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*Report of the*

American Society of
Mechanical Engineers'

# Technical Working Group on Inert Anode Technologies

*under contract to*

The U.S. Department of Energy
Office of Industrial Technologies

July 1999

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# CONTENTS

APPENDICES

# PREFACE

This report was prepared from July 1998 through July 1999 at the request of the U.S. Department of Energy's Office of Industrial Technologies (OIT), under Contract #DE-FC07-98ID13652, as part of OIT's Industries of the Future Initiative. It was coordinated and administered by the American Society of Mechanical Engineers' (ASME's) Center for Research and Technology Development. Eight seasoned experts in the field of aluminum technology, with backgrounds in industry, academia, and government laboratories, worked as a team to coordinate this study. The members of the team, which will be called the Technical Working Group (TWG), included the following:

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|---|---|
| 1. Dr. Rodney E. Hanneman | **Chairman**<br>Industry consultant; retired Vice President, Reynolds Metals |
| 2. Dr. H. Wayne Hayden | **Vice Chairman**<br>Manager, Engineering Materials Section, Oak Ridge National Laboratory |
| 3. Dr. Warren Goodnow | **Vice Chairman**<br>Industry consultant; retired Reduction Research manager, Kaiser Aluminum & Chemical Company |
| 4. Mr. Warren Haupin | Industry consultant; retired scientist, Alcoa |
| 5. Dr. Charles Windisch | Aluminum technology expert, Pacific Northwest National Laboratory |
| 6. Dr. Nolan E. Richards | Industry consultant; retired manager, Reynolds Manufacturing Technology Laboratory |
| 7. Prof. Donald Sadoway | Department of Materials Science & Engineering, Massachusetts Institute of Technology |
| 8. Dr. Ernest W. Dewing | Industry consultant; retired senior scientist, ALCAN |
| 9. Mr. Gregory Barthold | ASME Program Manager |

Grateful acknowledgment is given to the following individuals for their substantial contributions to the effort:

| | |
|---|---|
| 1. Dr. John Green | Vice President - Technology, The Aluminum Association; former manager, Martin-Marietta Aluminum |
| 2. Mr. George Hsu | Retired scientist and standards expert, Reynolds |
| 3. Dr. Euel Cutshall | Manager, Smelter Technology, Reynolds |

Appreciation is also expressed for the significant technical input and advice provided by Dr. Sara Dillich of the Department of Energy, as well as by numerous colleagues in industry during the preparation of this assessment report. Special thanks is given to Alicia L. Compere, Dr. Dane F. Wilson, and William L. Griffith of Oak Ridge National Laboratory for their work on the patent and literature search. Permission was obtained from the Minerals, Metals and Materials Society (TMS) to reproduce the paper by Dr. Barry Welch in Appendix A-6, and from the conference manager to reproduce the paper by Dr. Mark Taylor et al. in Appendix A-7.

# CHAPTER I — INTRODUCTION

This report provides a broad assessment of open literature and patents that exist in the area of inert anodes and their related cathode systems and cell designs, technologies that are relevant for the advanced smelting of aluminum. The report also discusses the opportunities, barriers, and issues associated with these technologies from a technical, environmental, and economic viewpoint.

The study was initiated as a result of a key recommendation made during the Inert Anode Workshop sponsored by the U.S. Department of Energy and The Aluminum Association, held in Arlington, Virginia, in November 1996.

## 1. Perspectives on Advanced Aluminum Smelting Technologies

Aluminum is a vitally important, highly versatile material that is widely used throughout the United States and the world. It has many economically attractive applications in the transportation sector; in numerous industrial products, packaging, and containers; and in components used in the nation's infrastructure and the construction sectors. The substitution of aluminum for common materials such as steel, copper, and certain composites can generate large energy savings over the net life of various products. It also reduces the production of the greenhouse gas, carbon dioxide, particularly in transportation applications because lightweight aluminum-intensive vehicles will use less fuel than conventional vehicles.

Over the years, aluminum has been extracted from nature by metallothermic, carbothermic, and electrolytic reduction processes. Although the earliest commercial method for producing aluminum involved a metallothermic process, the sodiothermic reduction of aluminum halides, such processes are no longer economical for the industry. The electrolytic Hall-Héroult process was adopted in the late nineteenth century, and continues as the process in commercial use today. The Hall-Héroult process involves the electrolytic decomposition of aluminum oxide dissolved in a molten cryolite ($Na_3AlF_6$) bath operating at temperatures below 1000° C. A carbon anode is consumed in the reaction that makes CO and $CO_2$. Molten aluminum is reduced at the cathode. Although there have been significant improvements in the scope and performance of this system, globally, virtually all aluminum is produced by the Hall-Héroult process.

However, scientists and engineers have sought alternative methods for producing aluminum for years in an attempt to reduce the energy intensity and capital investment required for aluminum production by this method. Moreover, world-wide concern about the effects of certain air emissions on global warming has more recently encouraged governmental, environmental, and industrial leaders to find ways to cost-effectively mitigate this potentially serious long-term problem. Producing aluminum by the conventional Hall-Héroult electrolytic cell process requires a large amount of energy and produces significant emissions of greenhouse and other detrimental gases. Some of the other approaches for aluminum production that have been attempted and the problems associated with them will be reviewed briefly.

Numerous approaches for carbothermic reduction have been studied. In all cases, electrical heating is generally used to attain high-temperature, carbothermic reduction reactions but these reactions provide reduced yields of aluminum owing to parasitic reactions, which produce substantial amounts of aluminum carbide and aluminum suboxide. They also generate high levels of carbon monoxide (CO), and subsequently of carbon dioxide ($CO_2$), per unit of aluminum produced. Other problems include costly purification and fluxing issues, huge scale-up costs for fully valid pilot testing, and issues concerning materials and maintenance. At least three major aluminum producers have spent many millions of dollars in research and development related to direct carbothermic reduction, without commercial success. Alcan investigated as far as pilot scale the carbothermic reduction of bauxite to produce an iron silicon aluminum alloy. The investigation was terminated owing to severe corrosion problems. Another approach to aluminum production combined a carbothermic reduction process using liquid tin to alloy the resultant aluminum phase of the aluminum-silicon eutectic, followed by a fractional crystallization and sodium treatment. That effort was terminated after significant testing.

The electrolytic reduction of aluminum chlorides was pursued worldwide by at least four aluminum producers during the 1960s, 1970s, and 1980s. The most advanced technology in this class used bipolar electrode cells to produce molten aluminum and chlorine gas. The chlorine was recycled to produce more aluminum chloride from alumina. Although energy-efficient, the reactors that never reached design capacity were expensive and difficult to maintain, and toxic products accumulated in the system. Total R&D expenditures for various chloride electrolysis efforts probably exceeded $100 million.

Industry recognizes the serious energy and environmental challenges of the methods just discussed. To date, they are technically mature and do not reduce energy use sufficiently to justify replacement of the existing Hall-Héroult process, nor have they yet proven to reduce the generation of greenhouse gases such as carbon dioxide. Consequently, industry has continued to pursue two technologies that could complement current methods of aluminum production and help resolve these energy and environmental challenges:

- Inert (or non-consumable) anode systems
- Wettable cathode systems

There are already emerging technical advances in materials which, coupled with innovative cell designs and operating procedures, offer the potential for significantly lower energy consumption and fewer emissions of greenhouse gases. Decades of research in these areas have already shown that this is not an easy task. Nonetheless, this “Technology Assessment” document will focus on these latter two technologies and on the technical and economic barriers that must be surmounted before they can be applied to commercial aluminum production.

If one or more of the technologies for primary aluminum production cited here is successful, it offers the following potential benefits over current commercial practices:

- Significant energy savings
- Large reductions in greenhouse gas emissions from aluminum smelters

- Significantly higher productivity
- Lower costs for the primary metal

This *Report of the American Society of Mechanical Engineers' Technical Working Group on Inert Anode Technologies* discusses the outlook for the direct retrofit of advanced reduction technologies to existing aluminum smelters. It also compares retrofits to "brown field" usage and "green field" adoption of the technologies. A number of observations and recommendations are offered for consideration concerning further research and development efforts that may be directed toward these advanced technologies. The opportunities are discussed in the context of incremental progress that is being made in conventional Hall-Héroult cell systems.

## 2. Statement of the Problem and the Approach

The aluminum industry has devoted more than four decades to developing an inert, non-consumable anode for the production of metallic aluminum in existing smelters, without success. Today, several factors are driving the effort to develop advanced technologies for producing aluminum for the commercial marketplace. **Environmental issues** include the need to reduce the risks of global warming as well as reduce hazardous waste products. Improvements in industrial energy efficiency fit well with the strategic government policy **to reduce U.S. dependence on foreign energy sources.**

The Technical Working Group's (TWG's) approach to this effort was to complete the following tasks prior to assessing the status of inert anode research for this document:

- Define the scope of the study and an overall implementation plan for meeting the *Inert Anode Roadmap's* specifications and expectations
- Identify and engage key experts in various aspects of inert anode systems and related reduction cell technologies to make presentations to the TWG
- Carry out in-depth literature and patent searches including computerized databases
- Define and classify the most significant abstracts, papers, and patents
- Solicit and receive independent input from interested parties
- Assess technical, environmental, and economic barriers
- Assess issues, and the impact and overall merit of various approaches for advanced reduction systems
- Prioritize recommendations for focused R&D efforts

# CHAPTER II — PATENT AND LITERATURE REVIEW AND CURRENT DEVELOPMENTAL EFFORTS

Technologies that are potential replacements for the conventional Hall-Héroult technology must be assessed in light of their technical, economic, and environmental attributes. This chapter summarizes selected patents and published literature that were found to be pertinent to this review. It also discusses current efforts to develop inert anodes, as well as wettable cathodes, based upon presentations made and other inputs provided recently to the TWG. Critical reviews of the status of the technology have been provided by Alcoa and by Reynolds Metals. A complete list of the patents and literature on inert anode technologies related to aluminum production may be found in Appendix A-1.

## 1. Patent and Literature Reviews

The patent selection procedure was done by "key word" search of the patent database provided by Corporate Intelligence Corporation, Browns Point, Washington. Initially, the time frame of the search went back to 1985 and resulted in more than 119 patents selected for review by the TWG. This was followed up by a search back to 1945, which brought forth another 229 patents for review. Review assignments were made on a random basis for the patents selected, and each of the patents listed in Appendix A-1 was reviewed by at least two members of the TWG. The assessments were made by completing an evaluation form (see Appendix A-2) and noting the results on the complete patent-listing matrix.

From the number of patents selected, it is apparent that a good deal of work on inert anodes has been carried out. However, a review of the state-of-the-art within the industry indicates that little of this work has been deployed. **To date, no fully acceptable inert anode materials have been revealed.** Topics reviewed in the patent literature included cell design, cathode development, connection schemes, alternative electrolytes, ideas for solid oxide fuel cells, and inert anode materials. The strategies employed by corporate patent attorneys in conjunction with the scientists they support became apparent when their broad claims and performance assertions were reviewed.

Among the research programs reviewed, scientists appeared to favor certain approaches. For example, the numerous patents awarded on behalf of the researchers working with the de Nora Group (Eltech and Moltech Companies) focus on cerium oxyfluoride coatings and the development of suitable substrates and barrier coatings and their method of manufacture. The developmental work on wettable $TiB_2$ cathodes conducted by several laboratories, including those affiliated with Alcoa, Pechiney, Comalco, Commonwealth, Reynolds, and Kaiser, has led to this technology being nearly ready for sustainable commercialization. On the other hand, viable "inert" anodes made from cermets of Ni-Fe-Cu or self-passivating metallic alloys are still only partially developed and their commercial success is quite uncertain. A new and quite novel solid electrolyte based on the "inert anode" concept that might eventually have a major impact primarily on the aluminum industry has been proposed. However, it is at an embryonic stage and it will require significant evaluation to verify its feasibility.

**Only a handful of the patents reviewed was rated unanimously as "highly relevant" by the assigned reviewers**. A discussion of the subjects covered in these important patents is provided here. In addition, the TWG considered the bulk of the inert anode research conducted by the de Nora group as relevant. For this reason, patents issued to Eltech and Moltech are also discussed in detail, but in a separate section (see Appendix A-3).

## Summary of the Patents Rated Highly Relevant by TWG

The highly rated patents fell into three areas: (1) bipolar cell and/or electrode designs, (2) cermet anodes using vertical electrode cell designs and low-temperature operation, and (3) a novel cell design using an aluminum chloride electrolyte.

### *Bipolar Electrode Designs*

As discussed in several sections of this report, the use of a bipolar electrode design in aluminum reduction cells may help realize the benefits of inert anodes. Since the bipolar arrangement affords the ability to pack the cells with many electrodes, the cells can be operated with much smaller anode-to-cathode distances and lower current densities. It was the opinion of at least one TWG member that inert anodes could not be used with any significant advantage in energy or cost savings unless they were incorporated in a bipolar electrode configuration. Unfortunately, there are several difficult problems associated with bipolar electrode designs and a lack of solutions has kept them from being deployed in commercial cells. Many of the problems are materials-related and include excessive corrosion of both anode and cathode materials, failure to identify successful materials and/or adequate strategies for bonding the anode and cathode materials, and the need for better resistive materials or coatings for edges and spacers so that the current flows efficiently between electrodes and the anode-to-cathode distance remains stable.

Two patents that the TWG identified as promising in this area were issued to Great Lakes Carbon (1985: 4,529,494) and Alcoa (1987: 4,664,760). The first of these describes a bipolar electrode composed of a cermet anode and a $TiB_2$ cathode bonded by an intermediate (Fe-Ni-Co) layer (with intermediate coefficient of thermal expansion [CTE]). The anode and cathode are treated (anode composition is graded while the cathode surface is metallized) and coated with metal foil to facilitate matching the CTE values of all the components. Finally, the pieces are joined together by brazing. While the survivability of the materials in a reduction cell is not demonstrated in this patent, the spirit of the invention is consistent with the need for novelty stressed by the TWG members. More research in this area could lead to new materials and bipolar cell designs that will facilitate the deployment of inert anodes. The Alcoa patent covers a novel cell design that incorporates a joined, horizontally oriented, free-standing, anode-cathode assembly. The configuration is applicable to both monopolar and bipolar electrodes, but its advantages would be exploited particularly by the bipolar design. The most important characteristic of the electrode assembly in this patent is the use of separators to establish a precise, spaced relationship in the form of an essentially fixed anode-to-cathode distance. While a suitable material for the spacers and other cell components still need to be demonstrated in long-term operation, the patent is nevertheless a very realistic portrayal of how inert anodes will probably have to be deployed in order to be successful. In particular, the patent highlights the systems issues that need to be addressed to reduce the inert anode concept to practice.

### *Cermet Anodes in Vertical Configuration*

Several patents were identified that used cermet inert anodes with promising results. Two related patents by Alcoa (1994: 5,279,715 and 1995: 5,415,742) are noteworthy because of the detail presented and because the concept couples Alcoa's cermet anode composition with a vertical configuration of electrodes and a low-temperature electrolyte. This perturbation of several systems variables involving both anode composition and cell design illustrates the multi-variable nature of the problem and its solution. The nickel-ferrite-based cermet anode compositions have received considerable attention over the last two decades. The materials have good electrical conductivity and acceptably low wear rates (good metal purities) under some conditions. Problems with the material have been mainly concerned with achieving these low wear rates in larger cells over long times, with developing an electrode geometry and configuration that exhibit adequate resistance to thermal and mechanical shock, and with controlling alumina concentration in the melt at sufficiently high levels so that the anode material does not dissolve. By thoughtfully addressing these issues and others in the indicated patents, Alcoa demonstrates its awareness of the necessity of a systems-type solution to the problem. Several surprises were also demonstrated in this patent, including the observation that electrowinning of metal is possible at high current densities and on low surface area anodes, producing oxygen at the anode with low fluoride emission and leaving the anode substantially free of corrosion even after periods of electrolysis. The legacy of the past two decades strongly suggests that some of the problems with this particular formulation may be insurmountable.

### *Novel Aluminum Chloride Cell*

A patent by Metallurgical, Inc. (1987: 4,670,110) was considered noteworthy because it addressed several systems issues related to using inert anodes and stood out as a rather novel design concept. Although $AlCl_3$ cells have been investigated by several laboratories, the results have been largely unsuccessful. Most recently, Alcoa abandoned the use of the $AlCl_3$ alternative in the further development of its cermet anodes. The cells have the advantage of lower temperature but suffer some problems including the production of chlorine gas and the difficulty in making $AlCl_3$ with acceptable purity. Unless high purity alumina is used in the $AlCl_3$ fabrication, other elements that are generally present such as iron, silicon, and titanium are also chlorinated and must undergo difficult separation from the $AlCl_3$. This contributes to the size and cost of the $AlCl_3$ plants. The indicated patent proposes a cell design that avoids both the chlorine collection and the independent production of $AlCl_3$ in a plant separate from the electrolysis plant by having the $AlCl_3$ generated in situ on the anode within the electrolytic cell. The $AlCl_3$ is produced at the anode by the reaction of an aluminous source and a reducing agent forming the anode with recycling chlorine produced at the anode during the electrolysis. The $AlCl_3$ produced at the anode during electrolysis is ionized in the molten bath and is deposited as aluminum metal at the cathode and chlorine at the anode. Details of the procedure are complicated and readers are encouraged to refer to the patent for further information. Nevertheless, the basic concepts presented in this patent are multifaceted and good examples of the systems approach that the TWG considered vital to success.

## 2. Discussion of Current Developmental Efforts

To broaden the sources of information available to the TWG, experts in anode technologies were contacted and offered a forum to present their approaches to the inert anode/cathode challenge. This section contains excerpts of their written or verbal presentations to the TWG. This is followed by a summary of a paper on Comalco's Composite Cell Program, information on other inert anode cell designs, and discussions by the Reynolds Metals Company on the Status of Cathode Development and by Alcoa on Previous and Ongoing Research on Oxygen Electrodes and Wetted Cathodes for Aluminum Smelting. A summary and analysis of the Eltech/Moltech patents appears in Appendix A-3.

### Opinions of Experts in Anode Technologies

The remarks of 10 experts follow.

#### *Dr. Ernest Dewing, retired Alcan*

Dr. Dewing presented a paper reviewing the general subject of inert anodes from several perspectives, including a critical review of life-cycle considerations, energy consumption, and global warming. His paper is presented in Appendix A-4.

#### *Curtis McMinn, Moltech*

Curtis McMinn, a consultant to Moltech, reviewed the company's capabilities and current efforts. Its wide-ranging technical efforts in aluminum cell technology are well-known, and there are a number of related technical publications. Two efforts are particularly relevant to the work of the TWG: (1) the development of TINOR, a wettable carbon cathode coating material, and (2) inert anode work, undertaken in the past by Prof. J.A. Sekhar at the University of Cincinnati.

The TINOR work, which is based on a $TiB_2$ composite, has been privately financed and has reached the stage of industrial trials in a number of locations. A full evaluation will take several months, and it is expected that results will be made public when it is complete.

The inert anode work has resulted in a composite non-carbon anode called NOVANOR, which will be tested in an industrial setting in 1999. McMinn described NOVANOR as having a metallic core of Ni, Cu, Fe, and Al, with a dense oxide coating on the surface. Tests in both the short (2–6 hrs), mid (10–50 hrs), and long term (100–600 hrs) have been carried out. These limited trials were described as promising with a dissolution rate of 0.05 mm/day cited as the "best test results." Moltech plans to continue trials of TINOR and retrofitted combinations of NOVANOR and TINOR. Cell voltages of as low as 3.00 to 3.50 volts were projected with a bipolar electrode cell. The real promise of NOVANOR and/or subsequent anodes developed by Moltech has not yet been determined since laboratory tests are incomplete.

#### *Professor Robert Rapp, Ohio State University*

Prof. Rapp presented a radically different approach to aluminum reduction. His proposed "inert anode" is a tubular solid oxide fuel cell (SOFC) electrolyte arrangement to oxidize reformed natural gas. "Rapp's Paradigm" provides a retrofit capability with the potential for reduced air pollutants and reduced energy consumption. Cost reductions of up to 7 cents per pound of aluminum were projected by Rapp. Material costs are likely to be extremely high and a good deal of developmental work will be required.

### *Craig Brown, Brooks Rand Ltd. of Seattle*

Craig Brown presented an inert anode concept (for Northwest Aluminum) whose initial development has been supported by a contract from the U.S. Department of Energy/Office of Industrial Technologies with Northwest Aluminum. The system would use low-temperature electrolyte (low ratio bath), vertical electrodes with inert anodes and $TiB_2$-based wettable cathodes, and an active anodic cell bottom to assist in reducing sludge in the cell. For the next 12 to 18 months, the technical effort will be devoted to evaluating metal alloy (Ni-Cu-Fe) anodes in bench-scale experiments. Various alloys will be subjected to small cell testing with the objective of selecting materials for 5KA pilot scale tests. According to Brown, "encouraging" results were claimed.

Northwest Aluminum's concept is a radical departure from conventional operations. Many technical hurdles will remain after a successful anode is tested, but the initial work is focused on the essential "inert" anode. At present, the trials constitute a go–no go approach to the concept.

### *John Hryn, Argonne National Laboratory*

John Hryn presented A Dynamic Inert Metal Anode as another approach to the inert anode problem. He proposes to use a metal-alloy anode whose surface would be protected by a film of alumina sufficiently thin that it can conduct current electronically. To achieve this very thin protective film, alumina will continually dissolve into the bath but constantly reform by oxidation of aluminum diffusing to the surface from a periodically replenished source of aluminum within the anode. There are major problems that must be solved here, for example, producing and maintaining an alumina film thick enough to prevent transport of the anode alloy to the aluminum product yet thin enough to conduct current without excessive voltage loss. It will be difficult to adjust diffusion lengths to supply aluminum to all anodic surfaces at the exact rate to match the dissolution of alumina, particularly for vertical plate anodes, which are the most promising configurations.

At present, there are no data on the alloy oxidation rate, nor on the dynamics of metal diffusion and the metal-anode/electrolyte interface. Hryn estimates that a $3-million, three-year effort is required to obtain the required data and demonstrate viability at the 100-amp, 100-hour test level.

### *Al La Camera, Alcoa*

Al La Camera presented a review of Alcoa's continuing efforts in inert anode/cell development. No written material was provided to the TWG for further study.

DOE has partially funded Alcoa, and R&D efforts have focused on metal-cermet anodes since the early 1980s. Alcoa's efforts have expanded to encompass a total cell system with vertical electrodes, a covered top, a conventional electrolyte, and a substantial concentration of dissolved alumina. This innovative system includes many novel components that require development. Until recently, electrolytic tests have not demonstrated the required stability/durability of anode materials. La Camera alluded to recent trials that yielded quite encouraging results in terms of the quality of the metal product. Further replication is required before researchers are confident of the results. La Camera spoke of the company's excellent facilities and resources, and advocated support for continuing Alcoa's efforts (see also page 21, *Integrated "Systems Approach"*).

### *Dr. Eric Frazer and Dr. Mark Twigg, CSIRO Minerals and CSIRO Manufacturing Science and Technology*

Drs. Frazer and Twigg described the work on inert anodes at CSIRO from 1993 to1996. The most successful anodes were made of tin dioxide-based materials. Low-temperature and low-ratio electrolyte trials yielded wear rates of ~2 cm per year. Copper depletion and a build-up of an alumina-rich surface layer were observed. They noted significant technical difficulties in expanding the inert anode developmental effort. To be successful, extensive investments of time and resources will be required. They foresee the development and demonstration of a promising material, followed by a five- to ten-year R&D implementation effort through an industry-government collaboration.

### *Dr. Tony Kjar, Comalco*

Dr. Kjar provided a written review of the work done at Comalco to develop $TiB_2$ cathode systems for an industrial application. A copy of his letter is presented in Appendix A-5. Comalco has had success in operating drained cathode cells at reduced anode-cathode separation and increased current density.

Although up to 700 day lives have been demonstrated, it is clear there are several hurdles to overcome. For example, a clean cathode must be maintained with no sludge or frozen material. A continuous pre-baked anode was advocated to further improve the results.

Rio Tinto Zinc (RTZ)/Comalco chose to reduce the priority of this foregoing program in the last few years because of the excessive developmental costs and other opportunities but is now showing renewed interest in the program.

### *Dr. Barry Welch, University of Auckland*

A recently published paper by Dr. Welch (*JOM*, May 1999) discusses the key aspects of any alternative process for aluminum production (a satisfactory chemical path, capital-cost reduction, a suitable material for the reactor and electrodes, and environmental considerations), and the common elements of all alternative processes (primary inputs of alumina, electrical energy, some carbon, and perhaps some other recyclable chemicals; outputs of aluminum and carbon oxides; releases of heat and perhaps by-products). He reviews several alternative processes investigated for aluminum production, and draws conclusions about the challenges facing the industry. His complete report is available as Appendix A-6 of this document.

## Comalco's Composite Cell Program

Dr. Nolan Richards has reviewed Dr. Mark Taylor's presentation on Comalco's Composite Cell Program at the New Zealand Aluminum Smelting Conference, November 26, 1998. A copy of Taylor's entire presentation appears in Appendix A-7 of this document. A summary of Nolan Richards' review of the paper follows immediately below.

Comalco has $TiB_2$-coated graphitic cathode cells in construction at one smelter and in operation at another. Taylor noted that Comalco's corporate objectives in conducting its research were to

- lower the operating inter-electrode distance,
- minimize cell instabilities from the cathode, and
- minimize instabilities from the anode (which, if achieved, could lead to new cell designs).

Researchers felt that after receiving technology from Martin Marietta, and conducting laboratory tests and prototype plant trials, they had reached "proof of concept." In practice they found that the anodes burned to the cathode profile. Achieving the correct cathode slopes and cell hydrodynamics were critical to success.

They also had to learn how to manage the heat balance, which was now dependent upon a 70 percent lower heat reservoir. The heat balance changed significantly when there was an error in the anode-cathode distance of only a few millimeters, or there was a variation in the thickness of aluminum flowing across the section (wetting the composite coating) and discharging into the center collection well. To inject more heat, researchers spliced in additional current from an extra rectifier, and later added extra insulation in the sidewalls. They also raised the anode current density from 0.95 $A/cm^2$ to 1.15–1.20 $A/cm^2$ (up from 90 to 110–120 kA. They also found it was important to avoid the formation or accumulation of sludge from the point feeders directly above.

During 1987-98, 25 drained cathode cells were built by Comalco, with a focus on improvements in a number of areas: (1) controls, (2) the composite formulation, (3) cell design, (4) operations, and (5) materials. For example, in improving the formulation for the composite, researchers wanted an initial 2–2.5 cm layer to deliberately shed particles to promote a viscous layer on the $TiB_2$ coating, which would impede both wear and dissolution. Many coated conventional cells have been operated over the same period. They now believe they have mastered the problems related to controls, cell design, and materials. The remaining issues are related to the operating and procedural changes needed to manage a potline of the drained cells. Coated graphitic cathode cells (with metal pads) need no further development for their commercialization.

## Other Cell Designs

Another route to achieving a heat balance with "inert" anodes is to pack more production capacity into the same volume. This can be accomplished by, for example, using bipolar electrodes. The “inert” anode plate (probably a cermet) must be joined to an “inert” cathode plate (probably made of a titanium diboride composite). Patents 3,930,967 and 4,529,494 claim to do this, but no long-term tests have been reported. In addition, an electrically insulating material, resistant to attack by the Hall-Héroult bath, is required to prevent current from bypassing the bipolar electrodes. Boron nitride and even thin chemical vapor deposited (CVD) diamond film have been suggested for this electrical insulating material, but they are expensive and not fully satisfactory in an oxidizing environment.

Alternately, an assembly could be made of multiple vertical anode and cathode plates with all anodes connected in parallel and all cathodes connected in parallel. These plates could be supported from above the bath and would not require any electrically insulating material to be in the bath. It would also avoid the problem of joining anode plates to cathode plates.

Baths with low melting points (e.g., $750^{o}$ C–$850^{o}$ C) have been proposed to reduce the attack on “inert” anodes, but these baths have low solubility for alumina. One way to alleviate this difficulty is to use a slurry of alumina in the bath. Northwest Aluminum Company is pursuing this concept. Another option is to cycle the alumina-depleted electrolyte to an externally heated and agitated reservoir containing alumina to replenish the alumina. On the other hand, Alcoa found that low-temperature baths caused passivation of the anode, which led to excessive voltage.

## Reynolds Metals Company’s Summary of the Status of Cathode Development

The majority of aluminum smelters in the United States have older, lower-amperage prebake or Soderberg cells that have higher electrical power requirements and are more labor intensive when compared with modern high amperage cells built in Canada and South Africa in the 1990s. U.S. aluminum producers have been able to stay competitive by making continuous improvements in the production process and by reducing costs. These older, more energy-intensive cells in the United States are better candidates for the wetted cathode technology.

From 1990 to 1996,$TiB_2$-graphite ceramic composite cathode elements manufactured by Sigri-Great Lakes were evaluated in industrial cells at the Kaiser Mead plant. The tests were supervised by Reynolds Metals Company and sponsored by the U.S. Department of Energy. The $TiB_2$-G material had shown promise in commercial cells as a stable, wettable cathode material demonstrating low dissolution rate and acceptable thermal shock resistance.

The use of $TiB_2$-G cathode elements also worked well to reduce the energy consumption in industrial prebake cells. However, the manufacture of a large number of high-quality, crack-free, $TiB_2$-G cathode elements proved to be too difficult for the supplier because of their complex “mushroom” shape. Consequently, a large number of $TiB_2$-G cathode elements failed during operations of the industrial prebake cell. The cathode elements were at risk of being damaged during cell startup and any operations involving anode bridge movements because they were positioned higher than the metal pad surface. Additionally, the economics of using the required number of the large 17-pound $TiB_2$-G elements per cell proved to be highly questionable.

Reynolds Metals Company, Kaiser Aluminum and Chemical Corporation, and Advanced Refractory Technologies (ART) are currently collaborating on a new effort to develop and evaluate materials and the necessary engineering package for retrofit of wettable, ceramic-based, drained cathode technology into existing aluminum reduction cells.

Internationally, there are at present three major non-U.S. companies pursuing the active development of $TiB_2$-based cathode technology for aluminum reduction cells: Comalco Aluminum (Australia), Alcan (Canada), and Moltech (Switzerland).

Comalco's $TiB_2$ cathode program has benefited from a very generous governmental policy of tax incentives, which promoted industrial R&D in Australia. It has been reported that significant commercial-scale testing by Comalco of $TiB_2$-carbon coatings in drained cathodes has been underway in Australia for almost 10 years. Comalco has been issued two U.S. patents (5,330,631 and 5,352,338) covering drained cell designs and cell startup practices.

Alcan International Ltd. and Eltech Systems Inc. made three unsuccessful attempts to start up prebake cells containing vertical $TiB_2$ bars in a non-carbon lining (see *Light Metals 1987*, 321–344). Research is continuing at Alcan in the evaluation of $TiB_2$-based materials specifically for drained cathode retrofits.

Moltech is actively promoting TINOR™, a $TiB_2$-based coating, for conventional reduction cells to extend cell life by reducing sodium penetration into the carbon lining and to control cathode block erosion. Moltech is working with Hoogovens (Holland) to develop and operate a drained cathode cell using the TINOR™ coating.

There is worldwide interest in the utilization of $TiB_2$-carbon based materials in drained cathodes by the major aluminum producers and companies developing wetted cathode technology. It now appears that promising Hall-Héroult cell-design concepts and promising candidate materials are both in the offing. Until recently, these design concepts and materials were not available simultaneously.

### Alcoa's Summary of Previous and Ongoing Research on Oxygen Electrodes and Wetted Cathodes for Aluminum Smelting

Currently, the inter-electrode spacing is not constant in aluminum processing. The anode reaction occurs at the bottom of the carbon anode and the cathode reaction occurs at the top surface of the aluminum pool. The aluminum pool spans the entire bottom cavity of the cell and is tapped from the cell on a regular basis to keep the height of the pool at between 3–5 in. Because of high currents in the process (i.e., 150 to 250 KA), large magnetic fields are produced in the aluminum pool. The combination of the current and the magnetic field causes the aluminum pool to circulate, resulting in waves forming on the surface of the aluminum that can extend 1 in. above the normal height of the aluminum. If an aluminum surface wave hits an anode, electrical current passes without producing aluminum, resulting in a major loss of power and production efficiency. Because the inter-electrode space is constantly changing, the anode must be far enough way from the metal surface to avoid contact. Typically this distance is about 1.75 in. A cathode material that is wetted by aluminum and that will drain so that the thickness of the remaining aluminum pool is less than 0.125 in. would eliminate the formation of waves. With a stable cathode surface, the constraint on the distance between the anode and cathode is eliminated, permitting the reduction of the spacing and the potential to improve power and production efficiency.

Anode changing can also cause waves on the aluminum surface of a cell that uses a deep metal pad. Because the anodes are consumed, they must be replaced every two weeks. This causes upsets in the distribution of the current, thermal field, and magnetic field in the cell. Upsets of this type initiate waves that result in a constantly changing spacing between the anode and cathode.

Combining an oxygen-generating anode, which has a life of over one year, and a wetted cathode with a thin aluminum film that can be drained results in a stable distance between the anode and cathode. This outcome, therefore, will achieve major improvements in energy and productivity efficiency for the Hall-Héroult cell. Alcoa presently is funding materials development programs for oxygen-generating anodes and wetted cathodes.

In addition, other federal, industrial, and academic research and development activities have been conducted, including the following:

- "Oxygen Electrodes for Aluminum Smelting," DOE-Alcoa Cooperative Agreement, 1980-1985.
- "Improvements of the Alcoa Cermet Anode Developed under the 1980-1985 Alcoa-DOE Cooperative
- "Research on CEROX Coatings for Cermet Anodes," Eltech Research Corporation
- "Tests of a Prototype Cermet Anode at 120 A," PNL-Reynolds Metals
- "Pilot Scale Tests Aimed at Assessing Anode Manufacturing and Stability," Reynolds Metals, Eltech Research Corporation, and Ceramic Magnetics Inc.
- "Water Models of Cell Concepts for Improved Electrolyte Flow," University of California, Berkeley
- "Programs for $TiB_2$-G Composite for Wetted Cathodes," Reynolds Metals and Great Lakes Carbon
- "Materials and Cell Design for a Wetted Cathode," Comalco
- "Studies of Low Temperature Slurry Electrolysis," Electrochemical Technology Inc.
- "Low Temperature Salt Systems for the Cermet Anode," DOE-Alcoa

Summaries of selected research efforts are presented below.

### *Development of Oxygen Electrodes for Aluminum Smelting (DOE/Alcoa)*

The cermet anode, a key element of this program, was developed during the DOE-Alcoa Cooperative Agreement, 1980–1985. The material is made of mixed oxide ceramic and metal constituents, as the name implies. The mixed oxide phase contains $Ni_xFe_{3-x}O_4$ and $Ni_yFe_{l-y}O$, and the metallic phase is Cu-rich, containing a Cu-Ni-Fe alloy. The motivation behind the cermet formulation was combining the characteristics of high corrosion and oxidation resistance of a ceramic with a metallic phase to improve electrical conductivity, thermal shock resistance, and the ability to make connections to metal conductors. Other technologies developed during the cooperative agreement were processes for anode manufacturing (forming and sintering) and the cermet to metal conductor connections.

During this program, anodes were tested in commercial Hall-Héroult conditions at 60 A (at 1.0 $A/cm^2$) for 265 hours. Two critical tests of anode performance were the purity of the aluminum produced and anode wear. These tests showed that the Cu-cermet performed the best. The purity of the aluminum produced was 0.19 percent Fe, 0.18 percent Ni, and 0.10 percent Cu. The anode wear rate was estimated at 1.8 cm/yr (0.70 in/yr). The material contained 17 percent Cu and an oxide power that contained 51.7 percent NiO and 48.3 percent $Fe_2O_3$. The oxide powder was designated 5324. The cermet was called 5324-17Cu.

It was believed that under optimal conditions, the cermet anode develops a passivating layer that leads to superior corrosion resistance. Cermet material fabrication practices and cell operating conditions can radically change the anodes' performance. These are the two important reasons why cermet corrosion has varied so dramatically in previous tests.

### *Improvements of the Alcoa Cermet Anode (Pacific Northwest Laboratory)*

At the end of the 1980–1985 cooperative agreement between Alcoa and DOE, Pacific Northwest Laboratory (PNL), under DOE contract, continued the development of the cermet anode. Emphasis was in the following areas: (1) anode material development and evaluation, (2) development of wetted cathode materials, and (3) sensor development. The objective of the PNL cermet anode program was to further improve the corrosion performance and electrical conductivity of the cermet anode. PNL investigators experimented with compositional changes to the anode. Additions of aluminum were found to improve the electrical conductivity of the cermet significantly, but the corrosion performance of the anode degraded. PNL scientists recommended the 5324-CU material developed by Alcoa as the preferred material for future cell studies. During the PNL work, the importance of controlling cell operating conditions on anode performance was recognized to be vitally important. The main concerns were the control of alumina and electrolyte composition.

PNL staff also evaluated wetted cathode materials. The materials tested were Alcoa-fabricated $TiB_2$ parts; Great Lakes $TiB_2$-G plates, and a $TiB_2$-based paint coating. Attempts also were made to produce in-situ $TiB_2$ coating. The best results were obtained with Alcoa sintered $TiB_2$ parts produced from $TiB_2$ powders produced by plasma processing. During this program the $TiB_2$-G produced mixed results. This was believed to be due to inconsistencies in materials and fabrications. But in recent long-term pilot tests at the Reynolds Metals Laboratories, $TiB_2$-G has performed very well. $TiB_2$-G is the preferred material today for wetted cathodes, although its cost is quite high.

Alumina control in cells that used cermet anodes is very important. At a low concentration of alumina, the corrosion resistance of the anode degrades. Recently, Alcoa has developed a method for rapidly measuring alumina that will be used to control alumina composition in the Phase III cell tests.

### *Research on CEROX™ Coatings for Cermet Anodes (Eltech Research Corporation)*

The Eltech Research Corporation's program focused on the development of a coating to improve the corrosion performance of the cermet anode. Eltech demonstrated that the addition of cerium fluoride to the oxyfluoride electrolyte formed a cerium-oxyfluoride coating (CEROX™) on the cermet anode. Corrosion tests conducted with and without cerium fluoride in the electrolyte showed substantial gains in the purity of the metal produced with cerium present, excluding increased cerium concentrations. However, the coating was not a good conductor, and therefore control of coating thickness was an important factor for achieving adequate current distribution, and minimizing the overall anode voltage drop. Poor current distribution and excessive anode voltage were found to degrade the anode corrosion performance and overall cell performance.

Another critical issue with this technology was the reaction of costly cerium fluoride with aluminum. This reaction formed cerium metal, which reports to the aluminum pool and is an impurity in primary aluminum. In most instances, this cerium would have to be removed substantially to achieve needed metal purity limits. A process for doing this was developed by E. Dewing at Alcan (U.S. Patent 4,668,251).

### *Tests of a Prototype Anode at 120 A (PNL and Reynolds Metals)*

The primary objective of this test was to determine if a commercially produced anode could survive normal Hall-Héroult cell conditions. The anode material was the Alcoa cermet. It was 15 cm in diameter and 20 cm high. The anode was operated at 0.50 A/cm$^2$, about 120 A. The main conclusions from this study were as follows:

1. Corrosion of the anode was higher than expected; after 120 hours of electrolysis, 6 mm were lost from the diameter of the anode.
2. Oxidation of the cermet above the electrolyte was extensive.
3. A high cathode area relative to the anode area may have increased anode corrosion.
4. Mismatch of thermal expansion between the anode and the metallic conductor caused cracks in the anode.

### *Operational Results of Cermet Anodes in a Pilot Scale Test (Reynolds, Eltech, PNL, and Ceramics Magnetics*

The main objectives of this program were to demonstrate cermet manufacturing capabilities and test the cermet in a commercial anode configuration. The tests were conducted in an internally heated cell using a six-cermet anode array as a replacement for a standard Hall cell anode. The goal was to maintain 90 A per anode and 540 A for the six-anode array. The energy generated through electrolysis by the cermet anodes alone was not sufficient to achieve a cell energy balance at the desired operating temperature. Auxiliary energy was supplied by electrolysis between an adjacent carbon anode and an aluminum pool common to the carbon and cermet anodes. The carbon anode supplied most of the thermal energy required for cell operation. Tests were conducted of cerium-free and cerium fluoride-containing electrolytes. The anode material of choice for this test was the cermet developed by Alcoa during the 1980–1985 DOE cooperative agreement. Issues identified included the following:

- Correcting the anode breakage and cracks caused by the conductor to anode connection
- Incorporating good current distribution and stress management in the anode design
- Operating the Hall-Héroult cell near alumina saturation without being limited by muck formation
- Achieving the cell energy balance without using carbon anodes as auxiliary anodes
- Achieving commercial anodes with the same composition, microstructure, and properties as those achieved at a bench scale

### *Assessment of New Cell Concepts (University of California, Berkeley)*

The objective of this program was to assess the design of new cell concepts for use with an oxygen-producing anode and a wetted cathode. This study listed three critical factors that must be considered in the design of such a cell:

- Sufficient electrolyte velocity in the inter-electrode space to suspend and dissolve alumina
- Adequate electrolyte velocity to achieve a negligible drop in alumina concentration from inlet to outlet of the inter-electrode space
- Minimal fluid turbulence, which influences reoxidation of aluminum

Physical modeling was used to determine the influence of electrode orientation (horizontal versus vertical); the use and geometry of grooves in the anode; and the use of flow enhancers on the velocity, turbulence, and ohmic losses in the inter-electrode space. The major findings were as follows:

1. The use and shape of grooves in the anode significantly influences the ohmic resistance in the inter-electrode space caused by gas evolution at the anode.
2. An anode without grooves operated in a horizontal configuration did not provide sufficient electrolyte velocity to keep alumina suspended.
3. The near vertical electrode configuration had recirculating loops near the outlet flow from the inter-electrode space that would enhance reoxidation of aluminum.
4. The near horizontal electrode configuration was recommended because it minimized recirculation, achieved an adequate velocity, and because it reduced the ohmic gas resistance in the inter-electrode space with properly designed grooves.

### *Development of TINOR Coating and Novanor Inert Anode (Moltech)*

Moltech has been aggressively investigating many new materials to improve cell performance or lifetime, and two are of interest. TINOR is Moltech's $TiB_2$ coating used to produce a wettable cathode. Moltech has installed test coatings in eight smelters worldwide. Chemical analysis indicates that the coating lasts about three years (from Ti and B analyses in the tapped Al). Preliminary results show a dramatic reduction in Na uptake by the carbon cathode. If this lower Na uptake translates into less cathode growth, the life of the pot should increase. Moltech has secured a $4-million contract from the European Commission to test a pilot scale TINOR-coated drained cell with conventional carbon anodes. Novanor, Moltech's inert anode, is the second material that relates to advanced cell concepts. In a recent paper, Sekhar et al. describe

Moltech's research on a series of progressively more complex metal alloys as they attempt to develop an inert (stable, nonconsumable) anode.

### *Plant Testing of TiB2-Carbon Coating in Drained Cells (Comalco)*

Comalco has been testing its $TiB_2$ cathode coating in drained cells in one of its smelters for about 10 years. Comalco's coating is a mixture of $TiB_2$ and C produced by baking out a mixture of $TiB_2$ and a carbonaceous cement. The coating permits good wetting of the Al and close anode-cathode distance in the drained cells. Coating life appears to be the problem as the Al metal pad apparently reacts with the carbon portion of the cement to produce $Al_4C_3$. Thus, the carbon portion of the coating slowly disappears, simultaneously releasing the $TiB_2$ particles. The coating typically lasts six to nine months. Once the coating is gone, the Al rapidly reacts with the carbon underneath leading to cell failure. Until Comalco can increase the lifetime of its coating, it does not appear the company can expand its testing beyond the limited group of test pots.

## Summary

If successfully implemented, aluminum reduction cells with inert anodes and wetted/drained cathodes have the potential to lower energy consumption, reduce greenhouse gases and other adverse environmental impacts, and improve the competitive position of the U.S. aluminum industry. Based on the present status of such R&D work, however, the TWG feels that the probability is still relatively low that current candidate materials for inert anodes will achieve ultimate commercial success. Nonetheless, because of the potentially large impact of a successful program, and some encouraging interim progress, further selective R&D support for inert anode-based systems is warranted on a stage-gated basis. Exploratory effort on promising unconventional inert anode approaches may well warrant limited support at this time to evaluate their preliminary feasibility.

After many years of work, $TiB_2$-based cathode technology appears close to commercial application and offers a good chance to achieve retrofits with up to 30 percent gains in productivity and the potential to extend the life of cells, with attendant environmental and economic benefits. Accordingly, support should be given to the development and demonstration steps that will ensure implementation of such technology.

# CHAPTER III—A SYSTEMS APPROACH

Insight gained from evaluation of numerous unsuccessful attempts to develop an inert anode (IA) suggests that this past work addressed only part of the task. The best way to improve cell efficiency and attain economic and environmental responsibility is by studying the whole system instead of only the anode. The most promising work to date has been on cathode development.

The electrolysis process requires an anode, a cathode, an electrolyte, a container, a method of delivering electricity, an alumina feeder, and an extraction system for the product. Each of these elements must work as part of the whole system and is defined by its performance in relation to the other elements of the system. The Hall-Héroult process required the discovery of an acceptable electrolyte that would be a solvent for aluminum oxide. The other elements of the cell (anode, cathode, container, delivery system for raw material, an anode replacement, and an extraction system for the product) were then optimized. This optimization continues today. There are prebaked carbon anodes and in situ baked anodes (Soderberg Process). Considerable work has been done to improve the cathode by using titanium diboride. However, if an inert anode material were successfully developed, it would be more favorable if a new cell design were also developed. The cell should probably be sealed since the anodes would seldom need to be replaced. Again, this is part of the argument for looking at the whole system instead of just the anode.

There are three possible methods for implementing IA technology. The first is a “brown cell retrofit” that uses current plant infrastructure and existing cells except for the anode. The carbon anode would be replaced with the IA with only minor changes to the cell design, which might be required to accommodate an anode with a different shape or electrical connection. The second approach is a “brown site retrofit” that would involve replacing cells in existing potlines with new, radically redesigned cells or reactors. Existing infrastructure would be used, including buildings, bus work, and raw material handling systems, but the cells themselves might bear very little resemblance to traditional Hall-Héroult cells. Finally, a “green field” approach is associated with new technologies that would be substantially different from existing plant infrastructure.

After extensive review and discussion of the patent literature, open published literature, and presentations of researchers currently working on IA developmental projects and proposals, the TWG has concluded that the brown cell retrofit is not a promising method for transitioning to a workable IA. It is very difficult to envision deployment of an IA without serious disturbances in the cell’s operation and significant changes in cell design. Many research projects have resulted in new anode materials that are promising in laboratory screening tests, but that are unsuccessful in a traditional Hall-Héroult cell configuration. Proposed solutions to make the materials “work” in larger cells usually consisted of modifications to the cell design and operation. Since many of these proposed modifications have never been tested and/or optimized, the proposed solutions are essentially “brown site retrofits.” The most workable solutions to developing a successful IA involve a “systems approach.” They require the development of a wide range of new technologies involving the anode material, cell design, and cell operation.

Below are seven examples of how the deployment of an IA in place of a carbon anode requires solutions to a cascade of cell-design and operational challenges. New technologies and materials must be developed or enhanced to solve these problems and harness the IA's potential. In most cases, the changes to cell design and operation are radical, which is why the TWG believes that only solutions that consider the entire "system" will have any chance of success.

## 1. Anode/Cathode Assembly

From a thermodynamic standpoint, the minimum reaction voltage in an inert anode cell for producing aluminum and oxygen is a full volt higher than that required in a Hall-Héroult cell for the production of aluminum and $CO_2$ with a carbon anode. If the IA-based cell is to be at least as energy efficient as a traditional Hall-Héroult cell, the extra volt must be recovered through cell design or operational modification. For example, the IA could present the opportunity to reduce the anode-to-cathode separation significantly. However, this change requires that a wettable cathode be in place so that the aluminum pad is stable enough to prevent shorting. Alternatively, the sidewalls or cell top could be insulated more efficiently. If more insulation is used, the cell will probably operate without a frozen ledge, and an inert sidewall material must be discovered. In summary, to achieve the required reduction in anode-to-cathode distance, a systems approach is required. Regardless of the corrosion resistance of the IA, if it is to be deployed to meet the energy performance levels of a current Hall-Héroult cell, it will require redesigning the cathode, the anode-cathode assembly, and/or the cell insulation (and possibly a cell cover) and sidewalls.

## 2. Bipolar Cell Design

A bipolar cell design helps to solve the problem in the first example (anode/cathode assembly) by packing many anodes and cathodes together in a cell. This design also saves space by bonding pairs of anodes and cathodes back-to-back. This solution is very attractive but involves many technological hurdles. It clearly amounts to a systems approach. The development of bipolar electrodes would include new materials for both the anode and cathode, and solutions to bonding anodes and cathodes together and electrically isolating certain parts of the assembly so that current flows in the desired direction. Additionally, unusual electrical requirements and chemical-management systems would be necessary.

## 3. Bath Composition Control

To minimize corrosion during the testing of a number of potential IA materials, it was necessary that dissolved alumina be maintained close to saturation in the molten electrolyte and/or that the cell temperature be lowered. Some promising candidate materials worked better with a very low bath ratio ($NaF/AlF_3$). Significant changes to the bath composition mean that the cell design and/or the design and operation of the control system will have to be modified. Maintaining the bath near saturation may require an accurate on-line sensor for alumina concentration, a very efficient way to mix alumina as it is added, methods to minimize agglomeration of the alumina in the cell, and an advanced control system. A lower-temperature bath means that the electrolyte composition will probably have to be changed and controlled very well, and cell operation and materials altered to be suitable for the lower temperature.

## 4. $CO_2$ Emissions – Cell vs. Power Plant

One of the proposed benefits of using an inert anode to manufacture aluminum is the reduction in $CO_2$ emissions from the aluminum reduction plant. This benefit is always realized when the analysis is restricted to the reduction plant. However, if the power plant is included in the estimate of the influence of IAs on total $CO_2$ emissions, the results may change significantly. The lesson here is that the evaluation of the IA as part of the "system" will require going beyond the boundaries of the reduction plant itself.

## 5. Additional Processing for Purity

One of the most important requirements of an IA material is that it must be able to survive in a hostile molten salt environment for an economically viable period, and to facilitate the production of high-quality prime metal. It is conceivable that additional processing steps (and costs) can be inserted in the process stream to improve metal quality if the electrodes survive and result in significant economic gains. However, these add-on processing steps complicate the "system" as well as make the product more expensive.

## 6. Integrated "Systems Approach"

During one of the TWG meetings, Alcoa described an improved cell using an IA similar to one that was patented by them in 1994. The cell used a "systems" approach and involved a new anode material, a new cell design using multiple vertical anode plates hung with wettable cathode plates interspersed between them, an insulated lid, and new sidewall materials that can survive in a ledge-free environment. In taking this approach, Alcoa has apparently reached the conclusion that an integrated system is necessary for implementation of inert anodes.

## 7. Novel Approaches

Another presentation made to the TWG was a proposal to develop a solid oxide electrolyte for use as a membrane in a cryolite bath so that natural gas could be used instead of carbon in the electrolytic reduction of dissolved alumina. The approach was quite novel, and despite numerous technological challenges was argued to have several potential advantages. The TWG views this proposal as another example of a systems approach to developing an IA, but one with a lower chance of commercial success at present than the more conventional approaches described above.

The TWG has concluded that it is highly improbable that IAs will succeed as a single-component modification, as in a brown cell retrofit. Rather, IAs must be coupled with other new technologies in a brown site retrofit to produce an economically attractive, system-based solution. Some of the required new technologies may be already developed (e.g., wettable cathodes), tested in the laboratory but still several years from realization (new sidewall materials); or they may be developed but completely untested (e.g., novel anode materials). In almost every scenario, it will probably be necessary to undertake significant upgrades in process sensing and control in order to successfully deploy IAs. In most R&D efforts on IAs, the IA was found to be more sensitive than carbon anodes to one or more operating conditions (e.g., bath composition and temperature). Since a successful IA must be long-lived, it is difficult to imagine how this could be realized without a system for accurate, on-line sensing and feedback control of important cell parameters.

Even if a successful IA is not developed in the near future, research that employs the systems approach may foster the development of spin-off technologies that could be applied to conventional Hall-Héroult cells. These technologies would be expected to achieve the industry goals of reduced energy consumption, low environmental impact, and improved domestic industrial competitiveness. Potential opportunities to improve conventional Hall-Héroult cell performance include the following:

- Wettable cathodes that are close to fruition and may well be deployed as a commercially viable stand-alone technology in the near future
- Improved insulation systems that could result in a more “thermally efficient” reduction cell with attendant energy savings
- Improved sensing and controls that would improve efficiency and reduce the generation of $CF_4$

In order to optimize all the independent parameters, the IA and reduction cell should be carefully modeled prior to running a single experiment. The approach is complex but so is the system. For this reason, the TWG believes that future researchers should address the system theoretically as much as possible before committing to developmental efforts on a new material or design for the IA.

In addition, it is the opinion of the TWG that the research and development efforts prior to any demonstration of IA materials should follow the “gated approach” recommended in the Inert Anode Roadmap. The TWG recommends that scale-up of research on IA materials be attempted only after specific criteria have been demonstrated in the prior stage of work. The order in which the criteria should be met follows:

- Successful performance in a laboratory cell at 100 amperes for 100 continuous hours of operation
- Successful performance in a laboratory or small-scale prototype cell at 1000 amperes for 1000 continuous hours of operation
- Successful operation in a prototype cell at 5,000 to 10,000 amperes for a period of continuous operation of at least six months
- Production-scale prototypes at projected plant-operating current

Accomplishing each of these criteria in this order is what is meant by a “gated approach.”

# CHAPTER IV—SYSTEMS ISSUES

Issues arise in three areas when one considers the systems approach to developing an inert anode. These areas are thermodynamic and power efficiency, the wetted cathode, and metal quality. Each of these issues will be discussed in turn. Refer to Appendix A-8 for a list of references cited by number in the text.

## 1. Thermodynamic and Power Efficiency

The efficiency of a reduction system using an inert anode system should meet or exceed the energy performance of a conventional system using carbon anodes. A comparative thermodynamic analysis of the two systems has been performed to determine the potential for achieving this goal.

### Thermodynamics of Aluminum Oxide Reduction Processes

Unlike the precious metals and copper, aluminum does not occur as a metal in its native state. In nature, aluminum is generally found in ores as aluminum oxide in combination with other metal oxides, or, in bauxite, an ore that is principally aluminum oxide. Aluminum oxide is highly stable chemically, and is difficult to reduce by heating it to elevated temperatures or by thermally treating it with hydrocarbon or carbonaceous reducing agents.

### Energy Requirements of the Hall-Héroult Process

The Hall-Héroult process involves the electrolytic decomposition of aluminum oxide dissolved in a molten cryolite ($Na_3AlF_6$) bath operating at temperatures below 1000° C. A carbon anode is consumed in the reaction that makes CO, $CO_2$, and molten aluminum, which is reduced at the cathode. Although there have been significant improvements in scope and performance of this system, globally, virtually all aluminum is produced by the Hall-Héroult process.

Under perfect conditions, where there are no reverse reactions and no parasitic reactions consuming additional anode carbon, the forward reaction for the Hall-Héroult process, at 100 percent current efficiency (ce), would be

$$Al_2O_3 + 3/2\ C \dashrightarrow 2\ Al + (3/2)\ CO_2$$

This is an endothermic (heat-consuming) reaction. The theoretical minimum energy requirements for the reaction would be determined by the enthalpy requirements for heating the reactants to operating temperature, plus the enthalpic requirements for carrying out the above reduction reaction. Using thermodynamic data from the JANAF tables, Grjotheim et al. [1] report the following theoretical energy requirements for cell operating temperatures of 977° C (1250° K) and 100 percent current efficiency:

|  |  |  |
|---|---|---|
| Heating | 0.70 kWh/kg Al | 0.32 kWh/lb Al |
| Reduction | 5.64 kWh/kg Al | 2.56 kWh/lb Al |
| Total | 6.34 kWh/kg Al | 2.88 kWh/lb Al |

In actual cell operations, current efficiencies of less than 100 percent result from reverse oxidation reactions between part of the aluminum metal and carbon dioxide gas produced by the forward reaction. The loss and net reactions are

$$\text{Loss Reaction: } 2n\ Al + 3n\ CO_2 \dashrightarrow n\ Al_2O_3 + 3n\ CO$$
$$\text{Net Reaction: } (1-n)\ Al_2O_3 + 3/2\ C \dashrightarrow 2(1-n)\ Al + (3/2-n)\ CO_2 + 3n\ CO$$
or
$$Al_2O_3 + (3/2ce)\ C \dashrightarrow 2\ Al + (3[2ce-1]/2ce)\ CO_2 + (3[1-ce]/ce)\ CO$$
Where: $ce = 1-n = \%\ \text{Current Efficiency}/100$

According to Grjotheim et al. [1], the total minimum energy requirement as a function of current efficiency for the Hall-Héroult process at 977° C is

$$\text{Minimum Energy} = (1.43/ce) + 4.91\ \text{kWh/kg Al}$$
$$\text{Minimum Energy} = (0.65/ce) + 2.23\ \text{kWh/lb Al}$$

In addition to the effects of the forward and back reactions for the electrolysis process, there are parasitic reactions between the carbon dioxide anode gas and the carbon anode. This reaction is known as the Boudouard reaction:

$$CO_2 + C \dashrightarrow 2CO$$

The extent of the Boudouard reaction varies with cell design and modes of operation. Haupin has made theoretical estimates for the effect of the reaction on the theoretical energy requirements, which are presented in Appendix A-9. The overall effect of the Boudouard reaction on the theoretical energy requirements is relatively small.

Today's state-of-the-art reduction cells are achieving current efficiency levels of 96 percent and energy consumption levels of 13.0 kWh/kg Al (5.9 kWh/lb Al). The theoretical minimum energy requirement at 96 percent current efficiency is 6.36 kWh/kg Al (2.90 kWh/lb Al). Thus, the energy efficiency levels of present state-of-the-art reduction cells are on the order of 49 percent.

## Inert Anode Cell Energy Requirements

A (permanent) inert anode reduction cell would utilize an anode material that would not engage in the reduction reaction and would be stable from the standpoints of wear, dissolution, and/or reaction with any of the cell components, feed materials, or reaction products. Despite the tremendous efforts that have been made throughout the world to develop inert anodes, a viable system has not yet been defined.

Under perfect conditions, with no reverse reactions, the forward reaction for an inert anode aluminum reduction process at 100 percent current efficiency would be

$$Al_2O_3 \text{ --> } 2\ Al + (3/2)O_2$$

This is also an endothermic (heat-consuming) reaction. The theoretical minimum energy requirements for the reaction would be determined by the enthalpy requirements for heating the reactants to operating temperature, plus the enthalpic requirements for carrying out the reduction reaction. Using a thermodynamic approach similar to that described above for the Hall-Héroult process, the minimum theoretical energy requirement for an inert anode aluminum oxide reduction process at 977° C would be

| | | |
|---|---|---|
| Heating reactants | 0.60 kWh/kg Al | 0.27 kWh/lb Al |
| Reduction | 8.69 kWh/kg Al | 3.95 kWh/lb Al |
| Total | 9.29 kWh/kg Al | 4.22 kWh/lb Al |

In actual cell operations, current efficiencies of less than 100 percent result from reverse oxidation reactions between part of the metallic aluminum and oxygen gas produced by the forward reaction. The loss and net reactions are

$$\text{Loss Reaction: } 2n\ Al + 3n/2\ O_2 \text{ --> } n\ Al_2O_3$$
$$\text{Net Reaction: } (1\text{-}n)\ Al_2O_3 \text{ --> } 2(1\text{-}n)\ Al + (3/2)(1\text{-}n)\ O_2$$
$$\text{or}$$
$$Al_2O_3 \text{ -->} 2Al + 3/2\ O_2$$

Inasmuch as the overall reaction and reaction products of inert anode cells do not vary with current efficiency, as with Hall-Héroult cells, the minimum energy requirement for an inert anode is independent of current efficiency. The minimum energy requirements are as follows:

Minimum Energy = 9.92 kWh/kg Al
Minimum Energy = 4.22 kWh/lb Al

These inert anode cell minimum energy requirements are about 47 percent higher than those for the Hall-Héroult process. On this basis, if the actual energy consumption levels for an inert anode cell are to be comparable to or less than the performance of state-of-the-art Hall-Héroult systems (13 kWh/kg Al, 5.9 kWh/lb Al), the operating efficiencies of such inert anode cells will have to be on the order of ***71.5 percent or higher***.

## Comparative Energy Requirements for Hall-Héroult and Inert Anode Cells

The foregoing estimates for theoretical minimum energy requirements for Hall-Héroult and inert anode cells have been made for the assumed case of 100 percent current efficiency and an operating temperature of 977° C. It should be noted that operating temperatures have a minor effect on theoretical energy requirements. Over the range of potential operating temperatures of from 1000° K to 1400° K (727° C to 1127° C), a change in operating temperature of 100° C has about a 1 percent effect of minimum energy need for the Hall-Héroult process and about 0.6 percent for the inert anode process.

Table IV-1, below, shows the effects of changes in current efficiency achieved in actual operations. The table also provides the actual energy efficiencies achieved at a performance level of 5.9 kWh/lb Al for a state-of-the-art Hall-Héroult cell, and the ***energy efficiency levels that would be required*** for an inert anode cell to achieve performance levels of 5.9 kWh/lb Al. These efficiencies are at the very high level of 71.5 percent. These thermodynamic estimates for theoretical energy requirements demonstrate that it is possible for an inert anode cell to attain similar (or lower) energy performance levels than the state-of-the-art Hall-Héroult cell, ***but the engineering designs for the inert anode cell systems must incorporate the very best approaches for minimizing thermal losses both from the reduction cells and the current-carrying bus systems and connectors external to the cell.***

Detailed presentation of the thermodynamic data and calculations appear in Appendix A-9.

**Table IV-1. Theoretical Energy Requirements Based on Enthalpy Requirements for Heating Reactants, Chemical Reaction, and Withdrawing Products at Cell Temperature**

| Current Efficiency | Theoretical kWh/kg Al | Theoretical kWh/lb Al | Ener. Effic. at 5.9 kWh/lb Al | Needed Ener. Effic.. for 5.9 kWh/lb Al |
|---|---|---|---|---|
| **Hall-Héroult Cell** | | | | |
| 92% | 6.46 | 2.94 | 49.8% | – |
| 94% | 6.43 | 2.92 | 49.5% | – |
| 96% | 6.40 | 2.91 | 49.3% | – |
| 98% | 6.37 | 2.89 | 49.0% | – |
| 100% | 6.34 | 2.88 | 48.8% | – |
| **Inert Anode Cell** | | | | |
| All | 9.92 | 4.22 | – | 71.5% |

## Practical Considerations in Cell Design

Theoretical energy requirements are the amounts of energy that must be delivered to the “process volume” in the cell where the reactants are heated and the reduction reaction is made to occur. In essence, the “process volume” is the molten bath and, particularly, the anode to cathode region, including the working surface of the anode, the molten bath, and molten metal layers. Heat generated in the process volume and heat flowing into the process volume can contribute to the reduction reaction. Heat flowing from the process volume is lost heat. Similarly, heat generated external to the process volume and flowing from the cell and external conductor surfaces cannot contribute to the reduction reaction, and hence is all lost heat.

The energy delivered per unit time in aluminum reduction processing operations is the product of the applied current and the sum of all the internal and external voltage drops. The total cell voltage drop includes the sum of the equilibrium electrode potentials, the anode and cathode overpotentials, and all of the cell IR drops. The IR drops include the external circuit (cell-to-cell busbar), bus-to-cell connectors, anode drop, interelectrode bath drop, cathode drop, and voltage drop attributable to anode effects. In advanced Hall-Héroult cells, the total cell voltage is about 4.1 volts. To match or exceed the energy efficiency of Hall-Héroult cells, the total voltage drop for an inert anode cell should be equal to or less than 4.1 volts, assuming that current efficiencies similar to those achieved in Hall-Héroult cells (about 96 percent or greater) are also attained. Clearly, these are going to be challenging targets to attain.

## 2. Wetted Cathode

The potential benefits of applying refractory hard metal (RHM) cathodes to reduction cells have been known for several decades. Several aluminum producers in Europe, Japan, Asia, and North America have sponsored research related to this concept. In this country, the Department of Energy has supported research on RMH cathodes for many years, at Kaiser Aluminum, Martin Marietta, or the Reynolds Metals Corporation. $TiB_2$ is being pursued as the material of choice for wettable cathodes.

Several features of the wetted cathode system provide a unique opportunity for designing cells in which the distance between the anode and cathode is significantly reduced, enhancing the thermal efficiency of the system. These features include the physical properties of $TiB_2$, high electrical conductivity, the chemical stability in aluminum and cryolyte electrolyte, and wettability by aluminum.

The economic potential of $TiB_2$ cathodes has been examined for two types of applications. A reduced anode-cathode distance (ACD) will reduce cell voltage. Potential energy savings are up to 1 kWhr/lb with these cathodes, even when used with conventional carbon anodes. Cell heat losses must be significantly reduced to achieve these savings; however, these losses tend to be limited by the side freeze constraint.

The second strategy for applying $TiB_2$ cathodes is to exploit the reduced ACD by increasing anode current density, i.e., increasing cell productivity. A significant reduction in ACD (e.g., from the standard 1.6 in to 0.75 in), at the same unit energy with an increase in current could lead to a 20 percent increase in productivity. This should prove to be an attractive economic return based on projected cathode and control costs.

Researchers looking for an economical application of inert anodes developed the notion of pairing an inert anode with an RHM cathode. Use of an RHM-inert anode bipolar electrode in a vertical array has appeal, at least on paper. Alcoa and Northwest Aluminum have conceived of vertical bipolar electrode cells, and have been awarded patents for their work. Comalco has demonstrated that $TiB_2$ materials can have a lifetime of more than two years, but a number of problems remain, including the following:

1. There is need for technology beyond a simple wettable cathode to operate at a significantly reduced ACD.
2. Wettable surfaces must be planar, i.e., devoid of sludge or frozen materials.
3. Anodes must be or must become precisely aligned and adjusted with great precision.

4. $TiB_2$ materials must maintain structural integrity during cell start-up, during normal operations, and during upset conditions.
5. $TiB_2$ materials must maintain chemical stability over the life of the cell and maintain their wetting characteristics. It is known that extended exposure of $TiB_2$ materials to oxidizing conditions at high temperatures can lead to the loss of wetting.
6. $TiB_2$ materials must be replaceable if parts fail prior to complete cell failure.
7. A $TiB_2$ cell operating at a reduced ACD with a drained cathode presents new problems in cell control. Alumina feed control must be very precise to minimize anode effects and eliminate sludge. Cell heat balance control has a new dimension, given the lack of a traditional metal pad with its stabilizing influence.

However, it is clear that RHM cathodes are much closer to commercialization than inert anodes. DOE is currently funding a team effort on RHM cathode research that includes Reynolds, Kaiser, and ART, a materials supplier.

The RHM cathode development program represents a significantly lower economic risk than the inert anode program. The TWG recommends that R&D in the area of RHM cathode development continue.

## 3. Metal Quality

The success of an aluminum reduction cell incorporating an inert anode will be judged by the impact of the technology on the kWh/lb and cost/lb of aluminum produced, if critical quality parameters are met. The TWG believes that barring regulatory mandate or fees on greenhouse gases, primary aluminum producers will only be interested in a revolutionary new cell based on inert anode technology if it decreases cost and/or energy requirements of the aluminum produced by at least 10 percent compared to conventional state-of-the-art technology. These parameters would justify the commercial risk and change-over expenses. Unfortunately, it is very difficult for the typical researcher to use these system performances or economic metrics when judging results of bench-scale experiments to evaluate potential inert anode materials. For simplicity, many laboratories use either **metal purity** or **wear rate** (also referred to as attrition or dissolution or corrosion rate) as a screening metric.

While such parameters are much easier to use as a relative developmental guideline in the laboratory than kWh/lb or cost/lb, they may prove to be misleading depending on the mechanism of wear, as discussed in Appendix A-10.

Based on the patent and literature survey conducted, at least a dozen failure modes were identified for the various inert anodes studied. An inert anode material (and encompassing cell) that produces aluminum that fails to meet existing quality standards will not be successful unless there is a reliable, cost-effective method for adequately removing the relevant impurities.

Researchers should emphasize the metric for metal purity in screening experiments in preference to that for wear rate, particularly where the failure mechanism and attrition mode are not thoroughly understood. The TWG concludes that the 10 mm/yr maximum wear rate cited in the *Inert Anode Roadmap* is not generally appropriate. In order to estimate the maximum acceptable rate of attrition of a new inert anode material, while staying within the aluminum-standards limits, researchers must include the impact of impurities released from the alumina, cathode, and other cell materials.

## Metal Purity Requirements

The American National Standard Designation System for Unalloyed Aluminum (ANSI H35.4), customarily known as the P-system, was developed as a designation for the purity of unalloyed aluminum. It includes the "workhorse" designation, P1020A, which can be used for most of the industry's requirements. The designation specifies limits for silicon (0.10 percent), iron (0.20 percent), zinc (0.03 percent), gallium (0.04 percent), and vanadium (0.03 percent). Depending on the end application, additional restrictions for certain impurities may be imposed on the producer, although these are seldom a practical problem for a conventional primary plant. It is conceivable that an unusual inert anode material could pose a problem. Examples of additional restrictions that may be placed on the producer include the following:

- For packaging and container uses: limits for beryllium (0.0001 percent), arsenic (0.01 percent), and lead, cadmium, mercury, and chromium (0.01 percent combined total)
- For premium casting applications: limit for phosphorus (0.001 percent) to avoid detectable adverse effects on strontium-modified microstructures
- For fracture-sensitive aircraft alloys: uses more restrictive P0507B or P061B designation with additional limits on iron (0.04 to 0.08 percent), titanium (0.06 percent), and manganese (0.06 percent)
- For electrical applications: uses more restrictive P0303B designation with added limits on manganese (0.01 percent), chromium (0.01 percent), boron (0.05 percent), and copper (0.05 percent)
- For welding electrode, rod, or wire: limit for beryllium (0.007 percent)
- For bright finish alloys: lower limits on silicon (0.08 percent) and iron (0.1 percent)
- For general applications such as in the construction, automotive, marine, and other sectors: limits on certain elements such as calcium and sodium (0.0007 percent or lower) to improve fabrication
- In certain sensitive applications, even more conservative limits for certain elements have been suggested: arsenic (0.002 percent), beryllium (0.0001 percent), cadmium (0.001 percent), cobalt (0.0001 percent), mercury (0.001 percent), lithium (0.0001 percent), lead (0.0005 percent), and antimony (0.001 percent)

The different alloying elements in aluminum, alone or in combination with another element, may be suitable for some applications but not for others. The chemical composition limits, including the maximum limit for certain elements, are always disclosed when an alloy is proposed for registration. However, the maximum tolerable limit of some elements is proprietary information and considered a competitive advantage. In these cases, the limits should be kept as low as possible.

The TWG believes that the impurity levels set for a given end-market application within any future inert-anode-based reduction plant will be comparable to those of P1020A, with the additional contamination limits appropriate for that end market. Consequently, these impurity levels should also be considered the criteria for potential inert anode materials.

### Additional Refining Steps

Finally, it should be mentioned that the foregoing arguments ignore adding refining steps to bring anode-derived impurities down to acceptable levels. Although such steps would increase the cost of producing the aluminum, in some cases these additional costs could be more than offset by the cost-savings or other benefits of using the inert anodes in the reduction process. Such add-on refining steps would be considered on an element-by-element basis, in terms of the amount of impurities to be extracted and the maximum amount of refining that can be achieved. Initially, potential materials should be evaluated without considering add-on processes so that competitive reduction technologies are considered on an equal basis. Industry is likely to prefer using inert anodes that are slightly more costly but that produce relatively pure metal, rather than inert anodes that cost less but corrode and produce impurities that must then be removed in a secondary process (at a cost equivalent to the higher-priced anodes). Any add-on process adds its own set of potential complications and unexpected costs.

# CHAPTER V—ECONOMIC AND ENVIRONMENTAL IMPLICATIONS OF THE SYSTEMS APPROACH

A number of economic and environmental implications can be drawn concerning the deployment of inert anodes. Before discussing these implications, several assumptions should be made. For example, it is assumed that a new electrolytic process system has been developed that will utilize an inert anode, a wettable cathode, and all the other design innovations mentioned in this study. The new system will be commercialized as a technology for use in a greenfield aluminum smelter. It is also understood that the search for the inert anode was driven by the desire to reduce emissions in the production of primary aluminum. Refer to Appendix 8 for a list of references cited by number in the text.

## 1. Economic Implications

The economic evaluation focuses on the potential for deploying inert anodes. It is assumed that this new technology will require a capital investment similar to that of a Hall-Héroult smelter of approximately $1 billion to $2 billion for a system operating at a capacity of 300,000 ton/year at 300 KA.

A cost model has been developed using these parameters that compares the costs of inert anode materials and their fabrication with the costs of typical conventional carbon anode cells. Average consumption rates for carbon anodes are about 0.5 pounds of carbon consumed per pound of aluminum produced. According to the *Aluminum Technology Roadmap*, the cost of carbon is about $120 per ton of aluminum produced or $240 per ton of carbon consumed. Since a viable inert anode material has not yet been demonstrated, an attempt has been made to estimate maximum "ballpark" costs per pound of anode material that would be competitive with present costs for carbon. A range of variables for inert anode materials has been assumed. These include the following:

- Inert anode thickness, 1 in to 10 in
- Inert anode material density, 0.09 to 0.27 $lb/in^3$
- Inert anode operating life before replacement, 1 year to 10 years

A summary of the range of predicted maximum costs for inert anode materials that permit anode operating costs of less than $120/ton Al are shown in Table V-1, below. It can be seen that inert anode systems using thin anode plates of low density materials that operate for long periods of time are still economical if expensive raw materials are used for the anode. On the other hand, systems with anodes that are thicker, of higher density, and shorter operating life can only be competitive based on the use of relatively inexpensive material systems for the inert anode.

The major cost-related hurdle for deploying new greensite Hall-Héroult aluminum smelters is the required capital investment of $1 billion to $2 billion. A smelter based on an inert anode technology will not be an attractive investment risk unless the projected costs of investing in and operating it are less than (or equivalent to) the costs of a conventional smelter. Projections must also show the potential of the new technology to address major environmental issues.

**Table V-1. A Comparison of the Costs of Inert Anodes Based on the Thickness, Operating Life, and Density of the Anode**

| Inert Anode Thickness (in) | Inert Anode Operating Life (yr.) | Inert Anode Density (lb/in$^3$) | Maximum Inert Anode Cost ($/lb of IA material) |
|---|---|---|---|
| 1 | 10 | 0.09 | $264.26 |
| 10 | 10 | 0.09 | $26.43 |
| 1 | 5 | 0.09 | $132.13 |
| 10 | 5 | 0.09 | $13.21 |
| 1 | 5 | 0.27 | $44.04 |
| 10 | 5 | 0.27 | $4.40 |
| 1 | 2 | 0.27 | $17.62 |
| 10 | 2 | 0.27 | $1.76 |
| 1 | 1 | 0.27 | $8.81 |
| 10 | 1 | 0.27 | $0.88 |

Statements made by Jon-Harald Nilsen, President of Hydro Aluminium Metals Products, during the TMS meeting in San Diego, California, March 3, 1999, best summarize the economic potential for the deployment of new technologies in the primary aluminum sector:

> “We have made great technological progress over the years. But when you look at the data from the world aluminum industry, one observation that can be made is that the difference between the most advanced cell, or technology, and the industrial average has actually widened during the last decade(s).”
>
> “The technology forefront of the aluminum reduction technology is now some 20 years ahead of average. Big smelters are projects with an expenditure of towards USD 2 billion. Only a limited number of highly qualified and financially strong companies can even consider undertaking such projects.”

## 2. Macro Environmental Implications

Inert anode (IA) technology would have distinct advantages over traditional carbon-anode technology in reducing emissions during the production of primary aluminum. A number of specific environmental benefits have been projected for IA systems related to increased energy efficiency and decreased production of greenhouse gases. The Aluminum Association in conjunction with the U.S. Department of Energy has made the following “best estimates” of the quantitative value of these benefits:

- Reductions in greenhouse gases of 7 million metric tons of carbon equivalent in the United States

- Increases in energy efficiency of up to 25 percent (when an IA is used in conjunction with a stable, wetted cathode)

(They also cited the additional non-environmental benefits of reducing operating costs by up to 10 percent, and increasing productivity by up to 5 percent.)

## Emissions

Inert anode technology can potentially have an enormous positive impact on reducing emissions from the smelter. A discussion follows of each of the major gaseous emissions associated with conventional smelting processes.

### *Carbon Dioxide ($CO_2$)*

The Hall cell is a device for converting alumina into aluminum and carbon dioxide. The cell relies upon stoichiometric consumption of the anode in order to fuel the reaction. Carbon consumption rates average 0.45 lb carbon per pound of aluminum metal product. Replacing consumable carbon anodes with nonconsumable anodes would totally eliminate $CO_2$ emissions from the Hall cell. Instead, the anode by-product would be oxygen gas. If the energy efficiency of the inert anode is less than that of the conventional carbon anode, increased $CO_2$ emissions will be shifted to fossil power plants where they are used.

### *Perfluorocarbons ($CF_4$ and $C_2F_6$)*

When the Hall cell goes on anode effect, the electrochemical reaction on the anode shifts from the reaction with oxygen to the reaction with fluorine. When this occurs, the production of $CO_2$ falls off as the production of the perfluorocarbons (PFCs) $CF_4$ and $C_2F_6$ rises [3]. These gases have been implicated in climate change because of their potential to contribute to global warming [4]. Aluminum smelting is the most significant point source of PFC emissions [5]. Replacing consumable carbon anodes with nonconsumable anodes would totally eliminate PFC emissions from primary reduction cells.

### *Hydrogen Fluoride (HF)*

Hydrogen fluoride is formed by reactions between fluorides in the electrolyte and hydrogen present either as moisture in the cell or as a component of anode carbon [6]. Replacing consumable carbon anodes with inert anodes would totally eliminate the second source of hydrogen and should significantly reduce the first source, because the IA cells must be kept more tightly sealed to minimize heat losses.

### *Polycyclic Organic Matter (POM)*

POM is the generic term for a class of compounds produced during the manufacture and consumption of carbon anodes. POM compounds include polyaromatic hydrocarbons (PAHs) such as naphthalene, phenantrene, and benzopyrene [7]. The predominant source of POMs is the anode paste plant. Replacing consumable carbon anodes with nonconsumable anodes would dramatically reduce POM emissions from the smelter, although a small amount of POM would still be produced in the manufacture of cathode block and potliner. However, the rate of consumption of these cell elements is trivial in comparison to that of the consumable carbon anode.

### *Sulfur Dioxide ($SO_2$) and Carbonyl Sulfide (COS)*

Industrial carbon contains sulfur as an impurity. Depending on the grade of carbon feedstock, sulfur content can range from as low as 0.25 wt percent to as high as 5.0 wt percent [8]. During electrolysis, these organic sulfur compounds react with alumina in the bath to form $SO_2$ [9]. Sulfur can also react with the carbon anode during electrolysis to form carbonyl sulfide (COS), which may subsequently oxidize in air to $SO_2$ [10]. Replacing consumable carbon anodes with inert anodes would totally eliminate sulfur emissions from the primary reduction cell.

### *Particulates*

Particulate emissions from aluminum reduction operations include fine particles of alumina, fluoride components of the bath system, and ash components from carbon anode baking and anode consumption. Replacing consumable anodes with non-consumable inert anodes will mean the cell hooding can be opened less frequently and this should result in a marked reduction of particulate emissions.

## Energy Efficiency and Carbon Dioxide Production

The argument has been made that the carbon utilization efficiency in the Hall cell is around 45 percent, while in old carbon-fired, electric-generating facilities the figure is about 35 percent. Therefore, deploying nonconsumable anode technology, which consumes more energy than Hall-Héroult cells, would be **regressive** from the standpoint of greenhouse gas emissions.

Dr. Dewing raised the issue by stating that an IA-equipped smelter would require an additional volt due to thermodynamic and electrochemical realities (see Appendix A-4). Since this would require an increase in electrical energy consumption, the question becomes whether it is more efficient to burn the carbon in the power plant or in the Hall-Héroult cell. Others suggested that the added volt needed for IA utilization could be countered by efficiencies gained from reducing anode to cathode distance and improving cell insulation. Moreover, modern combined cycle steam and gas turbine power plants boast hydrocarbon conversion efficiencies in the range of 50 to 55 percent. Another consideration is that on a worldwide basis, 56 percent of electricity for aluminum smelting is supplied by hydro power.

## Technological Imperative

Inert anodes are highly attractive from an environmental perspective, although a number of collateral technical issues need to be addressed if the full attributes of IA technology are to be realized. Research must go beyond simply discovering a material that can serve as a substitute for carbon. A systematic study of the entire Hall cell must be undertaken, addressing such issues as the following:

- Cell design (size, shape, electrode configuration, electrical operating parameters, bath chemistry, and others)
- Insulation (i.e., optimization of thermal balance for greater operating freedom)
- Cell cover (enabling containment of certain fugitive emissions)
- Sensors and actuators (for more precise control of the anode/cathode distance)
- A method for maintaining the electrolyte close to saturation

# CHAPTER VI—RECOMMENDATIONS

Research on inert anodes for the electrolytic production of aluminum has spanned many years. Despite the high quality of the work and the dedication of the scientists and engineers involved, most of these efforts have in large part resulted in technical dead-ends, bench-scale successes that could not be translated into workable commercial scale-ups, or solutions that were too expensive. Several examples of these research efforts have been provided earlier in this report along with explanations for their lack of success. Future R&D on inert anodes should be cognizant of this history, at the very least. Furthermore, based on its review of past work and the varied expertise of its members, the TWG has concluded that any future research and development program on inert anodes will only be successful if researchers adhere to the following priorities:

## 1. Take a Systems Approach

As discussed in Chapter III, all of the elements of an electrolysis system–anode, cathode, electrolyte, container, power and feedstock delivery system, and product-extraction system–must be considered in designing and implementing a cost-effective inert anode. Good performance in a bench-scale screening test does not necessarily mean that a material that is a candidate for an inert anode will perform well in a commercial Hall-Héroult cell. A promising inert anode material will more likely succeed if it is developed in the context of a cell or system that works specifically with the new material.

Highest priority for R&D at this stage should be directed at identifying, developing, and proving enhanced inert anode materials that will meet the multiple requirements of the following:

- Long life in a cell environment
- Acceptable impurity levels for major applications
- Compatibility with overall cell system and materials
- High energy efficiencies
- Major reductions in greenhouse gases
- Viable capital and operating costs compared to alternative technologies

As soon as such materials are identified, partially developed, and tested, the remaining systems considerations must be integrated into the overall R&D effort in a parallel, timely manner.

## 2. Maintain Current Metal Quality Standards

The primary aluminum industry is built on the premise that it will produce adequately pure metal. As discussed in Chapter IV, purity standards were derived from the operating characteristics of cells using carbon anodes, with carbon and alumina feedstocks meeting specifications on purity. A successful inert anode will present a new paradigm that may include the introduction of elements into the product that have not all been previously considered or dealt with by the industry. The recommendation of the TWG is that the resultant metal purity be equal to or greater than that currently fulfilling the industry standards. To achieve this, the TWG agreed that the maximum effective wear rate of a "successful" anode must be at least one order of magnitude less than 10 mm/yr, which was the value recommended in the *Inert Anode Roadmap*. A further strong recommendation is to de-emphasize the use of the wear rate parameter and put more weight on the metal quality values.

### 3. Follow a "Gated" Approach to Inert Anode Development

The TWG recommends that a gated approach be used for the scale-up testing of potential inert anode materials. This approach would involve a demonstration stage using 100 amps for 100 continuous hours of operation, followed by tests at 1,000 amps for 1,000 continuous hours of operation, followed by tests at 5,000 to 10,000 amps for a period of continuous operation of at least six months' duration. This screening process should be conducted before production-scale prototypes are tested in a new cell design.

The TWG also recommends that a special test facility be established that will be available to carry out the preceding types of tests on candidate materials and assemblies for inert anodes in a consistent and unbiased manner.

In addition to these global recommendations, the TWG members agreed that future research efforts should also follow certain recommendations related to cell design. These more detailed recommendations are derived from lessons learned from the literature and the cumulative years of experience of the TWG members themselves. These issues have been given a good deal of attention in past inert-anode efforts and they will probably need to be addressed in any future developmental project.

### 4. Strongly Encourage Aluminum Industry Consortia for Inert Anode Programs

R&D programs entail relatively high projected costs and a long-term commitment with substantial risks. Many potential investigators cannot or will not participate at any meaningful level in projects related to inert anodes. Multi-company consortia should be encouraged to lessen the costs and risks to individual companies to allow the industry to move forward more effectively in this major technology. This approach is also likely to increase the abundance of useful ideas and achieve other synergistic benefits.

### 5. Set Priorities for Inert Anode Materials

All of the "inert" anode materials characterized to date have had various shortcomings with respect to attributes needed for commercial success. The greatest proportion of development work, to date, is based on copper-iron-nickel oxide cermet systems. After millions of dollars of R&D, significant progress has been documented in the areas of materials synthesis, property characterization and improvement, and cell design and testing. However, major challenges remain before their commercial viability and acceptance can be achieved. The TWG supports further R&D on this class of materials as long as innovations continue to be developed and there is solid progress in line with the most important hard-stage-gated performance objectives.

TWG participants also believe that because of the risk and uncertainty, at least two or three parallel approaches to developing an inert anode are needed to increase the probability of success. The *concept* of the self-passivating, metallic-alloy anode has several *potential* advantages over the cermet and mixed conductive oxide electrode approaches. These include (1) lower resistive losses within the anode itself; (2) more uniform current distribution; (3) better thermal shock resistance, fracture toughness, and tolerance to damage; (4) less susceptibility to grain boundary or porosity-related degradation; (5) ease of achieving high-quality, low-resistance anode connections; and (6) ease of fabrication. Only very limited experimental work has been carried out, with mixed results. Nonetheless, further exploratory work on self-passivating metallic anodes with reasonably conductive film characteristics appears to be justified because of the potential conceptual advantages just cited and the magnitude of their impact if the anodes are successful.

Substantial work carried out until now on applied protective coatings for metallic anodes has led to limited successes at best. However, future novel approaches based on sound principles could warrant further support.

"Inert" anode systems based on two or more layers of "protective" applied coatings on a metal or alloy substrate, or monolithic ceramic anodes, appear to offer less promise of commercial viability based on information assessed by the TWG.

The Technical Advisory Committee of The Aluminum Association suggested that this report contain recommendations for the specific classes of materials that should be emphasized in future R&D work. Accordingly, the members of TWG were asked to rank their preference for three materials (cermets, metal oxides [ceramic], and metals [protected with in situ formed or applied coatings]. They were also asked to comment on what they saw as drawbacks in their second and third choices of materials. (Two individuals also chose to comment on the reasons for their first choice.)

The results of this poll are provided in Table VI-1. Seven members of TWG ranked the materials, and returned comments. Comments are quoted directly as they were received (with the exception that names of individuals and companies were removed to ensure anonymity, and a few acronyms were clarified), and immediately follow the table.

**Table VI-1. Materials Priorities of TWG for Future R&D on Inert Anodes**

| **Inert Anode Material Classes** | **How the Respondents Voted** | | | **Priority** |
|---|---|---|---|---|
| | **Ranked lst** | **Ranked 2nd** | **Ranked 3rd** | |
| Metals (protected with coatings) | 5 | 2 | 0 | 1st |
| Cermets | 2 | 5 | 0 | 2nd |
| Metal oxides (ceramic) | 0 | 0 | 7 | 3rd |

## Comments Received

### *Cermets*

*Cermets are attractive at first glance as they seem to combine the advantages of two classes of materials, namely, metals (desirable for their high electrical conductivity) and ceramics (desirable for their putative chemical inertness). In reality, the chain is as strong as its weakest link, and so the poor electrical conductivity of the ceramic phase becomes an issue unless one is willing to have so high a metal fraction that the cermet is effectively a metal anode containing a dispersion of oxide particles. To my knowledge, the cermets under investigation are dominantly ceramic with a dispersion of metallic phase. Hence, the poor electrical properties of the ceramic are an issue. Furthermore, the continuity of the ceramic phase leads to the question of ease making reliable electrical contact to the current lead. In parallel, there is the question of thermal shock resistance. Tests done at [one company] about 10 years ago showed that even relatively small electrodes (blocks measuring about 1 ft on edge) needed to be lowered into the Hall bath over a 24-hour period in order to avoid shattering from thermal shock. Furthermore, there is the question of stability of the metallic phase. What protects it? Lastly, there is the question of cell start-up. With carbon electrodes, the procedure involves placing carbon block between the anode and the floor. The cell is charged with electrolyte (which is solid of course at room temperature). Current passing between the anode and the floor causes the carbon blocks to glow and turn into heaters, which slowly melt the electrolyte. This is well and good for carbon anodes. But when the anodes are nickel ferrite or something of the sort, at 1000° C these materials will undergo carbothermic reduction. I could go on but suffice it to say there are problems with cermets. Just the same, cermets have their proponents, but I do not count myself among this group.*

*The cermets, as composites, will always have boundaries between the constituent particles. To date, these have, even at >97% theoretical density, proved to be the mechanism of destruction. Either gases permeate setting up corrosion/chemical attack/creation of new material leading to a volume expansion in the grain boundary, or molten bath permeates after the metal component has been extracted from the surface and sets up destruct modes similar to those just cited or potential gradients over the electronically differing materials initiates migration of "ions" or "radicals."(To wit, the gradation in composition from SEMs of used cermet anodes.)*

*Cermets combine the good features of metals (conductivity, toughness) with the good features of oxides (some have good solubility). Unfortunately, they also combine the bad features of each. To date, the experience with cermets indicates the bad features of the oxide* *components primarily limit success. These are (1) unacceptable solubility mainly due to difficulty in maintaining alumina saturation and uniform current density, (2) cracking due to mechanical and thermal shock, and (3) difficulty/cost in manufacturing specific shapes. An example of this is the [cermet system] containing Cu. Cu turns out to be a reasonably good metal phase, but only if it is "well-contained" within the ceramic matrix. If the electrolyte penetrates or dissolves the oxide, the Cu phase will corrode. It would seem to be more promising to use a direct approach: find a metal or alloy that gives rise to an oxide with good stability in the electrolyte. Part of the solution will also involve cell design no matter what material is selected.*

*The cermet anodes described in the literature to date are based on two-phase, metal-bonded ceramic materials. The relative reactivities of individual phases during operation will be critical. Preferential attack of either phase would lead to problems similar to carbon dusting in Hall-Héroult cells when the pitch binder phase is attacked faster than the coke aggregate phase. The question raised by others in the TWG are also issues that I second.*

### ***Metal oxides (ceramic)***

*Metal oxides are attractive because of their putative chemical inertness, but their electrical and thermomechanical properties make them a poor choice for this application. Many of the same problems cited above for cermets afflict metal oxide anodes.*

*Metal oxides, other than tin, have too high electrical resistance. Tin oxide puts too much tin into the aluminum. The tolerance for tin is very low.*

*Ceramics can only work if they are highly conductive. They are not. Those that are, are really semi-conductors. Electronic conduction can be improved by doping. However, all of these oxides have finite solubility in molten cryolite despite being anodically polarized. They are resistive so that any feasible [IA] has to be a very thin layer, thus dictating a limited life and, probably, a very expensive manufacturing cost. This also implies that the oxide (mixed oxide) has to be on a substrate for which there would have to be perfect compatibility of thermal expansion and the substrate would have to be resistive to AlF (g) and nascent oxygen since it is unlikely that the oxide layer would be 100% impermeable. Anything that has to be put together from particles has to be suspect for long term life. That is why I believe if there is to be a successful [IA], it will likely be based upon a metal or alloy in which there should be negligible porosity, continuous electronic conductivity, machinability, and no problem with differential CTEs. There is the opportunity to take advantage of some thermodynamics relative to* *alumina and several of the candidate metals have oxides that are both low in solubility in cryolite, semiconducting, and of higher negative free energy of formation (ΔG) than alumina.*

*Oxides tested to date are least promising because they are generally too resistive, and not tough enough to withstand mechanical and thermal shocking that will inevitably be part of cell operation. This is not to say that a new ceramic material may not possess all of the required characteristics of an inert anode, only that, at this point in time, achieving these goals appears more likely with a metal or metal-containing anode, or alternatively, developing a radically different cell design.*

*Metal oxide anode workability will require a compromise between mechanical, thermal, electrical, and chemical properties. Ceramics are generally brittle and would not withstand the handling operations required for cell installation, start-up, and operation. Most ceramics will thermal shock during operations. Most ceramics have very high electrical resistivities. This would lead to very high anode voltage drops at nominal operating current densities unless the oxides were extremely thin. Even if sparingly soluble in molten bath, dissolution over time would be a significant issue. Finally, because the fluorides of most metals are thermodynamically more stable than the oxides, there will be serious issues related to reactions between the metal oxide of the anode and fluoride constituents of the bath (probably* $AlF_3$*) through reactions such as*

$$3MO + 2AlF_3 \dashrightarrow Al_2O_3 + 3MF_2$$

*Once formed, it is likely that the metal fluorides will be quite soluble in the bath leading to a continuing erosion of the anode.*

### *Metals (protected with coatings)*

*Coatings dissolve and must be continually re-established. It is difficult to control coating thickness. If coatings are too thin, they do not provide adequate protection. If the coatings become too thick they cause excessive voltage drop. Thick coatings also tend to spall and contaminate the aluminum.*

*In my judgment, only metals have a reasonable chance of satisfying the stringent chemical, electrochemical, electrical, and thermomechanical requirements of a Hall-cell anode. Clearly, the electrode-electrolyte interface needs to be treated to impart the necessary level of protection against chemical and electrochemical destruction without adding a burdensome level of electrical resistance. [A TWG member] has advocated the use of alloying elements such as aluminum to form a thin reaction layer consisting primarily of alumina. [Another expert] has* *advocated the use of a protective coating. There may be other approaches, but unless the proposed inert anode is based upon the concept of a metal alloy monolith, I have little faith in the success of the enterprise.*

*For an oxide-protected metal anode to work, the oxide film must be stable relative to operations in a molten fluoride bath at elevated temperatures. Ideally, the film should reach a limiting (stable) thickness. During operations, if there is mechanical damage (through spalling, thermal shock, handling, etc.) or chemical damage (through dissolution in the bath, reaction with the bath, continuing oxidation, etc.) to the film (or parts of the film), such damage must be self-repaired through reaction with the oxygen being released by the electrolysis process. Through whatever set of conditions, the rates of film damage and film growth must be equivalent. Otherwise, the film will grow or shrink continuously. From a chemical point of view, the stability of a protective oxide film on a metal anode will be subject to the same questions as an oxide anode.*

*While still quite uncertain, the most promising opportunities for inert anode materials probably lie in a breakthrough in certain metallic alloy anodes with balanced self passivation and dissolution characteristics. Applied "protective" coatings (including multi-layer ones) do not appear at this stage to be as promising for long-term durability and commercial viability.*

## 6. Develop and Document an Understanding of the Following Basic Cell Operating Parameters:

- The critical current densities for the initiation of anode effect as a function of dissolved alumina content in the bath, of bath ratio ($NaF/AlF_3$), of bath additives ($CaF_2$ , $MgF_2$, LiF, etc.), and of operating temperature
- Similarly, for a given anode current density, the minimum alumina concentration before the initiation of anode effect
- The impact of brief periods of operation under anode effect on wear, erosion, or corrosion of the inert anode material
- For IA cell design concepts:
  – The kinetics of alumina dissolution under the operating conditions proposed with particular emphasis given to the effects of the fine, foam-like bubbles of oxygen anode gas compared to the larger bubbles of $CO_2$ typical of Hall-Héroult cells
  – The effect of excess alumina additions (supersaturation) on short-term and long-term cell operations with particular emphasis placed on the formation of sludge deposits and means for removing such deposits once formed
  – Demonstration that a slurry can be maintained for long-term operations without the formation of sludge deposits (for IA cell design approaches incorporating the use of "slurry" [supersaturated] electrolytes)

## 7. Reduce Anode to Cathode Distance and Improve Anode to Cathode Separation Control

Since both the theoretical minimum energy and the decomposition voltage for inert anode cells are much higher than Hall-Héroult cells, the total required voltage must be decreased in other parts of the cell to achieve break-even energy consumption levels. Reduction of the anode-cathode voltage through reduced anode-cathode distance is typically selected for such voltage (and energy) savings.

## 8. Improve Alumina Concentration Control

In the vast majority of papers describing inert anode materials, a near-saturation concentration of alumina (in the molten cryolite) is recommended to keep the solubility of the anode's oxide components (or the anode's protective film) at acceptably low levels. Unless a non-ceramic composition is developed for the inert anode, this requirement will probably have to be addressed again. To enhance the life and performance of the inert anode will require cell designs and operating procedures that maintain the electrolyte system at optimum concentrations of alumina. There will be serious problems if the concentration levels of alumina are inadequately controlled. Undersaturation will create "anode effects" with the generation of excessive cell voltage and heat. Oversaturation will lead to "sludge" formation, with potentially severe consequences. Operating cells with optimum concentrations of alumina requires a completely new set of procedures and guidelines, with which the industry is unfamiliar. Sensors and control devices that work effectively at high concentrations of alumina will be required. Development of this protocol and equipment will have to be part of any research effort involving anodes whose performance relies on a specific alumina concentration.

## 9. Improve Cell Insulation Materials and Insulation Design

Hall-Héroult cells operate today with frozen sidewalls of the cryolite bath. The frozen sidewalls protect the pot side lining from erosion. Maintaining the desired sidewall configuration requires careful design and control of sidewall heat losses. As with all other cell heat losses, lost heat must be supplied from increased cell voltage (IV heat generation). The development of sidewall materials with improved insulating abilities that are also more erosion resistant could help offset the increased energy requirements for an inert anode process. Similar arguments apply to the use of improved insulating materials for the cell cover. Once a very promising inert anode material is found, significant effort on improved insulation is justified.

## 10. Review Current Thinking with Regard to Anode Current Density Limits

Future research programs should consider the possibility of encountering wider ranges of anodic current density. The reasons for this are obvious: (1) There are power interruptions in any grid system, and (2) there are variations in current in any industrial pot line. Even in a series of "advanced" enclosed cells, with stable anodes and cathodes, the potential will exist for variations in internal resistance and hence, in line current. Therefore, an inert anode that cannot survive unless a certain (non-zero) current density is imposed will probably fail in the real world if the power is interrupted (almost certain to occur at some time) or if the established operating current density is momentarily exceeded (also probable). It is not constructive to simply advocate that an inert anode must operate in a range of current density. It must be demonstrated how these constraints will impact various aspects of the design, stability, and operation of the reactor. If the current densities are significantly less than the conventional cell limit, the inert anodes must be coupled with radically redesigned cells to offset the loss of production or they will be an obvious stumbling block for deploying the new technology. Clearly, if an inert anode will only survive by lowering the current density, any proposal must contain practical new cell designs that compensate for this production loss.

## 11. Encourage Deployment of Recent Cathode Developments

$TiB_2$ wettable drained cathodes and cathode coatings should be ready for deployment when cell operating protocols and durability issues are resolved. There would be energy and economic advantages to incorporating these developments into a Hall-Héroult cell. There would be further advantages if concepts of inert anode systems could also be incorporated. This combination will enhance the goals of the inert anode program.

## 12. Evaluate Novel Approaches

The various “conventional” inert anode systems proposed and/or partially developed to date still present a high degree of uncertainty and risk and any of them would require considerable future RD&D resources to have a chance to achieve commercial viability.

Accordingly, the TWG encourages further “out of the square” thinking and limited initial exploratory efforts on novel unconventional approaches including, for example, the solid oxide fuel cell derivative concept cited in an earlier chapter of this report.

# APPENDIX A-1

# PATENT AND LITERATURE SURVEY INVENTORY

# Patent Survey Inventory

**U. S. patents related to inert anodes for use in aluminium production, sorted by patent number**

| Interest | Type | Patent # | Title | Inventors | Asignee |
|---|---|---|---|---|---|
| | | EP0197003 | Elektrolyswanne für die Hertstellung von Aluminium | Scarpey, W., and Pawlek, R. | SCHWEIZERISCHE ALUMINIUM AG |
| | | EP0306101 | Non-consumable anode for molten salt electrolysis | Nguyenm T.; Lazouni, A.; and Doan, K. S. | ELTECH SYSTEMS CORPORATION |
| | | EP90/10735 | Anode substrate coated with rare earth oxycompounds | | |
| | | FR2,366,380 | Electrodes à base d'oxyde d'yttrium | | Diamond Shamrock Technologies S. A. |
| | | 3,400,061 | Electrolytic cell for production of aluminum and method of making same | Lewis, R. A.; Hildebrandt, R. D. | Kaiser Aluminum & Chemical Corporation |
| | | 3,433,749 | Glass electrode compositions | Nishimoto, K., and Iida, Y. | Matsushita Electric Industrial Co., Ltd. |
| | | 3,475,314 | Alumina reduction cell | Johnston, T. J. | Reynolds Metals Company |
| | | 3,502,553 | Process and apparatus for the electrolytic continuous direct production of refined aluminum and of aluminum alloys | Gruber, H. | |
| | | 3,661,736 | Refractory hard metal composite cathode aluminum reduction cell | Holliday, R. D. | Olin Mathieson Chemical Corporation |
| | | 3,666,654 | Furnaces with bipolar electrodes for the production of metals, particularly aluminum, through electrolysis of molten salts, equipped with auxiliary heating facilities | De Garab, G. O. | |
| | | 3,930,967 | Process for the electrolysis of a molten charge using inconsumable bi-polar electrodes | Alder, H. | Swiss Aluminium Ltd. |
| | | 3,960,678 | Electrolysis of a molten charge using incomsumable electrodes | Alder, H. | Swiss Aluminium Ltd. |
| | | 3,974,046 | Process for the electrolysis of a molten charge using inconsumable anodes | Alder, H. | Swiss Aluminium Ltd. |
| | | 4,002,551 | Process and apparatus for collecting the fumes given off during the production of aluminium in an electrolysis cell with a continuous anode | Duclaux, D.; Pontier, A. J. A.; and Ferret, G. P. | Aluminium Pechiney |
| | | 4,024,044 | Electrolysis cathodes bearing a mult-sprayed and leached nickel or coablt coating | Brannan, J. R., and I. Malkin | Diamond Shamrock Corporation |
| | | 4,039,401 | Aluminum production method with electrodes for aluminum reduction cells | Yamada, K.; Hashimoto, T.; Horinouchi, K. | Sumitomo Chemical Company |
| | | 4,049,511 | Protective material made of corundum crystals | Alder, H.; and Boving, H. | Swiss Aluminium Ltd. |
| | | 4,057,480 | Inconsumable electrodes | Alder, H. | Swiss Aluminium Ltd. |
| | | 4,069,058 | Porous silicon oxynitride refractory shapes | Washburn, M. E. | Norton Company |
| | | 4,108,741 | Process for production of aluminum | Tsumura, Y. | Mitsui Aluminum Co., Ltd. |

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| | | 4,121,983 | Metal production | Kinosz, D. L.; Das, S. K.; and Coffman, R. L. | Aluminum Company of America |
| | | 4,140,595 | Use of materials in molten salt electrolysis | Russell, A. S., and E. H. Rogers | Aluminum Company of America |
| | | 4,146,438 | Sintered electrodes with electrocatalytic coating | de Nora, V.; Spaziante, P. M.; and Nidola, A | Diamond Shamrock Technologies S. A. |
| | | 4,151,061 | Alkuminum electrolytic cell | T\Ishikawa, T.; Konda, S.; Iuchi, T.; and Ichikawa, H. | Nippon Light Metal Company Limited |
| | | 4,159,928 | Process for production of aluminum | Tsumura, Y. | Mitsui Aluminium Co., Ltd. |
| | | 4,170,533 | Refractory article for electrolysis with a protective coating made of corundum crystals | Alder, H.; and Boving, H. | Swiss Aluminium Ltd. |
| | | 4,173,518 | Electrodes for aluminum reduction cells | Yamada, K.; Hashimoto, T.; Horinouchi, K. | Sumitomo Aluminum Smelting Company, Limited |
| | | 4,179,345 | Controlled wettability graphite electrodes for selective use in electrolysis cells | Das, S. K. | Aluminum company of America |
| | | 4,179,346 | Selective use of wettable and non-wettable graphite electrodes n electrolysis cells | Das, S. K.; and P. J. Boget | Aluminum Company of America |
| | | 4,187,155 | Molten salt electrolysis | de Nora, V.; Spaziante, P. M.; and Nidola, A. | Diamond Shamrock Technologies |
| | | 4,219,400 | Electrolysis cell | Treptow, W.; Wunsch, G.; Meyer, H.; and Csizi, G. | BASF Aktiengesellschaft |
| | | 4,224,128 | Cathode assembly for electrolytic aluminum reduction cell | Walton, R. J. | PPG Industries, Inc. |
| | | 4,233,148 | Electrode composition | Ramsey, D. E., and Gridstaff, L. I. | Great Lakes Carbon Corporation |
| | | 4,243,502 | Cathode for a reduction pot for the electrolysis of a molten charge | Kugler, T. | Swiss Aluminium Ltd. |
| | | 4,251,344 | Porous nickel coated electrodes | Needles, C. R. S. | E. I. Du Pont de Nemous and Company |
| | | 4,285,785 | Metal producing method | Sullivan, D. A., Jr. | Aluminum Company of America |
| | | 4,308,113 | Process for producing aluminum using graphite electrodes having reduced wear rates | Das, S. K. | Aluminum Company of America |
| | | 4,308,114 | Electrolytic production of aluminum using a composite cathode | Das, S. K.; Foster, P. A., Jr.; and Hildeman, G. J. | Aluminum Company of America |
| | | 4,308,115 | Method of producing aluminum using graphite cathode coated with refractory hard metal | Foster, P. A., Jr.; Das, S. K.; and Becker, A. J. | Aluminum Company of America |
| | | 4,308,116 | Method and electrolyzer for production of magnesium | Andreassen, K. A.; | Norsk Hydro a.s. |

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| | | | | Bøyun, Øystein; Johnsen, H. K.; Ognedal, L. B.; and Solheim, P. R. | |
| | | 4,324,585 | Process for manufacture of aluminum | Hass, H. B. | |
| | | 4,357,226 | Anode of dimensionally stable oxide-ceramic individual elements | Alder, H. | Swiss Aluminium Ltd. |
| | | 4,362,647 | Electrode and the method for producing the same | Torigai, E.; Wakabayashi, N.; Kawami, Y.; Kamijo, E.; Nishimoto, T.; and Tani, K. | Sumitomo Ekectrc Industries<br>Agency of Indusfrial Science and Technology |
| | | 4,374,050 | Inert electrode compositions | Ray, S. P. | Aluminum Company of America |
| | | 4,374,761 | Inert electrode formulations | Ray, S. P. | Aluminum Company of America |
| | | 4,376,690 | Cathode for a cell for fused salt electrolysis | Kugler, T. | Swiss Aluminium Ltd. |
| | | 4,379,033 | Method of manufacturing aluminum in a Hall-Heroult cell | Clark, J. M.; Secrist, D. R. | Great Lakes Carbon Corporation |
| | | 4,392,925 | Electrode arrangement in a cell for manufacture of aluminum from molten salts | Alder, H.; Schalch, E. | Swiss Aluminium Ltd. |
| | | 4,396,481 | Eleotrolytic cell for the production of aluminum by fused salt electrolysis | Pawlek, R.; and Lagler, P. | Swiss Alminium Ltd. |
| | | 4,396,482 | Composite cathode | Das, S. K.; Foster, P. A., Jr.; and Hildeman, G. J. | Aluminum Company of America |
| | | 4,397,729 | Cermet anode electrowining metals from fused salts | Duruz, J.-J. R., and J. P. Derivaz | Diamond Shamrock Corporation |
| | | 4,399,008 | Composition for inert electrodes | Ray, S. P. | Aluminum Company of America |
| | | 4,402,808 | Gasket for sealing joints between electrodes and adjacent cell lining and for improving bath circulation in electrolysis cells | McMonigle, M. J. | Aluminum Company of America |
| | | 4,430,189 | Method of manufacturing aluminium in a Hall-Heroult Cell | Clark, J. M.; Secrist, D. R. | Great Lakes Carbon Corporation |
| | | 4,436,597 | Method and apparatus for producing aluminum in an electrolysis cell with tile lining | Hartley, L. A. | Aluminum Company of America |
| | | 4,437,950 | Method of controlling aluminum electrolytic cells | Arita, Y.; Seo, Y. | Itsubishi, Keikinzoku Kabushiki Kaisha |
| | | 4,439,382 | Titanium diboride-graphite composites | Joó, L. A..; Tucker, K. W.; and McCown, F. E., Jr. | Great Lakes Carbon Corporation |
| | | 4,443,314 | Anode assembly for molten salt electrolysis | Secrist, D. R.; Clark, J. M.; and Grindstaff, H. E. | Great Lakes Carbon Corporation |
| | | 4,450,061 | Metal stub and ceramic body electrode assembly | Rolf, R. L. | Aluminum Company of America |
| | | 4,457,811 | Process for producing elements from a fused bath using a metal strap and ceramic | Byrne, S. C. | Aluminum Company of America |

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| | | | electrode body nonconsumable electrode assembly | | |
| | | 4,459,195 | Cell for the electrolytic production of metals from metal halides | Bertaud, Y. | Aluminum Pechiney |
| | | 4,465,581 | Composite of TiB.sub.2 -graphite | Juel, L. H.; Joó, L. A.; and Tucker, K. W. | Great Lakes Carbon Company |
| | | 4,468,298 | Diffusion welded nonconsumable electrode assembly and use thereof for electrolytic production of metals and silicon | Byrne, S. C.; and Vasudevan, A. K. | Aluminum Company of America |
| | | 4,468;299 | Friction welded nonconsumable electrode assembly and use thereof for electrolytic production of metals and silicon | Byrne, S. C.; Ray, S. P.; and Rapp, R. A. | Aluminum Company of America |
| | | 4,468,300 | Nonconsumable electrode assembly and use thereof for the electrolytic production of metals and silicon | Byrne, S. C.; and Ray, S. P. | Aluminum Company of America |
| | | 4,478,693 | Inert electrode compositions | Ray, S. P. | Aluminum Company of America |
| | | 4,488,117 | Method of measuring backelectromotive forces of aluminum electrolysis cells | Seo, U. | Mitsubishi Keikinzoku Kogyo Kabushiki Kaisha |
| | | 4,488,955 | Sub-cathodic shield with deformable zones for Hall-Heroult electrolysis cells | Bertaud, Y.; and Leroy, M. | Aluminium Pechiney |
| | | 4,491,510 | Monolithic composite electrode for molten salt electrolysis | Clark, J. M.; and Secrist, D. R. | Great Lakes Carbon Corporation |
| | | 4,504,366 | Support member and electrolytic method | Jarrett, N.; and Hornack, T. R. | Aluminum Company of America |
| | | 4,504,369 | Method to improve the performance of non-consumable anodes in the electrolysis of metal | Keller, R. | |
| | | 4,529,494 | Bipolar electrode for Hall-Heroult electrolysis | Joó, L. A.; Secrist, D. R.; Clark, J. M.; Tucker, K. W.; and Shaner, J. R. | Great Lakes Carbon Corporation |
| | | 4,532,017 | Floating cathode elements based on electrically conductive refractory material, for the production of aluminum by electrolysis | Keinborg, M.; Varin, P.; Bertaud, Y.; and Leroy, M.. | Aluminium Pechiney |
| | | 4,544,457 | Dimensionally stable drained aluminium electrowinning cathode method and apparatus | Sane, A. Y.; Wheeler, D. J.; Kuivila, C. S. | Eltech Systems Corporation |
| | | 4,544,469 | Aluminum cell having aluminum wettable cathode surface | Boxall, L. J.; Buchta, W. M.; Cooke, A. V.; Nagle, D. C.; and Townsend, D. W. | Commonwealth Aluminum Corporation |
| | | 4,544,472 | Electrode coating and coated electrodes | Reven, F. V. | Nalco Chemical Company |
| | | 4,552,630 | Ceramic oxide electrodes for molten salt electrolysis | Wheeler, D. J.; Duruz, J.- | ELTECH Systemds Corporation |

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|  |  |  |  | J. R.; Sane, A. Y.; and Derivaz, J.-P. |  |
|  |  | 4,581,117 | Durable electrode for electrolysis and process for production thereof | Asano, H.Shimamune, T.; Hirao, K.; and Hirayama, R. | Permelec Electrode Ltd. |
|  |  | 4,582,553 | Process for manufacture of refractory hard metal containing plates for aluminum cell cathodes | Buchta, W. M. | Commonwealth Aluminum Corporation |
|  |  | 4,582,585 | Inert electrode composition having agent for controlling oxide growth on electrode made therefrom | Ray, S. P. | Aluminum Company of America |
|  |  | 4,584,084 | Durable electrode for electrolysis and process for production thereof | Asano, H.; Shimamune, T.; Hirao, K.; and Hirayama, R. | Permelec Electrode Ltd. |
|  |  | 4,585,618 | Cermets and their manufacture | Fresnel, J.-M.; Debély, P.-E.; and Wesfler, J.-P. | ELTECH Systems Corporatioin |
|  |  | 4,588,485 | Process for the production of a metal by electrolyzing halides in a molten salt bath, comprising a simultaneous and continuous double deposit | Cohen, J.; and Lorthioir | Pechiney |
|  |  | 4,592,812 | Method and apparatus for electrolytic reduction of alumina | Beck, T. R.; Brooks, R. J. | Electrochemical Technology Corp. and Brooks Rand, Ltd. |
|  |  | 4,596,637 | Apparatus and method for electrolysis and float | Kozark, R. L.; Hormakc, T. R.; and Harrett, N. | Aluminum Company of America |
|  |  | 4,602,990 | Low energy aluminum reduction cell with induced bath flow. | Boxall, L. G.; Gamson, B. W.; Green, J. A. S.; and Traugott, S. C. | Commonwealth Aluminium Corporation |
|  |  | 4,610,726 | Dense cermets containing fine grained ceramics and their manufacture | King, H. L. | EltechSystems Corporatioin |
|  |  | 4,614,569 | Molten salt electrowinning method, anode, and manufacture thereof | Duruz, J. J.; Derivaz, J.-P.; Debely, P.-E.; and Adorian, I. L. | Eltech Systems Corporation |
|  |  | 4,620,905 | Electrolytic production of metals using a resistant anode | Tarcy, G. P.; Gavasto, T. M.; Ray, S. P. | Aluminum Company of America |
|  |  | 4,639,304 | Apparatus for determination of aluminum oxide content of the cryolite melt in aluminum electrolysis cells | Báder, I.; Berecz, E.; Szina, G.; Horváth, J. | Nehezipari Muszaki Egyetem |
|  |  | 4,650,552 | Electrolytic production of aluminum | de Nora, V.; Gauger, J. F.; Fresnel, J.-M.; Adorian, I. L.; Duruz, J.-J. | Eltech Systems Corporation |
|  |  | 4,657,643 | Process for continuously controlling the proportion of metal dissolved in a bath of molten salts and the application thereof to the continuous feed of an electrolysis cell | Armand, M.; and Garnier, J.-P. | Pechiney |

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|  |  |  | with salts of said metal |  |  |
|  |  | 4,664,760 | Electrolytic cell and method of electrolysis using supported electrodes | Jarrett, N. | Aluminum Company of America |
|  |  | 4,668,351 | Method of producing aluminum | Dewing, E. W., and Reesor, D. N. | Alcan International Limited |
|  |  | 4,670,110 | Process for the electrolytic deposition of aluminum using a composite anode | Withers, J. C.; and G. V. Upperman | Metallurical, Inc. |
|  |  | 4,680,094 | Method for producing aluminum, aluminum production cell and anode for aluminum electrolysis | Duruz, J.-J. | ELTECH Systems Corporatioin |
|  |  | 4,681,671 | Low temperature alumina electrolysis | Duruz, J.-J. | ELTECH Systems Corporatioin |
|  |  | 4,683,037 | Dimensionally stable anode for molten salt electrowinning and method of electrolysis | Duruz, J. J. | ELTECH Systems Corporatioin |
|  |  | 4,717,692 | Composites comprising one or more interwoven matrix compositions each containing a refractory hard metal and method of forming same | Ray, S. P. | Aluminum Company of America |
|  |  | 4,737,247 | Inert anode stable cathode assembly | Jarrett, N.; Brown, M. H. | Aluminum Company of America |
|  |  | 4,824,531 | Electrolysis method and packed cathode bed for electrowinning metals from fused salts | Duruz, J.-J. R; and Derivaz, J.-P. | Eltech Systems Corporatioin |
|  |  | 4,919,771 | Process for producing aluminum by molten salt electrolysis | Wilkening, S. | VAW Vereinigte Aluminium-Werke AG |
|  |  | 4,929,328 | Titanium diboride ceramic fiber composites for Hall-Heroult cells | Besmann, T. M.; and Lowden, R. A. | Martin Marietta Energy Systems, Inc. |
|  |  | 4,948,676 | Cermet material, cermet body and method of manufacture | Darracq, D.; and Duruz, J.-J. | Moltech Invent S. A. |
|  |  | 4,956,068 | Non-consumable anode for molten salt electrolysis | Nguyen, T.; Lazouni, A.; and Doan, K. S. | MOLTECH Invent S. A. |
|  |  | 4,956,068 | Non-consumable anode for molten salt electrolysis | Nguyen, T.; lazouni, A.; and Doan, K. S. | MOLTECH Invent S. A. |
|  |  | 4,960,494 | Ceramic/metal composite material | Nguyen, T.; Lazouni, A.; and Doan, K. S. | MOLTECH Invent S. A. |
|  |  | 4,961,902 | Method of manufacturing a ceramic/metal or ceramic/ceramic composite article | Clere, T. M..; Abbaschian, G. J.; Wheller, D. J.; and Burnes, A. L. | Eltech Systems Corporation |
|  |  | 4,966,674 | Cerium oxycompound, stable anode for molten salt electrowinning and method of production | Bannochie, J. G., and R. C. Sherriff | MOLTECH Invent S. A. |
|  |  | 4,999,097 | Apparatus and method for the electrolytic production of metals | Sadoway, D. R. | Massachusetts Institute of Technology |
|  |  | 5,002,642 | Method for electrowinning a metal using an electrode unit consisting of assembled | Kaneko, K.; Kimura, T.; Ichinoseki, F.; and | Mitsubishi Kinzoku Kabushiki Kaisha |

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|  |  |  | anode plates and cathode plates and a frame body for forming such an electrode unit | Ohkoda, M. |  |
|  |  | 5,006,209 | Electrolytic reduction of alumina | Beck, T. R.; and Brooks, R. J. | Electrochemical Technology Corp. |
|  |  | 5,015,343 | Electrolytic cell and process for metal reduction | LaCamera, A.; Van Linden, J. H. L.; Pierce, T. V.; Parkhill J. O. | Aluminum Company of America |
|  |  | 5,017,217 | Ceramic/metal or ceramic/ceramic composite article | Clere, T. M.; Abbaschian, G. J.; Wheeler, D. J.; and Barnes, A. L. | Eltech Systems Corporation |
|  |  | 5,019,224 | Electrolytic process | Denton, D. A, and P. C. S. Hayfield | Imperial Chemical Industries PLC |
|  |  | 5,019,225 | Molten salt electrowinning electrode, method and cell | Darracq, D.; Duruz, J.-J.; and Durmelat, C. | Moltech Invent S. A. |
|  |  | 5,043,047 | Aluminum smelting cells | Stedman, I. G.; Houston, G.; Shaw, R. W.; Juric, D. D. | Comalco Aluminum Limited |
|  |  | 5,069,771 | Molten salt electroysis with non-consumable anode | Nguyen, T.; Lazouni, A.; and Doan, K. S. | Moltech Invent S. A. |
|  |  | 5,071,534 | Aluminum electrolysis cell with continuous anode | Holmen, H. K.; Naterstad, T.; Hurlen, J.; and Gjörven, S. | Norsk Hydro a. s. |
|  |  | 5,084,156 | Electrolytic cell | Iwanaga, N.; Yamaguti, T.; Fujieda, N.; Tsuzikawa, Y.; and Harada, I. | Mitsumi Toatsu Chemicals, Inc. |
|  |  | 5,085,752 | Electrolytic cell | Iwanaga, N.; Yamaguti, T.; Fujieda, N.; and Tsuzikawa, Y. | Mitsumi Toatsu Chemicals, Inc. |
|  |  | 5,089,093 | Process for controlling aluminum smelting cells | Blatch, G. I.; Taylor, M. P.; Fyfe, M. | Comalco Aluminum Ltd. |
|  |  | 5,185,068 | Electrolytic production of metals using consumable anodes | Sadoway, D. R. | Massachusetts Institute of Technology |
|  |  | 5,279,715 | Process and apparatus for low temperature electrolysis of oxides | La Camera, A. F.; Tomaswick, K. M.; Ray, S. P.; and Ziegler, D. P. | Aluminum Company of America |
|  |  | 5,284,562 | Non-consumable anode and lining for aluminum electrolytic reduction cell | Beck, T. R.; Brooks, R. J. | Electrochemical Technology Corp. and Brooks Rand, Ltd. |

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| | | 5,286,353 | Electrolysis cell and method for the extraction of aluminum | Wilkening, S. | VAW Aluminium A. G. |
| | | 5,286,359 | Alumina reduction cell | Richards, N. E.; Tabereaux, A. T. | Reynolds Metal Company |
| | | 5,340,448 | Aluminum electrolytic cell method with application of refractory protective coatings on cello components | Sekhar, J.; de Nora, V. | Moltech Invent, S. A. |
| | | 5,362,366 | Anode-cathode arrangement for aluminum production cells | deNora, V.; Sekhar, J. A. | Moltech Invent S. A. |
| | | 5,366,702 | Apparatus for generating ozone utilizing an oscillating plate electrode | Rimpler, M. | |
| | | 5,368,702 | Electrode assemblies and meultimonopolar cells for aluminium electrowinning | de Nora, V. | MOLTECH Invent S. A. |
| | | 5,378,325 | Process for low temperature electrolysis of metals in a chloride salt bath | Dastolfo, L. E.; LaCamera, A. F. | Aluminum Company of America |
| | | 5,378,327 | Treated carbon cathodes for aluminum production, the process of making thereof and the process of using thereof | Sekhar, J. A.; Zheng, T.; and Duruz, J. J. | Moltech Invent S. A. |
| | | 5,397,450 | Carbon-based bodies in particular for use in aluminium production cells | Sekhur, J. A.; and Liu, J. J. | Moltech Invent S. A. |
| | | 5,415,742 | Process and apparatus for low temperature electrolysis of oxides | La Camera, A. F.; Tomaswick, K. M.; Ray, S. P.; and Ziegler, D. P. | Aluminum Company of America |
| | | 5,486,278 | Treating prebaked carbon components for aluminum production , the treated components thereof, and the components use in an electrolytic cell | Mangianello, F.; Duruz, J.-J.; Bello, V. | Moltech Invent S. A. |
| | | 5,492,604 | Coating composition for carbon electrodes | Ray, S. P. | Aluminum Company of America |
| | | 5,498,320 | Method and apparatus for electrolytic reduction of fine-particle alumina with porous-cathode cells | Rendall, J. S. | Solv-Ex Corporation |
| | | 5,505,823 | Method for the electrolytic production of aluminum | Rendall, J. S. | Solv-Ex Corporation |
| | | 5,507,933 | Carbon masses for use in aluminium production cells and process | de Nora, V.; and Sekhar, J. A. | None |
| | | 5,510,008 | Stable anodes for aluminum production cells | Sekhar, J. A.; Liu, J. J.; and Duruz, J.-J. | |
| | | 5,518,829 | Solid oxide electrolyte fuel cell having dimpled surfaces of a power generation film | Satake, T.; Miyamoto, H.; and Yamamuro, S | Mitsubishi Jukogyo Kabushiki |
| | | 5,534,119 | Method of reducing erosion of carbon-containing components of aluminum production cells | Sekhar, J. A. | None |
| | | 5,578,174 | Conditioning of cell components for aluminum production | Sekhar, J. A. | Moltech Invent S. A. |
| | | 5,587,140 | Process for producing powders of transition metal boride | Fujiwara, S.; Tabuchi, H.; and Takahashi, A. | Sumitomo Chemical Company, Limited |

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| | | 5,658,447 | Electrolysis cell and method for metal production | Watson, K. D.; Juric, D. D. D.; Shaw, R. W.; and Houston, G. J. | Comalco Aluminium Limited |
| | | 5,667,664 | Ledge-free aluminum smelting cell M5,651,874 Method for production of aluminum utilizing protected carbon containing components | Juric, D. D.; Shaw, R. W.; Houston, G. J.; and Coad, I. A. | Comalco Aluminium Limited |
| | | 5,679,224 | Treated carbon or carbon-based cathodic components of aluminum production cells | Sekhar, J. A. | Moltech Invent S. A. |
| | | 5,725,744 | Cell for the electrolysis of alumina at low temperatures | de Nora, V., and J.-J. Duruz | Moltech Invent S. A. |
| | | 5,746,895 | Composite refractory/carbon components of aluminium production cells | Sekhar, J. A. | Moltech Invent S. A. |
| | | 5,794,112 | Controlled atmosphere for fabrication of cermet electrodes | Ray, S. P.; Woods, R. W. | Aluminum Company of America |

**Hot electron injection into aqueous electrolyte solution from thin insulating film-coated electrodes.** Kulmala. S.; Ala-Kleme. T.; Joela. H.; Kulmala. A. Department Chemistry. University Turku. Turku. SF-20014. Finland. J. Radioanal. Nucl. Chem. (1998). 232(1-2). 91-95. CODEN: JRNCDM; ISSN: 0236-5731. Journal written in English. AN 1998:455643.

**Abstract.** Hot electron injection into aq. electrolyte soln. was studied with electrochemiluminescence and ESR methods. Both methods provide further indirect support for the previously proposed hot electron emission mechanisms from thin insulating film-coated electrodes to aq. electrolyte solns. The results do not rule out the possibility of hydrated electron being as a cathodic intermediate in the redn. reactions at cathodically pulse-polarized thin insulating film-coated electrodes. However, no direct evidence for electrochem. generation of hydrated electrons could be obtained with ESR. only spin-trapping expts. could give information about the primary cathodic steps.

**Test of a dual electrode galvanic cell in binary carbonate melt.** Lee, Sung Kyu; Staehle, Roger W. Materials Research Lab., Research Development Center, Samsung Electro-Mechanics Co.. Ltd.. Suwon, 442, S. Korea. Mater. Corros. (1998), 49(1), 7-12. CODEN: MTCREQ; ISSN: 0947-5117. Journal written in English. CAN 128:130267

**Abstract.** Basicity of (Li0.62K0.38)2CO3, the current choice of electrolyte compn. for molten carbonate fuel cells (MCFC's), is defined as log (aM2O), where M represents an alkali metal and M2O is the net oxide ion activity. Net oxide ion activity is defined as the sum of the alkali oxides activities dissolved in the melt. To correlate measured cell emf values with basicity change in the (Li0.62K0.38)2CO3 melt, a dual electrode galvanic cell of the following arrangement was tested at 650° with PCO2, varying above the melt: Au, A-B, CO2, O2|mullite|A-B, CO2, O2|ZrO2 · Y2O3|O2, Au where A-B represents (Li0.62K0.38)2CO3. The response of the cell to PCO2 at const. PO2 can be explained by thermodn. model. which states that ion transference in the mullite tube is limited to Li+ and/or K+ and the dual electrode galvanic cell voltage is a direct measure of Δali2O or ΔaK2O for pure (Li0.62K0.38)2CO3 melt at const. Po2.

**A wall-jet electrode reactor and its application to the study of electrode reaction mechanisms. Part III: Study of the mechanism of the a.c. electrolytic graining of aluminum in hydrochloric acid.** Laevers, P.; Hubin, A.; Terryn, H.; Vereecken, J. Monroe Europe N.V., Sint-Truiden, 3800, Belg. J. Appl. Electrochem. (1998), 28(4), 387-396. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 129:9958

**Abstract.** The mechanism of the a.c. electrolytic graining of aluminum in hydrochloric acid is detd. from the anal. of the potentiostatic transient behavior of the system aluminum-electrolyte under anodic and cathodic polarization and comparison of exptl. detd. transients with calcd. values derived from a candidate mechanistic scheme. It was established. that the oxidn. of aluminum in the development of a distinct surface morphol. occurs according to Al + 3Cl- → AlCl3 + 3e- (k1) and AlCl3 → Al3+ + Cl- (k2) the Al3+ ions being dissolved from the surface and removed to the bulk of the soln., hence forming pits. AlCl3 is a solid intermediate. The morphol. developed, is detd. by the excess of Cl- ions created at the electrode surface. with respect to the bulk concn. The accumulation of Cl- ions is governed by the ratio between the rate const. for the formation of AlCl3, set by the flux of charges forced across the electrode-soln. interface per unit surface area taking part in the active dissoln. of aluminum and the mass transport rate of the Cl- ions. The redn. of H+ ions in the cathodic half period of the applied a.c. is mass transport controlled. The concomitant rise in interfacial pH causes Al3+ ions formed in the preceding anodic half period, which are not yet removed from the electrode-soln. interface. to ppt. as aluminum.

**Electrolyte for electrolytic refining of aluminum and its use.** De Vries, Hans. (Aluminal Oberflaechentechnik G.m.b.H., Germany). Ger., 4 pp. CODEN: GWXXAW. DE 19716495 C1 980520. Patent written in German. Application: DE 97-19716495 970419. CAN 128:327935.

**Abstract.** An electrolyte for the high-speed deposition of aluminum on end products contg. organometallic aluminum compd. is described. The compd. with a formula of MF·2Al(C3H7)3·nAlR3, where M = K, Rb, Cs and R corresponds to C3 alkyl group or a mixt. of C3 and C1-C2 alkyl group was used (n = 0.1-1). The electrodeposition was carried out in arom. or aliph. hydrocarbons as solvents.

**TiB2 composite-coated graphite electrode for aluminum three-layer electrolytic refining.** Zheng, Qingjun; Li, Dexiang; Ma, Xiufang. Beijing General Research Institute for Nonferrous Metals. Beijing, 100088, Peop. Rep. China. Youse Jinshu (1997), 49(2), 68-71, 76. CODEN: YSCSAE; ISSN: 1001-0211. Journal written in Chinese. CAN 128:195011.

**Abstract.** A new solid cathode was developed for 3-layer electrolytic refining of Al. The electrode consists of a graphite substrate and a composite coating contg. TiB2, a fine graphite powder having particle diam. <0.0074 mm, and a coarse graphite powder with a particle diam. 0.486-0.833 mm.

**ZnO-based Inert Anodes in Aluminum Electrolytes -The Influence of Dopants on the Electrical Properties of the Anodes.** Galasiu, I., R. Galasiu, N. Popa and V. Chivu, *Proceedings of the Ninth International Symposium on Light Metals Production* (ed., J. Thonstad), Norwegian University of Science and Technology, August 18-21, 1997, p. 189-194.

**Abstract.** No abstract available.

**Initial stages of aluminum electrodeposition in the presence of Co(II) ions.** Simanavicius, L.; Stakenas, A.; Sarkis, A. Inst. Chem., Vilnius, 2600, Lithuania. Chemija (1997), Issue 3, 60-63. CODEN: CHMJES; ISSN: 0235-7216. Journal written in English. CAN 128:120918

**Abstract.** A current min. along with its max. in the reverse scan of potential was detected while examg. cyclic voltammograms in AlBr3 solns. dissolved an arom. hydrocarbon contg. dimethylethylphenylammonium bromide. Anal. of the current-time transients indicated that a Co(II) addn. to the electrolute only insignificantly changed the character of nucleation and growth of Al electrodeposits.

**Thermodynamic and structural aspects of electrochemical deposition of metals and binary compounds in molten salts.** Danek, V.; Chrenkova, M.; Silny, A. Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dubravska cesta 9, Bratislava, 842 36, Slovakia. Coord. Chem. Rev. (1997), 167, 1-48. CODEN: CCHRAM; ISSN: 0010-8545. Journal; General Review written in English. CAN 128:160182

**Abstract.** A review with 140 refs. of the influence of the ionic structure of electrolytes used in the electrodeposition of molybdenum, titanium and aluminum on the mechanism and kinetics of metal deposition is discussed. Using electrochem. methods of study and a complex thermodn. and physico-chem. anal. it was detd. that in all the electrolytes investigated the electrodeposition process is significantly facilitated by the formation of complex anions with lower symmetry of the co-ordination sphere. In the case of molybdenum deposition, complex heteropolyanions are probably created in the melt by the addn. of B2O3 or SiO2 to the K2MoO4-based electrolytes. The electrodeposition of titanium from the K2TiF6-based electrolytes is enhanced by the formation of the less stable TiF73-, resp. TiF6Cl3- anions. In the electrolysis of aluminum from cryolite-alumina melts the creation of oxyfluoroaluminate anions facilitates the electrodeposition of aluminum.

**Method and device for water electrolysis to producing strongly acid water and alkaline water.** Deguchi, Katsuhiko; Sugiyama, Shigeshi. (Yugen Kaisha Art Project, Japan; Deguchi, Katsuhiko; Sugiyama, Shigeshi). PCT Int. Appl., 29 pp. CODEN: PIXXD2. WO 9745373 A1 971204. Designated States: W: KR, US. Designated States: RW: AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE. Patent written in Japanese. Application: WO 97-JP1779 970526. Priority: JP 96-129937 960524 CAN 128:66264

**Abstract.** Three electrolytic cells are arranged in an electrolytic bath contg. 1 % salt water as an electrolytic soln. In each cell, a cylindrical internal electrode constituted of an aluminum plate and a titanium plate is provided in an electrolytic membrane container which is made of a porous ceramic composed mainly of a cryst. clay mineral and contains water to be treated. In addn., a cylindrical external electrode is disposed facing the internal electrode on the other side of the container. A high-frequency a.c. contg. a d.c. component is supplied between the internal electrode and external electrode in each cell by periodically inverting the polarity of the current.

**Production of aluminum oxide involving the deposition of aluminum hydroxide in an electrolyzer, rinsing, drying and calcining.** Lamberov, Aleksandr Adolfovich; Liakumovich, Aleksandr Grigorev; Agadzhanyan, Svetlana Ivanovna; Vyazkov, Vladimir Andreevich; Levin, Oleg Vladimirovich. (Tovarishchestvo S Ogranichennoj Otvetstvennostyu Firma "kataliz", Estonia). Russ. CODEN: RUXXE7. RU 2083722 C1 970710. Patent written in Russian. Application: RU 94-94037737 941006. CAN 128:8249

**Abstract.** Title only translated.

**Production of an electrode mass for aluminum electrolyzers.** Derevyagin, Viktor N. (Ao O/t "bratskij Alyuminievyj Zavod", USSR). Russ. CODEN: RUXXE7. RU 2073749 C1 970220. Patent written in Russian. Application: RU 94-94015905 940428. CAN 127:196865
**Abstract.** Title only translated.

**The oxidation of heterogeneous carbon electrodes and furnace liners. Part II: overall reactivity correlations.** James, B. J.; Welch, B. J.; Hyland, M. M.; Hiltmann, F. Department of Chemical and Materials Engineering, The University of Auckland, N. Z. Light Met. (Warrendale, Pa.) (1997), 637-641. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 127:265838
**Abstract.** Using the method described previously (Light Metals, 1996) the oxidn. reactions of carbon cathode materials have been characterized for onset temp. and rate of oxidn. at low (less than 550°C) temps. Anal. of the product gases of oxidn. reactions has shown that the onset temp. is low (often below 200°C) for cathode carbons and the mechanism of oxidn. is controlled initially by oxygen adsorbed onto internal pore surfaces. Gas anal. in conjunction with SEM revealed links between the sample porosity and oxidn. rate. Structural anal. was conducted on heterogeneous cathode carbon blocks using X-ray diffraction (Part I), the change in intensity of the d002 peak for carbon showed the selective nature of the oxidn. process, more amorphous fractions oxidizing preferentially. Surface area anal. was conducted on powd. cathode carbons showing the development of surface area with extent of oxidn

**A study of CeO2 coated composite anodes for aluminum electrowinning in the Hall-Heroult cell.** Zhang, Hao. USA. Electrochem. Soc. Interface (1996), 5(3), 55-56. CODEN: ELSIE3; ISSN: 1064-8208. Journal written in English. CAN 125:226990
**Abstract.** The possibility of developing nonconsumable anodes in aluminum electrolyzers was studied by using Ni aluminide composites with or without CeO2 coating. Exptl data related to the corrosion and technol. properties of anodes made of alloy Ni 81, Al 9, Cu 10%, Ni3Al-Cu intermetallic alloy, and Ni3Al-Cu-CO2 composite in molten cryolite-alumina electrolyte in real conditions of Al electrowinning are given. Stable voltages were sustained with very low corrosion rate with the Ni-Al-Cu and Ni-Al-Cu-CeO2 anodes.

**Tin dioxide-based ceramics as inert anodes for aluminum smelting. A laboratory study.** Vecchio-Sadus, A.M.; Constable, D.C.; Dorin, R.; Frazer, E.J.; Fernandez, I.; Neal, G.S.; Lathabai, S.; Trigg, M.B. Division of Minerals, CSIRO, Port Melbourne, 3207, Australia. Light Met. (Warrendale, Pa.) (1996), 259-65. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 124:237814
**Abstract.** The behavior of tin dioxide-based ceramics as inert anodes was examd. in a lab.-scale aluminum smelting cell over a range of electrolyte compns. with operating temps. between 830 - 975°C. Anodes of a nominal compn. SnO2 (96 wt%), Sb2O3 (2 wt%) and CuO (2 wt%), were electrolyzed for 90 min at a c.d. of .apprx.1 A cm-2. The corrosion rate was detd. from the tin and copper concns. in the recovered electrolyte, aluminum metal and the fume. The corrosion rates were 12.5, 1.6 and 6.5 mg (Ah)-1 in electrolytes with bath ratios 1.5 (975°C), 0.89 (903°C) and 0.74 (830°C), resp. A four-fold increase in corrosion rate was obtained at open-circuit demonstrating the protection provided by oxygen evolution during electrolysis. A preliminary investigation of the dependence of corrosion rate on firing temps. and additive (Sb2O3 and CuO) concns. was conducted using a part-factorial design expt. Post-electrolysis examn. of the anodes using SEM coupled with energy dispersive spectroscopy anal. revealed a depletion of copper from the anode and a build-up of an alumina-rich surface layer under certain conditions.

**The behavior of nickel ferrite cermet materials as inert anodes.** Olsen, Espen; Thonstad, Jomar. Department of Electrochemistry, Norwegian Institute of Technology, Trondheim, N-7034, Norway. Light Met. (Warrendale, Pa.) (1996), 249-57. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 124:237813
**Abstract.** NiFe2O4-based cermet materials of varying compns. were fabricated using alternative techniques giving bodies with densities close to theor. The materials were used in aluminum electrolysis tests in a conventional electrolyte for 50 h with continuous bath and metal sampling. Good performance of the electrodes was dependant on the formation of a stable oxide layer on the anode surface. Corrosion rates corresponding to the range of 0.12 - 0.20 cm/yr were measured. The cathodically deposited aluminum was found to contain contaminants originating from the anode in the range of 3000 ppm. The anode dissoln. process as well as the mass transfer of the contaminating species from the electrolyte into the metal cathode were investigated. The microstructure of the

materials before and after testing was compared and very good characteristics were found, indicating that the anodes corroded in a controlled manner.

**An approach for a complete evaluation of resistance to thermal shock. Applying to the case of anodes and cathodes.** Dreyer, C.; Samanos, B. ALUMINIUM PECHINEY Research Center - LRF, St. Jean de Maurienne, 73300, Fr. Light Met. (Warrendale, Pa.) (1997), 585-590. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 127:265833
**Abstract.** The aim of this paper is to describe a new method for characterizing a material in terms of resistance to thermal shock. Such characterization takes into account the criteria of thermal shock resistance to initiation (KINGERY criterion) and propagation (HASSELMAN criteria). It can be applied equally well to hard or soft thermal shock. This next approach has the following main advantages:. .bul. Characterization of the material in terms of thermal shock is complete. .bul. Thermal shock tests or empirical formulas become unnecessary. Examples of utilization of this new approach are presented for anodes and cathodes of aluminum electrolyzers.

**Physical origin of the intrinsic cathodic luminescence of an oxide-covered aluminum electrode.** Hakanen, A.; Laine, E.; Haapakka, K. Department of Physics, University of Turku, Turku, FIN-20014, Finland. Europhys. Lett. (1997), 39(3), 311-316. CODEN: EULEEJ; ISSN: 0295-5075. Journal written in English. CAN 127:269736
**Abstract.** Photoluminescence spectra of thin-film Al oxide samples on Al show spectral lines at .apprx.330 and 420 nm that are attributed to the F+ and F centers of Al oxide, resp. The F centers are responsible for the intrinsic cathodic luminescence of an oxide-covered Al electrode, too. The mechanism of the luminescence is based on charge transfer reactions at the oxide/electrolyte interface.

**Visual observation of bubbles at horizontal electrodes and resistance measurements on vertical electrodes.** Qian, K.; Chen, J. J. J.; Matheou, N. Dep. of Chem. & Materials Eng., Univ. of Auckland, N. Z. J. Appl. Electrochem. (1997), 27(4), 434-440. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 127:72096
**Abstract.** In the Hall-Heroult process used in Al redn. cells, the electrodes are set in horizontal orientation and gas bubbles are generated on the underside of the anode which is immersed in the electrolyte. A comparison was made of the bubbles formed on a horizontal bottom-facing electrode in a phys. analog model with those formed electrolytically. Bubbles formed in a phys. analog model by forcing air through a porous plate are larger, with wetted clear areas between bubbles. By contrast, electrolytically generated gas bubbles are smaller and the electrode surface is covered with a foamy layer of tiny bubbles. To measure the bubble resistance on horizontal electrodes, a method was developed for vertical electrodes so that the measurements may be validated by comparison with published data. Voltage fluctuations were measured and analyzed by using a fast Fourier transform (FFT). The magnitude of the bubble impedance was obtained at a superimposed a.c. frequency f0. The phase angle caused by the effects of the double layer capacitance and the faradaic impedance on bubble resistance was detd. The effects of the faradaic impedance and the double layer capacitance were negligibly small under exptl. conditions.

**The initial stages of aluminum and zinc electrodeposition from an aluminum electrolyte containing quaternary aralkylammonium compound.** Simanavicius, Leonas; Stakenas, Algimantas; Sarkis, Albertas. Inst. Chem., Vilnius, LT 2600, Lithuania. Electrochim. Acta (1997), 42(10), 1581-1586. CODEN: ELCAAV; ISSN: 0013-4686. Journal written in English. CAN 126:348789
**Abstract.** The electrodeposition of aluminum and zinc from AlBr3-dimethylethylphenylammonium bromide solns. in arom. hydrocarbon was studied by the chronoamperometric technique. The diffusion coeffs. of the reducible species detd. by different methods are in satisfactory agreement with each other. Anal. of chronoamperograms indicate that the deposition process of aluminum and zinc alike involves progressive nucleation with diffusion controlled growth of the nuclei. The two maxima in the current-time transients are disclosed as apparently due to sep. nucleation of aluminum and zinc.

**Properties of a colloidal alumina-bonded TiB2 coating on cathode carbon materials.** Oye, H. A.; De Nora, V.; Duruz, J. - J.; Johnston, G. Institute of Inorganic Chemistry, The Norwegian University of Science and Technology, Trondheim, 7034, Norway. Light Met. (Warrendale, Pa.) (1997), 279-286. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 127:265807

**Abstract.** Lab. studies of colloidal alumina-bonded $TiB_2$ have been carried out. The following properties have been demonstrated: The thermal expansion was somewhat higher than for carbon materials, the elec. cond. was of the same order as graphite, while porosity of the coating was ≈ 30 %. The coating protected by infiltrated aluminum exhibited a high resistance to sodium attack. The material had a strong adherence to carbon materials even after thermal cycling. Other properties include high abrasion resistance of the coating and wettability by liq. aluminum. The coating is an effective barrier to sodium penetration. The barrier action is due to the ability to form a stable liq. aluminum layer in the pores of the coating. Then aluminum, electrolyte and the sodium stabilizing carbon are no longer in close contact and sodium penetration is limited by slow diffusion through the aluminum layer.

**Inert anodes for the primary aluminum industry. An update.** Pawlek, Rudolf P. Technical Info Services and Consulting, Sierre, CH - 3960, Switz. Light Met. (Warrendale, Pa.) (1996), 243-8. CODEN: LMPMDF; ISSN: 0147-0809. Journal; General Review written in English. CAN 124:237765
**Abstract.** A review with 24 refs. Recently developed non-consumable anodes for the primary aluminum industry are discussed. Development efforts have concd. on metal, cermet, ceramic and cerium-oxide coated anodes. Unfortunately problems such as oxidn. and corrosion, metal contamination of aluminum produced, anode life, elec. cond., and cost still remain to be solved.

**Aluminum and manganese electrodeposition from toluene solutions containing quaternary ammonium compounds.** Sarkis, A.; Stakenas, A.; Matulionis, E. Inst. Khim., Vilnius, 2600, Lithuania. Chemija (1996), Issue 4, 43-47. CODEN: CHMJES; ISSN: 0235-7216. Journal written in Russian. CAN 126:319821
**Abstract.** It was found that from Al2Br6·TMPAI or Al2Br6··DMEPAC solns. in toluene, contg. manganous stearate and TEA, the deposits of aluminum with manganese up to 4 wt. % can be obtained. The cathodic parts of cyclic voltammetric curves and anal. of coatings demonstrate that the deposition of aluminum and manganese occur simultaneously in the same potential region. After addn. of manganous stearate to aluminum electrolyte, a potential overlap on reverse scan curves show that the rate of aluminum-manganese electrodeposition is controlled by nucleation process.

**Towards energy saving in aluminum electrolysis.** Sen, Utpal. Central Electrochem. Res. Inst., Karai8kudi, 630 006, India. Bull. Electrochem. (1996), 12(9), 537-539. CODEN: BUELE6; ISSN: 0256-1654. Journal written in English. CAN 126:21257
**Abstract.** In the major aluminum producers in the world, the energy requirements for aluminum electrolytes are in the range of 14 to 15 kWh/kg of Al which is more than twice of the theor. energy requirement for the redn. process. It is also a fact that the operational temp. of Al-electrolysis is about 1233 K which is 573 K above the m.p. of Al-metal. A theor. calcn. of heat balance suggests that a redn. of about 373 K in the operational temp. of Al-electrolysis is the limitation of interelectrode spacing and frequent anode changing. A suitable inert anode would reduce energy losses besides saving high quality carbon uses as anode. The R & D activities undertaken by the CECRI to study such problems are discussed.

**Application of nonequilibrium thermodynamics to the electrode surfaces of aluminum electrolysis cells.** Hansen, Ellen Marie; Kjelstrup, Signe. Dep. Phys. Chem., Norwegian Univ. Sci. Technol., Trondheim, N-7034, Norway. J. Electrochem. Soc. (1996), 143(11), 3440-3447. CODEN: JESOAN; ISSN: 0013-4651. Journal written in English. CAN 126:149705
**Abstract.** A new method for modeling electrode surfaces, applied to aluminum electrolysis, is presented. The method uses nonequil. thermodn. for surfaces and describes the fluxes, the overpotential, and the dissipated energy at the surfaces in a new way. Examples are given for the interface anode- and cathode-bath to show how the model may be used to predict surface properties based on obsd. phenomena and the total energy dissipated in the cell. The method predicts apparent discontinuities at the surfaces in elec. properties, as well as in temp. and in chem. potentials. The overpotential is viewed as a discontinuity in elec. potential. Local surface heating or cooling effects can be simulated, and the results can be used to est. surface properties. The calcns. show that excess surface temps. of magnitude 0.1 K can occur under certain surface conditions. If the excess surface temp. is of magnitude 1 to 10 K, unrealistically high dissipated energy at the surfaces results. At the anode surface, elec. conductivities ≥10-7 times their resp. bulk values lead to the measured value for anodic overpotential. Even smaller conductivities lead to larger overpotentials, and a typical anode effect value results if the elec. conductivities are smaller than 10-8 times their resp. bulk values.

**Electrodeposition of aluminum from nonaqueous organic electrolytic systems and room temperature molten salts.** Zhao, Yuguang; VanderNoot, T. J. Chem. Dep., Queen Mary and Westfield Coll., London, E1 4NS, UK. Electrochim. Acta (1996), 42(1), 3-13. CODEN: ELCAAV; ISSN: 0013-4686. Journal; General Review written in English. CAN 126:66577
**Abstract.** Aluminum electrodeposition from nonaq. solvents and room temp. molten salts is reviewed with 140 refs. The feature of various arom. hydrocarbons, ethers and di-Me sulfone as Al-plating baths were assessed. Electrochem. processes and plating conditions of aluminum room temp. haloaluminate molten salts are described. The haloaluminate melts including alkylpyridinium, alkylimidazolium and alkylammonium are emphasized. Ionic equil. and electrode processes in these electrolytic systems are discussed.

**The Pt and Al electrode potentials in aluminum electrolyte containing dimethylethylphenylammonium bromide.** Simanavicius, L.; Stakenas, A.; Ragaleviciene, V. Inst. Chemistry, Vilnius, 2600, Lithuania. Chemija (1996), Issue 3, 64-67. CODEN: CHMJES; ISSN: 0235-7216. Journal written in English. CAN 125:126004
**Abstract.** The dependence of Pt electrode potential on the carbonium ion concn. in AlBr3 and dimethylethylphenylammonium bromide solns. in arom. hydrocarbons was studied and the potential-detg. reaction is proposed. The influence of both electrolyte compn. and the character of surface oxide film on the Al electrode potential was demonstrated.

**Recent developments of inert anodes for the primary aluminum industry. Part II.** Pawlek, Rudolf P. Tech. Info. Serv. Consult., Sierre, Switz. Aluminium (Isernhagen, Ger.) (1995), 71(3), 340-2. CODEN: ALUMAB; ISSN: 0002-6689. Journal; General Review written in English. CAN 123:68413
**Abstract.** A review with 28 refs.

**Sn02-based Inert Anodes for Aluminum Electrolysis, II. Properties Variation with Sinterization Temperature.** Galasiu, R., 1. Galasiu and E. Andonescu, *Proc. Of VIIth Aluminum Symposium,* Donovaly, Slovakia, (1995), p. 61-65.
**Abstract.** No Abstract available.

**Sn02-based Inert Anodes for Aluminum Electrolysis, I. Method for Increasing of Thermal Shock Resistance.** Galasiu, R., I. Galasiu and I. Comanescu, *Proc. Of the VIIth Aluminum Symposium,* Slovak -Norwegian Conference, Donovaly, Slovakia, (1995), p. 55-60.
**Abstract.** No Abstract available.

**Recent developments of inert anodes for the primary aluminum industry. Part 1.** Pawlek, Rudolf P. Tech. Info Services Consulting, Sierre, Switz. Aluminium (Isernhagen, Ger.) (1995), 71(2), 202-6. CODEN: ALUMAB; ISSN: 0002-6689. Journal; General Review written in English. CAN 123:20273
**Abstract.** A review with 53 refs. including an update of the ref. list of the review by P.

**Investigation of the aluminum electrodeposition process in cryolite-based melts using a rotating ring-disk electrode: evidence for the existence of a subvalent intermediate species.** Stojanovic, R. S.; Dorin, R.; Frazer, E. J. CSIRO Division Minerals, Institute Minerals Energy Construction, Port Melbourne, 3207, Australia. J. Appl. Electrochem. (1996), 26(3), 249-54. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 124:273086
**Abstract.** The rotating ring-disk electrode technique was used to study the reaction mechanism of the aluminum electrodeposition process in cryolite-based electrolytes. Lab. studies using high temp. gold-molybdenum and platinum-molybdenum rotating ring-disk electrodes provided evidence for the existence of a subvalent intermediate species (Al(I)). In a cryolite-alumina electrolyte (bath ratio: 1.5), two well sepd. convective-diffusion controlled oxidn. processes were obsd. at both a gold and a platinum ring during aluminum electrodeposition at the disk. From the data presented, a reaction scheme involving redn. of Al(III) to Al(0) via Al(I), followed by chem. dissoln. of Al(0) into the bulk electrolyte is proposed. The loss of current efficiency in aluminum smelting was primarily attributed to the chem. dissoln. of Al(0), rather than to the formation of a subvalent intermediate species.

**An electrical model for the cathodically charged aluminum electrode.** Wang, Mei-Hui; Hebert, Kurt R. Department Chemical Engineering, Iowa State University, Ames, IA, 50011, USA. Proc. - Electrochem. Soc. (1996), 95-15(Critical Factors in Localized Corrosion II), 355-67. CODEN: PESODO; ISSN: 0161-6374. Journal written in English. CAN 124:273053

**Abstract.** A math. model was formulated for the surface film on Al which considered the film to consist of an inner barrier high-field conducting layer and an outer, porous, ohmically-conducting layer. It included all relevant capacitive and faradaic processes. The model was used to study structural changes produced by cathodic polarization in acid solns., which was found to strongly promote anodic pitting in a.c. etching processes. The film's structural parameters were fit to exptl. current transients following anodic potential steps after cathodic charging. The model was found to represent exptl. current decays realistically over several orders of magnitude variation of c.d. (103 A/cm2) and time (105 s). To a 1st approxn., cathodic activation could be described in terms of a decrease of the inner layer thickness (V) from .apprx.30 to 15-20 .ANG. and an increase of the porosity (p) to 0.023; these changes were interpreted as being due to the formation of micropores in the outer portion of the initial film, possibly by electrochem. dissoln. of the oxide.

**Coating composition for carbon electrodes.** Ray, Siba P. (Aluminum Company of America, USA). U.S., 5 pp. CODEN: USXXAM. US 5492604 A 960220. Patent written in English. Application: US 94-364918 941228. CAN 124:214530

**Abstract.** A method for producing a metal in an electrolysis cell comprising an anode, a carbon cathode, and a chamber contg. a metal oxide dissolved in a molten salt bath, said method comprising: coating an outer surface portion of the cathode with a coating compn. consisting of a refractory metal, a paint comprising an org. polymeric binder, and aluminum powder, and optionally an org. solvent and an oil; and optionally a boron source; curing the coating compn. by heating it to an elevated temp., producing an aluminum-wettable coating on the cathode outer surface portion; and electrolyzing the metal oxide to a metal bypassing an elec. current in the molten salt bath between the anode and the coated cathode.

**A non-consumable metal anode for production of aluminum with low-temperature fluoride melts.** Beck, Theodore R. Electrochemical Technology Corp., Seattle, WA, 98109, USA. Light Met. (Warrendale, Pa.) (1995), 355-60. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 123:61865

**Abstract.** A dimensionally-stable alloy anode is being developed to operate in the eutectic NaF-AlF3 bath at about 750°C as described in Light Metals 1994. A small range of compn. of Cu-Ni-Fe alloy appears to have satisfactory low anodic oxidn. rate and high oxide cond. The anodic oxidn. rate is similar to air oxidn. rate at the same temp. Air oxidn. studies carried out to 6 mo appear to have satisfactory low rates. Operation with multiple, vertical, monopolar, metal anodes and TiB2 plate cathodes at 0.5 A/cm2 each side promises a 20-fold decrease in cell vol. compared to conventional H-H cells, and a specific energy consumption of 11 kWh/kg.

**Apparatus for electric-resistance preheating of unfired dry materials.** Fiesche, W. (Maschinenfabrik Gustav Eirich, Germany). Faming Zhuanli Shenqing Gongkai Shuomingshu, 9 pp. CODEN: CNXXEV. CN 1112233 A 951122. Patent written in Chinese. Application: CN 94-10562 940510. Priority: CH 93-1431 930510 CAN 124:264301

**Abstract.** The title app. comprises a vertical cylindrical casing (with lid), a core arranged on the center axis of the casing to form an annular path between them, an inlet at the top of the casing for downward supplying of an unfired dry material, an upper- and a lower electrode arranged in the casing for elec.-resistance heating the downward flowing dry material, and a rotary discharging device and an outlet at the bottom of the casing for discharging the preheated dry material. The app. is suitable for preheating of unfired C-contg. dry materials in manuf. of electrodes for prodn. of Al by electrolysis of molten electrolytes.

**Evaluation of low-temperature cryolite-based electrolytes for aluminum smelting.** Vecchio, A. M.; Dorin, R.; Frazer, E. J. CSIRO Institute Minerals, Energy Construction, Port Melbourne, 3207, Australia. J. Appl. Electrochem. (1995), 25(12), 1098-104. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 124:158717

**Abstract.** Aluminum was smelted in a lab.-scale cell at temps. down to 850° from cryolite-based electrolytes with bath ratios in the range 0.75-1.50. Electrolyses were conducted for 1-2 h using a c.d. of 1 A cm-2 on 5 cm2 electrodes with an anode-cathode distance of 2 cm. Current efficiencies of up to 95% were recorded. In low bath ratio electrolytes, operation at alumina concns. of ≤3% sometimes resulted in the aluminum deposit breaking into globules which clustered around the cathode. Under const. current conditions, the crit. alumina concn. for the onset of anode effect is .apprx.2%. The bubble evolution characteristics (i.e., size and frequency) which affect mass transfer and cell voltage were also evaluated. Overall, low-temp. cryolite-based electrolytes may offer a viable alternative to conventional compns. for aluminum smelting.

**Aluminum production cell and assembly.** De Nora, Vittorio. (Moltech Invent S.A., Luxembourg). U.S., 10 pp. CODEN: USXXAM. US 5472578 A 951205. Patent written in English. Application: US 94-307526 940916. CAN 124:69855
**Abstract.** A cell for the prodn. of aluminum by the electrolysis of a molten electrolyte, in particular the electrolysis of alumina dissolved in a molten halide electrolyte such as cryolite, comprises anodes immersed in the molten electrolyte above a cell bottom whereon molten product aluminum is collected in a pool contg. bodies of aluminum-resistant material. Under the anodes is at least one grid of side-by-side upright or inclined walls of aluminum-resistant material whose bottom ends stand on a ceramic-coated carbon cell bottom covered by the pool of molten aluminum. The bottom ends of the grid walls form a base which is large compared to the height of the walls, each grid standing on the cell bottom and being removable from the cell. These grids reduce movements in the aluminum pool and their top parts may act as a drained cathode.

**Characteristics of aluminum deposition and dissolution loss in low-melting-point electrolyte melts.** Tie, Jun; Qui, Zhuxian. North China University of Technology, Beijing, 100041, Peop. Rep. China. Youse Jinshu (1995), 47(3), 70-4. CODEN: YSCSAE; ISSN: 1001-0211. Journal written in Chinese. CAN 124:69802
**Abstract.** The aluminum deposition and dissoln. loss in low m.p. electrolyte melts were studied. The oxidn. of deposited aluminum involves reaction producing limited amt. of lower-valence aluminum ions. The dissoln. rate of aluminum is controlled by stationary mass transport through films at metal/melt interface and it is in the order of 14.2 mg. cm-2. h-1.

**Effects of additives on the electrolytic consumption of carbon anodes in aluminum electrolysis.** Kuang, Z.; Thonstad, J.; Soerlie, M. Dep. Electrochem., Norwegian Inst. Technol., Trondheim, N-7034, Norway. Carbon (1995), 33(10), 1479-84. CODEN: CRBNAH; ISSN: 0008-6223. Journal written in English. CAN 123:353034
**Abstract.** The effect of impurities on the anode carbon consumption in aluminum electrolysis was studied in a closed lab. cell, which allowed the detn. of the total carbon consumption (CC), the carbon gasification (CG) and the formation of carbon dust (CD). Addn. of $V_2O_3$ made CC, CG and CD all increase while LiCl addn. caused CC and CG to increase, and CD to remain const. Addn. of 0.5% $AlF_3$ lowered CC, but higher contents had a neg. effect. Increasing sulfur content in the petroleum coke caused a marked decrease in CG, which was partly counteracted by rising CD. Literature data on the effect of additives are discussed together with the results.

**Sodium fluoride sinter method for determining molecular ratio of aluminum electrolyte.** Qiu, Zhuxian; Ma, Zhicheng; Zhang, Jinsheng. (Lanzhou Aluminium Factory, Peop. Rep. China). Faming Zhuanli Shenqing Gongkai Shuomingshu, 9 pp. CODEN: CNXXEV. CN 1100807 A 950329. Patent written in Chinese. Application: CN 93-11581 930923. CAN 123:245661
**Abstract.** Sodium fluoride (0.25-0.5 g) is added to aluminum electrolyte (0.5-1.5 g) and followed by sintering at 550-700°C. After the sample is cooled down, fluoride std. soln. is added to the sintered sample. After the sample is completely dissolved and the ionic strength is adjusted, fluoride was detd. by fluoride-ion selective electrode. Aluminum can be calcd.

**Cathodic process and cyclic redox reactions in aluminum electrolysis cells.** Sterten, A.; Solli, P. A. Univ. Trondheim, Norwegian Inst. Technol. (NTH), Trondheim, N-7034, Norway. J. Appl. Electrochem. (1995), 25(9), 809-16. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 123:240226
**Abstract.** The cathode processes in aluminum electrolysis cells are discussed, with detailed descriptions of the chem. reactions and transport processes leading to loss of current efficiency with respect to aluminum. The cathode current consuming reactions can be described by (i) the aluminum formation reaction, and (ii) redn. reactions forming so-called dissolved metal species (reduced entities). The rate detg. steps for the aluminum forming process are mass transport of $AlF_3$ to the metal surface, and mass transport of NaF away from the metal surface. In com.

cells there is continuous feed of impurity species to the electrolyte, depressing the concn. of dissolved metal species to very low equil. values in the bulk phase of the electrolyte. However, the equil. values of reduced entities in the electrolyte at the metal surface are much higher than in the bulk phase. This means that polyvalent impurity species are involved in cyclic redox reactions in the electrode and gas boundary layers. The most important rate-detg. steps related to these cyclic processes are (i) mass transport of reduced entities from the metal surface to a reaction plane within the cathode boundary layer, and (ii) mass transport of impurity species from the electrolyte bulk phase to the reaction plane in the cathode boundary layer. This means that there is negligible transport of dissolved metal species through the bulk of the electrolyte phase during normal operation of com. cells.

**Investigation of aluminum electrolysis in vertical type electrolysis cell using carbon-composite cathode containing titanium boride II. Evaluation by gas analysis.** Sekine, Isao; Tsukakoshi, Hideki; Koizumi, Fumito; Yuasa, Makoto; Hayashi, Tatsuo; Fujimoto, Kazuhiro. Fac. Sci. Technol., Sci. Univ. Tokyo, Chiba, 278, Japan. Denki Kagaku oyobi Kogyo Butsuri Kagaku (1995), 63(7), 660-3. CODEN: DKOKAZ; ISSN: 0366-9297. Journal written in Japanese. CAN 123:125579

**Abstract.** To investigate the detailed evaluation for aluminum electrowinning in vertical type electrolysis cell using carbon-composite material titanium boride (TiB2) as a cathode, the current efficiency was deted. by in situ gas anal. The current efficiency detd. by the gas anal. was larger than those detd. by metal wt. anal. The current efficiency was influenced by the distance between anode and cathode, c.d., etc. The Al electrolysis could be carried out at the narrow distance of 1.5 cm. The current efficiency increased with increasing c.d. Based on the results obtained it can be expected to decrease a power consumption in Al electrowinning and increase output of Al.

**Insoluble electrode and its manufacture.** Kurisu, Yasushi; Amano, Masahiko. (Shinnippon Seitetsu Kk, Japan). Jpn. Kokai Tokkyo Koho, 6 pp. CODEN: JKXXAF. JP 07090693 A2 950404 Heisei. Patent written in Japanese. Application: JP 93-278936 930914. CAN 122:324869

**Abstract.** In the electrode comprising an elec. conductive mother material for the electrode and an outermost elec. conductive layer made mainly of IrO2, there is a metal layer for bonding on the mother material, a layer-structure porous nonconductive film parallel to the mother material and is between the outermost layer and the metal layer for bonding, and an intermediate layer comprising mainly IrO2 to fill in the voids in the porous nonconductive film. The corrosion resistance of the electrode is excellent even if electrolysis is carried out at a high c.d., thus it can be used not only in electroplating but also in electrorefining, etc.

**Simulation experiments on multi-compartment electrolytic cell.** Qiu, Zhuxian; Zhong, Zhonglin. Northeastern Univ., Shenyang, 110006, Peop. Rep. China. Youse Jinshu (1994), 46(3), 70-4. CODEN: YSCSAE; ISSN: 0513-3424. Journal written in Chinese. CAN 122:91455

**Abstract.** This work is aimed at a theor. introduction to the prepns. of multi-compartment cell in the aluminum electrolysis. In the expts. a 6-compartment cell was built, in which copper electrodes and cupric sulfate solns. were used. Under the various conditions of temps. and current densities, the anodic and cathodic current efficiency as well as the total cell current efficiency were measured. The current efficiency depression due to the existence of current by-path amounted up to about 50%. It seems that a decrease of by-path current can effectively increase the prodn. of the multicompartment electrolytic cell.

**Calculation of bypass currents in molten salt bipolar cells.** Rousar, I.; Thonstad, J. Department Electrochemistry, Norwegian Institute Technology, Trondheim, N-7034, Norway. J. Appl. Electrochem. (1994), 24(11), 1124-32. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 122:18746

**Abstract.** A theor. model is given for calcn. of parasitic currents (bypass currents) for a stack of bipolar cells used in molten salt electrolysis. A simplified bypass current calcn. was confirmed by the numerical soln. of the Laplace equation for Galvani potentials in the interelectrode space and in the free space of the cell stack for the aluminum cell of the Alcoa Smelting Process (AlCl3 electrolysis) with 11 bipolar electrodes. Due to the bypass currents the current efficiency of the electrochem. process was lowered to 82%-94%, depending on the height of the stack, i.e. the thickness of the bipolar electrodes. These values were in a good agreement with values obtained from the simplified approach. The numerical soln. of the Laplace equation allowed a detailed description of the influence of the bypass current flow on the current distribution at the edges of the bipolar electrodes.

**Energy efficiency considerations on monopolar vs. bipolar fused salt electrolysis cells.** Beck, T. R.; Rousar, I.; Thonstad, J. Electrochemical Technology Corp., Seattle, WA, 98109, USA. Metall. Mater. Trans. B (1994), 25b(5), 661-8. CODEN: MTBSEO; ISSN: 1073-5615. Journal written in English. CAN 121:288538
**Abstract.** The problem of the voltage efficiency for a set of monopolar cells (due to the voltage losses in bus connections between cells) and the current efficiency for a stack of bipolar electrodes (due to the bypass current) is analyzed. Both values are of the same order for the cases calcd. These values were calcd. for optimum bus cross section for monopolar cells, and the loss in current efficiency due to bypass current was calcd. for the case of bipolar electrodes for a given cell stack and free-space geometry designed for the prodn. of aluminum from a molten NaCl-LiCl-AlCl3 electrolyte.

**Graphite electrodes for electrolytic processing.** Takagi, Takashi. (Ibiden Co Ltd, Japan). Jpn. Kokai Tokkyo Koho, 3 pp. CODEN: JKXXAF. JP 06155167 A2 940603 Heisei. Patent written in Japanese. Application: JP 92-313314 921124. CAN 121:120275
**Abstract.** The electrode is a graphite substrate impregnated with an oxide ceramic. The electrolytic processing rate is increased.

**Electrodeposition of aluminum in molten AlCl3-n-butylpyridinium chloride electrolyte.** Yang, Chao-Cheng. Department of Humanities and Science, Chemistry Division, National Yunlin Institute of Technology, Touliu Yunlin, Taiwan. Mater. Chem. Phys. (1994), 37(4), 355-61. CODEN: MCHPDR; ISSN: 0254-0584. Journal written in English. CAN 120:333682
**Abstract.** Electrodeposition of aluminum was carried out by DC const. current and pulse current methods in the molten salt system AlCl3-BPC at 30°. The aluminum was unable to deposit from a basic AlCl3-BPC melt, whereas it could deposit from an acidic melt.. The influence of electrodeposition conditions and the morphol. of the layers were investigated by x-ray diffraction and SEM, resp. The properties of electrodeposited layers varied with the electrolysis time, the current form, the electrolyte compn. and the c.d. The c.d. increased and smaller particle size and better adhesiveness of the electrodeposited layer were realized by pulse current compared to d.c.

**Voltammetric study of the electrodeposition of cobalt and aluminum from toluene solutions.** Simanavitschius, L. Z.; Matulionis, E. L. Inst. Khim., Vilnius, Lithuania. Elektrokhimiya (1994), 30(2), 235-8. CODEN: ELKKAX; ISSN: 0424-8570. Journal written in Russian. CAN 120:309772
**Abstract.** Electrodeposition of aluminum and aluminum-cobalt and cobalt from org. solvents contg. org. acids was studied by voltammetry. A difference in deposition potentials of aluminum and cobalt are significantly lower in toluene than in aq. solns. The electrodeposition of cobalt started at about 0.6V more pos. potentials than aluminum and the process of cobalt electrodeposition was a quasi-reversible process.

**Energy efficiency considerations on monopolar vs. bipolar fused salt electrolysis cells.** Beck, T. R.; Rousar, I.; Thonstad, J. Electrochemical Technology Corp., Seattle, WA, 98109, USA. Metall. Mater. Trans. B (1994), 25b(5), 661-8. CODEN: MTBSEO; ISSN: 1073-5615. Journal written in English. CAN 121:288538
**Abstract.** The problem of the voltage efficiency for a set of monopolar cells (due to the voltage losses in bus connections between cells) and the current efficiency for a stack of bipolar electrodes (due to the bypass current) is analyzed. Both values are of the same order for the cases calcd. These values were calcd. for optimum bus cross section for monopolar cells, and the loss in current efficiency due to bypass current was calcd. for the case of bipolar electrodes for a given cell stack and free-space geometry designed for the prodn. of aluminum from a molten NaCl-LiCl-AlCl3 electrolyte.

**Effect of temperature and AlCl3 concentration on mass transfer rate during electrolysis of chloride melt with liquid aluminum electrode.** Blinov, V. A.; Mikhalev, Yu. G.; Polyakov, P. V. Russia. Rasplavy (1993), Issue 6, 37-41. CODEN: RASPEM; ISSN: 0235-0106. Journal written in Russian. CAN 121:120185
**Abstract.** An effect of temp. and the aluminum chloride concn. on the mass transfer rate was studied during the electrochem. polarization of a liq. aluminum electrode in chloride melts. Expts. were carried out in potentiostatic conditions. The current maxima were explained by a presence of dissipative structures at the interface due to the Marangoni effect.

**ZnO-based Inert Anodes for Aluminum Electrolysis.** Galasiu, I. and R. Galasiu, *Proc of VIIIth Aluminum Symposium,* Donovaly, Slovakia, (1993) p. 57-68 and 69-75.
**Abstract.** No abstract available.

**Materials characterization of cermet anodes tested in a pilot cell.** Windisch, C. F., Jr.; Strachan, D. M.; Henager, C. H., Jr.; Alcorn, T. R.; Tabereaux, A. T.; Richards, N. E. Pac. Northwest Lab., Richland, WA, 99352, USA. Light Met. (Warrendale, Pa.) (1993), 445-54. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 118:238108
**Abstract.** Cermet anodes were evaluated as nonconsumable substitutes for carbon anodes using a pilot-scale redn. cell at the Reynolds Manufg. Technol. Lab. After pilot cell testing, the anodes were subjected to extensive materials characterization and phys. properties measurements at the Pacific Northwest Lab. Significant changes in the compn. of the cermet anodes were obsd. including the growth of a reaction layer and penetration of electrolyte deep into the cermet matrix. Fracture strength and toughness were measured as a function of temp. and the ductile-brittle transition was reduced by 500° following pilot cell testing. These results imply difficulties with both the anode material and the control of operating conditions in the pilot cell, and suggest that addnl. development work be performed before the cermet anodes are used in com. redn. cells. The results also highlight specific fabrication and operational considerations that should be addressed in future testing.

**Systematic alumina measurement errors and their significance in the liquidus enigma.** Tarcy, G. P.; Rolseth, Sverre; Thonstad, Jomar. Alcoa Tech. Cent., USA. Light Met. (Warrendale, Pa.) (1993), 227-32. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 118:258491
**Abstract.** Modern Hall-Heroult.Cells often appear to operate for extended periods of time well below the calcd. liquidus temp. This paradox has been defined as the liquidus enigma. Last year five possible explanations for this enigma were proposed; this paper shows that a systematic alumina measurement error is the most likely explanation for the enigma. This systematic measurement error is larger at low alumina concns. than high alumina concns. and is caused primarily by the sampling procedure used. The measurement error can best be eliminated by switching to a new anal. procedure; however, less radical approaches involving the sampling procedure or post sample treatment will also eliminate the systematic errors.

**Cell testing of metal anodes for aluminum electrolysis.** Hryn, John N.; Sadoway, Donald R. Dep. Mater. Sci. Eng., Massachusetts Inst. Technol., Cambridge, MA, 02139-4307, USA. Light Met. (Warrendale, Pa.) (1993), 475-83. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 119:31928
**Abstract.** The tech. viability of a nonconsumable metal anodes was investigated. Chosen according to selection criteria previously disclosed, the metal anode is designed to form a protective oxide layer that under cell operating conditions is thick enough to prevent chem. attack of the underlying metal yet thin enough to allow electronic current to pass without a substantial increase in cell voltage. Testing involved electrolysis in a 10 A cell fitted with candidate anodes and TiB2 cathodes. Anode specimens were made of various Cu-Al, Ni-Al, Cr-Al, and Fe-Cr-Al alloys. During cell testing, the anodic c.d. was set at 0.25-2.4 A/cm2. The bath ratio was set at 1.15 and 0.56. When the bath ratio was 1.15, electrolysis was always conducted at 970°, whereas at a bath ratio of 0.56, expts. were performed at 750 and 840°. The alumina concn. was varied from satn. to exhaustion. The best results were obtained at a low temp. in melts with a bath ratio of 0.56. Cells generated O and produced Al contg. <0.1% Cu and Cr. The longest test lasted 47 h. Voltages compared favorably with that measured on a cell fitted with a C anode.

**Pilot cell demonstration of cerium oxide coated anodes.** Gregg, J. S.; Frederick, M. S.; Vaccaro, A. J.; Alcorn, T. R.; Tabereaux, A. T.; Richards, N. E. ELTECH Res. Corp., Fairport Harbor, OH, 44077, USA. Light Met. (Warrendale, Pa.) (1993), 465-73. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 118:217002
**Abstract.** Cu cermet anodes were tested for 213 to 614 h with an in-situ deposited Ce oxyfluoride (CEROX) coating in an Al electrolytic cell. At high bath ratio (.apprx.1.5) and low c.d. (0.5 A/cm2), a dense coating with a thickness of ≥1 mm was deposited on the anodes. At lower bath ratios and higher c.d., the CEROX coating was thinner and less dense, but no change in corrosion rate was noted over initial conditions. Regions of low c.d. on the anodes and sides adjacent to the C anode sometimes had thin or absent CEROX coatings. Problems with cracking

and oxidn. of the cermet substrates led to higher corrosion rates in a pilot cell than would be anticipated from lab scale results.

**Testing of cerium oxide coated cermet anodes in a laboratory cell.** Gregg, J. S.; Frederick, M. S.; King, H. L.; Vaccaro, A. J. ELTECH Res. Corp., Fairport Harbor, OH. 44077, USA. Light Met. (Warrendale, Pa.) (1993), 455-64. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 118:217001
**Abstract.** Cu/NiFe2O4/NiO cermets were evaluated with and without an in-situ deposited cerium oxyfluoride (CEROX) coating in 100 h lab. Al electrowinning tests. Bath ratio and c.d. were varied between tests and corrosion was judged by the contamination of the aluminum and cryolite by cermet components (Cu, Fe, and Ni). Higher bath ratios of 1.5 and 1.6 led to less corrosion and thicker CEROX coatings. Lower current densities led to slightly less corrosion but much less oxidn. of the Cu cermet substrate. Corrosion of the CEROX coated cermets was 1/7th that of an uncoated cermet. Corrosion of CEROX coated cermets in unsatd. alumina conditions was higher than in satd. tests. The elec. cond. of the CEROX coating was .apprx.0.2 Ω-1cm-1, resulting in a slight voltage penalty, depending on the thickness of the coating.

**Behavior and development of NiO-NiFe2O4 based cermets for aluminum reduction.** Yang, Jianhong; Wang, Huazhang; Liu, Yexiang; Xie, Xinjun. Dep. Nonferrous Metall., Central-South Inst. Min. Metall., Changsha, Peop. Rep. China. *Zhongnan Kuangye Xueyuan Xuebao (1993), 24(3), 326-31.* CODEN: CKYPDO; ISSN: 0253-4347. Journal written in Chinese. CAN 120:249787
**Abstract.** Several kinds of NiO-NiFe2O4 based cermet electrodes were developed. A better technique for prepg. cermets has been discovered. The elec. cond. of cermets prepd. by electroless copper plating was better than by mech. copper mixing. The corrosion rate of the cermets was detd. as inert anode in Al redn.

**Fabrication and corrosion of inert anodes in fluoride melt for aluminum electrolysis.** Li, Guoxun; Wang, Chuanfu; Qu, Shuling; Huang, Aiqin; Li, Guobin. Gen. Res. Inst. Nonferrous Met., Beijing, 100088, Peop. Rep. China. Youse Jinshu (1993), 45(2), 53-7. CODEN: YSCSAE; ISSN: 0513-3424. Journal written in Chinese. CAN 120:276077
**Abstract.** A no. of inert anodes including NiO-Fe2O3-base cermets and SnO2 ceramics were fabricated for Al electrolysis. Their properties were measured sep. The corrosion resistance of the anodes was detd. during electrolysis in NaF-AlF3 high-temp. and NaF-KF-AlF3 low-temp. systems, and the corrosion rates were .apprx.0.0015 and 0.0005 cm/h resp. Corrosion in the high-temp. system was a factor of 2-3 times greater than that in the low-temp. system.

**The behavior and improvement of tin(IV) oxide-based inert anodes in aluminum electrolysis.** Yang, Jianhong; Liu, Yexiang; Wang, Huazhang. Dep. Metall., Cent. South Univ. Technol., Changsha, 410083, Peop. Rep. China. Light Met. (Warrendale, Pa.) (1993), 493-5. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 118:178838
**Abstract.** The elec. cond. of typical SnO2-based and rare earth oxide-contg. SnO2-based inert anodes was detd. The elec. cond. of CeO2-contg. SnO2-based inert anodes was increased at both room temp. and elevated temp. The temp. coeff. of its elec. cond. was decreased. The corrosion tests of SnO2-based inert anodes under different conditions indicated that the corrosion resistance of CeO2-contg. SnO2-based anodes was increased, while its corrosion rate was decreased >4-fold. The wettability of SnO2-based electrodes at different compns. of electrolytes was detd., and the wettability between electrolytes and inert anodes was excellent.

**Operational results of pilot cell test with cermet "inert" anodes.** Alcorn, T. R.; Tabereaux, A. T.; Richards, N. E.; Windisch, C. F., Jr.; Strachan, D. M.; Gregg, J. S.; Frederick, M. S. Manuf. Technol. Lab., Reynolds Met. Co., Muscle Shoals, AL, 35661-1258, USA. Light Met. (Warrendale, Pa.) (1993), 433-43. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 118:238107
**Abstract.** The operational performance and corrosion rates of a six-pack of cermet anodes were evaluated in a six kA pilot redn. cell at Reynolds' Manufg. Technol. Lab. Two sep. tests were conducted with the cermet anodes; the first test was in conjunction with the Pacific Northwest Lab. and the second with ELTECH Research Corporation. Both tests used identical NiO-NiFe2O4-Cu anodes manufd. by Ceramic Magnetics, Inc. The ELTECH testing involved in situ coating of the anodes with cerium oxide. Primary evaluations for both tests were conducted at target conditions of alumina satn. and 0.5 A/cm2 anode c.d. Individual anodes remained in operation for 25 days

during the two and one-half month testing period. Operational difficulties developed throughout the test due to breakage of the anode conductor stems, cracking and breakage of the cermet anodes, unequal anode current distribution, and alumina muck build-up in the cell. These operational problems are discussed as well as an est. of anode corrosion rates based on metal impurity levels in the aluminum metal pad.

**The electrodeposition of Al3Ti from chloroaluminate electrolytes.** Stafford, G. R.; Janowski, G. M. Mater. Sci. Eng. Lab., Natl. Inst. Stand. and Technol., Gaithersburg, MD, 20899, USA. Proc. - Electrochem. Soc. (1993), 93-30(Corrosion, Electrochemistry, and Catalysis of Metastable Metals and Intermetallics), 296-310. CODEN: PESODO; ISSN: 0161-6374. Journal written in English. CAN 120:229832
**Abstract.** The electrodeposition and structural characterization of metastable titanium-aluminide alloys contg. up to 28 at. % Ti are reported. The alloys were electrodeposited from a 2:1 AlCl3:NaCl electrolyte contg. Ti(AlCl4)2. Electrodeposits are single phase and those contg. greater than 4 at. % Ti reveal electron diffraction patterns which are consistent with the ordered face-centered cubic (fcc) L12 structure (Al at the faces and Ti at the corners). Anal. of the current transient at the beginning of potentiostatic deposition on tungsten, indicates that Al3Ti forms by instantaneous 3-dimensional nucleation followed by hemispherical diffusion controlled growth.

**Electrodes for electrolysis of aluminum.** Hayashi, Tatsuo; Fujimoto, Kazuhiro; Sekine, Isao; Yuasa, Makoto; Wakasa, Tsutomu. (Nippon Light Metal Co, Japan; Nikkei Giken Kk). Jpn. Kokai Tokkyo Koho, 8 pp. CODEN: JKXXAF. JP 05263285 A2 931012 Heisei. Patent written in Japanese. Application: JP 92-91871 920317. CAN 120:147241
**Abstract.** The electrode comprises carboneous or graphite composite material contg. 40-70 wt.% Zr boride. Optionally in addn. to Zr boride, it can contains 1 or ≥2 kinds of borides selected from Ti, Nb, and Ta borides as a surface layer. Molten salt bath electrolysis can be carried out with a high current efficiency.

**Apparatus for the electrolytic production of metals.** Sadoway, Donald R. (Massachusetts Institute of Technology, USA). U.S., 10 pp. CODEN: USXXAM. US 5254232 A 931019. Patent written in English. Application: US 92-832748 920207. CAN 120:147216
**Abstract.** Improved electrolytic cells for producing metals by the electrolytic redn. of a compd. dissolved in a molten electrolyte are described. In the improved cells, ≥1 electrode includes a protective layer comprising an oxide of the cell product metal formed upon an alloy of the cell product metal and a more noble metal. In the case of an aluminum redn. cell, the electrode can comprise an alloy of aluminum with copper, nickel, iron, or combinations thereof, upon which is formed an aluminum oxide protective layer.

**Electrode and method for electrolysis of aluminum from molten salt bath.** Inai, Toshiaki; Irie, Yoshiro. (Nippon Light Metal Co, Japan; Nikkei Giken Kk). Jpn. Kokai Tokkyo Koho, 7 pp. CODEN: JKXXAF. JP 05247679 A2 930924 Heisei. Patent written in Japanese. Application: JP 92-81677 920303. CAN 120:119420
**Abstract.** The electrodes are a carbonaceous anode and a cathode comprising an integration of C and a heat-resistant and elec. conductive ceramic excellent in wettability with molten Al and the reacting face is arranged in vertical direction. The method involves placing the cathode opposite the anode, arranging a no. of electrodes horizontally with heat-resistant elec. insulators between them in a molten salt bath, and the Al formed is allowed to flow downward in the molten salt bath. A high productivity can be obtained in Al prodn.

**Cathodic processes at titanium diboride/carbon-composite electrodes during aluminum electrolysis.** Raj, S. C.; Skyllas-Kazacos, M. Sch. Chem. Eng. Ind. Chem., Univ. New South Wales, Kensington, 2033, Australia. Electrochim. Acta (1993), 38(5), 663-9. CODEN: ELCAAV; ISSN: 0013-4686. Journal written in English. CAN 118:221897
**Abstract.** The cathodic overpotential for Al deposition decreases gradually as the TiB2 content of the TiB2/C composite electrodes is increased. Increasing the TiB2 content of the composite electrodes makes it easier for them to sustain a thin and continuous film of molten Al metal on their surface, and hence less energy is required to achieve bulk deposition of Al. The overvoltage data can be plotted as straight lines on Tafel plots in the c.d. range of 0.1-0.7 A/cm2 for those composites which have TiB2 contents .gtorsim.60%. For those electrodes whose TiB2 content is .ltorsim.60% and which are not able to sustain a thin, uniform film of metallic Al on their substrates, the Tafel plots exhibited 2 distinct regions corresponding to Na and Al codeposition, resp. The cathodic overpotential on TiB2/C composite cathodes is of the order of 140-200 mV at 1 A/cm2.

**Electrode behavior for the electrolytic production of aluminum-lithium alloy by using molten chlorides.** Sato, Yuzuru; Saito, Sakae; Araike, Eiichi; Suzuki, Takeshi; Yamamura, Tsutomu. Fac. Eng., Tohoku Univ., Sendai, Japan. Keikinzoku (1993), 43(1), 33-9. CODEN: KEIKA6; ISSN: 0451-5994. Journal written in Japanese. CAN 118:201202

**Abstract.** Electrode behavior was studied for producing Al-Li alloys in molten salts contg. LiCl. A cathode is molten aluminum; and lithium electrodeposits into it. The anode is graphite and acts as a chlorine evolution electrode. The electrolysis were carried out at 973 K by using LiCl single melt, LiCl-NaCl and LiCl-KCl eutectic mixt. melts in order to study the electrochem. behavior of the cathode related to the current efficiency and the impurities such as sodium and potassium. For the case of LiCl single melt, required compn. of Al-Li alloy up to 10 mass% Li was easily obtained with high current efficiency, 93-99%, and low level impurities less than 20 ppm which is comparable to the level in the com. pure aluminum. For the case of LiCl-NaCl melt, the current efficiency somewhat decreased and about 320 ppm of sodium was contained in the alloy. For the case of LiCl-KCl melt, the current efficiency markedly decreased although no potassium increase was obsd. The reason for the decrease in the current efficiency is considered to be that the impurities deposit by concn. overvoltage and dissolve into the melt. However, these effects are negligible unless the melt contains large amts. of impurity salts.

**electrodeposition of aluminum-manganese ferromagnetic phase from molten salt electrolyte.** Stafford, G. R.; Grushko, B.; McMichael, R. D. Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA. J. Alloys Compd. (1993), 200(1-2), 107-13. CODEN: JALCEU; ISSN: 0925-8388. Journal written in English. CAN 120:17668

**Abstract.** The ferromagnetic Al-Mn $\tau$ phase was directly electrodeposited from a chloroaluminate molten salt electrolyte contg. $MnCl_2$. Electrodeposits were single phase in the compn. range 48-50 at.% Mn, significantly lower than the 55 at.% Mn reported in the literature for single-phase alloys made by other techniques. The $\tau$ electrodeposits were dense, fine grained, homogeneous, and exhibited strong texture which was primarily a function of deposition temp. Magnetic hysteresis loops generated from as-deposited samples yield magnetization values which are approx. half of literature values for bulk $\tau$ having a compn. of 55 at.% Mn. The measured coercivity, however, was twice as large as reported values, particularly for deposits having (112) texture and positioned perpendicular to the applied field.

**Model of conductivity in doped tin dioxide-base inert anodes for aluminum-electrowinning.** Yin, Zhoulan; Yang, Jianhong; Wang, Huazhang; Zhao, Qinsheng; Liu, Yexiang; Gao, Xiaohui. Cent. South Univ. Technol., Changsha, 410083, Peop. Rep. China. Trans. Nonferrous Met. Soc. China (1992), 2(3), 59-63. CODEN: TNMCEW. Journal written in English. CAN 118:25373

**Abstract.** Quantum chem. calcns. based on exptl. data were used to develop a model predicting the elec. cond. of chem. inert Al electrolyzer anodes made of $SnO_2$ with additives. The elec. cond. of anodes increased with 1-3% addn. of $Sb_2O_3$, ZnO, $MnO_2$, $TiO_2$, $Co_2O_3$, and $IrO_2$ without affecting the physicochem. properties of anodes operating in cryolite-$Al_2O_3$ melts.

**Effect of impurities on the combustion rate of electrode cokes.** Sigrist, K.; Jedamizik, J.; Schoen, G. Berlin, Germany. Freiberg. Forschungsh. A (1992), A826, 48-56. CODEN: FFRAA7; ISSN: 0071-9390. Journal written in German. CAN 119:186985

**Abstract.** The kinetics of coke oxidn. in anodes for the electrowinning of Al was detd. from thermogravimetric measurements at linear temp. rise. Synergistic effects in the presence of several impurities were taken into account. Unambiguous dependences of activation energy on the concn. of individual impurities were established. Fe, V, and Ca catalyze while Si and Ni + Na inhibit the oxidn. of coke.

**On the corrosion and the behavior of inert anodes in aluminum electrolysis.** Xiao, Haiming; Hovland, Rune; Rolseth, Sverre; Thonstad, Jomar. Lab. Ind. Electrochem., Norw. Inst. Technol., Trondheim, 7034, Norway. Light Met. (Warrendale, Pa.) (1992), 389-99. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 117:195599

**Abstract.** The corrosion rate of inert anodes based on either $SnO_2$ or Ni ferrite cermets was studied as a function of operating parameters. Low alumina concns. led to catastrophic corrosion of the inert anodes, and high current densities and high as well as low $NaF/AlF_3$ molar ratios were detrimental. Signs of electrolyte penetration into the anode and intergranular corrosion were obsd. To investigate the corrosion mechanism, the anodes were obsd. under extreme conditions, such as use of high-purity cryolite and high c.d. Electrochem. measurements and SEM studies were also conducted. Low alumina concn. and high c.d. give a high anodic potential, which cause the anode to decomp. into O and corrosion products. The current efficiency obtained with inert anodes in a lab. cell was slightly higher than that of C anodes.

**A review of RHM cathode development.** McMinn, Curtis J. Manuf. Technol. Lab., Reynolds Met. Co., Muscle Shoals, AL, 35661-1258, USA. Light Met. (Warrendale, Pa.) (1992), 419-25. CODEN: LMPMDF; ISSN: 0147-0809. Journal; General Review written in English. CAN 117:256328.
**Abstract.** A review, with 28 refs., of the development and manuf. of refractory hard-metal (RHM) cathodes.

**Corrosion mechanism of tin dioxide-based inert anodes.** Wang, Huazhang; Yang, Jianhong; Liu, Yexiang; Thonstad, J. Cent. South Univ. Technol., Changsha, 410083, Peop. Rep. China. Trans. Nonferrous Met. Soc. China (1992), 2(4), 8-13, 20. CODEN: TNMCEW. Journal written in English. CAN 119:54443
**Abstract.** According to the extent of their damage in cryolite melts, the corrosion of $SnO_2$-based inert anodes can be divided into three types: slight corrosion, marked corrosion, and catastrophic corrosion. The conditions under which these three types take place and their mechanisms are different. Our work shows that depletion of oxygen contg. ions in melts, high d., electrolyte penetration into the electrode, and intergranular corrosion contribute greatly to marked corrosion and catastrophic corrosion and that the redn. reaction by aluminum only attacks the electrode slightly.

**Electrodeposition of aluminum and magnesium from aprotic organic electrolyte solutions.** Eckert, J. Tech. Hochsch., Leuna-Merseburg, Germany. DECHEMA Monogr. (1992), 125(Elektrochem. Stoffgewinnung: Grundlagen Verfahrenstech.), 425-35. CODEN: DMDGAG; ISSN: 0070-315X. Journal; General Review written in German. CAN 117:120317
**Abstract.** A review with 16 refs. So far, only molten salts have been available as electrolytes for the electrodeposition of Al and Mg. Now these 2 metals can be deposited from org. electrolytes. As compared with molten salts, org. electrolytes have the advantage that they can be used at normal temp.

**Electrochemical studies on wettability of sintered titanium diboride electrodes in aluminum electrolysis.** Raj, S. C.; Skyllas-Kazacos, M. Sch. Chem. Eng. Ind. Chem., Univ. New South Wales, Kensington, 2033, Australia. Electrochim. Acta (1992), 37(8), 1395-401. CODEN: ELCAAV; ISSN: 0013-4686. Journal written in English. CAN 117:78626
**Abstract.** Electrochem. studies were conducted to better understand the behavior of sintered $TiB_2$ cathodes in cryolite-alumina melts. Cyclic voltammetry has also been used to identify the origin of the cathodic prewaves seen when the electrodes are cycled in the unsatd. melts. These cathodic prewaves have been attributed to the redn. of $TiO_2$ and $B_2O_3$ formed during anodic scanning of the $TiB_2$. Furthermore, microprobe anal. work has shown that the sintered $TiB_2$ substrate is susceptible to penetration by the melt components. This has been seen to affect the long-term wetting properties of the substrate by affecting the surface in contact with the molten bath. It has also been seen that subjecting the electrode to controlled oxidn. for long periods results in a black deposit formation on the $TiB_2$ surface, and this hinders the aluminum deposition process, particularly in the alumina-satd. melts. The overall wetting properties of $TiB_2$ have been compared to those of graphite as these two materials are the principal components of the $TiB_2$/C composite cathodes that are being investigated for use in low energy aluminum electrolysis cells.

**Low-temperature electrochemistry at superconducting electrodes.** Lorenz, W. J.; Saemann-Ischenko, G.; Breiter, M. W. Inst. Phys. Chem. Electrochem., Univ. Karlsruhe, Karlsruhe, Germany. Condens. Matter Phys. Aspects Electrochem., Proc. Conf. (1991), 454-73. Editor(s): Tosi, Mario P.; Kornyshev, Alexei A. Publisher: World Sci., Singapore, Singapore. CODEN: 58AUAB. Conference written in English. CAN 117:78606
**Abstract.** The charge transfer across the superconductor/ionic conductor interface represents a relatively unknown field at present. This paper deals with the 1st electrochem. studies in this area. Both n-type classical and p- and n-type high Tc superconductors (HTSC) are considered. Different solid electrolytes (Ag β"-alumina, $Ag^+$-conducting glass, and $RbAg_4$.perp.5) are used in expts. covering a temp. range down to 10 K. A transient technique in the time

domain and electrochem. impedance spectroscopy (EIS) in the frequency domain are used to study the Ag deposition as the faradaic charge transfer process at that interface. The results show an admittance peak in transient measurements or a corresponding neg. peak of the polarization resistance in EIS-measurements at T ≈ Tc. These findings are attributed to an increase of the exchange c.d. around Tc. The effect is much less on an A15 compd. (Nb76.1Al17.7Ge6.2) than on HTSCs. The effect can only be interpreted as a quantum electrochem. phenomenon caused by the contribution of Cu pairs crossing the electrochem. double layer as correlated charge carriers. A proximity-like phenomenon can be excluded.

**Improving the conductivity of carbon block cathodes.** Zhang, Zhuying. Guizhou Alum. Smelter, Guizhou, Peop. Rep. China. Youse Jinshu (1991), 43(3), 56-61. CODEN: YSCSAE; ISSN: 0513-3424. Journal written in Chinese. CAN 116:157338
**Abstract.** Methods for improving the elec. cond. of C block cathodes and new technol. used in full-scale testing are described. The potential application of high-cond. C-block cathodes in Al electrolysis and its energy-saving effects are assessed. The new technol. for manuf. of C block cathodes provides a new approach to energy conservation in Al manuf.

**Energy consumption in alumina reduction cells.** Kvande, Halvor. Hydro Alum. A/S, Stabekk, N-1321, Norway. Light Met. (Warrendale, Pa.) (1991), 421-6. CODEN: LMPMDF; ISSN: 0147-0809. Journal; General Review written in English. CAN 116:178062
**Abstract.** A review, with 24 refs., with emphasis on the cell voltage and the anodic c.d.

**Electrochemical and chemical reactivity of carbon electrodeposited from cryolitic melts containing aluminum carbide.** Oedegaard, Rolf; Midtlyng, Svein Haavard. SINTEF Metall., Trondheim, N-7034, Norway. J. Electrochem. Soc. (1991), 138(9), 2612-17. CODEN: JESOAN; ISSN: 0013-4651. Journal written in English. CAN 115:192416
**Abstract.** When used as an anode in Al electrolysis cells, C electrodeposited from cryolitic melts contg. Al carbide shows a much higher overvoltage toward the CO2 evolution reaction than do anodes of graphite and prebake anode material when tested under identical conditions. The chem. reactivity of electrodeposited C in gaseous CO2 (std. petroleum coke reactivity method) was significantly lower for electrodeposited C than for prebaked anode materials. It was demonstrated in lab. cells that it is possible to form a "spike" on 1 anode out of 2. These results give support to the hypothesis that there is a correlation between electrodeposition of C from dissolved Al carbide and formation of socalled "spikes" on anodes in Hall-Heroult cells.

**Study of pulsed electrolytic deposition of aluminum onto aluminum, platinum and iron electrodes.** Manoli, Georgia; Chryssoulakis, Yannis; Poignet, Jean Claude. Natl. Tech. Univ., Athens, Greece. Plat. Surf. Finish. (1991), 78(3), 64-9. CODEN: PSFMDH; ISSN: 0360-3164. Journal written in English. CAN 114:255772
**Abstract.** Expts. with electroplating aluminum on aluminum, platinum and iron electrodes from an acidic AlCl3 and N-butylpyridinium chloride 2:1 melt were made using square-wave pulsating currents at 25°. Results demonstrate the the main factor detg. the quality of the electrodeposit is the homogeneous formation of the first nuclei layer. This condition is achieved primarily by application of either a double cathodic pulse, followed by an off-time period, or a cathodic pulse followed by an anodic pulse of short duration, together with an off-time period.

**The electrodeposition of aluminum and aluminum alloys from alkylbenzene-hydrobromic acid electrolytes. Theoretical considerations and applications.** Capuano, G. A. Chem. Dep., Univ. Quebec, Montreal, PQ, H3C 3P8, Can. J. Electrochem. Soc. (1991), 138(2), 484-90. CODEN: JESOAN; ISSN: 0013-4651. Journal; General Review written in English. CAN 114:110517
**Abstract.** A review with 30 refs. is given. Theor. considerations pertaining to the electrodeposition of aluminum and aluminum alloys (Al-Cu, Al-Pb, Al-Sn, Al-Cd, and Al-Zn) from alkylbenzene-HBr electrolytes are reviewed. Applications of the aluminum plating process have been reviewed with special emphasis on aluminum alloys plating, thicker coatings realization by pulse plating and barrel plating of ordinary and aircraft fasteners.

**Generalized equations for determination of regime parameters for baking of cathodes of aluminum electrolytic cells and characteristics of baking with anode molding.** Panov, E. N.; Bozhenko, M. F.; Teplyakov,

F. K.; Damilenko, S. V.; Zverev, Yu. A. KPI, USSR. Tsvetn. Met. (Moscow) (1991), Issue 4, 20-4. CODEN: TVMTAX; ISSN: 0372-2929. Journal written in Russian. CAN 115:163512
**Abstract.** A generalized equation for calcg. the av. temp. of the bottom (cathode) of Al electrolyzers using the current intensity and voltage drop on the electrolyzer was derived. A math. expression is given for the detn. of the voltage drop rate as a function of the initial voltage drop and the optimum sintering time of the cathode. Exptl. data related to the firing of Al electrolyzers with molten metal (Al) at 150-175 kA with simultaneous forming of the anode are given.

**Current efficiency of a bipolar laboratory aluminum electrolysis cell.** Feng, Naixiang; Qiu, Zhuxian; Kai, Grjotheim; Halvor, Kvande. Northeast Univ. Technol., Shenyang, Peop. Rep. China. Light Met. (Warrendale, Pa.) (1990), 379-83. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 113:220185.
**Abstract.** A bipolar lab. aluminum electrolysis cell was studied exptl. with respect to current efficiency and back emf. The lower part of the cell, between the bipolar electrode and the cathode, had the higher current efficiency and the lower back emf. Both current efficiency and back emf. increased with increasing cell current. The leakage of current from the bipolar electrode directly to the side wall of the cell was reduced by increasing the cell current and by increasing the height of the bipolar electrode.

**Results of 100 hour electrolysis test of a cermet anode: operational results and industry perspective.** Peterson, R. D.; Richards, N. E.; Tabereaux, A. T.; Koski, O. H.; Morgan, L. G.; Strachan, D. M. Manufact. Technol. Lab., Reynolds Met. Co., Sheffield, AL, USA. Light Met. (Warrendale, Pa.) (1990), 385-93. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 114:10013
**Abstract.** The operating performance of a 15-cm diam. prototype cermet anode was evaluated in a lab. Al redn. cell. The anode was preheated in a muffle furnace and then hot transferred to the electrolysis cell without fracture. No major operational difficulties were encountered in the electrolysis test which lasted for 113.5 h. Av. current to the anode was 120.9 A or 0.69 A/cm2 based on conduction through the bottom surface only. A graphite anode of comparable size was used to start the test and provide a baseline for comparison purposes. The cell operating parameters including individual voltage components, anode c.d., alumina content, current scans, and anode bubble characteristics are discussed.

**A materials systems approach to selection and testing of nonconsumable anodes for the Hall cell.** Sadoway, Donald R. Dep. Mater. Sci. Eng., Massachusetts Inst. Technol., Cambridge, MA, 02139, USA. Light Met. (Warrendale, Pa.) (1990), 403-7. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 114:10014
**Abstract.** Based on an anal. of the Hall cell as a dynamic system, a set of selection criteria was set up to identify materials for use as nonconsumable anodes in Al prodn. New materials and anode designs were discovered. Beyond the question of choice of anode, a broader framework for success/failure anal. was constructed so that such factors as anode design and test conditions are systematically studied.

**electrolyte for electrolytic refining of aluminum.** Oblakowski, Ryszard; Jarosz, Piotr. (Akademia Gorniczo-Hutnicza im. Stanislawa Staszica, Pol.). Pol., 2 pp. CODEN: POXXA7. PL 163036 B1 940228. Patent written in Polish. Application: PL 90-287128 900928. CAN 122:117511
**Abstract.** The fluoride electrolyte contg. 18 wt. % of BaF2 was used for the aluminum refining. The electrolyte contg. addnl. 2-4 MgF2,, 2-4 LiF, 10-14 CaF2, 38-42 AlF3 and 22-24 NaF wt. %. The electrolyte provided decreases in the electrolytes and in the elec. energy usages.

**Preparation of carbon anodes and cathodes.** Deutzer, Manfred. (Elektrokohle Lichtenberg A.-G., Fed. Rep. Ger.). Ger. (East), 2 pp. CODEN: GEXXA8. DD 292936 A5 910814. Patent written in German. Application: DD 90-338803 900316. CAN 115:242493
**Abstract.** In the prepn. of C anodes and cathodes having holes or grooves, esp. for fusion electrolysis in Al prodn., by mixing coke and a binder, shaping, and heat treating, the anodes and cathodes are post-heat-treated in the vicinity of the holes or grooves.

**Results from a 100-hour electrolysis test of a cermet anode: materials aspects.** Strachan, D. M.; Koski, O. H.; Morgan, L. G.; Westerman, R. E.; Peterson, R. D.; Richards, N. E.; Tabereaux, A. T. Pac. Northwest Lab.,

Richland, WA, 99352, USA. Light Met. (Warrendale, Pa.) (1990), 395-401. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 114:27605
**Abstract.** A 15-cm diam. prototype NiO-NixFe3-xO4-17%Cu cermet anode was tested for Al prodn. The anode was cut in half, and samples were taken that were above, at, and below the electrolyte level. The microstructure and phases were different in each of these areas. The Cu oxidized to CuO above the electrolyte, but Cu2O was the favored oxidn. product in the anode in the electrolyte.

**Pilot reduction cell operation using titanium diboride-graphite cathodes.** Alcom, T. R.; Stewart, D. V.; Tabereaux, A. T.; Joo, L. A.; Tucker, K. W. Manufact. Technol. Lab., Reynolds Met. Co., Sheffield, AL, 35660, USA. Light Met. (Warrendale, Pa.) (1990), 413-18. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 114:11039
**Abstract.** A 4-wk operation of a pilot redn. cell using TiB2-graphite cathode elements demonstrated the com. viability of the material. Using 2 different TiB2-graphite cathode shapes under sep. anodes, the materials served as the primary cathode, effectively decreasing anode-cathode distance and cell voltage. Testing under various operating conditions, including close anode-cathode distances, demonstrated excellent cell stability using the cathode elements. The TiB2-graphite cathode material exhibited excellent thermal shock properties withstanding startup and removal from the cell during operation. Dissoln. of the TiB2-graphite material in the Al metal showed acceptable life; however, dissoln. rates of the SiC holders exposed to cryolite were unacceptable.

**Some important performances of titanium diboride-coated cathode carbon block.** Liao, Xianan; Liu, Yexiang. Dep. Metall., Cent. South Univ. Technol., Changsha, 410083, Peop. Rep. China. Light Met. (Warrendale, Pa.) (1990), 409-12. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 114:28833.
**Abstract.** Elec. cond., resistance to corrosion, and wettability by molten Al of TiB2-coated cathode C blocks were examd. The coating had better cond. than common cathode block. The modified M. B. Rapoport test (1957) showed that the expansion of C block from Na penetration of coated block is 40% less than that of uncoated block. The wetting angles of molten Al on graphite or C block are .ltorsim.180° in the cryolite melt-Al electrode system, but <70° between molten Al and TiB2-coated block. No polarization effects were obsd. on the wetting angle.

**Reversibility of aluminum electrode potential in aluminizing electrolyte containing dimethylethylphenylammonium bromide.** Simanavicius, L.; Sarkis, A. Inst. Khim. Khim. Tekhnol., Vilnius, USSR. Chemija (1990), Issue 1, 31-6. CODEN: CHMJES. Journal written in Russian. CAN 114:236488
**Abstract.** The current-voltage characteristics and the concn. dependence of the Al electrode potential were analyzed. The elec. potential of the Al electrode was reversible in toluene contg. dimethylethylphenylammonium bromide. The studied system can be used as a ref. electrode.

**Anode current density distribution in an aluminum electrolysis cell with sloping electrodes.** Kasherman, Djen; Skyllas-Kazacos, Maria. Sch. Chem. Eng. Ind. Chem., Univ. New South Wales, Kensington, Australia. Aluminium (Duesseldorf) (1990), 66(12), 1157-60. CODEN: ALUMAB; ISSN: 0002-6689. Journal written in English. CAN 114:216703
**Abstract.** Math. models were developed to est. the effects of changing mode-cathode d. distribution for an Al electrolysis cell employing a sloping inert-wettable cathode material and a sloping C anode. The models show that the anode c.d. at the bottom section (sloping) increases as anode-cathode distance decreases, which leads to a higher anode overvoltage and a higher local C consumption rate. The current distribution in the presence of bubbles has also been math. modeled. The magnitude of anode c.d. variations depends strongly on the nature of the bubble layers so that any parameter which influences the gas vol. fraction or layer thickness (e.g., cryolite temp., additives or interfacial properties of C anode), could have a marked effect on the anode current distribution in Al electrolysis cells. Therefore, the significance of these changes will have to be accounted for in the design and operation of new long-energy cells.

**Electrochemical study of the aluminum carbide or oxycarbide formation in acidic cryolite-alumina melts at 1300 K.** Chryssoulakis, Y.; Righas, G. Dep. Chem. Eng., Natl. Tech. Univ., Athens, 15773, Greece. Bull. Soc. Chim. Fr. (1990), Issue Sept.-Oct., 635-40. CODEN: BSCFAS; ISSN: 0037-8968. Journal written in French. CAN 114:71091

**Abstract.** The electrochem. reaction was studied of the aluminum carbide or oxycarbide formation in acidic-cryolite-alumina m. 1300 K using triangular voltammetry on graphite electrodes. Five reoxidn. peaks are obsd. The first of them (obsd. at the most cathodic potential) is attributed to the aluminum reoxidn. reaction, while the other four characterize the reoxidn. of the aluminum carbides or oxycarbides which are formed during the cathodic potential sweep. The study of the voltammograms obtained and the comparison of the obsd. reoxidn. peak potentials with the calcd. ones using appropriate available thermodn. data permit to propose three reoxidn. schemes for the compds. Al4C3, Al4O4C and Al2OC.

**Electrodeposition of aluminum, aluminum/magnesium alloys, and magnesium from organometallic electrolytes.** Mayer, Anton. Mater. Sci.-Technol. Div., Los Alamos Natl. Lab., Los Alamos, NM, 87545, USA: J. Electrochem. Soc. (1990), 137(9), 2806-9. CODEN: JESOAN; ISSN: 0013-4651. Journal written in English. CAN 113:180250

**Abstract.** The possibility was explored of plating an alloy of Al from organometallic solns. Also Mg was considered as an alloying constituent because Mg alkylds are inexpensive and readily available com. chems. All the operations were carried out under pos. pressure with a continuous flow of dry N or Ar to prevent reactions with air or water. Most electrolysis expts. were conducted with liq. vols. of 100-500 mL. In the plating solns. for the Mg, an attempt was made to form complexes of Mg alkylds and alkali metal fluorides analogous to the Ziegler organoaluminum electrolytes, but complex formation did not occur. The plating solns. can be prepd. by combining the alkyl Mg/diethyl ether soln. with the alkyl Al and slowly heating the mixt. to .apprx.100° to boil off the ether solvent. Toluene is then added to the soln. followed by slow addn. of the alkali metal fluoride. The soln. is then heated and stirred to form the complex salts that are elec. conductive species of the electrolyte. A typical bath compn. for depositing pure Mg was: CsF 1, Et2Mg 2, Et3Al 4, (iso-Bu)3Al 2 and toluene 3 (mol ratio). A foil electroformed in this bath at 1 A/cm2 under moderate agitation at 40° was 99.4 at% Mg. A typical bath for depositing a Mg/Al alloy was: KF 1.Et2Mg 0.67, Et3Al 2.5, (iso-Bu)3Al 0.83, and toluene 1.5 (mol ratio). A brass panel plated in this bath at 1 A/dm2 at a cell voltage of 1-5 V and 109° produced a bright deposit of .apprx.50 at.% Mg - 50 at.% Al as analyzed by x-ray fluorescence spectroscopy. The alloy deposits were generally smooth and bright in the 10-90% compn. ranges of both metals.

**Viscosity, specific conductivity, and density of organic electrolytes used in electrodeposition of aluminum.** Ladouceur, M.; Capuano, G. A. Dep. Chim., Univ. Quebec, Montreal, PQ, H3C 3P8, Can. Can. Metall. Q. (1990), 29(1), 87-92. CODEN: CAMQAU; ISSN: 0008-4433. Journal written in French. CAN 112:109388

**Abstract.** The viscosity, cond. and d. of solns. of Al2Br6 in several arom. solvents and solvents mixts., have been detd. The cond. and viscosity increase spontaneously with time. At a cond. of 2.5 × 10-3 Ω-1 cm-1 and 20°, pseudocumene gives the highest viscosity value and ethylbenzene-toluene (1:1 vol.) produces the lowest viscosity. The obsd. results have demonstrated a non-Stokesian behavior for all the solns. studied and a relay type mechanism for the cond. The data presented should be useful in the design of industrial plating systems for aluminum electrodeposition from org. electrolytes.

**Electrodeposition of metals from nonaqueous organic electrolytes.** Landau, Uwe. MIB Metall., Berlin, Fed. Rep. Ger. Jahrb. Oberflaechentech. (1990), 46, 163-74. CODEN: JBOFAN; ISSN: 0075-2819. Journal; General Review written in German. CAN 113:63413

**Abstract.** A review with 79 refs. on the electrodeposition of metals from org. electrolytes with special attention to the electrodeposition of Al and Al alloys.

**Electrode for electrolysis.** Hirakata, Kaoru; Fujii, Akihiko; Okabe, Yoshio. (Japan Carlit Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho, 6 pp. CODEN: JKXXAF. JP 01298189 A2 891201 Heisei. Patent written in Japanese. Application: JP 88-125984 880525. CAN 112:206646

**Abstract.** An electrode comprising a Pt-group metal and/or its oxide on a valve-metal substrate has an ion-irradiated middle layer of Pt, Ir, Ru, Os, Rh, Pd, Ti, Ta, Nb, Zr, Mo, W, Fe, Co, Ni, Mn, Pb, Sn, Sb, Bi, In, Tl, Al, and/or their oxides. The electrode is durable.

**Steel cathode rod system for aluminum electrolysis bath.** Zhang, Zuming. (Zhengzhou Light Metals Institute, Peop. Rep. China). Faming Zhuanli Shenqing Gongkai Shuomingshu, 6 pp. CODEN: CNXXEV. CN 1032682 A 890503. Patent written in Chinese. Application: CN 88-10677 880913. CAN 115:37460

**Abstract.** A steel cathode rod system used in an Al electrolysis bath comprises an upper steel rod, a lower steel rod, an internally connected steel rod, and an externally connected steel rod with the upper and the lower steel rods parallel to each other and connected through the other steel rods by welding to form an integral structure. The structural parameters of the rod system are so selected to give an optimum magnetic field distribution in the electrolysis bath, resulting in high current efficiency, reduced electricity consumption, and prolonged bath life.

**Electric-conductivity meters for determination of electrolyte concentration.** Sato, Kimiyasu; Miyaki, Yoshuki; Hirao, Kazuhiro; Matsumoto, Yukie. (Tosoh Corp., Japan; Permelec Electrode Ltd.). Jpn. Kokai Tokkyo Koho, 5 pp. CODEN: JKXXAF. JP 01203952 A2 890816 Heisei. Patent written in Japanese. Application: JP 88-29886 880210. CAN 112:201272
**Abstract.** The metal electrodes (e.g., Ti, Ta, Nb, Zr) for the elec.-cond. meters are coated with oxides of Pt, Ir, Os, Pd, Ru, and/or Rh, with optional Pt, Ir, Os, Pd, Ru, and/or Rh, Ti, Ta, Nb, Zr, Hf, Al, Si, Sn, Sb, and/or Bi to increase the corrosion resistance.

**Electrochemically producing a desired product from a reactant during electrolysis in a molten salt composition.** LaCamera, Alfred F.; Van Linden, Jan H. L.; Pierce, Thomas V.; Parkhill, James O. (Aluminum Co. of America, USA). PCT Int. Appl., 23 pp. CODEN: PIXXD2. WO 8906289 A1 890713. Designated States: W: AU, BR, NO, US, US. Designated States: RW: AT, BE, CH, DE, FR, GB, IT, LU, NL, SE. Patent written in English. Application: WO 88-US4565 881219. Priority: US 87-138391 871228; US 88-197889 880524 CAN 111:183124
**Abstract.** In the cell and process, metals and metal alloys are formed from oxides or nitrides in a molten salt, without the evolution of halogen or halogen compds., with less corrosion and reduced power consumption, by the use of an electrode having an extended or substantially increased surface area, effective for the evolution of O and C oxide, and a molten salt electrolyte effective at low temp. Preferably, Al is produced from Al2O3 using the cell and process.

**Electrodeposition of aluminum from solutions based on triethylaluminum.** Kazakov, V. A.; Titova, V. N.; Petrova, N. V. Inst. Fiz. Khim., Moscow, USSR. Elektrokhimiya (1989), 25(7), 1006-9. CODEN: ELKKAX; ISSN: 0424-8570. Journal written in Russian. CAN 111:104495
**Abstract.** The electrodeposition of Al was studied from org. solvents (toluene, xylene, mesitylene) contg. NaF.2AlEt3. The effect of temp., c.d., and Al salt content was examd. The elec. cond. of the electrolyte bath and the surface structure of the Al electrodeposits were also investigated.

**The behavior of inert anodes as a function of some operating parameters.** Wang, H.; Thonstad, J. Lab. Ind. Electrochem., Norweg. Inst. Technol., Trondheim, Norway. Light Met. (Warrendale, Pa.) (1989), 283-90. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 110:234976
**Abstract.** The corrosion behavior of SnO2-based anodes was studied at varying bath compn., and also Ni ferrite anodes. With the SnO2-based material, high LiF contents and high as well as low NaF/AlF3 molar ratios had a detrimental effect on the anode performance. At > 5% LiF, the corrosion rate increased sharply at 2 A/cm2 c.d., whereby the anode disintegrated. The effect of increasing excess AlF3 was far less dramatic, but it appears that the optimum NaF/AlF3 molar ratio is 2.6-3.0. The Ni ferrite anodes also showed increased corrosion rates at high excess AlF3 contents. The corrosion mechanism is discussed.

**The development of cerium oxide coatings from cryolite melts. A self-forming anode for aluminum electrowinning.** Walker, J. K.; Kinkoph, J.; Saha, C. K. ELTECH Res. Corp., Fairport Harbor, OH, 44077, USA. J. Appl. Electrochem. (1989), 19(2), 225-30. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 110:221429
**Abstract.** The anodic deposition of Ce oxide from cryolite melts onto Sn oxide substrates was investigated. Such a coated structure offers promise as an O-evolving anode in Hall-Heroult cells. The development and dimensional stability of the coating is established by the equil. between the bath components and the Ce oxide. The coating thickness and morphol. is shown to be dependent on the initial Ce oxide bath concn. and, to a lesser extent, on c.d. The presence of the Ce oxide coating greatly diminishes dissoln. of the anode substrate and increases the purity of the electrowon Al. The protection afforded by the coating is achieved by reducing the exposed substrate surface area.

**Studies on inert electrodes in aluminum electrolysis.** Xue, Jilai; Qiu, Zhuxian. Northeast Inst. Technol., Shenyang, Peop. Rep. China. Zhenkong Kexue Yu Jishu (1988), 8(5), 55-9, 49. CODEN: CKKSDV; ISSN: 0253-9748. Journal written in Chinese. CAN 111:30232

**Abstract.** SnO2-based inert anodes with oxides or metal as modifier was prepd. for Al electrorecovery. The apparent d. of the cathode was 4.6-6.7 g/cm3 and the resistivity was 0.0082-0.021 Ω.cm (960-1000°). Graphite cathode with an intermediate layer and coated with TiB2 (on the intermediate layer, i.e. outermost layer) was prepd. for Al electrorecovery. In the electrorecovery of Al in a 100 A exptl. cell with the above anode and cathode, the current efficiency reached .apprx.90% and the anode corrosion rate decreased to 0.0035 g/cm2.h.

**Studies on inert electrodes in aluminum electrolysis.** Xue, Jilai; Qiu, Zhuxian. Northeast Inst. Technol., Shenyang, Peop. Rep. China. Youse Jinshu (1988), 40(4), 55-9, 49. CODEN: YSCSAE; ISSN: 0513-3424. Journal; General Review written in Chinese. CAN 117:35556

**Abstract.** SnO2-based inert anodes with oxides or metal as modifier was prepd. for Al electrorecovery. The apparent d. of the cathode was 4.6-6.7 g/cm3 and the resistivity was 0.0082-0.021 Ω.cm (960-1000°). Graphite cathode with an intermediate layer and coated with TiB2 (on the intermediate layer, i.e. outermost layer) was prepd. for Al electrorecovery. In the electrorecovery of Al in a 100 A exptl. cell with the above anode and cathode, the current efficiency reached .apprx.90% and the anode corrosion rate decreased to 0.0035 g/cm2.h.

**Preparation of carbon electrodes for use in aluminum electrolyzers.** Romovacek, George R.; Lytmak, Edward P.; Buxton, James H.; Pascoe, Frank J. (Koppers Co., Inc., USA). Braz. Pedido PI, 12 pp. CODEN: BPXXDX. BR 8606516 A 880712. Patent written in Portuguese. Application: BR 86-6516 861230. CAN 110:123905

**Abstract.** The electrodes are prepd. by mixing C particles with tar, molding the resultant mixt. to the shape desired, measuring the packing state of the article, remolding it with altered proportions of tar and C if necessary to obtain the desired packing properties, and then baking the electrode to its final hard condition.

**Baking process and apparatus for production of carbon electrodes.** Dreyer, Christian; Thomas, Jean Claude; Vanvoren, Claude. (Aluminium Pechiney, Fr.). Faming Zhuanli Shenqing Gongkai Shuomingshu, 22 pp. CODEN: CNXXEV. CN 87104218 A 880106. Patent written in Chinese. Application: CN 87-10421 870615. Priority: FR 86-8987 860617; FR 87-5466 870414 CAN 110:103911

**Abstract.** C blocks which are used as electrodes in electrolytic cells for prodn. of Al or in electrolytic alloying processes are produced by mixing coke with asphalt at 120-200° to form a melt, shaping into blocks, and baking at 1100-1200° under vacuum for 100 h in an app. comprising preheating, baking, and cooling chambers. The app., in which the vacuum and temp. are carefully controlled and monitored, is also claimed.

**Method of controlling an aluminum electrolyzer.** Borzykh, S. D.; Kapp, V. A.; Timofeev, N. A. (Bratsk Aluminum Plant, USSR). U.S.S.R. CODEN: URXXAF. SU 1435666 A1 881107. Patent written in Russian. Application: SU 87-4219103 870402. CAN 110:65728

**Abstract.** The interelectrode distance is controlled by monitoring resistance.

**Electrocatalytic activity of doped carbon anode in aluminum electrolysis process.** Xiao, Haiming; Liu, Yexiang; Liu, Longyu. Dep. Nonferrous Metall., Inst. Min. Metall., Changsha, Peop. Rep. China. Zhongnan Kuangye Xueyuan Xuebao (1988), 19(3), 279-85. CODEN: CKYPDO; ISSN: 0253-4347. Journal written in Chinese. CAN 110:47334

**Abstract.** The anode overvoltage of C anode in the existing Al electrolysis process is 0.4.apprx.0.6 V. The reducing of anodic overvoltage to save energy was carried out by increasing the catalytic activities of the C anode with dopants. The anodic overvoltage of C anodes in Na3AlF6-Al2O3 (satd.) melt was measured by means of steady state technique. Obvious electrocatalytic activities were obsd. on the C anodes with Ru, Cr and Li dopants. The anodic overvoltage was reduced by >0.2 V under the industrial c. ds. The estd. energy savings were 6.0% when this technique was used. A primary discussion related to the function of dopants in C anode and the mechanism of the above mentioned electrochem. process are also described.

**Pilot plant testing of the petroleum cracking pitch in the preparation of anodes.** Itskov. M. L.; Denisenko. A. G.; Skripnik, A. G.; Belik, T. M.; Konyaeva, A. P. USSR. Tsvetn. Met. (Moscow) (1988), Issue 6, 58-9. CODEN: TVMTAX; ISSN: 0372-2929. Journal written in Russian. CAN 109:153546

**Abstract.** Petroleum cracking pitch (softening temp. 78°, α1-fraction content 0.12%, α-fraction content 4%, ash content 0.13%) can be used in place of coal pitch as a binder in self-baking anodes in Al electrolyzers. The petroleum cracking pitch is less carcinogenic than coal pitch.

**Improving the quality of self-baking electrodes.** Kulesh. M. K.; Frizorger, V. K.; Zalivnoi, V. I.; Teplyakov, F. K. USSR. Tsvetn. Met. (Moscow) (1988), Issue 6, 53-5. CODEN: TVMTAX; ISSN: 0372-2929. Journal written in Russian. CAN 109:153545

**Abstract.** The quality of self-baking anodes in Al electrolyzers was improved and consumption of anode mass decreased by decreasing the level of liq. coke-pitch mixt. in the anodes during the winter season.

**D.C. pulse plating and barrel electrodeposition of aluminum and aluminum alloys from alkylbenzene electrolytes.** Capuano, G. A. Dep. Chem., Univ. Quebec, Montreal, PQ, H3C 3P8, Can. Can. Metall. Q. (1988), 27(2), 155-61. CODEN: CAMQAU; ISSN: 0008-4433. Journal; General Review written in English. CAN 109:114384

**Abstract.** A review is given with 28 refs. An increase in coating thickness is achieved by using pulse plating. Barrel plating of steel and Ti fasteners promotes enhanced corrosion resistance following a chromating.

**A new bath for the electrodeposition of aluminum. III. The electrochemical behavior of the rotating aluminum disk electrode in pure aluminum trichloride/THF-toluene solutions.** Badawy, W. A.; Sabrah, B. A. Fac. Sci., Cairo Univ., Cairo, Egypt. J. Appl. Electrochem. (1988), 18(2), 220-4. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 108:228368

**Abstract.** The kinetic parameters controlling the electrode processes were investigated. The effect of the concn. of AlCl3, the speed of rotation of the rotating disk electrode and the temp. on the cathodic and anodic c.d. was analyzed. The results were compared with those for AlCl3-LiAlH4/THF-toluene solns.

**Future uses of inert materials for the electrolysis of aluminum chloride.** Delimarskii, Yu. K.; Makogon, V. F.; Gudymenko, A. M.; Chesnokov, A. S. Inst. Obshch. Neorg. Khim., Leningrad, USSR. Ionnye Rasplavy Tverd. Elektrolity (1988), 3, 46-50. CODEN: IRTEEE; ISSN: 0234-4483. Journal; General Review written in Russian. CAN 108:212331

**Abstract.** A review with 7 refs. is given on some electrode materials based on borides and carbides used as cathodes in the electrochem. prodn. of Al from chloride melts. Also some electrode materials used as anodes are described. The comparison between the properties of the graphite as the electrode material and several other was made.

**Effect of certain organic additives on the electrodeposition of aluminum from a m-xylene electrolyte.** Spiridonov, B. A.; Bobryashov, A. I.; Falicheva, A. I. Voronezh. Politekh. Inst., Voronezh, USSR. Zashch. Met. (1988), 24(2), 316-20. CODEN: ZAMEA9; ISSN: 0044-1856. Journal written in Russian. CAN 108:194721

**Abstract.** Cathodic and anodic polarization studies were made during the electrodeposition of Al from a bath contg. AlBr3 (50 wt.%), m-xylene with the addn. of paraffin additives, polynuclear arom. compds. not contg. amino groups (biphenyl, diphenylmethane, naphthalene) and those contg. such groups (4,4'-diaminobiphenyl; 4,4'-diamino-3,3'-dimethoxydiphenylmethane (I)). The concn. of the additives varied from 1 to 10 g/L. Polarization curves were measured on a potentiostat. Fine-cryst., corrosion-resistant Al electroplates of good quality and ≤5 μm thick can be obtained from a bath of the following compn.: AlBr3 500-550, I 5.0, and m-xylene the remainder; at cathodic c.d. 1-1.5 A/dm2 and electrolysis duration 20-30 min. The anode was Al and the anodic potential was -0.1 to +0.2 V.

**Rotating disk electrode studies in cryolitic melts.** Tellenbach, J. M.; Landolt, D. Mater. Dep., Swiss Fed. Inst. Technol., Lausanne, CH-1007, Switz. Electrochim. Acta (1988), 33(2), 221-5. CODEN: ELCAAV; ISSN: 0013-4686. Journal written in English. CAN 108:84146

**Abstract.** A rotating disk electrode assembly for use in molten cryolite at 1020 K is described. The electrodes, press-fitted into a BN insulator, were made of W plated with Au or of TiB2. The performance of the rotating disk system was tested by measuring limiting currents for Mn2+ redn. on Au at rotation rates up to 1600 rpm. The rate of Al loss from a TiB2 cathode was measured as a function of the rotation rate and found to be mass transport-controlled.

**Mol-ratio determination of aluminum smelting electrolyte by potentiometric titration with fluoride-ion selective electrode.** Geissler, Manfred; Kunze, Reiner; Roeder, Heino. Forschungsinst. NE-Met., VEB Mansfeld-Komb. "Wilhelm Pieck", Freiberg, DDR-9200, Ger. Dem. Rep. Z. Chem. (1987), 27(8), 306-7. CODEN: ZECEAL; ISSN: 0044-2402. Journal written in German. CAN 107:249147
. A titrimetric detn. of the NaF/AlF3 ratio in the smelting electrolysis of Al is described. The samples were sintered with NaF at 600°. The cooled sinter was dissolved in H2O and titrated with a La(NO3)3 soln. The end point of the titrn. was indicated by a F--sensitive electrode.

**Overvoltage on Inert Anode Materials in Cryolite Melts.** Thonstad, J., Y. X. Liu and S. Jarek, *International Light Metals Congress*, Leoban, Vienna *(Aluminium Verlag)* (1987) p. 150-154.
**Abstract.** No abstract available.

**Electrochemical polarization studies on copper and copper-containing cermet anodes for the aluminum industry.** Windisch, Charles F., Jr.; Marschman, Steven C. Pac. Northwest Lab., Richland, WA, 99352, USA. Light Met. (Warrendale, Pa.) (1987), 351-5. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 106:164520
**Abstract.** Recent work showed that a Cu-contg. oxide cermet has promise as an inert anode material for the primary Al prodn. industry. In order to understand the reactions occurring at the Cu/ceramic/melt interface during polarization in cryolite melt electrochem. polarization techniques were applied to Cu metal and Cu-contg. oxide cermets. Distinct oxidn. and redn. waves were obsd. for the materials; these waves are correlated with electrochem. reactions involving Cu in cryolite melt. Addnl. material characterization was used to support the proposed reaction mechanisms.

**Selection and testing of inert anode materials for Hall cells.** McLeod, Alan D.; Lihrmann, Jean Marc; Haggerty, John S.; Sadoway, Donald R. Dep. Mater. Sci. Eng., Massachusetts Inst. Technol., Cambridge, MA, 02139, USA. Light Met. (Warrendale, Pa.) (1987), 357-65. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 106:164521
. A new set of criteria for Hall cell anode materials is given and fundamental thermodn. data used to est. how well a variety of oxides will satisfy these criteria is discussed. The decompn. potentials and the soly. of the oxides in the Al electrolyte consisting of Na3AlF6, AlF3, CaF2 and Al2O3 were also taken into account. Data are given for many oxides.

**of aluminum-tin alloys from organic electrolytes.** Platis, F. S.; Capuano, G. A. Dep. Chem., Univ. Quebec in Montreal, Montreal, PQ, H3C 3P8, Can. J. Electrochem. Soc. (1987), 134(10), 2425-9. CODEN: JESOAN; ISSN: 0013-4651. Journal written in English. CAN 107:224917
**Abstract.** Al-Sn alloys were electrodeposited onto steel from alkylbenzene, AlBr3-HBr electrolytes. Bright, adherent, and coherent Al-Sn plates were obtained at cathode efficiencies approaching 100%. The compn. of the cathode deposit can be readily controlled by using Al-Sn anodes of specified Sn content. If the c.d., agitation, and specific conductance are maintained const., the electrolyte Sn concn. acquires a const. value after a working up period. With electrolytes having conductivities of 3-6 × 10-3 Ω-1 cm-1, 100% of the Sn dissolved from the anodes is transferred to the cathode, whereas, with electrolytes having conductivities of 2-3 × 10-3 Ω-1 cm-1, only about half the Sn content from the anodes is actually electroplated. The codeposition of Sn in the electrodeposition of Al-Sn alloys was found to be a diffusion rate controlling process.

**Studies of the anodic process at tin dioxide-based electrodes in aluminum electrolysis.** Liu, Yexiang; Xiao, Haiming. Dep. Metall., Cent. South Univ. Technol., Changsha, Peop. Rep. China. Proc. - Electrochem. Soc. (1987), 87-7(Proc. Jt. Int. Symp. Molten Salts), 751-2. CODEN: PESODO; ISSN: 0161-6374. Journal written in English. CAN 107:185944

**Abstract.** The use of inert anodes and stable cathodes in the Al electrolysis industry is of significance for saving energy. The electrochem. characteristics of SnO2-based electrodes in Al electrolysis are interesting not only for understanding the mechanism of the anode process and infering indirectly the structure of cryolite-alumina melt, but also for developing new techniques for Al metallurgy with inert anodes. The anode process on SnO2-based electrodes in Al electrolysis was studied by several electrochem. methods and some initial results were obtained.

**Electrodeposition of aluminum-zinc alloys from organic electrolytes.** Bizabalimana, S.; Capuano, G. A. Dep. Chim., Univ. Quebec, Montreal, PQ, H3C 3P8, Can. Can. Metall. Q. (1987), 26(1), 13-19. CODEN: CAMQAU; ISSN: 0008-4433. Journal written in French. CAN 107:164044
**Abstract.** Al-Zn alloys were electrodeposited onto steel substrates from org. electrolytes. Adherent plates, usually brighter than deposits obtained with pure Al, were obtained with the same electrolyte. The compn. of the cathodic deposit can be readily controlled by using Al-Zn anodes of specified Zn content, if the c.d. and specific conductance are maintained const. With electrolytes having conductivities of (2-4) × 10-3 Ω-1 cm-1, about half the anode Zn content is transferred to the cathode, whereas with electrolytes having conductivities of (4-6) x 10-3 Ω-1 cm-1, 100% of the dissolved Zn from the anode is electroplated at the cathode. The codeposition of Zn in the electrodeposition of Al-Zn alloys was controlled by diffusion.

**Cathodic processes in the electrodeposition of aluminum from ethylbenzene electrolytes.** Petrova, N. V.; Titova, V. N.; Kazakov, V. A.; Biallozor, S. Inst. Fiz. Khim., Moscow, USSR. Elektrokhimiya (1987), 23(1), 56-60. CODEN: ELKKAX; ISSN: 0424-8570. Journal written in Russian. CAN 106:109949
**Abstract.** Cathodic processes occurring during the electrodeposition of Al from ethylbenzene electrolytes, as a function of the operating time of the electrolyte, were examd. Together with the basic process (Al redn. on the cathode), the electroredn. of H occurs, as well as of the solvent, with the formation of the anion-radical and its further protonation.

**Effect of cell operating parameters on performance of inert anodes in Hall-Heroult cells.** Ray, S. P. Alcoa Lab., Alcoa Center, PA, 15069, USA. Light Met. (Warrendale, Pa.) (1987), 367-80. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 106:184898
**Abstract.** Recently, the selection and evaluation of a no. of cermet anodes having compns. in the Ni-Fe-O and Ni-Fe-Cu-O systems have been described. A discussion is given on the effect of electrolyte parameters, e.g., temp., Al2O3 concn., bath ratio, and additives on the performance of anodes. The Al2O3 concn. in the electrolyte has a strong effect on the anode performance. Anodes perform best when Al2O3 concns. in the electrolyte are at or near satn. Anodes tend to decrepitate and fluorinate in tests with low (NaF/AlF3) ratio electrolytes with low Al2O3 level.

**Corrosion and passivation of cermet inert anodes in cryolite-type electrolytes.** Tarcy, Gary P. Smelt. Process Dev. Div., Alum. Co. America, Alcoa Center, PA, 15069, USA. Light Met. (Warrendale, Pa.) (1986), 2, 309-20. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 104:190200
**Abstract.** Expts. on reaction-sintered Ni-56 NiFe2O4-14 NiO [101995-91-9], isolated Ni metal Ni-64 NiFe2O4-16 NiO [101995-92-0], reaction-sintered Ni-3 Cu-56 NiFe2O4-14 NiO [101995-93-1], isolated metal particle Cu-4 Ni-64 NiFe2O4-16 NiO [101995-94-2], and Pt-64 NiFe2O4-16% NiO [101995-95-3] cermets show that Ni is an unacceptable metal phase in a cermet anode due to its anodic dissoln. The Cu-rich Cu-Ni alloy cermet is recommended. The stability of the metal phase depends on: (1) the use of a cermet to provide a mech. barrier to spalling, (2) the use of Cu-Ni alloys to cathodically protect the Cu metal during the initial phase of electrolysis, and (3) high Al2O3 activity in the electrolyte to assure the formation of a passivating CuAlO2. The resistance of various alloys and metals to anodic dissoln. in cryolite-base melts is given.

**Manufacturing Processes Used for the Production of Inert Anodes.** Weyard, J. D., *Light Metals 1986*, p. 321-339.
**Abstract.** Manufacturing processes have been developed for the production of commercial size inert anodes. These inert anodes can be used to replace carbon anodes in Hall-Heroult electrolytic cells for the production of aluminum. Commercially available raw materials in cluding FeA, Fe2O3, NIO, Fe, Ni and Cu were evaluated and selected for fabrication of anode shapes. Several manufacturing process flow sheets have been developed and used to produce inert anodes ror testing in 60 and 2500 ampere electrolysis cells. Raw materials were agglomerated by spray drying

in open and closed systems to produce free flowing pressable powders. Consolidation of shapes was completed by cold isostatically pressing at 100 to 207 MPa and sintering in an inert atmosphere furnace at 1200* to 1400*C. Electrical-mechanical connections were made to the manufactured inert anodes by several methods including diffusion welding, mechanical connections and the use of braze alloys. Final sintered properties, including physical and microstructural, were evaluated before Hall cell testing.

**Inert anodes for Hall cells.** Ray, S. P. Ceram. Div., Alum. Co. America, Alcoa Center, PA. 15069, USA. Light Met. (Warrendale, Pa.) (1986), 2, 287-98. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 104:176572

**Abstract.** It is well known that the use of inert electrodes may lead to compact cell designs and improved efficiency in Hall cells for Al prodn. Refractory hard metal, e.g., $TiB_2$ is clearly the leading inert cathode material. In the past no materials have been proposed for use as inert anodes, but most of these materials lacked the stringent requirements that must be met. The selection and evaluation of a no. of cermet materials in the Ni-Fe-O and Ni-Fe-Cu-O systems were selected and evaluated. The cermet materials have acceptable elec. cond. The Al produced during bench scale electrolysis tests using these anodes contains low levels of anode constituents. The effect of Hall cell operation on anode microstructure is discussed.

**One hundred years of carbon for the production of aluminum.** Wilkening, S. Ver. Alum.-Werke A.-g., Bonn, D-5300/11, Fed. Rep. Ger. Erdoel Kohle, Erdgas, Petrochem. (1986), 39(12), 551-60. CODEN: EKEPAB; ISSN: 0014-0058. Journal written in English. CAN 106:83578

**Abstract.** A history is given of the use of C in the electrode material for the molten salt electrolysis of alumina in Al prodn.

**Manufacturing Processes Used for the Production of Inert Anodes.** Weyard, J. D., *Light Metals 1986, p.* 321-339.

**Abstract. No abstract available.**

**Solubilities of oxides for inert anodes in cryolite-based melts.** DeYoung, David H. Alcoa Lab., Alum. Co. America, New Kensington, PA, 15068, USA. Light Met. (Warrendale, Pa.) (1986), 2, 299-307. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 104:190199

**Abstract.** The solubilities of $Fe_2O_3$, NiO, and $NiFe_2O_4$ were measured in $NaF-AlF_3-CaF_2-Al_2O_3$ melts as a function of temp. and melt compn. The solubilities of $Fe_2O_3$ and NiO for melts contg. 1.5-6.5% $Al_2O_3$ and for bath ratios 0.7-1.5 are represented as $\log[\% Fe] = 4.71-7080/T$ and $\log[\% Ni] = 6.27-9740/T$, resp., T = abs. temp. The solubilities of $Fe_2O_3$ and NiO increase with decreasing concns. of $Al_2O_3$ in the melt, esp. at <1% $Al_2O_3$. The soly. of $Fe_2O_3$ decreases moderately with decreasing bath ratio (wt. NaF/wt. $AlF_3$), while no change occurs for NiO. The soly. of $NiFe_2O_4$ is less than the solubilities of $Fe_2O_3$ and NiO, and there is good agreement between the free energy of formation of $NiFe_2O_4$ calcd. from the measured solubilities of $Fe_2O_3$, NiO, and $NiFe_2O_4$ and the free energy of formation reported in the literature.

**Anodic process of tin dioxide-based electrode in aluminum electrolysis.** Xiao, Haiming; Liu, Yexiang. Cent. South Univ. Technol., Changsha, Peop. Rep. China. Youse Jinshu (1986), 38(4), 57-62. CODEN: YSCSAE; ISSN: 0513-3424. Journal written in Chinese. CAN 106:40415

**Abstract.** The anodic overvoltage on a $SnO_2$-based electrode of 0.1-0.2 V at industrial c.d. was found by the steady-state technique. The occurrence of 2 straight segments on the anodic Tafel plot implied a 2-step O discharge reaction. The linear potential sweep curves obtained from $SnO_2$-based anode showed that O and F discharged sep. No anode effect appeared at high c.d. 12 A/cm2, which could be explained from the good wetting of $SnO_2$ materials by the molten electrolyte. The chronoamperometric measurements showed that O evolution on a $SnO_2$-based anode was an irreversible process. The chronopotentiometric measurements showed that the O evolution on a $SnO_2$-based electrode was an irreversible process accompanied by a chem. reaction preceding it. The rate-detg. step was a 2-electron transfer step.

**The effect of anode-cathode distance on the current efficiency in aluminum electrolysis. Part I: mechanical stirring in laboratory cells.** Muftuoglu, T.; Thonstad, J. Metall. Div., Norweg. Inst. Technol., Trondheim, Norway. Aluminium (Duesseldorf) (1986), 62(8), 589-92. CODEN: ALUMAB; ISSN: 0002-6689. Journal written in English. CAN 105:142066
**Abstract.** A study was made of the relationship of the anode-cathode distance (ACD) and the current efficiency (CE) in the electrowinning of Al in the Hall-Heroult cell. The CE measurements were made in a closed cell without Al2O3 feeding. In addn. to the ACD/CE relationship a series of expts. were made in cells with forced convection using a mech. stirrer. The CE was detd. as a function of the stirring intensity and of the location of the stirrer within the cell at a fixed ACD. Results are given in several graphs and they show that the CE decreases with increasing intensity of stirring and the effect of stirring on CE is far more pronounced when the stirrer is located near the metal-bath interface or within the metal pad.

**Reaction of electrode products in aluminum electrolytic cells.** Burnakin, V. V.; Polyakov, P. V. Krasnoyarsk. Inst. Tsetn. Met., Krasnoyarsk, USSR. Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall. (1986), Issue 3, 47-52. CODEN: IVUTAK; ISSN: 0021-3438. Journal written in Russian. CAN 105:122962
**Abstract.** A possible method was examd. for calcg. the losses of Al in the chem. reactions of electrolysis products in the electrorecovery of Al. It is 1st necessary to det. the basic characteristics of 2-phase flow. The method of successive approxns. was used. The calcd. values are presented of the sp. flows of CO2 (106 kg/m2-s) for electrolyzers with baked and self-baking anodes. The conducted anal. agrees well with exptl. data and with data obtained in practice and allows one to det. the principal directions for solving the problems of improving the tech.-economic indicators of the electrolysis process.

**observation of the dissolution process of aluminum in cryolite-alumina electrolyte through a transparent quartz cell.** Fan, Liman; Qiu, Zhuxian; Kai, Grjotheim. Northeast Inst. Technol., Shenyang, Peop. Rep. China. Dongbei Gongxueyuan Xuebao (1986), 46, 97-101, 4 plates. CODEN: THYPDK; ISSN: 0253-4258. Journal written in Chinese. CAN 105:68997
**Abstract.** Direct observation was made through a transparent quartz cell for the dissoln. of metallic Al in cryolite-Al2O3 melt and the anode effect. The compn. of the electrolyte was 85% cryolite + 5% Al2O3 + 10% NaCl. When Al was dissolved, a large amt. of small bubbles was formed followed by floating of blue brown metallic fog. The dissoln. of Al was regarded as electrochem. nature and the cathodic polarization controlled the dissoln. of Al.

**Carbon electrodes in the Hall-Heroult cell: a century of progress.** Belitskus, David. Alcoa Lab., Alum. Co. American, Alcoa Center, PA, 15069, USA. Light Met. (Warrendale, Pa.) (1986), 1, 130-43. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 104:185537
**Abstract.** A history is presented that reviews the state of the art of C electrode technol. a century ago and traces the developments in raw material processing and electrode manuf.

**Correlations between ability of pitch to penetrate coke and the physical characteristics of prebaked anodes for the aluminum industry.** Couderc, P.; Hyvernat, P.; Lemarchand, J. L. Soc. H.G.D., Lens, 62304, Fr. Fuel (1986), 65(2), 281-7. CODEN: FUELAC; ISSN: 0016-2361. Journal written in English. CAN 104:92772
**Abstract.** With respect to pitch selection for electrode prodn., the optimum exptl. conditions for the use of an automatic app. that monitors pitch penetration into a coke bed are investigated. The penetration test described can be used to select pitches with good affinity for petroleum coke and to correlate this quality with the phys. properties of electrodes produced therefrom. The test suggests the suitability of certain pitches which would not satisfy the usual selection criteria. The temp.-dependent ability of a pitch to penetrate a coke bed, in conjunction with the traditional criteria, assists in the selection of binder pitches used in the Al industry.

**Electrode processes preceeding the deposition of aluminum in a toluene electrolyte.** Simakavicius, L. E.; Sarkis, A. USSR. Issled. Obl. Osazhdeniya Met. (1985), 96-101. Publisher: Akad. Nauk Lit. SSR, Inst. Khim. Khim. Tekhnol., Vilnius, USSR. CODEN: 55OQAE. Conference written in Russian. CAN 106:204072
**Abstract.** Exptl. data show that in a toluene electrolyte contg. Me2EtPhNBr for Al electroplating on metals with a low or intermediate H overvoltage, the electroplating of Al precedes the evolution of H, which on a Pt (and probably on Ni also) electrode under conditions of mixed kinetics is also complicated by passivation, and on a Cu (and probably also on Ag, Sn and glassy C) electrode is detd. basically by diffusion limitations.

**Electrodeposition of aluminum in low-temperature molten hydride electrolytes.** Kazakov, V. A.; Nakamura, N.; Ioshio, M. Inst. Fiz. Khim., Moscow, USSR. Elektrokhimiya (1985), 21(10), 1331-4. CODEN: ELKKAX; ISSN: 0424-8570. Journal written in Russian. CAN 104:12255
**Abstract.** The kinetics were studied of the electrodeposition and dissoln. of Al in concd. THF hydride baths for Al electroplating. A modified THF bath was used, which contained an increased concn. of Al (15-20 mol%). The studied baths consisted of AlCl3-LiAlH4-THF-benzene. All the tests were conducted at 35°. By using baths with a low value of diffusion overvoltage and high concn. of Al, one can obtain high-quality electroplates at considerable cathodic c.d. values, attaining ≥100 mA/cm2.

**of anode carbon during aluminum electrolysis (III).** Houston, Geoffrey J.; Oeye, Harald A. Inst. Inorg. Chem., Univ. Trondheim, Trondheim, Norway. Aluminium (Duesseldorf) (1985), 61(6), 426-8. CODEN: ALUMAB; ISSN: 0002-6689. Journal; General Review written in English. CAN 103:108114
**Abstract.** Part III of a review with many refs. is given. Calcination of the filler coke, baking the anodes, effect of temp. differences, pitch quality, anode addns. and impurity levels, and anode protection are considered.

**A rotating ring-disk study of the aluminum electrode in molten aluminum chloride + sodium chloride + potassium chloride electrolytes.** Takahashi, Setsuko; Koura, Nobuyuki. Fac. Sci. Technol., Tokyo Univ. Sci., Noda, 278, Japan. J. Electroanal. Chem. Interfacial Electrochem. (1985), 188(1-2), 245-55. CODEN: JEIEBC; ISSN: 0022-0728. Journal written in English. CAN 103:61354
**Abstract.** It is thought that the electrode kinetics of Al in a AlCl3 + NaCl + KCl melt proceed by a 3-electron reaction, but there is some doubt as to the existence of certain intermediate products. Rotating ring disk electrode (RRDE) measurements were carried out to analyze the electrode reaction and to confirm the existence of the intermediates. The disk electrode was of glassy C or 99.99% Al and the ring was of glassy C. When the disk was cathodically polarized at a sweep rate of 100 mV s-1 and the ring was potentiostated at a certain potential, 2 waves were obsd. on the disk polarization curve and a significant anodic current was detected at the ring as soon as the disk current reached the 2nd stage of rise. The anodic ring current is considered to confirm the existence of the intermediates. The ratio of the no. of electrons for the intermediate formation reaction on the disk to the no. for the disappearance reaction on the ring was calcd. to be 2. It is therefore assumed that Al(III) (i.e., AlCl4-) is reduced to Al(I) on the disk and that the Al(I) is oxidized to Al(II) on the ring. Some intermediates were also detected in the anodic reaction of Al, but the details are still under investigation.

**Determination of the lithium content of molten aluminum using a solid electrolyte.** Yao, P. C.; Fray, D. J. Chung Shan Inst. Sci. Technol., Taiwan. Metall. Trans. B (1985), 16B(1), 41-6. CODEN: MTTBCR; ISSN: 0360-2141. Journal written in English. CAN 103:16032
**Abstract.** A Li probe was used for the detn. of the Li content of molten Al alloys. The electrolyte was a 2-phase mixt. of Li3PO4 and Li4SiO4 to give an overall compn. of Li3.6Si0.6P0.4O4. This electrolyte was slightly attacked by pure liq. Li, but no attack was detected in the Al-Li melts. However, exposure to high humidity caused the electrolyte to degrade. A satisfactory ref. electrode was decompd. Li2Ti3O7 consisting of Li4Ti5O12 and TiO2. An activity vs. compn. plot showed that Henry's law was obeyed, and the activity coeff. was 0.17 at 984 K and 0.26 at 1050 K.

**A study of the voltage and current efficiencies of fused salt aluminum chloride electrolysis using bench scale cells.** Hauksson, Trausti; Foulkes, Frank R. Dep. Chem. Eng. Appl. Chem., Univ. Toronto, Toronto, ON, M5S 1A4, Can. Can. J. Chem. Eng. (1985), 63(2), 237-43. CODEN: CJCEA7; ISSN: 0008-4034. Journal written in English. CAN 102:228168
**Abstract.** The fused salt electrolysis of AlCl3 dissolved in LiCl-NaCl m. 700° was studied using bench scale cells using graphite electrodes. The effects of AlCl3 concn., forced convection, interelectrode spacing, and c.d. on the voltage, current, and energy efficiencies of the process were investigated. At a practical cell voltage of 3.05 V and c.d. of 15 kA.m-2 the elec. energy consumption per kg of Al produced by the AlCl3 process was .apprx.32 MJ, compared with a typical value of 52 MJ.kg-1 for the Hall-Heroult electrolysis.

**Operation of a ring chamber furnace for the production of electrodes containing carbon.** Oderbolz, Stefan; Bouwmeester, Gerhard. (Swiss Aluminium Ltd., Switz.). Eur. Pat. Appl., 18 pp. CODEN: EPXXDW. EP 133842

A1 850306. Designated States: R: CH, DE, FR, GB, IT, LI, NL. Patent written in German. Application: EP 84-810355 840720. Priority: CH 83-4381 830811 CAN 102:194019

**Abstract.** A procedure is described for operating an open ring chamber furnace with firewalls at least partially fastened together for the prodn. of C-contg. workpieces, esp. electrodes for Al prodn. from molten salts. Esp. in combination with control of the operation, the procedure leads to uniform qualities independent of the position of the workpiece in the furnace. Control of the temp. and vacuum in the furnace is described. The control devices are removable slide values operated by a servomotor.

**Cycling of β-lithium-aluminum (LiAl) in organic electrolytes - effect of electrode contaminations and electrolyte additives.** Besenhard, J. O.; Fritz, H. P.; Wudy, E.; Dietz, K.; Meyer, H. Anorg.-Chemisches Inst., Tech. Univ. Muenchen, Garching, D-8046, Fed. Rep. Ger. J. Power Sources (1985), 14(1-3), 193-200. CODEN: JPSODZ; ISSN: 0378-7753. Journal written in English. CAN 102:188009

**Abstract.** The mobility of Li in β-LiAl formed by cathodic Li incorporation is drastically reduced by small amts. of Si in the parent Al; this is shown by $^7$Li NMR and electrochem. expts. During long-term cycling, the detrimental effect of lower Li mobility is compensated by the less spongy morphol. of Si-doped electrodes. Addn. of >100 ppm 1,2-propanediol [57-55-6] or 2-methoxyethanol [109-86-4] improves the 1st cycle Li recovery from Si-doped β-LiAl in propylene carbonate electrolytes; paraffin oil is a non-reactive surfactant which slightly decreases the corrosion of β-LiAl.

**Reactivity of pitch cokes as a function of the group composition of pitch.** Litwinowicz, Andrzej; Golec, Marian; Zmuda, Wieslaw. Pol. Gornictwo (1984), 8(1), 71-5. CODEN: GORNDL. Journal written in Polish. CAN 101:57471

**Abstract.** The reactivity towards oxidn. by $CO_2$ of semicokes produced by carbonizing coal-tar pitches increases as the $\alpha$1 and $\alpha$2 group content (Polish anal. method BN 79/0511-34) is increased. The foregoing is significant when coal-tar pitches are used as binders for anodes in the electrolytic prodn. of Al. The durability of these anodes depends on the resistance of binders to oxidn.

**iron for conductors for carbon blocks of aluminum electrolysis cells.** Frizorger, V. K.; Koz'min, G. D.; Shpakov, V. I.; Nepomnyashchii, V. N.; Abramov, A. A.; Mozhaev, V. M.; Gromov, B. S.; Polyakov, P. V.; Kulinich, G. G.; Kunichkin, S. M. (USSR). U.S.S.R. CODEN: URXXAF. SU 1073318 A1 840215. Patent written in Russian. Application: SU 82-3515161 820928. CAN 100:196034

**Abstract.** The voltage drop is decreased in the carbon block-conductor contact by adding 0.01-0.05% Ga to the cast iron [90144-44-8] contg. C 3.2-3.6, Si 2.6-3, Mn 0.35-0.5, Al 0.15-0.25, and Cu 0.08-0.15%.

**Energy reduction in the manufacture of prebaked carbon containing electrodes for electrolytic production of metals such as aluminum.** Withers, James C.; Upperman, Gary V. (Metallurgical, Inc., USA). U.S., 6 pp. CODEN: USXXAM. US 4431503 A 840214. Patent written in English. Application: US 81-275940 810622. CAN 100:147506

**Abstract.** Improved C-contg. anodes for Al recovery are described. The anodes are formed in 7.5 cm diam. molds with pressure of 8500-28000 psi at 100°. After the anode was set it was cooled, removed from the mold and coked to 1100°. Holes 0.6 cm diam. and 2.5 cm apart were drilled after pre-curing prior to coking. Good results were obtained from the anodes contg. holes by coking for 24 or 48 h.

**Studies on wettability of carbon electrodes in aluminum electrolysis. II.** Qiu, Zhuxian; Wei, Quingbin; Yuo, Kwantsung. Dep. Non-ferrous Met., Northeast Inst. Technol., Shenyang, Peop. Rep. China. Aluminium (Duesseldorf) (1983), 59(10), 753-6. CODEN: ALUMAB; ISSN: 0002-6689. Journal written in English. CAN 99:202402

**Abstract.** Improvement of wettability of C electrodes is influenced by many factors, the 2 most important of which are addn. of Al to the electrolyte and increasing the c.d. Electrolytic polarization curves and motion pictures were used to study the wetting of C electrodes by the $Al_2O_3$/cryolite melt. A short period of reverse electrolysis may be beneficial in the Al electrowinning process. These results are also helpful in understanding the mechanism of the anode effect and of penetration of electrolyte into the cathode blocks.

**DSA in aluminum reduction cells.** Horinouchi, Kazuo; Tachikawa, Noboru; Yamada, Koichi. Kikumoto Works, Sumitomo Alum. Smelting Co., Ltd., Niihama, Japan. Proc. Int. Symp. Molten Salt Chem. Technol., 1st (1983), 65-8. Publisher: Molten Salt Comm. Electrochem. Soc. Jpn., Kyoto, Japan. CODEN: 53FZAG. Conference written in English. CAN 102:139783
**Abstract.** Several electroconductive complex oxides e.g. NiMn2O4, SnZn1.8Ni0.2O4, Sn0.3Ni1.3Fe1.4O4 are presented as candidates for dimensionally stable anode (DSA) for use in Al redn. cells. Properties of oxides such as the stability in cryolite melt, reactivity with the dissolved alumina, and anodic oxidn. by oxygen evolved were studied. Anodic behavior of complex oxides were studied by the electrolysis of alumina in the melt. Their anodic overpotentials were detd. by a current interruptor method at 1000°. The loss of Al during electrolysis was measured in relation to the rate of reoxidn. of Al produced. The redn. of energy requirement of the newly designed cell with DSA is roughly estd.

**Ceramic electrode material. Energy balance in aluminum electrolysis.** Windfeldt, A. Sentralinst. Ind. Forsk., Oslo, Norway. Report (1983), Issue SI-R-790101-1; Order No. DE84750388, 11 pp. Avail. NTIS (U.S. Sales Only). From: Energy Res. Abstr. 1984, 9(9), Abstr. No. 16811. Report written in Norwegian. CAN 101:100188
**Abstract.** The report compares the energy balance when using C anodes and ceramic anodes for industrial electrolysis of Al2O3 melts. The ceramic anodes can be made permanent. The calcns. show that it is possible to at least maintain the present specific energy consumption by reducing the electrode distance.

**Studies on wettability of carbon electrodes in aluminum electrolysis. I.** Qiu, Zhuxian; Wei, Qingbin; Yuo, Kwantsung. Northeast Inst. Technol., Shenyang, Peop. Rep. China. Aluminium (Duesseldorf) (1983), 59(9), 670-3. CODEN: ALUMAB; ISSN: 0002-6689. Journal written in English. CAN 99:148418
**Abstract.** The wettability of C electrodes being polarized in Al electrowinning melts was studied. The melts consisted of NaF/AlF3 and Na3AlF6/Al2O3 as well as salt additives. Photog. was used in the study of the anode effect in addn. to the wetting phenomena of the C electrodes at current intensities of 0.1-5.0 A or c.ds. of 0.08-4.0 A/cm2. Anodic and cathodic polarizations were carried out and the influence of c.d. and concn. of alumina was studied.

**Electrode for determining alumina concentration in an electrolytic aluminum cell.** (Sumitomo Aluminium Smelting Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho, 5 pp. CODEN: JKXXAF. JP 57100344 A2 820622 Showa. Patent written in Japanese. Application: JP 80-177700 801215. CAN 97:192459
**Abstract.** An app. for the potentiometric detn. of Al2O3 present in the melt of an electrolytic Al cell consists of a main electrode prepd. by immersing a metal lead into a fused salt satd. with Al2O3 and contained in a multiporous elec. insulator tube with a closed end and a metal wire serving as a counter electrode to be immersed in the test melt.

**Charge transfer reaction on a bromine electrode in molten aluminum bromide-potassium bromide.** Krasnoperov, A. V.; Nekrasov, V. N.; Ivanovskii, L. E. Inst. Elektrokhim., Sverdlovsk, USSR. Deposited Doc. (1982), Issue VINITI 5178-82, 10 pp. Avail. VINITI. Report written in Russian. CAN 99:202354
**Abstract.** Direct measurements were made of the fast charge-transfer reaction rate by using the method of dual pulses on a Br electrode in a melt of the eutectic AlBr3-KBr (25.8 mol%) at 370-470 K. The expts. were conducted in a cell with 2 electrodes of glassy C. The method allows one to obtain direct exptl. information on the kinetic parameters of the charge transfer reaction, a knowledge of which is necessary for understanding the process on the stated electrode.

**Application of solid oxide electrode in aluminum electrolysis - continuous determination of aluminum oxide concentration in aluminum electrolytes.** Wang, Huazhang. South Cent. Coll. Metall., Peop. Rep. China. Youse Jinshu (1982), 34(6), 28-33. CODEN: YSCSAE. Journal; General Review written in Chinese. CAN 99:186391
**Abstract.** A review with 9 refs. on the emf. method for continuous detn. of Al2O3 concn.

**Electrodes for aluminum electrolyzers.** Berdnikov, Yu. I.; Ryzhov, V. A.; Nikishev, A. A.; Kiselev, V. S. (All-Union Scientific-Research and Design Institute of the Aluminum, Magnesium, and Electrode Industry, Irkutsk, USSR). U.S.S.R. CODEN: URXXAF. SU 933808 A1 820607. Patent written in Russian. Application: SU 80-2938010 800602. CAN 97:117489

**Abstract.** Electrodes for Al electrolyzers were prepd. by mixing coke with a binder.adding an inorg. additive and then baking the raw material of the anodic mass. A high quality anode was obtained by using as inorg. additive a H3BO3-Al powder mixt. in a (0915-093) to (5-1) ratio.

**Electrode for electrolytic aluminum production.** (Sumitomo Aluminium Smelting Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho, 4 pp. CODEN: JKXXAF. JP 57051277 A2 820326 Showa. Patent written in Japanese. Application: JP 80-127428 800912. CAN 97:46553
**Abstract.** In manufg. an electrode for Al electrowinning by blending fine, medium, and coarse coke powder with a binder, precalcined coke mostly in the medium particle-size range is used constituting up to 30% of the total amt. of coke. Energy conservation is achieved during electrode prodn.

**Electrodeposition of aluminum from an aromatic hydrocarbon electrolyte.** Kume, Michiyuki. Nagoya Munic. Ind. Res. Inst., Nagoya, Japan. Nagoya-shi Kogyo Kenkyusho Kenkyu Hokoku (1982), Issue 64, 9-12. CODEN: NASKAR; ISSN: 0369-3333. Journal written in Japanese. CAN 97:13992
**Abstract.** The electroplating of Al on Cu was studied. As a bath, a soln. of AlBr3 in the mixt. of ethylbenzene and naphthalene was used. The optimum conditions obtained were as follows: concn. of AlBr3 2-2.5 moL/L, temp. 25° and c.d. 1 A/dm2. Under these conditions, a silvery white, compact deposit was obtained. The activation overpotential vs. c.d. curves, obtained by a galvanostatic method. showed a good linear relation at c.d. 0.6-3 (15°), 0.4-3 (25°), and 0.6-3.6 A/dm2 (35°), resp., and in these Tafel regions, the charge-transfer process: Al3+ → Al2+, was the rate-detg. step.

**Electrode processes in production of aluminum by electrolytic reduction of aluminum chloride in molten chlorides of alkali metals.** Orman, Zofia; Oblakowski, Ryszard; Jarek, Stanislaw. Inst. Non-Ferrous Metall., Univ. Min. Metall., Krakow, Pol. Metal. Odlew. (1981), 7(3), 287-305. CODEN: MEODD6. Journal written in English. CAN 96:171066
**Abstract.** Anode and cathode potentials, as well as the overall potential drop, were measured during electrolytic redn. of AlCl3 in equimol. mixts. of NaCl-KCl and NaCl-LiCl for AlCl3 concns. of 5-20%; temps. of 970, 1020, and 1070 K; and c.d. values of 0.1-1.2 A/cm2. The potential drops between the electrodes and the anode potentials were higher in NaCl-KCl mixts. than in the NaCl-LiCl system. In both electrolytes, the cathodic polarization was negligible. The preferred concn. of AlCl3 was 5%. Some increase in potential was obsd. at higher concns.

**Inert electrodes in Hall-Heroult cells.** Billehaug, K.; Oeye, H. A. Norw. Tech. Sch., Trondheim, Norway. Int. Leichtmetalltag. (1981), 7th, 250-2. CODEN: INLEDD. Journal; General Review written in German. CAN 96:131934
**Abstract.** A review with 16 refs. is given, based on patent literature of Al manuf. in the title cells.

**Electrode for detecting alumina concentration in an electrolytic aluminum cell.** (Sumitomo Aluminium Smelting Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho, 6 pp. CODEN: JKXXAF. JP 56158889 A2 811207 Showa. Patent written in Japanese. Application: JP 80-63136 800513. CAN 96:115164
**Abstract.** In an Al2O3 concn. detecting electrode for an electrolytic Al cell and consisting of a monitor electrode and a ref. electrode, that part of the electrode which comes into contact with the fused salt is the monitor electrode which is a metal (e.g. Ti, Zr, Hf, Si, V, Nb, Ta, Cr, Mo, W) coated with a chem. stable and redn.-resistant carbide (carbides of Ti, Zr, Hf, Si, V, Nb, Ta, Cr, Mo, W).

**Arrangement of the electrodes in a fused bath electrochemical cell for producing aluminum.** Alder, Hanspeter; Schalch, Eugen. (Swiss Aluminium Ltd., Switz.). Fr. Demande, 17 pp. CODEN: FRXXBL. FR 2482629 A1 811120. Patent written in French. Application: FR 81-9625 810514. Priority: CH 80-3873 800514 CAN 96:94039
**Abstract.** The manuf. of Al by electrolysis in a salt melt was carried out in a cell with dimensionally stable anodes and a cathode of deposited liq. metal. The Al surface which is in direct contact with the electrolyte melt is opposite the active surface of the anodes but placed lower. On the floor of the C vessel is a device for collecting the liq. metal and this is sepd. by an insulating material. The basin filled with liq. Al communicates with all the various parts by tubes or channels. The total of all the surfaces of Al exposed in the bath amts. to 10-90% of the active surface of the anodes. In an example, the anode consists of SnO2 with 2 wt.% CuO and 1 wt.% Sb2O3.

**Products formed from titanium diboride.** Hazel, John Grant; Steiger, Roger Arthur. (PPG Industries, Inc., USA). Fr. Demande, 21 pp. CODEN: FRXXBL. FR 2468564 A1 810508. Patent written in French. Application: FR 80-23344 801031. Priority: US 79-90840 791102 CAN 96:90537
**Abstract.** TiB2 articles of d. >95% for use in electrolytic cells for the manuf. of Al are prepd. from TiB2, produced by reaction of TiO2, B2O3, and C, by grinding the particles in an inert O-free liq. in a mill which does not introduce any impurities to spec. surface >3 m2/g, cold-forming, and firing at 1800-2500°. The inert grinding liq. is a liq. C5-8 hydrocarbon or a halogenated C2-4 hydrocarbon. Thus, 300 g of TiB2 contg. Ti 69.2, B 30.8, C 0.28, O 0.35, N 0.05, and Fe 0.5% and having spec. surface 0.8-1.1 m2/g was ground in 750 cm3 heptane for 168 h, dried, and passed through a 495 µ screen giving a powder of spec. surface 9.9 m2/g and av. particle size 1.03 µ which was formed into plates and fired at 2100° for 1 h giving articles of d. 96.2%.

**Electrode arrangement in a fusion electrolysis cell for producing aluminum.** Alder, Hanspeter; Schalch, Eugen. (Swiss Aluminium Ltd., Switz.). Ger. Offen., 19 pp. CODEN: GWXXBX. DE 3022232 A1 811224. Patent written in German. Application: DE 80-3022232 800613. CAN 96:59998
**Abstract.** The deployment of the dimensionally stable anodes in relation to the melt and the liq. Al is described. The anodes are ceramic oxides and are held vertically in contact with the molten Al which is collected in the lower part of the C vat in sumps divided by insulating material. The total of all the melt of the discharged Al amts. to 10-90% of the anode surface. This arrangement increases the stability of the anodes.

**Electrode kinetics of the aluminum deposition from tetrahydrofuran electrolytes.** Eckert, J.; Galova, M. Sekt. Chem., Tech. Hochsch. "Carl Schlorlemmer", Merseburg, DDR-4200, Ger. Dem. Rep. Electrochim. Acta (1981), 26(8), 1169-75. CODEN: ELCAAV; ISSN: 0013-4686. Journal written in English. CAN 95:227911
**Abstract.** The kinetics and mechanism were studied of the electrode process for Al deposition from an electrolyte consisting of AlCl3 and LiAlH4 in THF or THF- benzene mixts. Kinetic parameters such as the exchange c.d. and transfer coeffs. depend to a great extent upon the molar ratio of both components. An electrode mechanism was suggested in agreement with the exptl. results obtained.

**Apparatus for jammed tap or similar rod, mandrel removal or placing, especially for mandrels applied in aluminum electrolysis baths.** Karoly, Ede; Titli, Janos. (Inotai Aluminiumkoho, Hung.). Hung. Teljes, 12 pp. CODEN: HUXXBU. HU 19393 810128. Patent written in Hungarian. Application: HU 78-IO269 781130. CAN 95:46888
**Abstract.** A mech. device is described for the removal and placing of spent electrode-holding mandrels applied in Al-electrolysis cells.

**The effect of an alumina layer at the electrolyte/aluminum interface. A laboratory study.** Thonstad, Jomar; Liu, Yexiang. Norwegain Inst. Technol., Univ. Trondheim, Trondheim, Norway. Light Met. (N. Y.) (1981), 303-12. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 94:164639
**Abstract.** Alumina particles can accumulate at the interface between Al and cryolite-alumina melts, due to the high interfacial tension (.apprx.450 mN/m). Theor. calcns. indicate that alumina spheres of sizes up to 7.5 mm diam. can rest at the interface. Alumina which was carefully added to the system, accumulates at the interface, as evidenced by chem. anal. and by microscopy. The rate of oxidn. of dissolved metal when CO2 was passed over the melt, decreased strongly when excess alumina was added. Correspondingly, current efficiency of a lab. electrolytic cell increased in the presence of an alumina layer at the interface. The concn. of dissolved metal in the bulk of the melt decreased, and a concn. gradient was set up within the alumina layer. Evidently, mass transfer of dissolved metal was impeded by the presence of the layer. Settling of alumina at the bath/metal interface probably plays a part in the mechanism of alumina dissoln. in com. Al cells.

**Submicron titanium boride powder.** Hoekje, Howard H. (PPG Industries, Inc., USA). U.S., 31 pp. Cont.-in-part of U.S. Ser. No. 546,838, abandoned. CODEN: USXXAM. US 4282195 810804. Patent written in English. Application: US 75-546838 750203. CAN 95:174250
**Abstract.** Submicron TiB2 powder (and/or ZrB2 and HfB2) is prepd. by vapor phase reaction of the corresponding metal halide (e.g. TiCl4) and a B source (e.g. BCl3) in the presence of H and substantial absence of O in a reaction zone. The TiCl4 and BCl3 are mixed in a hot stream of H from a plasma heater. The reaction zone is maintained at metal boride-forming temps. and the boride powder is removed promptly from the reactor and cooled. The TiB2

powder, contg. TiB2 ≥99, metal impurities <0.4, C <0.1, O <0.20, and halogen <0.15 wt.% and having surface area of .apprx.3-25 m2/g with ≥90% of the TiB2 particles having diam. <1 μ, well-developed faces, and a no. mean particle size of 0.08-0.6 μ, is suitable for hot- and cold-pressing and sintering to prep. articles of d. ≥90%. A metal boride powder contg. a minor concn. of C, e.g. 0.1-5 wt.% is prepd. by adding a source of C, e.g. 1,1,2-trichloroethane [79-00-5], in the reaction zone or by adding submicron metal carbide powders or finely divided C and blending with the powd. metal boride product. Thus, TiB2 powder was prepd. by vapor reaction of TiCl4 and BCl3 in a stream of H, HCl, and Ar, recovered, and degassed under H to give a TiB2 powder contg. B 32.3, O 0.44, and Cl 0.03% and having a surface area of 3.3 m2/g. A portion of this powder was hot-pressed to a plate of d. 97% and resistivity 7 μΩ-cm contg. 0.05% O which when operated as the cathode in an Al redn. cell for 100 h had no signs of deterioration or penetration of the electrolyte.

**Use of modified solvent refined coal as an electrode binder.** Bullough, V. L.; Daley, L. O.; Gates, E. J.; Pipes, William D. Reynolds Metals Co., Sheffield, AL, 35660, USA. Light Met. (N. Y.) (1980), 483-8. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 95:84127
**Abstract.** The suitability of modified solvent-refined coal (SRC) as a binder in the prodn. of C electrodes was investigated. The SRC can be used as a starting material for the manuf. of satisfactory electrode pitch. While the properties of this pitch are marginal, the plant evolution and electrode formulation adjustments will produce satisfactory anodes for Al manuf. by the Hall-Heroult process.

**Electrode for determining alumina concentration in an aluminum electrolysis cell.** (Sumitomo Aluminium Smelting Co., Ltd., Japan). Jpn. Tokkyo Koho, 10 pp. CODEN: JAXXAD. JP 55036104 800918 Showa. Patent written in Japanese. Application: JP 76-62556 760528. CAN 94:57593
**Abstract.** The monitoring electrode (to be used with an Al, Pt, or TiB2 ref. electrode) used to det. the Al2O3 concn. in an Al electrolysis cell is made of a complex oxide having precise compn. (SnO2.Ta2O5, LaYO3, CoCr2O4, LaCrO3, La2Sn2O7, or NiO.Nb2O5).

**Study of the kinetics of aluminum electrodeposition in electrolytes based on aromatic hydrocarbons.** Kuznetsov, V. V.; Kazakov, V. A.; Grigor'ev, V. P.; Titova, V. N.; Davidenko, T. N.; Skibina, L. M. Nauchno-Issled. Inst. Fiz. Org. Khim., Rostov, USSR. Elektrokhimiya (1980), 16(5), 646-50. CODEN: ELKKAX; ISSN: 0424-8570. Journal written in Russian. CAN 93:56756
**Abstract.** The kinetics and mechanism were studied of the electrodeposition of Al from org. electrolytes. The introduction of MBr (KBr, LiBr) in the system AlBr3-ArH, (where ArH is arom. hydrocarbon) increases and stabilizes the elec. cond., not affecting the realkylation of ArH. The role of diffusion limitations in the kinetics of electroredn. of Al decreases in the order: benzene > mesitylene > toluene > m-xylene > ethylbenzene. The connection was established between polarization, elec. cond., the stability of complex species and the magnitude of the ratio MBr-AlBr3 in Al electroplating baths based on arom. hydrocarbons. The principal effects on the kinetics of the process are the dissocn. and adsorptive properties of the solvent.

**Secondary anode paste for Soderberg-type electrode for aluminum electrolysis cells.** Mochizuki, Shogo; Sawai, Mitsugi; Hayashi, Tatsuo; Fujimoto, Kazuhiro; Yano, Kunihiro. (Nippon Light Metal Co., Ltd., Japan; Nippon Light Metal Research Laboratory, Ltd.). Jpn. Kokai Tokkyo Koho, 3 pp. CODEN: JKXXAF. JP 55002724 800110 Showa. Patent written in Japanese. Application: JP 78-73987 780619. CAN 92:188262
**Abstract.** The anode paste used to fill the spike holes when replacing the vertical anode spikes in a Soderberg-type Al electrolysis cell is prepd. by using a layer proportion of fine powder in the aggregate (pitch coke) as well as a larger proportion of binder (pitch) compared to the prepn. of the primary anode paste. The anode potential is lower when a paste having the above compn. is used.

**Carbon electrode coated with antioxidants for aluminum electrolysis.** Inao, Junichi; Yamada, Koichi; Matsui, Atsuro; Murase, Mitsutoshi. (Sumitomo Aluminium Smelting Co., Ltd., Japan). Jpn. Kokai Tokkyo Koho, 5 pp. CODEN: JKXXAF. JP 54137412 791025 Showa. Patent written in Japanese. Application: JP 78-45765 780417. CAN 92:118539
**Abstract.** A C electrode for Al electrolysis is coated with a flux (A, being solid at the electrolysis temp.) contg. ≥1 of Ca, Mg, and Al oxides and binder and then with a flux (B being liq.) contg. ≥1 compds. of K, Na, Ca, Mg, and Li fluorides, and 1 compd. from NaBF4, B2O3, HBF4, and KBF4, and a binder. Loss due to combustion of the

electrode exposed to air is prevented. The binder used is an alkali metal silicate or AlPO4 for the former (flux A), and 1 compd. from alkali. alk. earth metal, and Al nitrates, alkali metal and Al phosphates for the latter (flux B) and an electrode is coated with the former and the latter in a (30-90):(10-70) ratio in 0.2-20 mm total thickness. Thus a 3 diam. × 7 cm petroleum coke electrode was coated with a 5:4 mixt. of Al2O3 and No. 3 water glass (36% solid, Na2O:SiO2 1:3) and then with a mixt. of CaF2 42, NaF 42, NaBF4 16, and 50% NaH2PO4 50 parts, and dried so as to be coated to a 1.5 mm thickness in a 1:1 ratio. When heated at 500, 600, or 800° for 16 h in a vertical elec. furnace with free access of air, the wt. loss was 12, 15, or 13 g/m2-h, vs. 350, 920, or 970 g/m2 without the coating.

**Electrodes for producing aluminum.** Fischer, Werner Karl; Keller, Felix; Haenni, Max. (Swiss Aluminium Ltd., Switz.). Ger. Offen., 22 pp. CODEN: GWXXBX. DE 3013294 801023. Patent written in German. Application: DE. Priority: CH 79-3194 790405 CAN 93:227570

**Abstract.** A procedure is described for prepg. the material to be mixed (dry material and electrode binder), for producing the title electrodes, by mixing, degassing and temp. variation. The dry material and/or the material to be mixed are simultaneous fluidized, degassed and homogenized, as well as heat treated, in an at least partially dust- and gas-tight system. During the mixing a coolant liq., such as water, can be added to completely wet the mixt. The mixed material is then led to molding equipment. In an example, the following operating parameters are presented: throughput of material to be mixed 14 ton/h, temp. at the lower mill exit 150 ± 3°, temp. of the pressed anode 104 ± 6°, quantity of cooling air 28,000 ± 2000 m3/h, anode wt. (green) 456 kg ± 6, anode height (controlled) 512 ± 2 mm. The finished anode had a d. of 1.539 kg/dm3, sp. elec. resistance of 60.4 μΩ-m, and breaking strength 85 daN/cm2.

**efficiency in the electrolysis of aluminum chloride.** Ichikawa, Hachiro; Iuchi, Toshiaki; Ishikawa, Tatsuo., Nippon Light Met. Res. Lab., Ltd., Shizuoka, Japan. Light Met. (N. Y.) (1979), 363-72. CODEN: LMPMDF; ISSN: 0147-0809. Journal written in English. CAN 94:147420

**Abstract.** The redn. of AlCl3 to Al was studied with graphite electrodes in a 20 A cell at 750°. The AlCl3 gas was continuously fed to the electrolyte. The current efficiency was detd. by the metal wt. Relations between the operating and design parameters and current efficiency were found. The following electrolysis conditions are recommended in view of energy saving: electrode angle of 30°, electrode distance of 13 to 16 mm, c.d. of 0.7 to 1.5 A/cm2, and solvent comp. of 20 to 30 mol.% MgCl2 and/or CaCl2 and 80 to 70 mol.% of NaCl and/or LiCl.

**Electrode processes in the electrolysis of an aluminum bromide-potassium chloride molten system.** Vashchenko, V. B.; Chovnyk, N. G. USSR. Fiz. Khim. Elektrokhim. Rasplavl. Tverd. Elektrolitov, Tezisy Dokl. Vses. Konf. Fiz. Khim. Ionnykh Rasplavov Tverd. Elektrolitov, 7th (1979), 2, 67-9. Publisher: Akad. Nauk SSSR, Ural. Nauchn. Tsentr, Sverdlovsk, USSR. CODEN: 43RCAU. Conference written in Russian. CAN 93:139905

**Abstract.** In a polarog. study of AlBr3-KBr and AlBr3-KCl fused systems, varying the ratio of components affected the shape of the polarograms. In the AlBr3-KBr system, increasing the excess of AlBr3 above the theor. increased the limiting current in the cathodic wave, and increasing the excess KBr increased the limiting current in the anodic wave. The excess KBr may have been dissolved in KAlBr4. The AlBr3-KCl fused system behaved similarly. The shape of anodic wave for a system contg. excess KCl was explained by the reaction (AlBr3Cl)- + Cl- = (AlBr2Cl2)- + Br-.

**Correlations between special tar sagging point and dynamic viscosity determined at various temperatures.** Dumitrescu, C.; Dan, Valeria; Mititelu, Tincuta. Inst. Cercet. Metal., Bucharest, Rom. Metalurgia (Bucharest) (1979), 31(5), 213-16. CODEN: MTURAA; ISSN: 0461-9579. Journal written in Romanian. CAN 91:213519

**Abstract.** The relation between the viscosity and the softening point of petroleum tar, which is used as binder in the manuf. of electrodes for Al electrolysis, was studied. Nomographs are given for detg. the ring-and-ball softening point of the tar as a function of its viscosity.

**Characteristics of the electrodeposition of aluminum from an ethylbenzene electrolyte.** Kazakov, V. A.; Titova, V. N.; Smirnova, S. A. Inst. Fiz. Khim., Moscow, USSR. Zashch. Met. (1979), 15(2), 235-7. CODEN: ZAMEA9; ISSN: 0044-1856. Journal written in Russian. CAN 90:212148

**Abstract.** Al can be electroplated from relatively stable baths contg. 1 mol AlBr3 in 3 mols of ethylbenzene (I) [100-41-4]. Upon aging, the sp. cond. (λ) of the bath increases and transalkylation of I occurs. At λ = 2 × 10-3 Ω-1 cm-1, the current efficiency falls from 80% to 35% as the c.d. increases from 5 to 50 mA/cm2. The ductility of the electroplate decreases, but the microhardness changes little as the c.d. increases. Deposits become more coarse as the c.d. increases.

**Electrodeposition of aluminum-copper alloys from alkyl benzene electrolytes.** Capuano, G. A.; Ducasse, R.; Davenport, W. G. Dep. Chem., Univ. Quebec, Montreal, Que., Can. J. Appl. Electrochem. (1979), 9(1), 7-13. CODEN: JAELBJ; ISSN: 0021-891X. Journal written in English. CAN 90:94294
**Abstract.** Al-Cu alloys (0-3.5 wt.% Cu) can be plated on steel with the resulting plates being bright, adherent, and less porous than equiv. plates of pure Al. The compn. of the plates can be readily controlled by using Al-Cu anodes of specified Cu content. About half the Cu dissolved from the anodes is transferred to the cathode, the remainder is pptd. from the electrolyte as CuBr. Plate compn. varies with c.d. and this parameter can also be used to control the process. In a parallel investigation, the p.d. between Al and a no. of other metals (Zn, Pb, Cd, Sn, Cu, Ag) was measured. The p.ds. in the alkyl benzene baths were 10-30 fold less than in aq. baths which indicates that the alkylbenzenes should be used for plating other alloys in addn. to those of Al and Cu.

**Continuous treatment of electrode materials.** Chevroulet, Leon; Meier, Robert Reinhard. (Buss A.-G., Switz.). Swiss, 7 pp. CODEN: SWXXAS. CH 606498 781031. Patent written in German. Application: CH 76-14460 761117. CAN 90:31125
**Abstract.** The continuous treatment of electrode materials is described, in which pitch, coal dust, and other solids are treated by mixing and kneading with addn. of heat to form a C-contg. paste. Such anode material can be used in Al recovery by electrolysis of a melt.

**Pitch for electrodes used in aluminum electrolysis.** Wada, Tetsuo; Iguchi, Kenji. (Mitsui Coke Co., Ltd., Japan). Japan., 3 pp. CODEN: JAXXAD. JP 53006976 780313 Showa. Patent written in Japanese. Application: JP 74-14419 740206. CAN 89:149384
**Abstract.** Coal-tar pitch is mixed with heavy oil and heated continuously in a reactor at 350-450° and 0.1-1.0 kg/cm2. Thus, 144 vol. parts pitch (contg. C6H6 insols. 22.1, quinoline insols. 5.5, and fixed C 52.1%) was mixed with 16 vol. parts heavy oil and heated in a reactor at 400° and 0.7 kg/cm2 for 5 h to obtain a pitch (softening point 87.1°, d. 1.307 g/cm3, C/H ratio 1.68, and contg. C6H6 insols. 32.6, quinoline insols. 9.0, and fixed C 56.8%), which is suitable for the manuf. of electrodes.

**Firing of carbon electrode for aluminum electrolysis.** Ishiwara, Yoshio; Sakae, Tadashi; Uno, Tetsuo. (Sumitomo Toyo Aluminium Seiren K. K., Japan). Japan. Kokai, 6 pp. CODEN: JKXXAF. JP 53033206 780329 Showa. Patent written in Japanese. Application: JP 76-107521 760907. CAN 89:97132
**Abstract.** To prevent damage from taking place at the point when the electrode rod is connected to a C electrode for Al electrolysis, the raw C electrode obtained from pitch coke or petroleum coke and pitch (binder) is covered with powd. coke (particle size <0.2 mm) at the point when contact is to be made with the electrode rod and then fired.

**Significance of coal tar pitch for aluminum manufacture.** Collin, Gerd; Gemmeke, Wilfried. Ruetgerswerke A.-G., Duisburg-Meiderich, Ger. Erdoel Kohle, Erdgas, Petrochem. (1977), 30(1), 25-9. CODEN: EKEPAB. Journal written in German. CAN 86:109442
**Abstract.** Coal-tar pitch, the main binder for C electrodes used in electrolytic Al prodn. contained 14% quinoline-insol., and 25% benzene-insol. components. During the process of manuf. by distn., the lower and medium mol. wt. components are polymd. Aromaticity and binder properties are discussed with respect to the manuf. of C electrodes.

**Electric current and voltage during alternating current electrolysis of aluminum.** Ono, Yukiko; Sato, Toshihiko. Shibaura Kogyo Univ., Tokyo, Japan. Aruminyumu Kenkyu Kaishi (1977), 122, 39-40. CODEN: AKKADN. Journal written in Japanese. CAN 89:81887
**Abstract.** The cathodic and anodic current passing through the oxide coatings during a.c. treatment of Al were measured for the cases when Al and Pt counter electrodes were used. The anodic treatment showed very little effect on the electrode surface area ratio regardless of the counter electrode, but the cathodic current showed a significant dependence on the ratio when an Al counter electrode was used. The voltage dependence of barrier layer thickness showed a linear relation at low voltage, but deviated from the straight line at higher voltage.

**Nonconsumable electrode for aluminum electrolysis.** Yamada, Koichi; Hashimoto, Tadanori; Horinouchi, Kazuo. (Sumitomo Chemical Co., Ltd., Japan). Japan. Kokai. 4 pp. CODEN: JKXXAF. JP 52153816 771221 Showa. Patent written in Japanese. Application: JP 76-71860 760617. CAN 88:112535
**Abstract.** The part of the anode (optionally cathode) contacting the melt is perforated. The evolved O is readily removed, and the melt is homogenized to lower the electrolysis potential and extend its life. Thus, ZnO, SnO2, and NiO were mixed to obtain spinel-type Zn1.7Ni0.3SnO4, calcined at 1200° for 10 h, vibration-milled to -400 mesh, plasma-sprayed on a Ni lattice of 100 × 100 cm of perforation area ratio 40%. When 10% Al2O3 in cryolite was electrolyzed with this anode and a Ni lattice of 100 × 100 cm of perforation area ratio 25% plasma-sprayed with TiB -400 mesh as cathode for 3 mo, the current efficiency was 94 vs. 88% with floating Al on the melt when the perforation area ratio for both electrodes was 0 %.

**Electrode for electrolytic aluminum manufacture.** Yamada, Koichi; Hashimoto, Tadanori; Horinouchi, Kazuo. (Sumitomo Chemical Co., Ltd., Japan). Japan. Kokai, 5 pp. CODEN: JKXXAF. JP 52140411 771124 Showa. Patent written in Japanese. Application: JP 76-58208 760519. CAN 88:96670
**Abstract.** The title electrode, at least the part in the molten salt, is of spinel-type oxide, (NixM1-x)(FeyN2-y)O4 (M = Sn, Zr, or Ti; N = Zn, Ni, or Pb; $0.5 \leq x < 1$; $1 \leq y < 2$), is chem. resistant to the molten salt and is electron conducting. Thus, NiO 40.1, Fe2O3 36.7, and SnO2 23.2 parts was ball-milled for 15 h, rubber-pressed at 1000 kg/cm2, and sintered at 1400° for 24 h to give Ni0.6Sn0.4Fe1.2Ni0.8O4. The elec. cond. was 5 Ω-1 cm-1 at 1000°. When used at 950° in a cryolite melt contg. Al2O3 at 1 A/cm2 and 4.0 V for 3 mo, the decompn. potential was 2.2 V with little overvoltage and current efficiency 95%.

**"In situ" determination of the alumina content in aluminum electrolysis baths.** Mazza, B.; Pedeferri, P.; Re, G. Ist. Chim. Fis. Elettrochim. Metall., Politec. Milano, Milan, Italy. Metall. Ital. (1976), 68(12), 582-90. CODEN: MITLAC. Journal written in Italian. CAN 88:57898
**Abstract.** The crit. c.d., .hivin.ic, for onset of the anodic effect in cryolite (Na3AlF6)/Al2O3 electrolytic baths depends on the Al2O3 content. Factors affecting its use in the detn. of the Al2O3 content are the nature, shape, size, and positioning of the electrodes. The min. value of the deviation in .hivin.ic vs. Al2O3 content relation is obtained with wire-shaped electrodes of glassy C, a material for which .hivin.ic shows little temp. dependence. Industrial use of the method will depend on com. availability of electrode materials resistant to anodic attack and obtainable in the required geometry.

**Effect of anthracite properties and formulation on properties of bench scale cathode blocks.** Belitskus, David. Alcoa Lab., Alcoa Cent., Pa., USA. Light Met., Proc. Sess., AIME Annu. Meet. (1976), 1, 411-32. CODEN: LMPMDF. Journal written in English. CAN 87:87612
**Abstract.** Calcined anthracite was formed with pitch binder into cathode liner blocks for Hall electrolysis cells. Bench-scale cathode blocks having an aggregate of 70% anthracite calcined at 1135°C and 30% ball-milled graphite and a coal tar pitch binder were fabricated, baked at 1135°C, and tested for elec. resistivity and expansion during electrolysis in a test cell. Cathode expansion during electrolysis increased with increasing S content of the anthracite but appeared to decrease with increasing Si content. Elec. resistivity decreased with an increase in the fraction of green anthracite exhibiting a conchoidal rather than laminar fracture. Aggregate size and binder also had effects.

**Calcined electrode for aluminum molten salt electrolysis.** Morimoto, Shingo; Kawamoto, Kiyoyoshi. (Showa Denko K. K., Japan). Japan. Kokai, 3 pp. CODEN: JKXXAF. JP 76132107 761117. Patent written in Japanese. Application: JP 75-56036 750514. CAN 86:124805
**Abstract.** The terminal part of the C electrode is coated with a mixt. of coke, pitch, Al2O3, and cryolite. Thus, the C electrode was coated with (1) a 2:1:1:1 mixt. of coke, pitch, Al2O3, and cryolite, or (2) a 3:2:5 mixt. of coke, pitch, and ppt. contg. cryolite 44.5, (CaF2 − AlF3) 8.3, and balance α-Al2O3. Erosion was 10 and 3% for electrodes coated with 1 and 2, resp. When a conventional 4:1 mixt. of coke and pitch was used for coating, 17.5% electrodes were eroded.

**Study of the mechanism of an anodic process during electrolytic production of aluminum using a rotating electrode.** Vetyukov, M. M.; Dyblin, B. S.; Ivanov, S. N. USSR. Tr. Leningr. Politekhn. In-ta (1976), Issue 348, 53-7. From: Ref. Zh., Khim. 1976, Abstr. No. 18L462. Journal written in Russian. CAN 86:23419
**Abstract.** Title only translated.

**Carbon materials used for smelting aluminum.** Watanabe, Tohru. Nippon Light Met. Res. Lab., Ltd., Shizuoka, Japan. Nenryo Kyokai-Shi (1975), 54(8), 644-52. CODEN: NENKAU. Journal; General Review written in Japanese. CAN 85:163985
**Abstract.** A review with 23 refs. on the use as anodic and cathodic electrodes of C materials in the electrolytic smelting of aluminum.

**Prevention of sulfiding of iron material in contact with carbonaceous material containing sulfur (in Soederberg aluminum electrolysis cell).** Ikeuchi, Haruhiko; Tomita, Takeshi. (Mitsubishi Chemical Industries Co., Ltd., Japan). Japan. Kokai, 2 pp. CODEN: JKXXAF. JP 7659005 760522. Patent written in Japanese. Application: JP 74-133386 741120. CAN 85:127743
**Abstract.** At least 1 alkali metal or alk. earth oxide, carbonate, or fluoride is added to the title paste. A Li compd. is preferred. Thus, petroleum pitch contg. 2.5% S was mixed with an equiv. amt. of powd. Fe and Li2CO3 and heated at 900° for 3 hr in a graphite crucible in a N stream; 6.8% S as FeS was formed, vs. 15.9% without Li2CO3.

**Carbon electrode for an aluminum electrolysis furnace.** Natsume, Isamu; Sasaki, Yoshito; Ito, Keiichi; Fujii, Takayuki. (Mitsubishi Chemical Industries Co., Ltd., Japan). Japan. Kokai, 4 pp. CODEN: JKXXAF. JP 7654011 760512. Patent written in Japanese. Application: JP 74-127771 741106. CAN 85:101251
**Abstract.** Calcined anthracite (I) is mixed with 5-30% of powd. coke whose macro-pore vol. is larger than the micro-pore vol. Thus, a mixt. of I calcined >1300° and sieved to give 5-10, 0.2-5, and <0.2 mm in 23:40:29 parts was mixed with coke (macro-pore vol. of 74 and micro-pore vol. 55 mm3/g) 8 parts. Pitch 30 parts were added to the above mixt. of 100 parts at 150° for 20 min, extruded at 90° and 50-60 kg/cm2 to a slab of 590 × 520 × 2600 mm size, and heated at 1200° for 2 wk. The compressive strength was 350 kg/cm2, sp. resistance 7100 cm, swelling 0.9%, apparent d. 1.55, and porosity 13.9%, vs. 360, 6700, 0.8, 1.51, and 16.1 with micro powder of I in place of the coke.

**Mechanism of the electrolytic working of ether baths for aluminum electrodeposition.** Levinskas, A. USSR. Elektrokhimiya (1975), 11(12), 1905. CODEN: ELKKAX. Journal written in Russian. CAN 84:127950
**Abstract.** Addnl. data considered in abstracting and indexing are available from a source cited in the original document. High quality Al electrodeposits from ether baths are detd. by the high degree of Lewis basicity of the ether medium. During Al electrodeposition, with the decrease in cathodic current and simultaneous increase in c.d. (0.06-0.08 A/cm2), the current efficiency of metal increased (.apprx.100%). The mechanism of electrolytic working of an ether-ammoniacal bath is confirmed by ir data, chem. anal., change in the Al deposit structure, and transport.

**Aluminum electrodeposition in the presence of Lewis bases.** Levinskas, A.; Armalis, S.; Ingaunyte, B. Vil'nyus. Gos. Univ. im. Kapsukasa, Vilnius, USSR. Deposited Doc. (1975), Issue VINITI 1073-75, 13 pp. Avail. BLLD. Report written in Russian. CAN 87:92537
**Abstract.** With the presence in the compn. of ether electrolytes of Lewis bases with strong donor action such as pyrrolidine, bipyridine, hexamethylenimine, ethylaminocyclohexane, diethylamine, triethylamine, butylamine, NH3, etc., the high basicity of the medium required for optimal electrocrystn. of Al is attained by the supplemental operation of purifn. by electrolysis. The process of purifn. of ether electrolytes by electrolysis possesses a no. of general features, to which belong the disappearance of the limiting current ilim by the complex H·ether+ and a decrease in cathodic polarization, a spasmodic increase in the basicity of the medium at the end of the process, and an increase in the content of Al in the cathodic deposit as a result of disappearance of parallel org. transformations.

**Apparatus for producing carbon electrodes for the aluminum industry.** (Fives-Cail Babcock, Fr.). Fr. Demande, 11 pp. CODEN: FRXXBL. FR 2263051 751003. Patent written in French. Application: FR 74-07925 740308. CAN 84:124828

**Abstract.** A vibrating molding machine comprises a solid mold on a vibrating table resting on rubber blocks. The mold is fastened to a fixed structure by several rods disposed in a horizontal plane and distributed around the mold. so as to restrict its horizontal movements.

**Device for connecting bus bars of aluminum or copper with electrical conductors of steel in electrolysis furnaces, especially for producing aluminum.** (Vereinigte Aluminium-Werke A.-G., Ger.). Fr. Demande, 3 pp. CODEN: FRXXBL. FR 2246091 750425. Patent written in French. Application: FR. Priority: DE 73-2349151 730929 CAN 84:78460
**Abstract.** Use is made of a composite element clad by explosion, for instance Al or Cu on steel. The element has a high mech. strength and an improved elec. cond.

**Calcined carbon electrode of aluminum electrolyzers.** Ryaguzov, V. N.; Turchenkov, V. I. U.S.S.R. CODEN: URXXAF. SU 378524 730418. Patent written in Russian. Application: SU 710928. CAN 79:99898
**Abstract.** The title anode includes a C block with adapter receptacle, and adapter, and a cast Fe lining between the adapter and the walls of the adapter receptacle. To reduce the loss of elec. energy, in the body of the C block around the adapter receptacle are placed vertical cast Fe rods connected by cast Fe crosspieces with the cast Fe lining. The cast Fe rods in cross section have an oval form and have a corrugated surface. The cast Fe rods are tapered downwards.

**Electrode system for electrolytic cells.** Jacobs, Stanley Carlton. (Aluminum Co. of America). Ger. Offen., 17 pp. CODEN: GWXXBX. DE 2244040 730329. Patent written in German. Application: DE. Priority: US 71-178282 710907 CAN 78:143232
**Abstract.** The electrode system for passing current into and out of a chamber in a corroding surrounding comprises a conducting member extending into the chamber which would be exposed to the corrosive action, a conducting casing which is impermeable for gases and liqs. which surrounds the conducting member and protects it against contact with the corroding medium, addnl. elements to maintain a protective gas shield around the conductor, the pressure of said gas being sufficient to keep away the corroding medium, and addnl. coolant means which ensure freezing of the corroding medium and thus also inhibits the contact between the corroding medium and the conductor. Preferably, the conducting member is part of an electrode system in an electrolytic Al cell which contains a corroding mixt. of gaseous Cl and AlCl3 dissolved in a molten solvent having a higher decompn. potential that AlCl3.

**Equipment for producing high-density green carbon electrodes.** Hirt, Wilhelm; Ringelmann, Heinz; Weckesser, Ernst; Weinhold, Gottfried. (Vereinigte Aluminium-Werke A.-G.). Brit., 5 pp. CODEN: BRXXAA. GB 1253908 711117. Patent written in English. Application: GB. Priority: DE 680904 CAN 76:135107
**Abstract.** A method of and a vibrating app. for producing a high-d. green C electrode for the Al-producing industry are disclosed. A mass comprising C and a binding or cementing agent is deposited in a mold and compacted by vibration, wherein the mold and its charge are evacuated before or during compaction of the mass. In the vibrating app. an addnl. sealing plate is spaced above and rigidly attached to the covering wt. in such a manner that the sealing plate, the addnl. sealing plate, the covering wt., and the mold define (between themselves) 3 superposed chambers, the lower 2 of which are in communication through a peripheral clearance gap and are evacuable through an evacuating connection. The upper chamber can be vented at any time through a valve before or during the vibrating process.

**Electrochemical behavior of the aluminum electrode in molten salt electrolytes.** Del Duca, Betty S. Lewis Res. Cent., NASA, Cleveland, Ohio, USA. J. Electrochem. Soc. (1971), 118(3), 405-11. CODEN: JESOAN. Journal written in English. CAN 74:93779
**Abstract.** The kinetics for dissoln. and deposition of solid Al in molten AlCl3.N aCl and AlCl3-(LiCl-KCl eutectic) electrolytes were studied by mean s of galvanostatic and potentiostatic techniques at 175-313°. The apparent exchange c.ds. varied from 1 to 56 mA/cm32 Surface diffusion was the rate-detg. step at low overpotentials, and char ge transfer the rate-detg. step at high overpotentials. The most probable anodic rate-detg. step was Al → Al+ + e-; the most probable cathodic rate-detg. step was Al+++ + e- → Al++ in AlCl3- (LiCl-KCl eutectic) electrolyte and Al+ − − e- → Al+ in AlCl3.NaCl electrolyte. Current efficiencies for dissoln. were close to 100%.

**Cooling apparatus for newly compressed carbon electrodes used for electrolytic aluminum production.** Wilkens, Kurt. (Kloeckner-Humboldt-Deutz A.-G.). Ger. Offen., 12 pp. CODEN: GWXXBX. DE 1928424 701210. Patent written in German. Application: DE 690604. CAN 74:70999

**Abstract.** Green electrodes for Al prodn. are cooled immediately after compacting them by feeding the upper side of the conveyor belt through a shallow pan with coolant, while coolant sprinklers are arranged on both sides of the belt above the pan. Sufficient electrode stability for removal and storage is claimed.

**Model of the aluminum-electrolysis cell and its electrodes.** Schwarz-Bergkampf, Erich. Leoben, Austria. Int. Leichtmetalltag., 5th (1969), 347-9. Publisher: Aluminum Verlag, Duesseldorf, Ger. CODEN: 22MEAG. Conference written in German. CAN 74:60151

**Abstract.** Aluminum Verlag: Duesseldorf, Ger. Graphs are constructed to aid in detg. the most economical operation in terms of cell voltage, c.d., and cell configuration.

**Carbon for aluminum electrolysis electrodes.** Maugweiler, Gottfried. (Swiss Aluminium Ltd.). Ger. Offen., 23 pp. CODEN: GWXXBX. DE 2005064 700813. Patent written in German. Application: DE. Priority: CH 690204 CAN 73:89634

**Abstract.** This carbon is prepd. by compacting a mixt. contg. powd. coke, additives, and binders, e.g. pitch, in a shaking app. The app. consists of a container on a shaking table and a cover which is pressed down with increasing pressure during the process, optionally while being vibrated.

**Aspects on potential-current curves of aluminum electrolyte (preliminary experiment on electrode reaction in aluminum electrolyte).** Matsushima, Tomoo. Res. Inst. Miner. Dressing Met., Tohoku Univ., Sendai, Japan. Keikinzoku (1969), 19(9), 373-82. CODEN: KEIKA6. Journal written in Japanese. CAN 73:31004

**Abstract.** The potential-current curves of fused electrolyte with or without Al were measured at 1000° by chronoamperometry with linearly variable potential. The electrolytes consist of cryolite, Al2O3, and one of the following fluorides; NaF, BaF2, CaF2, AlF3, and MgF2. The electrodes were graphite anode, Mo or Al cathodes, and Mo as the reference electrode. Concn. polarization of Al2O3 resulted in each case. The difference between acid and base electrolytes were observed with respect to polarization potentials and the mechanism of cathodic polarization are discussed.

**Correlations between pitch binder properties and properties of Soderberg electrodes.** Mason, Clifford Robert. Coal Tar Res. Assoc., Cleckheaton, Engl. Fuel (1970), 49(2), 165-74. CODEN: FUELAC. Journal written in English. CAN 73:20838

**Abstract.** Eight coal tar pitches, of similar softening point but of varying coking values and solvent anals., have been evaluated for their suitability as electrode binders, particularly in producing electrodes for aluminum electrolysis. The correlations found between pitch properties and properties of lab. made test electrodes indicate that current specifications tend to select those binders giving carbonized electrodes of greatest strength and lowest porosity, although desirable levels of the electrode properties do not coincide with the min. binder content to give desired flow properties of the uncarbonized electrode-paste. The results also indicate a relation between electrode compressive strength and the wetting properties of the pitch used as a binder and that the rate of consumption of the electrode is influenced by the coking value of the lower mol. wt. constituents of the binder pitch.

**One solution to the anode problem in the electrolytic production of aluminum.** Stender, V. V.; Trofimenko, V. V. Dnepropetrovsk. Khim.-Tekhnol. Inst., Dnepropetrovsk, USSR. Khim. Tekhnol. (1969), No. 12, 41-5. CODEN: KTRMAQ. Journal written in Russian. CAN 72:23726

**Abstract.** The principle of working "gaseous" anodes has been discussed. Certain gas reducing agents, e.g. natural gas, CO, and H, have been tried. Porous, conducting, and corrosion-resistant anodes of graphite and magnetite in hermetically sealed construction (to allow the access of gas under any requisite pressure) were used. Electrodes were prepd. from graphite of porosity ≈50% in the form of truncated cones of 30 mm av. diam. and 10 mm height. Electrolysis was done at 970° in the electrolyte having a cryolite ratio of 2.7. With natural gas, depolarization of the order of 0.4 V was observed, but the process soon changed over to anodic oxidn. of C due to the blocking o f electrode pores by soot formed by cracking of hydrocarbons. A const. value of depolarization was obtained with H and CO. The depolarization occurred at a high rate in the presence of H. It was due to strong disintegration of porous graphite electrodes. The surface oxides decomp. to give CO, CO2, and C. Magnetite electrodes having a porosity of 40-5% were prepd. by powder metallurgy from Fe at a pressure of 600 kg/cm2, and were baked in a mild reducing atm. at 1400°. De-polarization of the order of 0.2 V was observed. These electrodes was more stable in the presence of CO.

**Electrochemical behavior of the aluminum electrode in molten salt electrolytes.** Del Duca, Betty S. Lewis Res. Center, Cleveland, Ohio, USA. NASA Tech. Note (1969), Issue NASA-TN-D-5503, 29 pp. Avail. CFSTI. CODEN: NASCA3. Report written in English. CAN 71:118951
**Abstract.** The kinetics of dissoln. and deposition of solid Al in molten AlCl3.NaCl and AlCl3.-(LiCl-KCl)eutectic electrolytes were studied by means of galvanostatic and potentiostatic techniques at 175-313°. The apparent exchange currents varied from 1 to 56 ma./cm.2 Surface diffusion was the rate-detg. step at low overpotentials, and charge transfer the rate-detg. step at high overpotentials. The most probable anodic rate-detg. step was Al → Al+ + e-; the most probable cathodic rate-detg. step was Al3+ + e- → Al2+ in AlCl3-(LiCl-KCl)cutectic electrolyte and Al2+ + e- → Al+ in AlCl3.NaCl electrolyte. Current efficiencies for dissoln. were close to 100%.

**Change of the reactivity of graphite by additions of mineral substances.** Robozerov, V. V.; Vetyukov, M. M. USSR. Khim. Tverd. Topl. (1968), Issue 3, 128-33. CODEN: KTVTAX. Journal written in Russian. CAN 69:56525
**Abstract.** The effect of the inhibitors in the electrolysis of Al2O3 was studied with graphite electrodes, evaluating the activity by the rate of oxidn. by CO2. At 1200 and 1250° in a const. current of CO2 the most effective inhibitor of oxidn. was B2O3. The rate of oxidn. decreased as the content of B2O3 increased to 0.17%. The activation energy of graphite contg. B2O3 and Na2O was 114.8 and 64.5, resp. This compared with that of graphite without additive of 80.1 kcal./mole. Much weaker inhibitors were B2O3 + Al2O3, Na2B4O7, and Al2(SO4)3. But Al2O3, MgO, and WO3 were weak catalysts and CaO, BaO, Na2O, and Cr2O3 were effective catalysts. The results confirmed the hypothesis of the electron mechanism of inhibition.

**Activation of cryolite-alumina compositions.** Diller, Isaac M. U.S., 3 pp. CODEN: USXXAM. US 3392092 680709. Patent written in English. Application: US 630830. CAN 69:48730
**Abstract.** A cell for the electrolytic redn. of Al (U.S. 3,244,604) was modified by inserting into the pot walls auxiliary firing anodes of Ti and Zr diboride contained in a resistant-ceramic tube. A single auxiliary electrode (area .apprx.2% of the regular electrode) can be used in conjunction with the regular electrodes. The refractory hard metal or other firing electrodes should contain <10 ppm. V. A low voltage was applied to the pair of firing electrodes several sec. before use for firing and was maintained during the moderate high-energy firing. To avoid excessive loss of surge energy, low voltage conditioning current was conducted through an impedance to a fast rise surge. Thus, Ti diboride and Zr diboride electrodes were placed in tubes made of SiC bonded with Si oxynitride and inserted in a pot contg. 10 lb. cryolite (contg. 3% LiF), 1 lb. Al2O3, and 3 oz. Al at 990-1010°. A polarizing d.c. voltage was placed across electrodes to deliver 40 amp. After 10 sec. of the 1st firing, the bath temp. dropped to 30° and was restored in 1 min. The current rose to 450 amp. and, after lowering the voltage from the source, was restored to the initial value. The new voltage between the electrodes was 1.9 v.

**Effect of electrolyte sorption on the physicochemical properties of carbon blocks.** Nikitin, V. Ya. Tsvetn. Met. (1967), 40(8), 65-8. CODEN: TVMTAX. Journal written in Russian. CAN 68:8647
**Abstract.** The concns. of F, Na, and Al2O3 sorbed by carbon blocks, lining the bottom of electrolytic Al cells, increased with service life. The apparent and the true ds. of the blocks increased curvilinearly with the amt. of electrolyte sorbed. The phase compn. of the sorbate approximated the triple eutectic 12.3% Al2O3 + 11.0% AlF3 + 76.7% NaF of the system Na3AlF6 + 3NaAlO2 → 2Al2O3 + 6NaF, m.872°. The electrolyte sorption probably assists the graphitization of the blocks, although the mechanism is not clear. Sorption data confirm observations that the carbon bottom lining expands during the operation of the cell.

**Effect of lithium on the carbon materials of an aluminum electrolysis cell.** Rapoport, M. B.; Kudryavtsev, V. I.; Shifman, G. A. Izv. Akad. Nauk SSSR, Met. (1967), Issue 5, 151-9. CODEN: IZNMAQ. Journal written in Russian. CAN 68:5155
**Abstract.** Li, as all alkali metals added as salts to the Al electrolytic cell, penetrates at certain temps. into the interlayer space of coke, thermoanthracite, or graphite. The deforming effect of the penetration decreases gradually with increasing temp. and ultimately ceases. The degree of deformation during the penetration is lower than that of

Na and much lower than during the penetration of K, which is to be expected in view of the considerably smaller ionic radius of Li. Addns. of LiF to an ordinary electrolyte of an Al bath considerably reduce the deformation of a C cathode. The effect of Li on ungraphitized materials is much greater than the effect of Na. It promotes a reversible structural change and the attainment of a higher degree of structural order than that of the initial material on removal of the vapor of the penetrated metal. The basic difference between Li and all the other alkali metals is its capacity for spontaneous formation of Li2C2, for which a temp. range of 500-800°, a relatively high Li content, and an adequately long reaction with C materials are essential. In this temp. range, dependent on the last 2 conditions, products of 2 different processes, namely the penetration of Li into the interlayer space and the formation of Li2C2, can be observed. 18 references.

**Electrode processes during electrolytic deposition of aluminum from xylene solutions.** Simanavicius, L.; Levinskiene, A. Liet. TSR Mokslu Akad. Darb., Ser. B (1966), Issue 4, 39-47. CODEN: LMDBAL. Journal written in Russian. CAN 67:60247
**Abstract.** The cathodic polarization of xylene contg. 25 mole % AlBr3 and of the 3-component system xylene-AlBr3-HBr was measured. On polarization curves, 2 waves were established. The height of the 1st wave [E1 = 0.65-0.75 v. (Pt-electrode) or E2 = 0.15-0.20 v. (Cu-electrode)] was proportional to the HBr concn. and to the water content of the soln. The mechanism of the cathodic processes for the 1st wave was: C6H4Me2 + Al2Br6 + HBr .dblarw. [C6H4Me2H]+ + Al2Br7-; 2[C6H4Me2H]+ + 2e → C6H4Me2 + C6H6Me2 (dihydroxylenes). The 2nd wave (E = -0.10 to -0.15 v.) represented the Al electrodeposition by the scheme: [AlBr2.nC6H4Me2]+ + 3e → Al + nC6H4Me2 + 2 Br-. The depolarization effect of HBr on Al deposition was established. The Al deposition from solns. contg. ≥8 mole% HBr was interrupted, because of the increased rate of Al dissoln. The effective energy of activation for Al deposition [9-12 kcal./mole] was calcd. from the dependence of the cathodic polarization on the temp. During electrolysis, the Al anode dissolved and and AlBr3 was formed: with a Pt anode, Br sepd. and interacted with xylene.

**Fluid coke aggregate and electrode.** Loevenstein, Hirsch. (Harvey Aluminum). U.S., 4 pp. CODEN: USXXAM. US 3322663 670530. Patent written in English. Application: US 620801. CAN 67:46163
**Abstract.** Fluid coke electrodes used for obtaining Al from its ores are described. The process includes briquetting fluid coke particles, calcining the briquets, grinding the briquets such that a compn. of 33-46% total fines, 14-26% medium, and 37-47% total coarse is obtained. This compn. is mixed with a suitable binder, e.g., hard pitch, to produce a paste. The paste is compressed and baked to form a conventional electrode or it may be used to form a self-baking electrode. The proportion of very fines to total fines should be 60-70% by wt. Previously desulfurized fluid coke may be used. To illustrate, fluid coke briquets were ground to size and mixed with 33.1% hard pitch to form a paste. The paste was then used in a 100,000-amp. vertical stud cell. The anode filled with this paste was ready to be put into operation in 12 days, as compared with the normal prebaking time of 3 weeks. The following properties were observed: 190% elongation; 1.371 apparent d.; 3625 psi. crushing strength; 0.00337 ohm/cu. in. resistivity. The percentage of very fines of the total fines in the aggregate was 69.2%.

**Molded carbon materials.** Metrailer, William J. (Esso Research and Engineering Co.). U.S., 5 pp. CODEN: USXXAM, US 3320150 670516. Patent written in English. Application: US 630906. CAN 67:46162
**Abstract.** The C electrodes used in the manuf. of Al by electrolytic redn. of alumina contain relatively active and relatively inactive coke material to provide uniform oxidn. to minimize dusting of the electrode. The cokes used are delayed cokes formed by destructive distn. and fluid cokes formed by surface deposition. Both are calcined. The relative reactivity, which is the wt.% C which reacts with CO2 at 1740°F., is listed for the delayed and fluid coking petroleum residues and delayed coking coal tar pitch. The samples are 14-35 mesh. The coarse aggregate particles have a wt. av. size 10/1 to 40/1 times the wt. av. particle size of the fines aggregate. The ratio of coarse particles to fines particles is 1/1 to 10/1. Depending on the size distribution and relative size, the coke fines material has a ratio of relative reactivity to the relative reactivity of the coarse material of 1/2 to 1/5. The coarse aggregate has ≥90 wt.% of the particles 300-10,000 μ. The fines aggregate has .apprx.90 wt.% of the particles <150 μ and ≥40 wt.% <44 μ. The overlap of coarse and fines aggregate is <20 wt.% of the total aggregate. Samples prepd. by mixing the coke aggregate and pitch binder 30 min. at 300°F. were molded and baked at 1800-2000°F. for 10-50 hrs., then contacted with CO2 up to 16 hrs. When the coarse aggregate is .apprx.3 times as reactive as the fines, it is consumed at approx. the same rate as the binder – fines, resulting in essentially no dust. The source of coke, fluid or delayed, is not important.

# APPENDIX A-2

# SAMPLE OF FORM FOR ASSESSING PATENTS

**Reviewer**________________________________________

**Patent #/**
**Paper**________________________________ **Title**__________________________

**Inventor/**
**Author** --______________________________ **Assignee/**
**Affliiation**________________________

**Material:** __Ceramic __Cermet __Metal __Cathode __Other

**Merit** __High __Medium _Low

Technical________________________________________________________________

Environmental/OSHA_________________________________________________________

Economic_________________________________________________________________

**Viability** __High __Medium __Low

Failure
Mechanism______________________________________________________________

Show
Stoppers_______________________________________________________________

**Implications**

Follow-Up
Steps__________________________________________________________________

Does it Address Roadmap Selection
Criteria?_______________________________________________________________

# APPENDIX A-3

# REVIEW OF THE ELTECH/MOLTECH PATENTS

# APPENDIX A-3

# REVIEW OF THE ELTECH/MOLTECH PATENTS

## Review of the Eltech and Moltech Patents

The de Nora group, which includes Eltech and Moltech, has obtained an impressive array of patents in the area of inert anodes and related technologies over the past two decades. For this reason, the TWG felt it was appropriate to set aside a special section of this report to summarize the content of these patents and make recommendations for future research using the Eltech/Moltech approaches.

### CEROX Patents

The original 1986 CEROX patent (1986: 4,614,569) describes the novel use of a cerium-based coating to protect an anode from corrosion in molten cryolite. The patent covers coatings formed by either in-situ deposition of an oxide in the melt or ex-situ fabrication on an anode substrate (ceramic, cermet, or metal). In the most common embodiment, a cerium fluoride compound is added to the molten bath with the result that a protective cerium oxyfluoride (CEROX) coating forms on the anode. Later work showed that the electrolyte could, in fact, penetrate the CEROX coating, mainly through cracks and other defects. Not surprisingly, the penetration resulted in excessive corrosion of the anode substrate. Several patents followed that tried to address this difficulty. The basic strategies were either to change the composition of the coating so that it had fewer defects or to promote the formation of a "barrier layer" between the substrate and the CEROX coating.

Changes in coating composition were effected by adding other rare earth elements to the bath in addition to cerium, including yttrium, lanthanum, and praseodymium (1987: 4,683,037). The presence of the additional rare earth elements appeared to seal the cracks in the CEROX coating. A later patent (1990: 4,966,674) extended the range of "additional additives" to include all pentavalent metals and also covered ex-situ application of the coating where a mixture of the pentavalent metal and cerium components were sintered onto a substrate.

The barrier-layer approach took several forms. These included the in-situ formation of a "contaminant inhibitor barrier" of spinel composition (1987: 4,680,094) by addition of magnesium fluoride to the bath along with the cerium fluoride. The magnesium (lithium behaved similarly) fluoride penetrated imperfections of the CEROX coating to block channels and cracks. Another form of the barrier layer (1989: EP-030611, 1991: 5,069,771) was a separate film, usually of chromium oxide deposited or formed prior to use in the reduction cell (patents also include Pt, Pd, Au, and several alloys). With chromium oxide, it is preferred that a chromium-containing alloy (including nickel, iron, aluminum, and other elements) substrate be used and the film be formed by heating in oxidizing atmospheres (1990: 4,956,068). Patent 5,069,771 also covers the application of a third "oxide ceramic" layer, on top of the oxygen barrier layer, to serve as an anchorage for the CEROX coating to be formed later. Several compositions are proposed for the oxide ceramic layer, including copper oxide and copper oxide in solid solution with other oxides or oxyfluorides.

A very recent patent (1996: 5,578,174) discusses an alternate method for preparing anodes with a CEROX coating. In this case, a microporous anode is infiltrated with a colloid containing CEROX precursors, typically using a stabilized aqueous liquid carrier. prior to its deployment in a reduction cell. When the anode is first used, a CEROX coating forms early, so that the anode is protected even in the beginning stages of operation. The patent also calls for adding alumina precursors to the colloid so that alumina forms at the anode where it can be consumed instead of the anode material, should conditions favor corrosion. The patent also refers to a similar use of colloids for pretreating carbon anodes.

## Manufacturing of Non-Carbon Components

These patents address the fabrication of non-carbon components for both anodes and cathodes. Cathode-related patents cover mainly boride-based cermets (1986: 4,585,618, 1986: 4,610,726, 1987: 4,650,552) made by pressing/sintering or hot pressing mixtures of aluminum or aluminum alloy and ceramic powders. Sintering or pressing takes place at temperatures up to 1700°C and a chemical reaction actually occurs during fabrication. When the metal is in excess, the result is a cermet containing an aluminum metal-containing phase and a boride. In one case, cerium oxide, boron oxide, and aluminum were the starting materials and the cermet contained cerium boride, alumina, and aluminum metal. This cermet was supposed to be useful as a wetted cathode. Two other patents (1990: 4,961,902, 1991: 5,017,217) refer to a process for making fine-grained ceramic or cermet composites, again with their application to boride-type cathodes primarily in mind, by using a unique heating schedule. The result was a smaller grain size (of 1 μm) in the finished product than in the original powders and improved interconnectivity and mechanical properties.

Two patents (1990: 4,956,068, 1990: 4,960,494) covered fabrication of anodes with both oxygen barrier layers and ceramic layers to be used in conjunction with the CEROX coating. Barrier layers of chromium oxide were grown on chromium-containing alloys by heating them in oxidizing atmospheres, while the copper oxide ceramic layers were generally made by oxidizing a copper-containing metal layer previously put down on the non-copper-containing substrate. The copper oxide layer could reportedly be stabilized by being in solid solution with nickel or manganese oxide. One patent (1985: 4,552,630) was very similar to patents by Alcoa on spinel-based inert anodes but, instead of adding a metal phase, the Eltech anodes were made more conductive by partial substitution of another ion, using a nonstoichiometric composition, or by doping. The lowest dissolution rate reported for these anodes was about 8.8 cm/yr for a ferrite/zirconia composition.

Finally, fabrication of a (ceria/alumina)/(Ce + Al or Ni or Fe or Co) cermet was described (1990: 4,948,676). (The metallic phase would be mainly $Al_2Ce$, which melts at 1360°C.) This was reported to be a good candidate for a substrate for the CEROX coating in aluminum reduction cells since the main corrosion products would be cerium or aluminum, which would be in the bath anyway. Hot pressing powders generally make the cermet and the powders react during hot pressing. Dopants can be added to increase conductivity.

## New Cell Designs

Two patents on cell design (1987: 4,681,671, 1998: 5,725) cover a vertical arrangement of inert anode plates. The earlier design is unusable (as noted in the latter patent) because the cathode is under the plates, resulting in significant current flowing from the bottom of the plates instead of from the faces as anticipated. The latter patent places the anodes and cathodes in parallel in a multi-monopolar arrangement with a spacer between them. The design is reported to be advantageous because it uses gas lift to facilitate circulation of electrolyte.

Other patents describe a multi-monopolar arrangement of inert anode tubes with wettable cathode rods inside them (1994: 5,368,702), a true bipolar electrode design that uses a cerium oxyfluoride-type anode material and a cerium hexaboride cathode bonded to a common cerium metal substrate (1991: 5,019,225), and a modification of the Hall cell cathode that calls for putting chunks of a refractory material in the molten aluminum pad to reduce magnetohydrodynamic movement (1989: 4,824,531).

## Additional Remarks on the CEROX Coating and Accompanying Modifications

The original CEROX patent is an elegant portrayal of a novel idea to protect "partly consumable" anodes from corrosion and thus render them "nonconsumable" within the currently established boundaries for that rather vague term. The key advantage of the CEROX process is that it uses a constant supply of cerium ions in the bath to maintain a protective coating of cerium oxyfluoride on the anode. The anode material is not involved so it is not consumed in making or maintaining that coating. The primary disadvantage is that the cerium has to be removed from the aluminum metal later, but all indications are that this can be done economically.

Unfortunately, the cerium oxyfluoride coating was found to be unsuitable after early testing due to the presence of cracks or channels in the coating. Electrolyte penetrated these defects and reacted with the anode substrate. To rectify the problem with cracks in the coating, Eltech/Moltech investigated essentially three strategies: (1) Incorporating other elements (in addition to cerium) in the bath so the coating that forms has no defects, (2) using another coating *in addition* to the CEROX coating, and (3) modifying the anode composition completely.

The first of these strategies is not practical because it involves spiking the bath with more impurities. Getting the aluminum companies to accept cerium is arguably feasible, but compounding the problem by requiring the separation of elements like yttrium or praseodymium is probably not feasible.

The third approach, completely modifying the anode composition, is intriguing. The idea, discussed at length in patent 4,552,630, involves making a cermet anode composed of a cerium-containing oxide and an aluminum-cerium intermetallic phase. This idea is faithful to the original CEROX approach with the added benefit that a reduced amount of corrosion from the substrate only results in putting more cerium in the bath. Since the industry would already be prepared to remove cerium from the aluminum, the additional "impurity" would have very little impact on operations. Unfortunately, this idea was not pursued in later research, apparently due to excessive dissolution of the cerium-based anodes and their high resistance. Currently, Eltech/Moltech have focused on the micropyretic/NOVANOR anodes and their modification.

The second approach listed above, using an additional coating, has received the most recent and intensive attention from Eltech/Moltech researchers. It has many embodiments. The most comprehensive description involves using a chromium-containing metal as a substrate and coating it with a layer of copper-containing alloy. Both the copper-containing layer and the substrate are oxidized to give two oxide layers. The layer next to the remaining metal substrate, termed the "oxygen barrier layer," is a chromium-rich oxide that protects the substrate from attack by the electrolyte, even if the CEROX coating leaks. The second layer, called the "ceramic oxide layer," is on top of the barrier layer. It is rich in copper (oxide) and porous, and serves as an anchor for the CEROX coating that forms on top of it. Recent work has adapted this multi-coating approach to use with micropyretic NOVANOR anodes. These anodes are porous multi-component, compositionally graded, metal anodes designed to give both a protective coating during oxidation and a morphology that is optimal for binding to the CEROX coating. The results of recent testing are promising with wear rates from 100-amp tests reported at about 1.8 mm/yr. This is reasonably close to the most stringent requirements recently considered by the Inert Anode Technical Working Group for a successful inert anode. In spite of these promising results, however, reviewers remain somewhat skeptical.

There are two main concerns regarding the NOVANOR anodes. First, as far as can be determined, the recently reported successes were not accompanied by diagnostics of the anode microstructure after testing. For this reason, it is unclear whether the anodes are changing internally or not, i.e. oxidizing, despite injecting small quantities of impurities into solution or remaining dimensionally stable. Chemical changes in the anode can alter their mechanical and electrical properties so that they may "fail" despite giving acceptable metal quality or remaining the same shape.

A second difficulty is that the approach involves the formation and maintenance of several layers to succeed. Unfortunately, with more components in the system, the more failure modes become possible and the more potential impurities are present for the aluminum product. This is not to conclude that Eltech/Moltech discovered an inert anode with NOVANOR. If wear rates of 1.8 mm/yr are achievable in bench-scale tests, longer term testing is clearly warranted.

## Cell Redesign

Several designs call for vertical anodes and cathodes, and other laboratories have proposed similar versions, as well. There are distinct advantages to gas lift in a vertical design and this has been demonstrated and modeled numerous times. In fact, work has been done to determine optimal anode shapes and orientations for gas bubble-induced circulation and alumina dissolution. It is probable that a successful deployment of inert anodes will use a vertical design or some orientation off-horizontal to take advantage of this mixing effect. The tubular design by Moltech is novel but not necessarily superior to the parallel vertical plate design. (The tubular design will give lower anode current densities but changing the size and number of vertical plates may also accomplish this.) The tubular design may also make less efficient "use" of cell space. Large portions of electrolyte between the anode tubes appear to be unutilized, compared to the plate design where only electrolyte between the plate array and the sidewalls is unused. Current efficiency and bubble flow may also not be optimized in the tubular arrangement so that the alumina does not dissolve and circulate efficiently. Under these conditions, most inert anode materials will corrode. Another problem with the tubular design is that some spacer will probably be required to keep the anode tube and cathode rod apart, especially if the annulus is kept small. Since there needs to be room for gas to flow up and aluminum to flow down, designing spacers that do not contribute to plugging up the tubes will not be trivial.

Another interesting design patent by Eltech/Moltech is the proposed bipolar electrode that uses a cerium oxide/oxyfluoride anode and a cerium hexaboride cathode, bonded to a common cerium metal substrate. It is not clear if the materials would exhibit adequate performance as the patent describes (e.g., the cerium oxide anode is probably not conductive enough and may be too soluble, based on other reports), but the basic idea is clearly within the spirit of a "new approach." Variation of composition of the two cerium-based electrodes may solve some of the problems and, coupled with the distinct advantages of a bipolar configuration, would take inert anode research onto a new and exciting path.

# APPENDIX A-4

# PAPER BY DR. ERNEST DEWING

# INERT ANODES FOR ALUMINUM PRODUCTION

by

ERNEST W. DEWING

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## INTRODUCTION

The primary purpose of this paper is to give a critical analysis of the logic for seeking an inert (i.e. non-consumable) anode for use in the production of aluminum by electrolysis of alumina dissolved in molten cryolite. A secondary purpose is to look at the generic problems which face all such anodes, and the cell-systems in which they would be used, without going into much detail about specific materials. The two areas overlap: it is obviously useless to consider that something would be nice if there are fundamental reasons for believing that the objective is unattainable.

The author was closely associated with ALCAN's research in this field for over ten years, and indeed had, for much longer than that, responsibility for looking into and considering any possible novel ideas for making aluminum. It is on that background that the present work is based, but it should be made clear that, although the author has permission from ALCAN to discuss what was done, the views expressed are entirely the views of the author and not of ALCAN. The author retired from ALCAN eight years ago, and has no knowledge of any research ALCAN may have pursued since that time.

## ENERGY CONSIDERATIONS

The usual reasons advanced for wanting inert anodes for aluminum production cells relate to saving fossil carbon consumption, producing oxygen instead of $CO_2$, thereby reducing greenhouse warming, and generally having a much "greener" operation. Analysis shows, however, that these considerations ultimately boil down to considerations of energy; how, and from what, it is generated, and how much of it is consumed in making a kilogram of aluminum.

The first thing to understand is the equivalence between energy consumption and the voltage on the electrolysis cell. In an electrolytic process Faraday's law requires that 96,485 coulombs of charge be passed through the cell to generate one gram-equivalent (9 g) of Al. Coulombs are amperes times seconds. Multiplying by the cell voltage gives the energy consumption as volt-ampere-seconds, or watt-seconds; conversion to kWh/kg is a straight multiplicative relationship, and, to a convenient first approximation, each volt corresponds to 3 kWh/kg. There is a correction for loss of Faradaic efficiency, but efficiencies of commercial cells are over 90 % and vary little from one to another, so the matter can be ignored for the current discussion.

The chemical reaction taking place in a conventional cell is

$$2\ Al_2O_3 + 3\ C = 4\ Al + 3\ CO_2 \qquad [1]$$

The thermodynamic minimum energy required (i.e. the reversible energy) can again be expressed as a voltage, and is 1.2 V. For an inert anode the reaction becomes

$$2\ Al_2O_3 = 4\ Al + 3\ O_2 \qquad [2]$$

and the reversible voltage is 2.2 V. The difference of 1 V naturally corresponds to the reversible energy of burning carbon:

$$C + O_2 = CO_2 \qquad [3]$$

The *heat* absorbed in reactions [1] and [2] is not the same as the energy used because there is a significant increase in entropy involved in the production of the gas. In fact, for reaction [1] the voltage equivalent to the heat absorption is 1.7 V, and for the inert anode it is 2.7 V. *All other voltage on the cell, regardless of its origin, generates heat* .

The consumption of carbon in a conventional cell is not, in fact, reversible; there is an overvoltage of 0.5 - 0.6 V. This means that only 40 - 50 % of the theoretically available combustion energy is recovered. That, however, is better than can be achieved in a thermal electricity generating station, which runs at about 35 % efficiency. This fact is central to the whole of the discussion which follows.

As I understand it, the oil industry must produce petroleum coke - it is an unavoidable by-product. What is going to be done with it if the aluminum industry does not take it? Answer: it will be burned as fuel to generate electricity *with less efficiency than if it is used in an aluminum cell* . Thus, the argument that going to inert anodes saves $CO_2$ generation is inherently specious. The extra volt needed will be generated by burning more carbon than is burned now.

The above argument, which has been given in its simpiest form in order that the principle may be clearly seen, is in fact overstated because it ignores the fact that energy was used in calcining the green petroleum coke to make anodes, that energy was used in baking them, and that there is a certain amount of air oxidation of an anode in a cell. The energy for the calcination is supplied by burning the volatiles in the green coke; if the green coke were burned in a power station that energy would generate power. I do not have figures available to do any more detailed sums, but my guess is that the outcome would be somewhere around break-even, i.e. that the extra power needed could be generated by burning the coke, but that any overall benefit would be marginal.

The above discussion applies to the case of full retrofit where carbon anodes are pulled out of a cell and similar-size inert ones are put in, and nothing else changes. The cell *must* operate 1 V higher or it will not stay hot. If something is done to reduce voltage in order to save power, then something must also be done to give an equivalent reduction in heat losses. Subsequent discussion thus comes down to: An inert anode carries an inherent penalty of a volt; what can be done to take advantage of its other inherent properties (notably that its face can be shaped to release gas and that the cell can be better closed since access to change the anode regularly is no longer required) to reduce power consumption and heat losses?

The voltage breakdown on a conventional cell looks something like this:

| | |
|---|---|
| Reversible Voltage | 1.2 |
| Anode Overvoltage | 0.55 |
| Electrolyte Drop | 1.5 |
| Extra for Gas Bubbles | 0.15 |
| Cathode | 0.4 |
| Anode | 0.4 |
| Busbar (external to next cell) | 0.3 |
| Total | 4.5 |

Where can one hope to reduce voltage with an inert anode? Let us look at each of the items in turn.

(a) Overvoltage.

This can only be determined by experimental measurements on the individual materials which may be proposed. However, in my experience I have not come across any candidate materials with overvoltages substantially less than with carbon.

(b) Electrolyte Drop.

Here there is real room for improvement *if and only if the inert anode is combined with a stable (drained) cathode* . Then the anode - cathode distance (acd) could be reduced substantially with savings up to 1 V (?). However, the comparison must be made with similar cells with carbon anodes. Unless one goes to a multipolar cell (see below), all the advantages of the stable cathode can be obtained by combining it with carbon anodes just as well as by combining it with inert anodes.

(c) Gas Bubble Drop.

Even if it could be reduced 50 % by suitable anode design, it is probably not enough to be worth all the trouble and complication.

(d) Cathode Drop.

The cathode drop could probably be reduced. but the question arises: do we *want* to reduce it? The question stems from the fact that good electrical conductors are also good thermal. conductors. The situation was analyzed by Seager who showed that, in the case of a conducting bar in a temperature gradient, the overall energy consumption was minimum when the bar was sized such that the heat flowing out of the bar at its cold end was equal to the heat generated in the bar from its electrical resistance. This means that no heat was flowing in or out at the hot end. Quite apart from the mathematics, the Seager condition makes intuitive sense. If too much heat is generated in the bar (because it is too small), then the bar is being used as a resistance heater to heat the cell. This is obviously silly. Conversely, if the bar is too big, then heat flows to it out of the cell and it becomes a cold spot with risk of freezing in. Real linings, of course, do not consist solely of conducting bars; there is a lot of non-conducting insulation there as well. But the basic principle applies; in the general case the heat lost from the cell through the cathode lining should be balanced by the heat generated in the lining, and it is unlikely that dramatic savings can be achieved. To make the cathode drop too low is asking for trouble with freeze and sludge, especially if the cell is operating close to alumina saturation. (See below.)

(e) Anode Drop.

All the above considerations apply to the anode just as much as the cathode: one cannot risk freezing in the anodes because the anode connectors are not generating enough heat, especially if one is relying on any specialized gas-flow channels which would become blocked.

(d) Busbar Drops.

Busbars are sized for minimum overall cost (material plus energy loss); the only way to achieve anything is to eliminate them by going to a multipolar cell construction. This is discussed below, but inert anodes would be vital to such a development and a major part of the savings would be attributable to them. Indeed, it is only in such cells that inert anodes make any sense and have any possible future.

So, on the other side of the ledger, what can be done to reduce heat losses?

All existing aluminum cells are insulated thermally at the sides by frozen cryolite; this prevents erosion of the carbon side linings by formation and dissolution of aluminum carbide. The top of the bath is also allowed to freeze in and it and the anodes are then covered with powdered alumina to prevent air oxidation and excessive heat loss. This not only gives a cheap (in fact free) top cover, but it can be broken without causing any harm or chemical contamination when an anode needs changing.

In order to maintain the freeze a relatively high heat flux is needed. If this flux is to be reduced by adding insulation, then the inner temperature will come up and freeze will no longer form. In conventional operation this is regarded as a disaster. In a low-loss, inert anode cell new materials, designs, and construction techniques would be called for to contain the system. No suggestions can be made in a general paper such as this, but the difficulties of finding suitable materials, and the operational problems that arise when access to the cell becomes restricted should not be underestimated. (See the next section for a note on the behavior of metals.)

## INERT ANODE MATERIALS

Structural metals can be divided into two classes - those that do not form an oxide film in air (the noble metals), and the rest. It does not take much calculation to realize that, from an economic point of view, bulk noble metals are out. A coating of platinum 1 mm thick on the faces of the anodes of a single 200 kA cell would weigh 400 kg, and it is not worth attempting to calculate its cost since a new use for the metal would send the price far higher than it is today. Only if one considers coatings of the order of microns thick do the economics come down into a reasonable range. There are, however, two problems. If the coating is on a metallic substrate (e.g. Fe or Cu) it will diffuse into it and disappear in a matter of a day or so, and, on any substrate, Pt and the other noble metals are not barriers to oxygen. Oxygen has a sufficient solubility in the solid metal that it readily diffuses through and. owing to the overpotential for oxygen discharge, the inside of the metal is supersaturated and oxygen bubbles can nucleate either internally or at the interface with the substrate. In any case, a coating only microns thick is so fragile that damage to it while handling and installing the anodes would be virtually inevitable. Noble metals can thus be ruled out.

All that remains are electronically conducting oxides. From the chemical point of view it matters not whether it is a large block of oxide connected to a metallic support and current lead, or a thin oxide coating on a metal, or a cermet; the problems are exactly the same. The surface in contact with the bath is oxide; by definition any exposed metal would have to be one of the noble metals to be stable. All further discussion is thus in terms of the oxides.

## INERT ANODES - GENERIC PROBLEMS

All oxides have some solubility in cryolite. This is inevitable - cryolite is used precisely because it dissolves alumina. In general the solubility of the oxide goes up as the alumina content of the melt goes down. This can be explained generically in terms of the common ion effect - the equilibrium

$$MO_{(solid)} = M^{2+}{}_{(soln)} + O^{2-}{}_{(soln)} \qquad [4]$$

is obviously driven to the right as the oxide content goes down. Although other considerations may enter in specific cases, they always work in the same direction.

There are few, perhaps no, oxides with solubilities sufficiently low that they can be contemplated for use as anodes, even at alumina concentrations close to saturation. In most cases the limiting factor is not so much the physical disappearance of the material, but the appearance of the foreign metal as an impurity in the aluminum produced. The industry is based on making pure metal, and indeed the need becomes more stringent as time goes on, first to meet the requirements of special alloys, and second because with increasing recycling of scrap it becomes more and more necessary that the new metal entering the stream be "sweet" in order to dilute the inevitable impurities in the scrap. (I note that the **Inert Anode Road Map** says that "almost any element" can be tolerated at up to 0.1 %, Fe at up to 0.1 %, and Si at up to 0.2 %. That is absolutely untrue. For some elements (e.g. Sn) even ppm are not acceptable, for Ni the limit is certainly less than 0.1 %, and metal containing 0.1 % Fe and/or 0.2 % Si would be unsalable for any purpose other than making low-grade "garbage" alloys. The specifications for "commercial grade metal" being quoted bear no relation to the real commercial market and the needs of modern high-performance alloys. And do not forget that there are other sources of impurities beside the anodes, notably the raw materials; there is already enough trouble keeping purity acceptable in the conventional process without a new source of problems in the supposedly inert anodes. Depending on the elements contained in the anodes, the quoted "acceptable" erosion rate of 10 mm/year is high by up to a factor of ten.)

From time to time one hears suggestions that a plant could be built to make a special alloy where the contamination coming from the anodes was acceptable as a useful part of the product. This is, in my view, completely unrealistic. The industry could not accept such a loss of flexibility. If the particular product to which that alloy was going lost market, the plant would be totally useless. The lack of flexibility would extend also to the personnel because people could not be transferred in (or out) without retraining for a totally different operation.

Apart from the slow erosion of the anodes due to solubility, and the question of how long it can be tolerated, there are three mechanisms which can lead to specific failure of an anode: ionic conduction; surface alteration; and internal electrolysis in porosity. This is apart from the obvious - but rarely mentioned - problem of breakage. Carbon anodes have pieces break off from time to time, but they do no damage. The fragments float on top of the bath and burn off. If they do happen to bridge the electrode gap and cause a short circuit they heat up so rapidly that they probably disintegrate from thermal shock. A fragment of an inert anode, on the other hand, will sink to the bottom and contaminate the metal produced. Such a sudden spike in contamination would be diluted exponentially as new metal was produced, but the metal coming from the cell could be unacceptable for an extended period of time.

It was specified above that the oxide must be *electronically* conducting. Unfortunately, most oxides are not inherently electronically conducting; they become so in general only when they contain ions of metals with more than one valency. Examples are iron oxides ($Fe^{2+}/Fe^{3+}$) and cerium oxides ($Ce^{3+}/Ce^{4+}$). Other oxides which in pure form are insulators or ionic conductors can have electronic conduction induced by doping with suitable impurities, or in some cases by treating them in a reducing atmosphere. Unfortunately, all of these materials must, in the nature of the system, retain a residual ionic conduction, and it causes trouble in that the oxide behaves partly as an electrolyte, and the metallic substrate or connector becomes to the same extent an electrode and suffers corrosion. The only figure I can quote is for cerium oxide where the ionic conduction is about 0.1 %. It seems small, but the resulting current density of the order of a milliamp per square centimeter can cause a lot of corrosion over a period of months or years.

The problem of surface alteration can take several forms, and can best be illustrated by events that I have witnessed in practice.

(a) ZnO is electronically conducting when reduced during manufacture. But it is being used to generate oxygen, and the surface becomes oxidized and loses its conduction. Materials based on $Fe_3O_4$ should similarly convert to $Fe_2O_3$.

(b) Materials which have been doped (e.g. with Mn) to induce electronic conduction may have the dopant preferentially leached out. After all, it was chosen for its electrical properties, not because of its low solubility. (c) Some oxides are converted to aluminates in the presence of high alumina concentrations. ZnO is again a case in point; the surface converts to $ZnAl_2O_4$. I have also seen $NiFe_2O_4$ (one of the favorite candidate materials) convert to $NiAl_2O_4$, and I think its long-term stability is questionable. $NiAl_2O_4$ is an insulator. For any particular oxide there is a critical activity of alumina above which the aluminate becomes thermodynamically stable: obviously the closer to alumina saturation one succeeds in operating, the more likely one is to encounter this problem.

The effect of porosity in an anode is perhaps poorly understood in detail, but its result is all too obvious in practice. If some oxygen discharge takes place inside a pore, then the *liquid inside becomes depleted in alumina because there is insufficient circulation to replace it* . As a result the solubility of the anode material increases, and the anode is literally eaten away from the inside. Being short of alumina, the anode electrolyzes itself! This is not what one terms non-consumable!

One last point may be mentioned in this section, although it does not really belong, and that is the question of the oxidation of metals to form protective oxide films. This is of relevance more to the construction of hoods and covers than to anodes themselves, although one can conceive ideas for anodes made simply by taking an oxidation-resistant metal and letting it form its own coating. Unfortunately many metals (notably the ferrous metals) which are protected in air are not protected in an atmosphere containing fluoride. This is because the $F^-$ ion is exactly the same size as the $O^{2-}$ ion, and substitutes for it in the lattice. The charge deficit leads to compensating vacancies in the cation lattice, ionic conduction ensues, and the film is no longer protective. Inconel, for example, which will last for years in air at 1000 °C will survive barely days if the atmosphere contains fluoride, and steels are similarly affected.

## CONTROL OF ALUMINA CONCENTRATION

It has already been stated that the solubility of all oxides from which anodes might be manufactured increases as the alumina concentration goes down. The effect can be dramatic; $ZnAl_2O_4$ at 1020 °C, for example, has a solubility of 0.02 % Zn in a melt saturated with alumina, and 2 % Zn at 1 % alumina. The corollary is that alumina concentrations must be kept as close to saturated as possible; if alumina is depleted the product metal will be scrap and the anodes will be severely damaged or completely destroyed.

One must first understand the situation in a typical conventional cell. The saturated concentration is 7 wt % $Al_2O_3$. The normal operating level is 3 %. If it goes above 4 % some of the added alumina does not dissolve but forms sludge on the bottom; if it goes below 1 % an anode effect (when fluorine is discharged instead of oxygen) ensues.

For a mass transfer process to proceed at a finite rate a concentration gradient is needed, and the above figures give us the vital information. There are two such processes involved: dissolution of the alumina, and transport of the dissolved alumina to the working face of the anode. With the conditions of stirring existing in a conventional cell a gradient of 3 % (between 7 % saturation at the surface of the particles to 4 % in the bulk) is needed to get the alumina to dissolve fast enough, and a 1 % gradient is needed to transport the alumina from the bulk to the anode interface. Thus the highest *interface* concentration which can be achieved is 3 % (=

7 - 3 - 1), less than half of saturation, and the normal interface operating level is 2 %. This dramatically illustrates the unreality of supposing that it will be easy to operate inert anodes close to saturation. The biggest problem is getting the alumina dissolved; it will almost certainly need a special stirrer to reduce the 3 % gradient currently existing.

The other point to note is the conventional method of control of alumina concentration. Periodically (every few days or oftener) alumina feeding is stopped until the cell has an anode effect with a conspicuously high voltage. At that point the concentration is known to be 1 %, and feeding is resumed. *No chemical analysis is ever done in routine operation* . An anode effect leads to the formation of $CF_4$, but that causes the cell no harm. An analogous event with "inert" anodes would be an utter disaster. They are inert to oxygen, not fluorine, and there would not even be a sharp voltage rise as a warning. The anodes would just quietly dissolve.

## THE MULTI-POLAR CELL

Near the beginning of this paper it was indicated that the only application of inert anodes that seems to make any sense is in a multipolar cell. Such a cell contains several electrolysis units in electrical series in one pool of electrolyte; it is constructed from a series of slabs each of which acts as an anode on one side and a cathode on the other. This is the route that the magnesium industry has taken to achieve dramatic reductions in power consumption, but the magnesium cell has three advantages which are not present in the aluminum case. Firstly, the same material (graphite) can be used for both the anode and cathode sides of the slab since magnesium does not form a carbide, and the anode product is chlorine, not oxygen. Secondly, the chloride electrolyte used has a low solubility for oxides, so oxide refractories can be employed for linings and for electrical insulators. Thirdly, the cell is not working close to the liquidus temperature of the bath (i.e. it is not close to saturation with anything), so coolers can be used to extract unwanted heat without becoming frozen up. Additional points are that the metal produced floats on top of the electrolyte and is easy to reach for tapping, and that the $MgCl_2$ feed is readily soluble in the bath (or it may be dissolved externally and fed as a liquid).

In addition to *all* the problems of inert anodes already discussed, a multipolar cell for aluminum production brings some new ones of its own. Firstly, the slab construction becomes a sandwich, since the anode material and the cathode material cannot be the same. The cathode will undoubtedly be a $TiB_2$ complex of some sort. The anode is currently unknown, but one has the problem of obtaining a good mechanical and electrical bond between materials with different coefficients of expansion and very likely incompatible chemistries. Thus, $TiB_2$ is a reducing agent, especially if it is porous and permeated with liquid aluminum, and it will react with the oxides of all the ferrous metals such as iron and nickel. Likewise, permeating aluminum would destroy any cermet with which it came in contact. And the shearing forces due to differential expansion in the joint of a slab, say, one meter square heated from room temperature to nearly 1000 °C are more easily imagined than calculated. In any case, what does one use for glue?

Another compatibility problem arises at the edges of the slab. One face is at an anodic potential, the other is at a cathodic potential; in between a gradient exists, and the joint in the sandwich must be situated at exactly the right place or one or other of the materials will find itself in a potential range where it is not stable. The ideal solution is to cover the edges of the slab with an insulator, but that is by no means straightforward either.

The other problem is control of heat generation. As mentioned above, a magnesium cell is fitted with coolers (steel pipes through which air is blown). As the inevitable erosion of the anodes occurs (mainly due to traces of oxides) the acd increases and heat generation goes up. The cell has to be taken out of service and rebuilt when the coolers no longer have the capacity to keep the temperature where it should be.

In a cryolite electrolyte close to saturation any cool surface becomes covered with a crust of corundum crystals. Air coolers are thus not feasible. It is hard to see how a variable and controllable heat removal can be achieved.

## GENERAL DISCUSSION

There is always a risk when assessing new technology of ascribing to it benefits which arise from modifications to existing practice that, although essential to the new technology, could equally well be implemented on the old. A case in point is the elimination of 2,500 t of perfluorocarbon emissions (≈ 2 Mt $CO_2$ equivalent). If an inert anode cell can be made to run with high alumina concentrations, so can a carbon anode cell, and with vastly less technological risk if something goes wrong. It would seem that one initiative that the panel should sponsor on an urgent basis is a demonstration that a conventional cell can be run for, say, a year without an anode effect and without the cell becoming sludged up. Success would do three things: it would immediately give technology that could be implemented to save the perfluoride emissions, it would give an experimental number for the level of alumina concentration that can be maintained in practice, leading to a more realistic assessment of the performance of inert anodes, and, ironically, it would reduce the justification for wanting an inert anode because the potential for saving emissions would be reduced. Failure, on the other hand, would make the chances of a successful inert anode so remote that any R&D program in place could be abandoned.

The first conclusion to emerge in the general analysis was that full retrofit of existing cells was not feasible, nor even desirable. Since that is a very important conclusion the logic will be repeated and amplified here.

On an existing cell it is virtually impossible to reduce heat losses. The cell is designed to run with certain heat fluxes to maintain freeze, and replacing carbon anodes with inert ones would do nothing to change them. Consequently the cell would run 1 V higher. This would involve new rectifiers and transformers (to give the higher voltage and handle the extra power), new transmission lines and, somewhere, a new power station to generate the extra power. That power station (or another one somewhere else) would be fuelled by unwanted petroleum coke. To a first approximation, the coke which would have gone into the carbon anodes would be just about the quantity needed to generate the extra power. Meanwhile a new plant has been built to make the anodes, while the existing carbon plant has been abandoned. So what has been gained for all this expenditure of capital? Nothing, except the technological risk of operating inert anodes, and increased impurity levels in the metal produced. Plus the problem, well understood but not previously mentioned here, of operating the cell when the volume of the metal produced is no longer compensated by the reduction in volume of the carbon consumed.

Full, direct, retrofit is out of the question.

Suppose, now, that an inert anode is to be combined with a stable cathode in an otherwise conventional cell. What advantage could be gained with inert anodes that could not be gained just as well with carbon anodes? The only answer apparent is that one might be able to better remove the gas bubbles from under the anodes with special channels, which could be important when operating at low acd. On the other hand, one has the level control problem referred to above. There does not seem to be any incentive to justify the technological risk and research effort involved.

The only prospect to have any real advantage is the multipolar cell; that is where one can genuinely begin to save power and capital investment. However, it means that *from the outset* research must be aimed at that, with the development, not just of inert anodes, but of the requisite anode-cathode sandwich as the only objective. Developing little anode structures with individual current connectors is a dead end since the retrofit-type installation in which they might be used is known to be a non-starter. And that electrical connection, which will give so much trouble, will not be needed in a multipolar cell except for the end electrode which will have problems all its own. In fact, it could well be advantageous to make the end anode of carbon, especially if the cell had horizontal slab electrodes so that the end anode was on top and accessible for changing.

The overall tone of this paper has been pessimistic; I make no secret of the fact that I do not think that any further work on inert anodes can be justified. This is not because I am so conceited as to feel that if I cannot solve the problems no-one else can either. It is because at the end of ten years work (involving many others beside myself in several different companies and with a very wide background of experience), *none* of the problems had been solved, and a lot of new ones had been found. Although I am not in touch with everything which has happened since 1990, I am not aware of anything on the horizon which could transform the situation.

# CONCLUSIONS

1. Regardless of the availability of suitable materials, retrofit of inert anodes in existing cells is neither feasible nor desirable. Green-house gas emissions would be essentially unchanged, energy use would increase, capital expenditure would be enormous, and the modified plant would be faced with very severe operating and control problems.

2. No research or development of inert anode systems intended for replacement of carbon anodes in existing or modified conventional cells should be pursued.

3. The only use for inert anodes which carries with it any advantage is in a multi-polar cell. This raises a whole new set of problems, but is the only objective which could be worth pursuing. However, unless specific and plausible ideas are available as to how the requirements could, at least in principle, be met, there is no justification for going beyond the study stage.

4. The author is not aware of any materials and/or anode systems which have any prospects of satisfying the requirements for satisfactory long-

term operation.

5. Regardless of other considerations, work should be undertaken on an urgent basis to find out whether a conventional cell can be operated indefinitely (minimum one year) without an anode effect. Such technology would be valuable in its own right to reduce green-house gas (fluorocarbon) emissions. The experiment would also provide data on what alumina concentrations are reasonably attainable in practice: such data are essential for assessing and predicting the performance of any inert anode materials and cell systems which might be proposed.

# APPENDIX A-5

# PAPER BY DR. TONY KJAR

**Gibson Crest Pty Limited**
ACN 008 924 844

**Anthony R Kjar**
BE(Hons), PhD, FTSE, FIEAust, MAusIMM
Managing Director

**Strategy, Technology and**
**Project Management**
23 Laurel Grove
Blackburn Victoria 3130
Australia
Phone +61 (0) 3 9878 1843
Fax + 61 (0) 3 9894 8879

24 September 1998

**Dr Rodney Hanneman**
**Chairman, Aluminium Inert Anode Technical Working Group**
**(DOE Sponsored/ASME Facilitation)**

**Fax 0015 1 804 323 6948**

Copy John Green
Aluminum Association

Fax 0015 1 202 862 5164

Dear Dr Hanneman,

Thank you for your fax of 10 September 1998 concerning details of your panel to carry out an in depth review of aluminium inert anode research and related cell design issues in the context of other state of the art cell technologies and performance.

It is two years since I left Rio Tinto Ltd, and now four years since I led the Comalco Limited reduction cell improvement program, and so I am both constrained in what I know as well as what I can say.

Nevertheless, it is public knowledge:

> Comalco Annual Report 1997.
>
> "Plant trials of a composite titanium diboride cathode demonstrated satisfactory power efficiency and excellent operating stability. A decision on further expanding these trials will be made in 1998."

| | |
|---|---|
| US Patents | sloped drained cells |
| | double sloped cells |
| | low metal cells |
| | coating formation |
| | $TiB_2$ slurry etc |

These statements describe the results, but of course not the detail.

It is common knowledge that Comalco has operated drained cathode cells for up to 700 days, and at ACD of 2.5cm. These cells were in an operating line, and necessarily had to be operated at current densities well above the 0.8A/cm$^2$ normally used for new lines. Hence comparing power use is not the best measure. Nevertheless, results were in line with predictions based on the change in ACD, and no fundamental reasons were found as to why the technology will not be successful.

However there are some enabling technologies which need to be developed to be able to use the technology in a full operating potline. These include control issues for the anode that necessarily must be operated very close to a solid material cathode surface. Again, nothing has come up that cannot be solved with people, time and money. However, with tighter budgets this is taking longer than anticipated. Separately Rio Tinto/Comalco Ltd have chosen to focus on existing operations than build new greenfields or modernise existing plants and have modified the program to suit.

I believe the improvement path for the Hall Herouit cell is to develop a stable cathode, with no sludge and frozen bath, then other improvements can be added on. It is then a question of whether to pursue a continuous carbon anode or an inert anode, as well as lower temperature electrolytes In combination with the clean cathode a quantum leap can be obtained, and I still favour the continuous carbon route as

(i) only mechanical problems have to be solved
(ii) there are less inherent voltage drops.

I suggest that it is important for your committee to look at the road map forward, without limitation of technology, then address the issues of access as a second step.

You may also be interested to follow the Tri annual Aluminium Smelting workshop to be held at Queenstown, New Zealand an 23 November 1998. Details can be obtained from Prof B Welch on Fax =64 9 373 7463. I understand that Comalco will Discuss some aspects of their program at this meeting.

If I can be of further help please advise.

Yours sincerely,

Tony Kjar

# APPENDIX A-6

# PAPER BY DR. BARRY WELCH

# Aluminum Production Paths in the New Millennium

Barry J. Welch

**Editor's Note:** A hypertext-enhanced version of this paper can be found on JOM's web site at www.tms.org/pubs/journals/JOM/9905/9905-Welch.html.

*In the last two decades, the aluminum industry has seen the demise of the ASP chloride process as an alternative production path and a reduction of papers on carbothermal production options. At the same time, there has been a steady stream of articles proposing the use of drained-cathode technology (by a wettable titanium-diboride coating) and others extolling the virtues and potential materials for inert-anode technology. There was also a rush of smelter technology papers in the early 1980s claiming an achievable energy consumption of less than 12.5 kWh/kg. However, the recent emphasis has been a shift to high amperage technologies that are less energy efficient but more cost efficient. Current efficiencies in excess of 96 percent can be routinely obtained by new technologies, and even aged technologies can be retrofitted to perform at 95 percent. The challenge is to lower cell voltages, but one of the key limitations is the need to maintain adequate superheat to avoid sludge formation and electrolyte-concentration gradients. Electrochemical technologies face the same problems and challenges as present technology; the requirements are even more acute and demanding. These challenges can probably be met, however, and the industry is undoubtedly faced with interesting times as it continues to strive to be competitive.*

## INTRODUCTION

The driving force for developing new processes for aluminum smelting usually revolves around one of three major cost factors: electrical-energy reduction demands (because of the so-called inefficiency), capital-cost reduction of the reactor per annual production tonne, and environmental considerations (because of both the high cost of compliance with existing fluoride regulations and also because of greenhouse considerations).

Earlier analysis and discussions of alternative processing[1] demonstrated that the fundamental energy requirements for all options do not differ substantially since all start with an aluminous (oxide) raw material and all finish with aluminum at a temperature above its smelting point, with oxygen and carbon oxide byproducts. From a theoretical energy consideration, different processes do not hold much potential to make substantial differences, although there can be a tradeoff between electricity and carbon as the energy source used. Thus, from an energy perspective, the differences in processes usually revolve around differences in efficiencies of both the reactions unsolved in the process and the energy utilization. Some of the alternative processes considered and investigated have been based on an incomplete analysis of the process energy requirements, while others have not considered either economics or practicality.

Monopolar electrochemical cells are always capital intensive because the reaction rates are low per unit reaction area and also low per unit reactor volume. These cells have a limited finite size based on feeding technology and the need to have a liquid-metal cathode. Thus, if there is to be a significant breakthrough in the capital cost barrier, electrode arrangements and design need to be considered so that there is an increase in reactor area per unit volume. Another contributor to the capital cost is the limited cell life through corrosion and erosion of materials. Although cell lives have increased, so too has the cost of the better materials of construction.

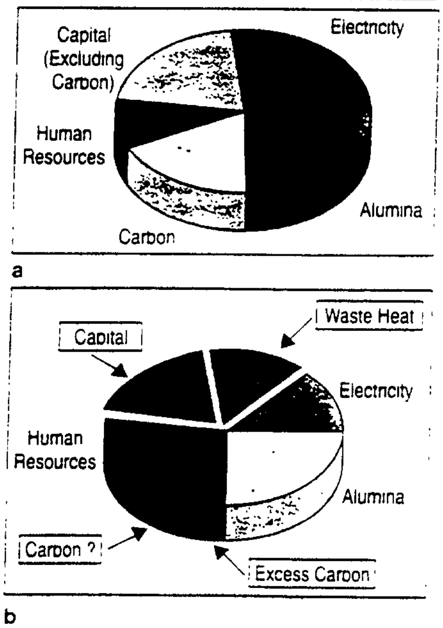

Figure 1. (a) Contributions to the cost of aluminum production and (b) potential areas for cost reduction with alternative technology.

Whenever alumina is used in the presence of fluorides, as seen in Figure 1, the capital cost of the smelters is a significant contributor to the overall metal production cost. Typically, equipment for environmental compliance contributes about ten percent of this cost while extensive occupational health and compliance monitoring programs are also significant contributors to the production costs. Fluoride emissions are generated at the cell because of hydrolysis reactions. Thus, environmentally, smelters must get away from either the moisture-bearing oxide or the fluoride solvent. Alternatively, cell redesign for the much more efficient capture of all cell emissions may help costs. Candidate nonoxide feed materials have been anhydrous aluminum chloride and aluminum sulfide.

The second environmental driver is linked to the carbon-oxide greenhouse emissions. On a tonnage basis, the amount of carbon oxide produced is greater than a tonnage of metal produced. However, the only alternative to carbon oxide is electricity, since a form of energy is always required for metal production. With incremental electrical energy usually being generated by inefficient combustion processes, the potential for reducing the greenhouse impact depends on how electricity generation is accounted.

There is much more to alternative processes than simply getting the chemistry right or lowering the energy demands for any process. Four key aspects for any alternative process are

- A need for a satisfactory chemistry path for achieving the production of the metals from the raw materials.
- A suitable and practically operable reactor system that is much less capital-intensive on an annual tonnage basis than the present process.
- A suitable material to construct the reactor and electrodes.
- The ability to meet stringent environmental standards without increasing costs excessively.

## MODERN HALL-HÉROULT TECHNOLOGY—THE BENCHMARK

Beginning in 1980, new cell technology broke through the 175,000 A barrier, while being magnetically compensated fitted with point feeders and resistance-tracking process control.[2] This enabled operation in a narrower alumina solubility range, which led to electrolyte chemistry modification for high current efficiencies and low energy consumption. The practical annual operating minimum was typically between 12.9 DC kWh/kg Al and 13.2 DC kWh/kg Al. The anode-effect frequency was also typically lowered by an order of magnitude.

By the mid-1980s, key engineering design features of the new breed of even larger cells included point feeders discharging less than 2 kg $Al_2O_3$ per addition; single- or dual-draft hooded emissions collection systems; a microprocessor-based process control system that takes readings of cell-energy parameters every five seconds or less and utilizes feeding and energy-change strategy according to predetermined logic; and, typically, an automated conveying system for introducing the alumina to the hoppers at the cell for a more dust-free environment.

As a consequence of further gains in process control, the trend in the 1990s has shifted further toward increasing the amperage[3] or size of the cells because of the economic gains through reduced capital expenditure per unit annual production. The larger cells (especially when exceeding 310,000 A) do not achieve the low energy consumption of the slightly smaller cells of the early 1980s. This is as a result of a number of issues, including operation at higher (cathode) current density; the existence of concentrated gradients through less efficient mixing end-to-end in the cell; reduced cell life because of the more stringent heat balance requirements for freeze protection and the increased cathode corrosion with current density; and the tendency to form sludge because of the higher feed frequency and limited mixing. Despite these limitations, the overall economics are more favored through the reduction of the capital cost section of Figure 1 than through the increase in the energy-cost sector.

In reviewing all new technology and developments since the early 1980s, the following features stand out:

- Current efficiencies in excess of 96% can be achieved.
- The present process energy efficiency is approximately 50%, with the excess energy being dissipated as heat loss from cells.
- Despite concerns about excess anode consumption, its utilization efficiency exceeds 85%, thus offering limited scope for future gain.
- The limit to reducing cell voltage is no longer the anode-cathode distance constraint from the turbulent metal pad that leads to the risk of direct shorting. Rather, it is to ensure sufficient heat is generated to maintain stable operation.
- Despite design and materials advances, it remains imperative that the cell sidewalls maintain a protective freeze. Otherwise, metal quality and cell life are unacceptable.
- Because of constraints through operating procedures and the emphasis on the capture of emissions, there are only limited variations for reducing the top heat loss from the cell. Thus, the present technology is constrained by both upper and lower limits for heat generation.

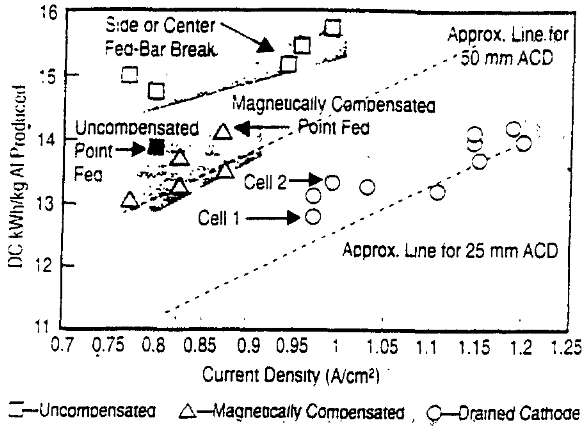

Figure 2. Reductions in energy consumption achieved by Comalco[10] using drained cathodes in existing technology.

Based on these features, as illustrated in Figure 1b, it is evident that the greatest scope for reducing metal production costs is to reduce capital cost, have a reactor design that can operate with a lower heat loss per unit production, or eliminate the anode carbon and substitute a more cost-efficient option. This shifts the future emphasis to operable reactor designs with a low capital cost per annual tonne while complying with environmental requirements. Hence, it becomes understandable why increasing line current has become favored. This increases productivity at near constant heat loss but, for an installed technology, it is invariably less energy efficient.

## ALTERNATIVE ALUMINUM PRODUCTION PROCESSES

Regardless of the methodology proposed, all alternative processes have some common elements. The primary inputs will be alumina, electrical energy, some carbon, and possibly some other recyclable chemicals; outputs are aluminum and varying amounts of carbon oxides. Heat will always be released, because all alternatives involve high temperatures. If an impure alumina source is used, the processing would be similar, but with a secondary metal or alloy as a by-product. In several of the process options, the alumina is converted to a more easily decomposed (relative to the process) intermediate, such as $AlCl_3$,[4]

**Table I. Alternative Processes Investigated for Aluminum Production**

| Production Process | Features |
|---|---|
| Drained-Cell Technology* | Cathode sloping and coated with aluminum-wettable $TiB_2$.<br>By eliminating metal pad, anode-cathode gap could be halved to ~25 mm, enabling substantial voltage lowering.<br>Other basics would remain the same as present technology ($E° \sim 1.2$ volts, $\Delta H_{\text{min. electrolysis}} = 6.34$ kWh/kg). |
| Inert Anode Cells* (Oxygen Evolution) | Eliminate consumable carbon anode by having an electrode material that evolves oxygen.<br>Although the electrochemical potential would increase by 1 V ($E° \sim 2.2$ volts), the voltage increase would be (hopefully) less because of lower anode polarization ($\Delta H_{\text{min. electrolysis}} = 9.26$ kWh/kg).<br>The superstructure of the existing cell could be refined, reducing capital costs.<br>If drained-cell materials development were successful, further design options are possible. |
| Chloride Process† | Aluminous material converted to (anhydrous) $AlCl_3$ of adequate purity.<br>$AlCl_3$ electrochemically decomposed in a multi-electrode cell at ~700°C ($E° \sim 1.8$ volts, $\Delta H_{\text{min electrolysis}} = 6.34$ kWh/kg).<br>Electrochemically generated chlorine is recycled. |
| Sulfide Process† | Aluminous material converted to (anhydrous) $Al_2S_3$ of adequate purity.<br>Aluminum sulfide electrochemically decomposed to recyclable $S_2$ and aluminum ($E° \sim 1.0$ V) in a multipolar ($\Delta H_{\text{min.electrolysis}} = 5.24$ kWh/kg) cell. |
| Carbothermal Reduction† | Convert aluminous material to an intermediate $Al_4C_3$ (or oxycarbide) chemically at $T > 1{,}700$°C.<br>React carbide with further oxide to evolve CO and produce aluminum (or alloy) at $T > 2{,}000$°C.<br>Refine the metal quality to a usable grade ($\Delta H_{\text{minimum}} = 9.0$ kWh/kg). |

* Substantial retrofits using cryolite-alumina electrolytes.
† Processing using intermediates derived from alumina.

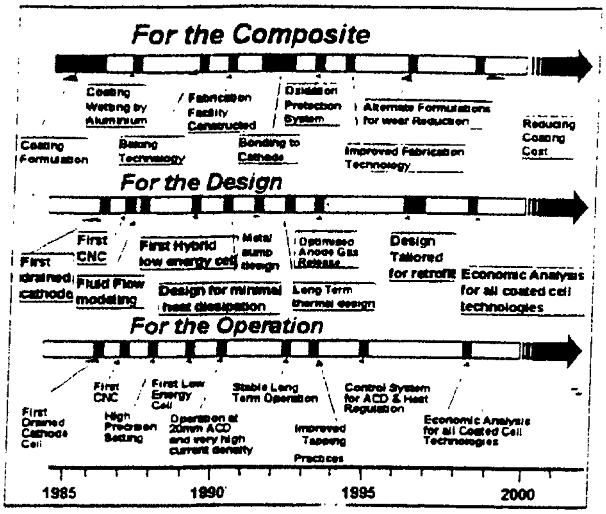

Figure 3. The parallel development paths followed by Comalco[10] in developing coated drained technology.

$Al_2S_3$,[5] $Al_4C_3$, or aluminum oxy carbide.[6] These all involve separate reactors and associated heat losses, materials recycling challenges, and materials transfer needs. Intermediates involve additional reactor systems. Problems with reactor life and construction materials do not disappear simply by bringing in a new process—all processes have material-restricting constituents, such as reactive aluminum and slags or salt melts.

Based on these general features, the best process would be one that occurs at as low a temperature as possible, but with the highest productivity per unit volume while possessing the fewest number of processing stages in the overall conversion process. In the last 25 years, there has only been sustained R&D on the first two of five discussed alternative processes (Table I).

## Drained-Cell Technology

Titanium diboride was first promoted as a useful cathode material for aluminum smelting cells in the 1950s.[7] It has an exceedingly low solubility product in the metal, while the metal contamination is sometimes considered an advantage because of the refining processes to which the metal is subject. Titanium diboride is wetted by aluminum, thus potentially lowering interfacial voltage drops. Other potential advantages have included lowering the cathode-lining ohmic drop, enabling a drained cell configuration, and acting as a barrier to sodium penetration into a subdiboride carbonaceous lining.

Because of its refractory nature, high melting point, and the high cost of the raw materials from which $TiB_2$ is produced, there have been significant economic and practical challenges to fully testing and implementing wetted cells. In order to reduce the costs and fabrication difficulties for $TiB_2$, considered approaches have included bonding tiles and other shapes to the carbon substrate[8] or alternatively applying a composite coating.[9,10] In the last two decades, the main driver has been to develop drained cells that, by elimination of the metal pad and, hence, its magnetically induced turbulence, enable cells to be operated at a much reduced interelectrode distance. This would lower the energy consumption through the lower voltage. However, the external design and features of the cell would essentially be the same, and, therefore, a reduction in voltage must be accompanied by a reduction in heat loss.

Theoretically, increasing the thickness of the crust cover and reducing drafting at the top of the cell would lower the heat loss. However, with increasing the thickness of the top cover, the crust becomes softer and risks collapsing. Likewise, reducing the drafting velocity leads to a greater rate of release of emissions to the environment. Therefore, the reductions in top heat loss are extremely constrained. The bottom heat loss of the cell has generally already been reduced as much as possible with modern insulation materials and is a small contributor to the total.

Insulating the sides of the cell, which typically account for a quarter of the heat loss, results in a loss of the protective sidefreeze because of the consequential increase in superheat. The importance of retaining this has already been noted. Practically, it is of even greater importance for $TiB_2$-coated cells because of the accentuated corrosion that would occur at the three-phase interface between the liquid bath, carbon, and aluminum-wetted coating.

Drained cells have other design and operating challenges that must be met before implementations, including

- How should the alumina be fed to the cell so that it mixes uniformly with the reduced electrolyte volume?
- How will the metal be tapped from the cell, and how frequently will it be tapped if there is little or no metal pad?
- How will the anodes be changed and set without forming a freeze on the bottom that extends and adheres to the $TiB_2$-wetted coating?
- How will an anode effect be extinguished automatically since there is no metal pad to splash onto the anode surface, as is done in the present automatic process?
- What should be the optimum slope and direction for the drained cathode, and how should the slope be developed for new anodes?
- How can a new cathode be preheated and started with such a reactive material as the coating ($TiB_2$ in the powder form is a pyrophoric substance)?

Design innovation and hard slog R&D can answer these questions satisfactorily, but inevitably solutions will have a price tag that detracts from the perceived economics.

The coating material itself must also satisfy several criteria. First, its thickness must be sufficient to give the desired cell life after recognizing the metal it dissolves to saturation in the metal. Second, any binding phase of the composite must corrode at a similar rate to the $TiB_2$. Third, the coefficient of thermal expansion should match that of the substrate to which it is bonded. Finally, the material must be impervious to the electrolyte (or electrolyte uptake totally prevented), since the electrolyte can lead to galvanic corrosion if it is also in contact with a carbonaceous substrate.

With the existing cathode potential gradient, the formation of $Al_4C_3$ becomes enhanced by the thermodynamically favored galvanic corrosion reaction within any coating material that has also taken up electrolyte. With the aluminum-wetted cathode surface being at a more anodic potential, and there being a continuing supply of aluminum and carbon, we have

$$4\ Al \rightarrow 4\ Al^{3+} + 12e$$

in the zone above the electrolyte that has penetrated the coating, and

$$12e + 3C \rightarrow 3C^{4-}$$

at the carbon surface with the consequential reaction in the electrolyte phase

$$4\ Al^{3+} + 3C^{4-} \rightarrow Al_4C_3\ (solid)$$

The growth of this deposit can lead to debonding and accelerated coating failure.

Three separate approaches have been used for developing coatings—a colloidal alumina-bonded $TiB_2$ composite (Tinor™ and Thicknor™) developed by Moltech,[7] a plasma-sprayed $TiB_2$ coating developed by SGL Carbon,[11] and a carbon-bonded $TiB_2$ composite developed by Comalco.[10] Plant trials of the Moltech coatings have been conducted with positive indications of enhanced cell performance, especially in reducing the sodium uptake.[12] While there have been no performance data published for the plasma coating, more extensive details have recently been revealed for the Comalco coating.[10]

The energy performance gains achieved by Comalco's trials in test cells are presented in Figure 2. Of particular interest is the overcoming of a heat deficit when operating at a low interelectrode spacing in a drained cell by increasing the line current. The magnitude of the line-current increase (~30%) is similar to that predictable from an appropriate cell-voltage equation and energy-balance models.[13,14]

When increasing the line current, the gains are lowered by consequential issues, such as cathode voltage drop increases, higher anode stub drops, and the resistivity losses of the interconnecting busbars. Perhaps equally revealing is that they found it necessary to develop not only the coating to meet the specifications, but also the cell design and operating strategy (Figure 3).

The data presented,[10] together with other publications on the performance of Tinor,[12] demonstrate that while the era of wetted-cathode technology is now a practical option, the economic and production gains are not likely to be dramatic unless the design and heat-balance constraints can be overcome.

### Oxygen-Evolution Options

Considerable laboratory-scale effort has been directed toward developing a suitable material that will result in oxygen evolution at the anode when electrolyzing either a conventional or low-temperature[15,16] fluoride-alumina electrolyte. For this path, the overall electrochemical reaction

$$2\,Al_2O_3 \rightarrow 4\,Al + 3O_2$$

would require an electrochemical voltage of approximately 2.2 V as compared to 1.2 V when using a conventional carbon anode. While it has been argued that the anode polarization will be less and will, thus, lower the necessary voltage increase, this feature can only be beneficial if the heat-balance constraint can be overcome. This means that electrical-energy reductions will not be achieved unless a major design change is also implemented. The increased power cost would, however, be partly offset by simpler operations and elimination of the carbon-anode costs.

Hitherto, no suitable anode material has been found as technical difficulties arose through corrosion and subsequent metal contamination (at a time when the industry is shifting to more high-purity metal applications); the loss of electronic conduction of the oxide surface, causing passivation and high voltages; and problems of adhesion of the oxide surface coating to the metal substrate when manufacturing at the necessary electrode size. At best, it appears the electrode design will necessitate the ability to periodically remove the electrode from the cell for surface refurbishment in a similar manner to the practice for the chlor-alkali industry. This, coupled with the challenges for heat insulation (especially to reduce top-heat losses) and alumina feeding, also emphasizes that design and operating challenges must be addressed.

### Carbothermal Processing

This is the only nonelectrochemical process that has been considered, although the high temperatures necessitate the use of considerable electrical energy in order to achieve these temperatures. It is based on the idea of an aluminum reduction process analogous to the old iron-making blast furnace, which is a high productivity unit per volume reactor. However, direct translation is not possible for a number of reasons.

- $Al_4C_3$ formation is favored at temperatures below aluminum and, therefore, becomes a necessary intermediate.
- The process temperatures are high (in excess of 1,900°C for any reaction stage), resulting in significant heat losses for all designs.
- CO is the overall gaseous product, leading to a high greenhouse penalty (even though some energy credit could be achieved).
- Aluminum has significant vapor pressure at the reaction temperature, thus lowering reaction efficiencies. This is aggravated by a potential for suboxide formation. Both can be reduced by alloy formation (as has been proposed).

The considered two-stage reduction process first forms a carbide (T > 1,900°C)

$$2\,Al_2O_3 + 9C \rightarrow Al_4C_3 + 6CO$$

(although, the presence of excess $Al_2O_3$ could also lead to an oxycarbide phase) and then react the carbide with more oxide (at T > 2,000°C)

$$Al_4C_3 + Al_2O_3 \rightarrow 6Al + 3CO$$

The staging of the reactions reduces potential dusting problems through the high gas volumes otherwise released. However, it necessitates accurate temperature control for two reaction sequences in an environment that is difficult to control. Furthermore, the viscosity-composition-temperature relationships for the reacting charges present enormous challenges for operations and design.

When evaluating the process from the reactor design and operations perspectives, it changes from an extremely attractive alternative to the most challenging one. On an energy analysis, it is also extremely poor. No trials have been successful in obtaining reaction efficiencies that hold promise for refinement.

### Multipolar-Electrolysis Processes

As seen in Table I, the remaining proposed alternative processes involve electrolysis of a purified intermediate aluminum-containing compound. The electrodes are assumed to be nonconsumable or inert. The various compounds considered at different times are aluminum chloride (e.g., the ASP process[4]), aluminum sulfide,[5] and conventional purified alumina (as per the inert anode).

When writing the sequence of reactions, it is interesting to note that, like the carbothermal option, carbon is involved as a significant material in all of these processes (except the oxygen-evolving cell). Consequently, they will all have similar overall theoretical energy efficiencies. Differences will revolve on the varying proportions of chemical versus electrical energy input and varying reaction efficiencies.

For any of these three options to be successful, inert anodes are required. Other requirements include an operating temperature above 700°C to form liquid aluminum; an inert drained cathode; an anode that is unreactive to the anode products (e.g., chlorine, sulfide or oxygen); a corrosive electrolyte, because of the need to have it in an ionic form at elevated temperatures; a design that en-

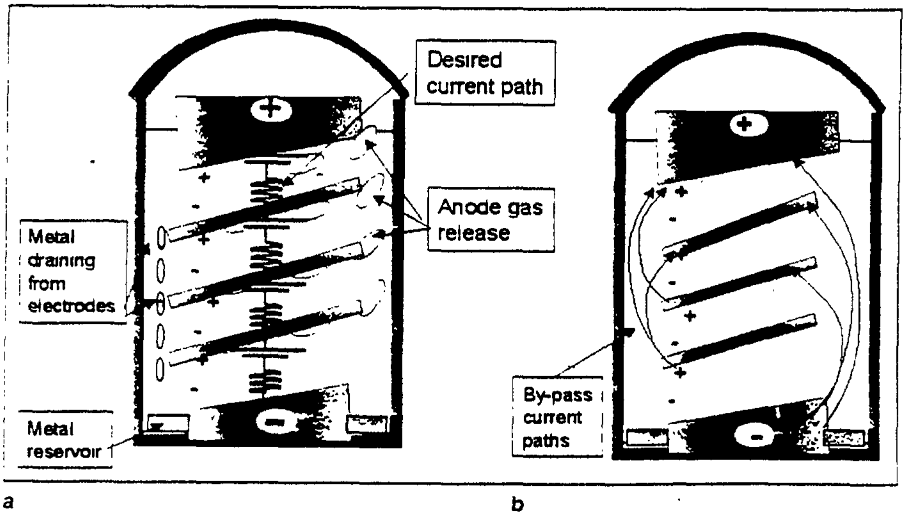

Figure 4. A schematic of the key features of a horizontally oriented multiple bipolar cell showing (a) the desired current path and (b) the by-pass current paths.

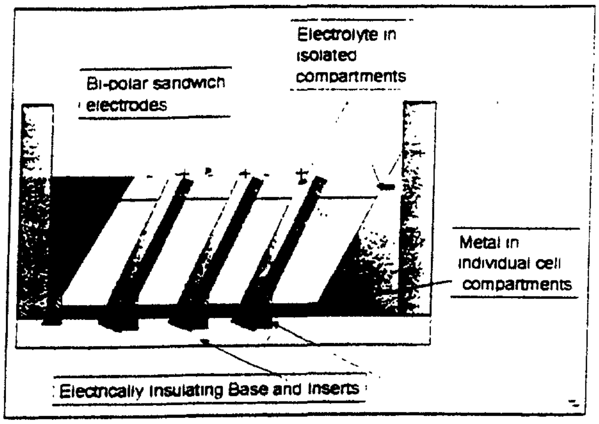

Figure 5. A schematic of a compartmentalized vertically oriented multiple bipolar cell highlighting the necessary design features.

ables the efficient separation of the liquid aluminum product from the gaseous anode products; and energy efficiencies that reduce heat loss per unit production. Not only in aluminum smelting, but in all other metallurgical and high-temperature processes, the best reactor protection is a layer of frozen reacting mixture, and if the design does not achieve this, there is another challenge.

Multipolar electrodes such as the multiple bipolar design patented for the ASP[4] have the obvious advantage that higher productivities per unit reactor volumes are possible. However, these cannot operate at the high current efficiencies currently experienced because of by-pass currents that are inevitably present. Figure 4 schematically illustrates a multiple bipolar cell that has near horizontally oriented electrodes together with the preferred current flow path. The electrolyte in both the cavity that enables the gas to be released (Figure 4b) and in the cavity where the metal drains (Figure 4a) presents an alternative path for by-pass current flow. The equivalent circuit is complex, and the design challenges to obtain high-current efficiencies are considerable. Beck, Rouser, and Thonstad[17] have compared these with the inefficient monopolar arrangement and shown energy efficiencies are likely to be the same as a consequence.

Compartmentalized multiple bipolar cell designs[18] similar to that in Figure 5 overcome the by-pass current problem, but present new materials, design, and operating challenges. For example,

- How short can the interelectrode separation (versus electrode height) be made because of the rising gas volume?
- How would the metal be tapped or drained from each (isolated) electrode compartment?
- What insulating material can be used for electrode support and containing the metal reservoir?
- How will the anodic and cathodic sides of the bipolar electrodes be bonded?

Cell designs probably need to incorporate readily replaceable multiple electrodes.

## CONCLUSIONS

In reviewing each alternative, it is evident that there are several considerations for developing any new or alternative technology, including having the right materials for the key reactions or electrodes (this has been fairly heavily researched); having a feasible reactor design that has a much higher rate of productivity per unit volume than current technology (this must include design features for feeding and removing the reactants and products); maintaining heat balance; and, after all other aspects are addressed, determining good, safe, and environmentally responsible operating practices. If the research is carried out sequentially it will take a very long time. The experience in developing drained-cell technology[10] is important in that it emphasizes that design and practice are as important as having favorable chemistry and suitable materials.

The economic gains of alternatives are, however, not likely to be dramatic. The development costs when considering the above facets are considerable—so much so that it is impractical for any one company to do it alone. Thus, it will necessitate consortiums "picking a winner," unless there is a change in driving force from economics alone.

The challenge becomes even harder when it is recognized that there are several viable paths open to improve the existing process, so any new technology is faced with a moving target. When picking a technology, it is crucial that the concept be developed in its entirety with parallel effort on design, operating practices, materials, and reaction concepts as otherwise the development time could extend to half a century.

Titanium-diboride cathode technology is, however, just around the corner. While a need exists for further development, cost reduction, and design improvements, there are already two distinct benefits: the ability to do substantial retrofits (with 30% productivity gains) to existing aging technologies and the ability to extend the life of cells and cathodes. More importantly, however, it is a start for further development, since it opens the door for innovative multi-electrode cells.

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*Barry J. Welch is a professor in the Chemical and Materials Engineering Department at the University of Auckland.*

**For more information, contact B.J. Welch, University of Auckland, Department of Chemical and Materials Engineering, Private Bag 92019, Auckland, New Zealand; telephone 64-9-373-7515; fax 64-9-393-7463; e-mail b.welch@auckland.ac.nz.**

# APPENDIX A-7

# PAPER BY DR. MARK TAYLOR

(Presented at the Queenstown (New Zealand) Aluminum Smelting Conference, November 26, 1998.)

# $TiB_2$ Coated Aluminium Reduction Cells: Status and Future Direction of Coated Cells in Comalco.

*G. D. Brown, G. J. Hardie, R. W. Shaw and M. P. Taylor*

## BACKGROUND

Since 1985, following early work by Martin Marietta Corp, Comalco has been developing a $TiB_2$ based coating for use on the cathode of aluminium reduction cells. This development program has involved extensive fundamental research into wear mechanisms, material properties, fabrication technologies and cell fluid dynamics as well as ongoing full scale operation of high performance cell designs. The driver for this work is the achievement of major reductions in power consumption compared to those possible with the present best magnetically compensated cell designs. This paper reviews some of the steps taken toward this goal and outlines the intended future direction.

## THE $TiB_2$/C COATING

The enabling technology which has allowed trials of lower anode cathode distance, high performance cell designs, is the Comalco composite coating. The coating is a combination of titanium diboride particles and carbon, bonded by a novel phenolic resin based binder system. The key property of the material is wettability by aluminium, which under certain cell conditions, results in an extremely low wear rate of the coating, when compared to any of the available cathode carbon types.

Wear of cathode carbons, in aluminium reduction cells, is believed to be driven primarily by three interacting mechanisms[1]: chemical removal, (particularly aluminium carbide dissolution), physical abrasion, (by sludge or the moving metal pad) and particulate detachment. Wear is found to be particularly severe in turbulent regions and where electrolyte has regular access to the cathode[1],[2]. These conditions allow rapid removal and / or dissolution of corrosion products ($Al_4C_3$), by the electrolyte, followed by further combined chemical and / or electrochemical attack. Industry experience also shows that graphitised cathodes wear significantly faster than those with an anthracitic binder matrix[3].

The $TiB_2$/C coating material reduces wear by ensuring an aluminium film is maintained over the cathode at all times. The metal film excludes the electrolyte from accessing the $Al_4C_3$ corrosion product and thereby significantly slows the carbide removal and reformation rate. In addition, as slow wear of the carbon matrix does progress, $TiB_2$ is released from the upper millimetres of the coating, but remains on the cathode surface, thereby helping to stabilise the metal film to give a more effective barrier. This viscous slurry layer effectively provides a thicker aluminium film/barrier[4],[5],[6], further slowing the rate of removal of carbides and carbon by diffusion or electrolyte access to the cathode.

The protective mechanisms described above, have allowed development of a group of cell technologies, which utilise the coating properties to fundamentally change the fluid mechanics and physical operation of the cell. This enabling technology can be practically applied both to improve cathode life and to make improvements in cell performance.

## COATED NORMAL CELL (CNC) TECHNOLOGY

The simplest application of the wettable coating is on conventional, horizontal cathode cells. The initial advantage of this approach is significant improvement in cathode life. Multiple full scale cells of this type have been operated at two different test sites A and B. ***Table 1*** below shows the average, wear rate observed on coated cells, when compared to standard cathodes of different grades.

**Table 1:** Cathode Wear Rates for Coated and Uncoated Cells

| CATHODE GRADE | CATHODE MANUFACTURER | AVERAGE WEAR RATE, (mm/year) |
|---|---|---|
| **Site A** | | |
| Coated Fully Graphitised | MLI SG | 4 [7],[8] |
| Uncoated 30%-Graphitic | Carbone Savoie HC3 <u>or</u> SGL 5BDN | 8 [9] |
| Uncoated Fully Graphitised | MLI SG | 40 [10] |
| | | |
| **Site B** | | |
| Coated 30%-Graphitic | Carbone Savoie HC3 | 4 [7] |
| Coated Fully Graphitised | Carbone Savoie G | 4 [11] |
| Uncoated 30%-Graphitic | Carbone Savoie HC3 | 8-12 [9] |
| Uncoated Fully Graphitised | MLI SG | 30 [10] |

The wear rate of 4mm per year measured for coated cells, is the wear rate of the coating itself. This wear rate means that the coating can be expected to provide protection for the current lifetime of a normal cell (~2000 Days). Beyond this age, the viscous slurry continues to offer ongoing cathode protection. Clearly this offers a corresponding extension in cathode life, which is normally limited by cathode erosion.

### Site A

At the first smelter where trial cells have been operated, excessive cathode erosion is known to cause a high percentage of cell failures through localised, accelerated erosion, or "potholing"[12]. As seen above, the cathode wear experienced was significantly reduced for those cells using the $TiB_2$ coating. Fully graphitised cathodes without a protective coating, were found to experience an unacceptably high level of general wear (40mm/y), limiting their use in the unprotected form at this site, despite the potential voltage savings. Cell failure through collector bar attack typically occurs when general wear reaches 150-160mm at Site A. Hence the maximum expected life for a cell using this cathode grade would be 1460 days. In contrast, coated cells using this grade have operated for 2500 days without cathode failure.

Importantly, autopsied cells also showed a complete absence of potholing, although uneven wear was still found in the tap hole region. This is significant because cathode erosion failures rarely occur due to general wear at Sites A and B, rather failure typically occurs as a result of localised "potholing". While the depth of potholes found in uncoated cells has been excluded from the general wear data in Table 1, wear rates across the coated cells were very even, with all heights measured falling within a 20mm range (Results are from 3 cells with an average age of 1500 days). Coated cells have therefore consistently provided excellent protection from cathode erosion as a failure mechanism at Site A.

### Site B

The protective ability of the $TiB_2/C$ coating also offers opportunities for cost and voltage savings via the use of more graphitised cathodes, reduced height cathodes, and lower metal heights, without sacrificing cell life. The second full scale trial of CNC technology examined these factors in addition to cathode wear.

Results again showed a significant reduction in erosion rate, comparable to that experienced at Site A, (see Table 1). The average voltage savings achieved during 12 months monitored operation is given in Table 2.

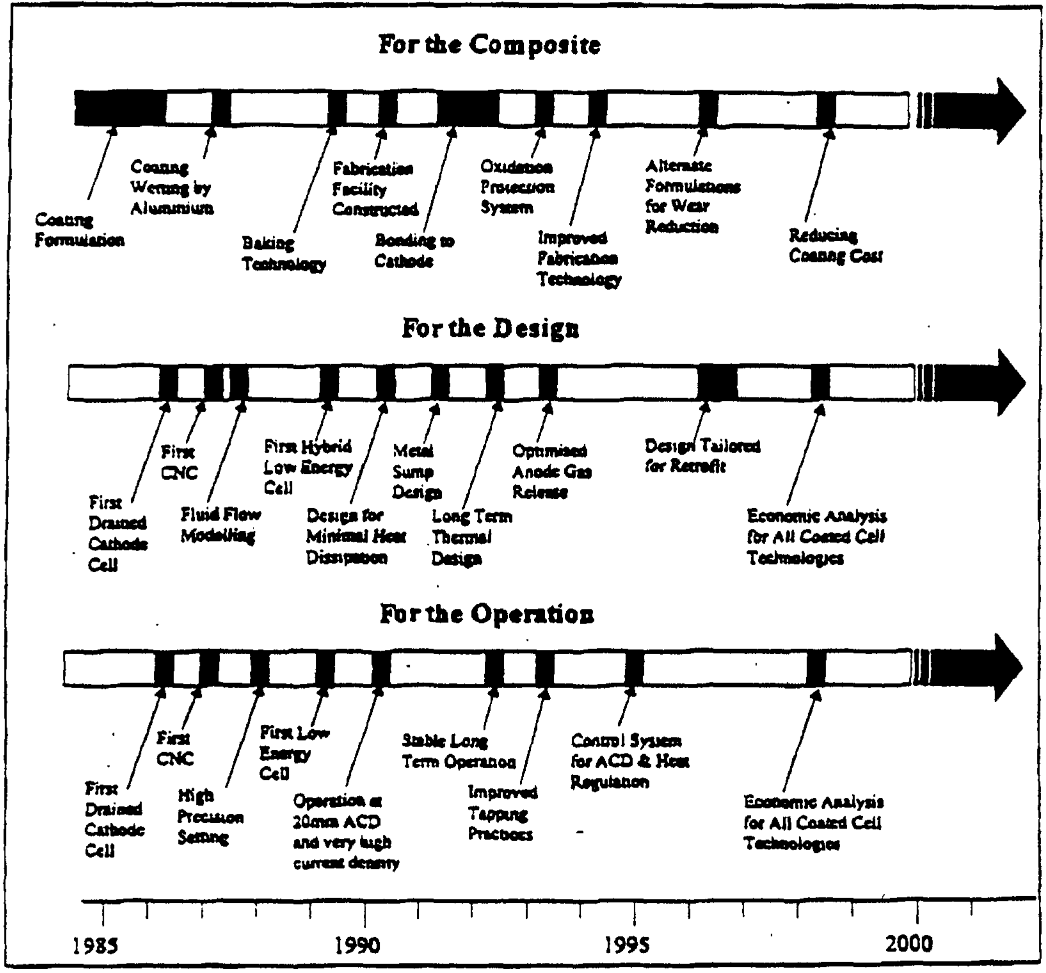
**Table 2:** Voltage Savings Achieved by Coated Normal Cells at Site B.

| **HC3 Cathode (30% Graphitic)**<br>**-Low Metal Height -** | **G Grade Cathode (Graphitised)**<br>**-Low Metal Height,**<br>**-Reduced Cathode Height** |
|---|---|
| VOLTAGE SAVING | VOLTAGE SAVING |
| 160mV[13] | 220mV[13] |

While the cathode wear was significantly reduced, the cell life potential was not realised due to cells failing through the sidewall. This mode of failure was not specific to the technology and has since been removed by better side wall design[11]. Autopsies of these cells showed similar cathode coating performance to that observed at Site A. Hence, for cell technologies limited by cathode erosion, the composite coating provides a very effective pathway to improved cell life.

Even in the case of coated conventional cells, there were a number of technical challenges to be overcome, as shown in the technology development path for the coating. (**Figure 1**).

**Figure 1:** Development Paths for Key Elements of Drained Cathode Technology.

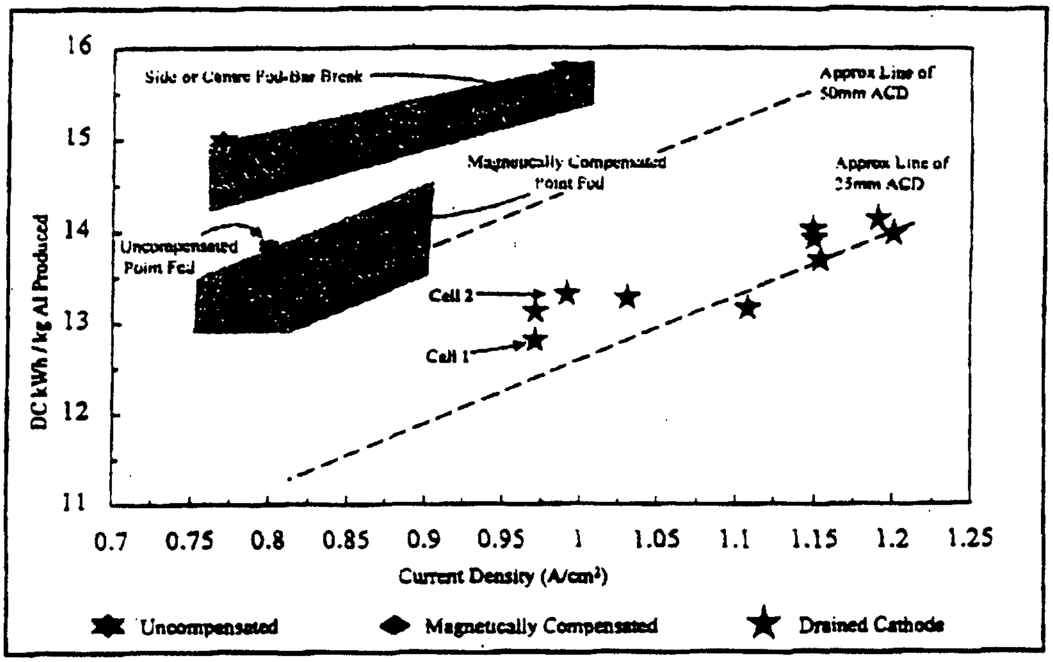


## DRAINED CATHODE CELLS

The ultimate goal for a sufficiently resistant cathode material is development of a cell design able to operate without a metal pad. Elimination of the metal pad promises large power savings both through allowing operation at very low anode to cathode distances (ACDs), without an unstable metal interface and through minimising convective heat loss to the cell walls.

A significant number of drained cells have been operated at the Comalco test site. These cells have been operated either at high current density, to produce additional metal or at line amperage to achieve power savings. Typical operation was at 20 to 30mm ACD and 0.97 to 1.2 A/cm$^2$ current density. **Figure 2** plots the power efficiencies achieved for these cells against the anode current density. Typical performance for conventional, magnetically compensated and uncompensated technologies is also shown[14]. The comparison clearly demonstrates the potential of the technology, with the drained cell performance representing a significant step improvement over magnetically compensated technologies at similar current densities. This offset results from the ability to run drained cells at low ACD. Approximate lines of constant ACD are also plotted. These indicate that the step change in power performance is maintained over a range of current densities. Work to date gives confidence that this performance gain will be transferable to larger cells, with the added benefit of reduced specific heat loss.

**Figure 2:** Drained Cathode Cells on the DC kWh/kg versus Current Density Map Compared to Other Australasian Smelters[14].



Once the potential of the drained design was confirmed, cell life became a major focus of development work. **Figure 3** shows the increase in cell age achieved during the development program so far. Significant improvements have been achieved as a result of improved composite robustness and evolution of the cell design. Development of construction, start up and cell operating practices during this period also contributed significantly to improved performance and life. These advances in materials, design and operations are summarised in the technology development path **Figure 1**. It should also be noted in **Figure 3** that many of the drained cells had their lives curtailed prematurely so that cell autopsies could be done and an improved cell constructed with the newly acquired knowledge.

**Figure 3:** Life of Drained Cells Operated at Site A

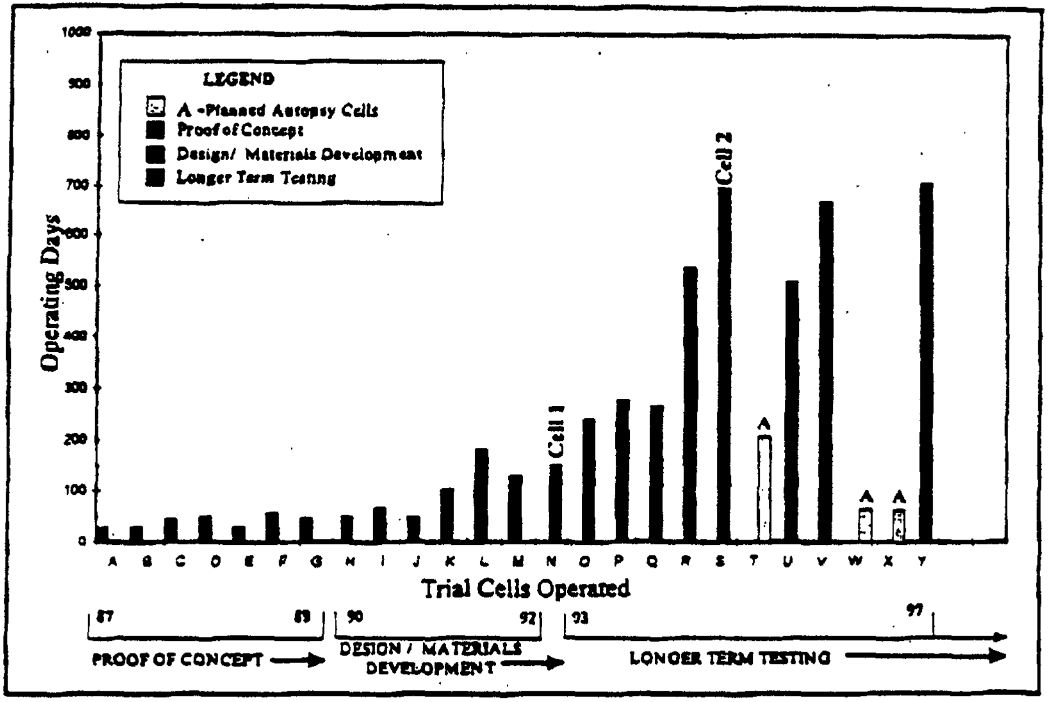
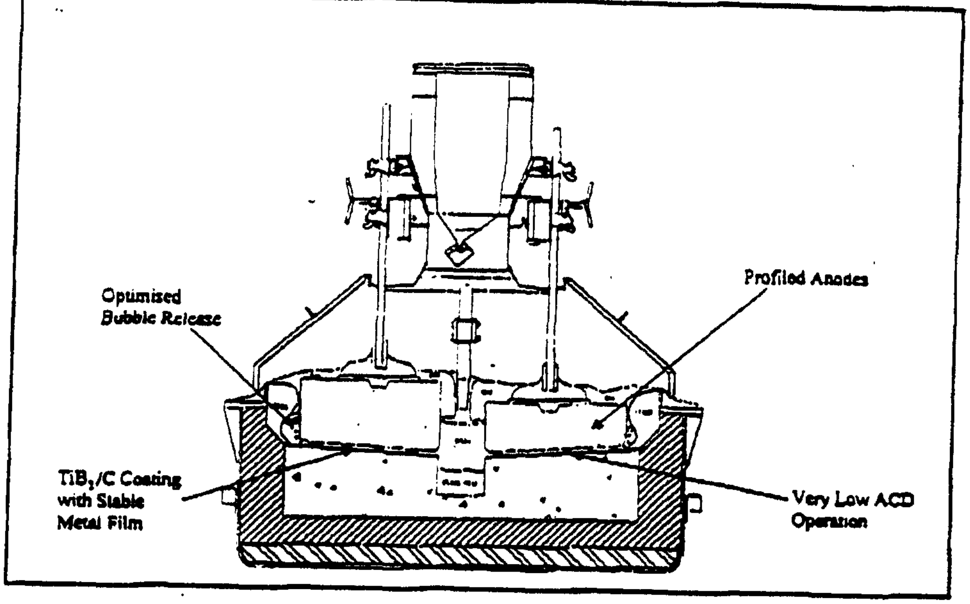


**Figure 4** shows the basic detail of a typical drained cell in cross section. Appropriate cathode angles have been found to be important to minimise cell voltage and cathode wear.

Performance results over the lifetime of one of the more recent long term drained cell designs, (Cell 2 of Figures 2 and 3), are shown in **Figure 5**. This trial was operated under similar operating conditions (line current, bath chemistry and temperature) to the normal smelter operation to provide a sound basis for comparison. The potential of the technology to operate with equivalent current efficiency, at greatly reduced power consumption, for an extended period is clearly demonstrated. Due to the absence of a metal pad in a drained cell, noise can also be seen to be extremely low until late in the cell's life.

**Figure 4:** Cross Section of a Typical Drained Cathode Cell



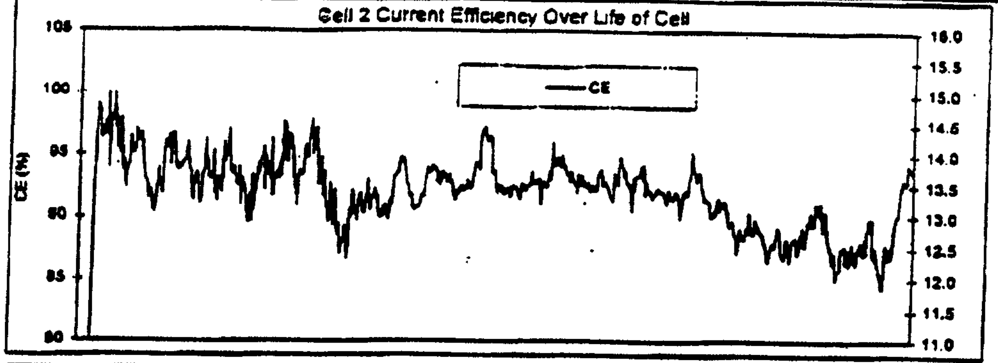
The average performance of Cell 2, shown in **Figure 5**, does not indicate the full potential of the technology due to the deterioration in the current efficiency seen at the end of the cell life. Cell performance deteriorated due to partial detachment and degradation of the cathode coating. Sidewall degradation was also observed to have contributed to coating damage. Solutions to these problems have since been successfully trialed at full scale in the planned autopsy cells of **Figure** 3.

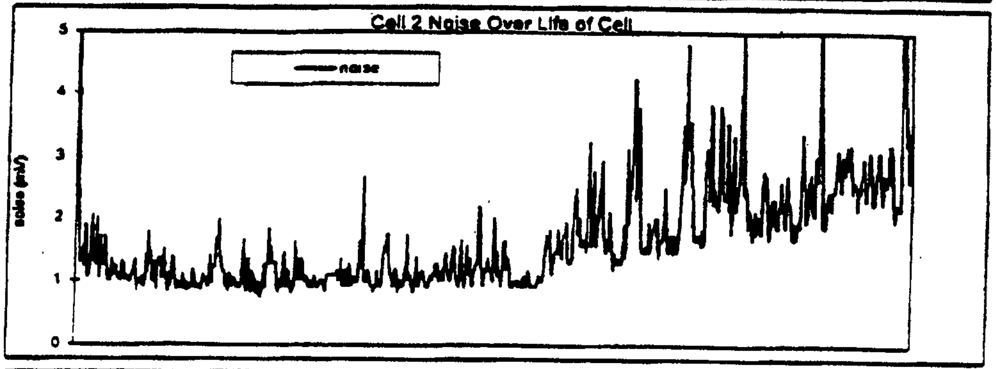
It should also be noted that the data shown in **Figure** 5 is now more than two years old. The intervening period has seen significant, cell design independent, improvement in performance at Site A, which would also be expected to flow on to drained cell operation.

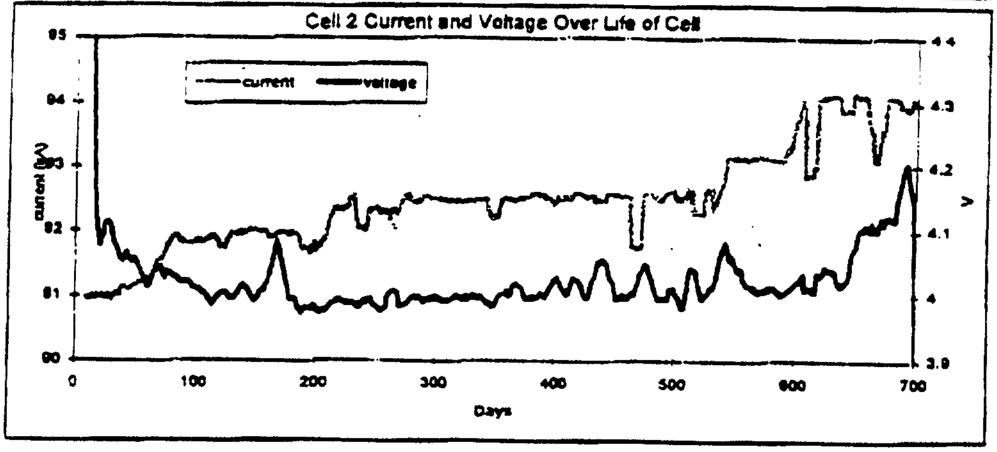
The restriction of operating within an existing potline, using a small cell by modern standards, has imposed limitations on the DC kWh/kg performance due to heat balance constraints. The ability to more fully utilise the potential of drained cell technology, has been successfully demonstrated in a short term test cell, which deliberately compromised the longevity of the cell lining, to further reduce heat loss. The power savings achieved were increased to 2.4 kWh/kg (Cell 1 of **Figure** 2). A larger cell, similar to those in most operating smelters today, with a more advantageous surface area to volume ratio, is better suited to the future application of drained cell technology. As a minimum however, it can be expected that the application of drained cathode technology in any smelter will provide an opportunity for 20% higher amperage and substantially improved DC kWh/kg performance as shown in **Figure 2**.

**Figure 5:** Performance Comparison Between Cell 2 and Standard Site A Results

| - | Cell 2 (life) | Plant Avg. (operating cells) |
|---|---|---|
| Cell Age | 701 days (total) | 804 (days) (Avg. of operating cells) |
| Cell Avg Measured* Volts | 4.02 V | 4.63 V |
| Cell Avg. Current | 92.6 kA | 92.1 kA |
| Cell Avg. Resistance | 25.5 µΩ | 32.4 µΩ |
| Cell Current Efficiency. | 91 7 % | 92.6 % |
| Cell Avg. Noise | 1.7 mV | N/A |
| Anode Effects per cell day | 0.05 | 0.89 |







Specific achievements of the drained cell program to date are:

- Cell operation for 150 days at an average ACD of 20mm, yielding a power efficiency of 12.8 DCkWh/ kg, at Current density of 0.97 A/cm$^2$
- Stable, controlled operation in drained mode for 700 days, averaging 13.3DC kWh/kg, at a current density of 0.99 A/cm$^2$.
- Sustainable long term coating wear rates of between 2 and 6mm/ year on drained cells.
- Robust sump design allowing drained operation.
- Optimised cathode slopes.
- Development of technologies and a facility for coating manufacture.
- Operating practices appropriate for drained cathode cells.

There are still practical operating challenges to be overcome and optimisation of composite cathode fabrication for quality and cost. These issues are in front of us today but are not fundamental limitations to the commercialisation of the drained cathode technology.

## LOW ENERGY CELLS

A third design variation based on a semi drained system is also under development. A group of these hybrid drained cells is presently under trial, again taking advantage of the $TiB_2/C$ coating's ability to resist erosion and thereby enable design of novel cathode geometries. This cell design has already demonstrated 50% of the voltage and power savings of the fully drained cell and is better matched to the specific retrofit requirements of the Comalco smelter site.

## FUTURE DIRECTION

Comalco remains committed to the commercial exploitation of the coating technology. A team of research and operating staff is working toward implementation of low energy cells at the test site. Current and future work involves establishing the potential of the hybrid design, followed by a large scale, multi-cell proving trial for the technology within the reduction lines.

Work is also progressing to determine the most appropriate commercialisation route for both fully drained and coated normal cell technologies.

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# APPENDIX A-8

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# APPENDIX A-9

# DETAILED PRESENTATION OF THE THERMODYNAMIC DATA, CALCULATIONS, TABLES, AND BOUDOUARD REACTION

## Thermodynamics of Electrochemical Reduction of Alumina

Thermodynamic calculations are required to analyze power consumption and cell voltage in aluminum production. The standard Gibbs energy of reaction is used to calculate the standard potential. This and activity are used to calculate the equilibrium, reversible or Nernst potential sometimes called the decomposition potential. The enthalpy of the overall cell reaction is required for calculating the heat balance of the cell and energy efficiency.

Definition of Terms

$a$ = Activity (thermodynamic concentration)

Bemf = Back electromotive force or counter electromotive force (V)

$b$ = Mole or volume fraction of $CO_2$ reaction with carbon (Boudouard reaction)

CE = Current efficiency (%)

$E^\circ$ = Standard potential

$E^\circ_E$= Equilibrium or reversible potential (V)

$E_{Al}$ = Aluminum production potential (V)

$E_{cl}$ = Voltage within the heat loss boundary (V)

$E_{cell}$ = Total voltage of cell (V)

$F$ = Faraday's constant 96.485 kJ /volt equivalent

$\Delta H^\circ$ = Standard enthalpy of reaction (kJ)

$I$ = Cell current (kA)

$n$ = Number of electrons transferred in the reaction as written

$\eta$ = Overvoltage (V)

$R$ = Electrical resistance (ohm)

ROS = Relative oxide saturation

$T$ = Temperature of electrolyte (K)

$T_b$ = Temperature of electrolyte (°C)

$T_r$ = Ambient temperature (°C)

$l$ = Liquid state

$g$ = Gaseous state

$s$ = Solid state

$\gamma$ = Gamma crystalline state

$\alpha$ = Alpha crystalline state

$Rg$ = Ratio $CO/CO_2$ of unburned cell gas

$x$ = Fractional current efficiency, $x$ = %CE / 100

Subscripts:

el = electrolyte
bub = bubbles
an = anode
ca = cathode
ex = external
sa = surface overvoltage at anode
ca = concentration overvoltage at anode
cc = concentration overvoltage at cathode

## Cell Voltage

The voltage in a cell is the sum of the back emf (counter electromotive force), the electrolyte's ohmic voltage drop, the additional ohmic voltage drop caused by anode gas bubbles in the electrolyte, the voltage drops through the anode and cathode, and voltage drops external to the cell. In heat balance calculations we are interested in the voltages within the heat boundary and will omit the voltages external to the cell. However, the external voltage drop must be included in calculating the energy consumption (kWh/kg A1) and in calculating the costs ($/kg AL).

$$E_{cell} = Bemf + IR_{el} + IR_{bub} + IR_{an} + IR_{ca} + IR_{ex} \qquad 1.$$

The Bemf is made up of the equilibrium potential plus overvoltages. The equilibrium potential (reversible potential or Nernst potential) is the voltage required to hold the cell in equilibrium. The kinetics of producing products requires additional voltage at both electrodes (overvoltages). These overvoltages result from concentration gradients and surface reactions at the electrodes.

$$Bemf = E_E + \eta sa + \eta ca + \eta cc \qquad 2.$$

Knowing the cell reaction, the equilibrium potential can be calculated from thermodynamics. Overvoltages are caused by electrode kinetics and must be measured.

## Equilibrium Potential

The standard potential, $E^\circ$, is calculated from $\Delta G^\circ$ the Gibbs free energy change for the cell reaction with all reactants and products at electrolyte temperature and at unit activities:

$$E^\circ = \Delta G^\circ/(nF) \qquad 3.$$

By thermodynamic convention, $\Delta G^\circ$ in the above equation should have a negative sign. This would make $E^\circ$ negative. By this convention the cell voltage and all components of it are negative because energy is consumed rather than produced. However, engineers and cell operators consider the cell voltage to be positive; hence the sign of all cell voltage components has been made positive.

The cell reaction for Hall-Héroult cells with carbon anodes is

$$2Al_2O_3(\alpha,T_b)) + 3C(s,T_b) = 4Al(1,T_b) + 3CO_2(g,T_b) \qquad 4.$$

With inert anodes, the reaction is:

$$2Al_2O_3(\alpha,T_b) = 4Al(1, T_b) + 3O_2(g, T_b) \qquad 5.$$

Alpha alumina was used in the cell reaction because gamma and other non-alpha aluminas convert to alpha as they go into solution. The primary anode gas with carbon anodes is $CO_2$. Substituting n = 12, F = 96,485 J/volt equivalent and numerical values for $\Delta G^\circ$ as a function of T K, $E^\circ$ for cells with carbon anodes becomes

$$E^\circ = 1.898 - 0.0005728\,T \qquad 6.$$

For cells with inert anodes, $E^\circ$ is

$$E^\circ = 2.922 - 0.0005712\,T \qquad 7.$$

This means that the cell voltage would be about 1.0V higher for inert anodes if the overvoltages were the same. However, measurements of overvoltage indicate that the overvoltage on inert anodes is about 0.4 V less than on carbon anodes. The net effect of inert anodes will be about a 0.6 V increase in cell voltage.

The Nernst equation corrects the standard potential for the actual activities to give the equilibrium potential, $E_E$:

$$E_E = E^\circ + \frac{RT}{nF}\ln\frac{a_{Al}^4 a_{CO_2}^3}{a_{Al_2O_3}^2 a_C^3} \qquad 8.$$

Al, $CO_2$, and C are close enough to their standard states that they can be assigned unit activities. The activity of alumina must be obtained from measurements.

Activity of Alumina

A recent analysis by Dewing and Thonstad[4] of cryoscopic data, showed that the slope of log $[a(Al_2O_3)]$ vs. log $(\%Al_2O_3)$ was 3 in dilute solutions and 1.5 in concentrated solutions corresponding to species containing, respectively, 1 and 2 atoms of oxygen. The entire range can be fitted with the equation:

$$a(Al_2O_3) = -0.03791\,(ROS) + 2.364(ROS)^2 - 2.194(ROS)^3 + 0.868(ROS)^4 \qquad 9.$$

$$ROS = \%\,Al_2O_3/(\text{sat}\,\%\,Al_2O_3) \qquad 10.$$

At 960°C the equilibrium potential, $E_E$, for cells with carbon anodes is 1.191V for electrolyte saturated with alumina. At 1/3 saturation, $E_E$ is 1.222V. For an inert anode at 960°C, $E_E$ is 2.217V at saturation and 2.278V at 1/3 saturation.

Voltage Equivalent of Energy to Make Aluminum

Haupin[2] coined the term "$E_{Al}$" to simplify the calculation of a static heat balance. Multiplying the cell current by $E_{Al}$ gives the energy in kW used producing aluminum. The remaining energy becomes heat. This avoids having to make a materials balance to calculate the heat balance.

In deriving $E_{Al}$, Haupin chose for heat loss boundaries the steel pot shell, the top of the ore cover, and the top and exposed sides of the anodes. $E_{Al}$, the voltage equivalent of the total energy (enthalpy) to make aluminum becomes

$$E_{Al} = \Delta H^\circ (x)/(nF) \qquad 11.$$

Where $\Delta H^\circ$ is the standard enthalpy of the cell reaction for reactants entering at ambient temperature and products leaving at electrolyte temperature. In the static state, the route from input to output need not be considered. Intermediate steps do not change $\Delta H^\circ$ for the overall reaction. Current efficiency as a fraction, x, enters into the equation because only the aluminum actually made consumes energy.

The primary reaction in the cell is:

$$Al_2O_3(\gamma,T_r) + 1.5C(s,T_r) \rightarrow 2Al(1,T_b) + 1.5\ CO_2(g,T_b) \qquad 12.$$

However, some of the metal made at the cathode, through a series of reactions, dissolves into the electrolyte and back reacts with $CO_2$ made at the anode forming alumina and CO.

$$2(1\text{-}x)Al(1,T_b) + 3(1\text{-}x)CO_2(g,Tb) \rightarrow (1\text{-}x)Al_2O_3(\alpha,T_r) + 3(1\text{-}x)CO(g,T_b) \qquad 13.$$

In addition to the $CO_2$ reacting with dissolved metal, a small fraction, b reacts with carbon to make CO (the Boudouard reaction).

$$bCO_2(g,Tb) + bC(s,Tr) \rightarrow 2bCO(g,Tb) \qquad 14.$$

Adding reactions 12 + 13 + 14 we get

$$x\ Al_2O_3(\gamma,T_r) + (1.5+b)\ C\ (s,T_r) \rightarrow 2x\ Al\ (1,T_b) + (3x - 1.5-b)\ CO_2\ (g, Tb) + (3\text{-}3x+2b)CO(g,T_b) \qquad 15.$$

Calculating $\Delta H^\circ$ for reaction 15 allows us to calculate $E_{Al} = \Delta H^\circ (x)/(nF)$.

The number (n) of electrons transferred = 6 (x). Therefore,

$$EA1 = \Delta H^\circ\ (x) / [6(x)F] = \Delta H^\circ / 6F \qquad 16.$$

To calculate $\Delta H^{\circ}$ for the overall cell reaction, equation 15, requires knowledge of b, the mole fraction of the $CO_2$ reacting with carbon. Its value can be calculated by equation 17, if one knows the current efficiency, x, and the $CO/CO_2$ ratio, Rg.

$$b = [3\,(x)\,Rg - 1.5Rg + 3x - 3]/(2+Rg) \qquad 17.$$

The $CO/CO_2$ ratio can be estimated using equations 18 and 19 from Beck[3].

$$\%CO = [200G - 2\,(\%CE) - 8]\,/G \qquad 18.$$

$$\%CO_2 = 100 - \%CO \qquad 19.$$

**G~= 1.05 for cells with prebaked anodes**
**G~= 1.19 for cells with Soderberg anodes**

**The value of G for cells with Soderberg anodes is larger than for cells with prebaked anodes because Soderberg anodes are of poorer quality leading to more dusting, more Boudouard reaction, and a higher amount of CO in the unburned gas from the cell. Indeed, the Boudouard reaction is about 20 times greater for Soderberg anodes.**

Using equations 17, 18, and 19 we can estimate b for prebakes and Soderbergs.

For prebaked anodes: $b \sim= -0.1132 + 0.198\,(x) - 0.0704(x)^2$ 20.

For Soderberg anodes: $b \sim = 0.0712 + 0.2252\,(x) - 0.08\,(x)^2$ 21.

The $CO/CO_2$ ratio can be obtained more accurately from a chemical analysis of the unburned cell gas. Then equation 17 can be used to calculate b accurately.

With inert anodes, the cell reaction for calculating $\Delta H^{\circ}$ is

$$Al_2O_3(\gamma,Tr) \rightarrow 2Al(l,T_b) + 1.5\,O_2\,(g,T_b) \qquad 22.$$

Tables I, II, and III give $\Delta H^{\circ}$ calculated for several electrolyte temperatures, several current efficiencies, and several values of b. Table IV gives $\Delta H^{\circ}$ calculated for inert anodes using reaction 22. Ambient temperature was assumed to be 25°C. JANAF table[4] values were used to make the calculations.

Table I. Enthalpy Increase Per Equation 15, Prebaked Anodes, No Boudouard Reaction

| **100(x) =** | | **$\Delta H^{\circ}$ in kJ for 6 Faradays Current** | | | |
|---|---|---|---|---|---|
| **% CE** | **b** | **950°C** | **960°C** | **970°C** | **980°C** |
| 100 | 0.00000 | 1211.46 | 1212.93 | 1214.41 | 1215.89 |
| 95 | 0.00000 | 1164.73 | 1166.14 | 1167.55 | 1168.96 |
| 90 | 0.00000 | 1118.37 | 1119.35 | 1120.69 | 1122.04 |
| 85 | 0.00000 | 1071.27 | 1072.55 | 1073.83 | 1075.11 |

Table II. Enthalpy Increase Per Equation 15, Prebaked Anodes with Boudouard Reaction

| **100(x) =** | | **ΔH° in kJ for 6 Faradays Current** | | | |
|---|---|---|---|---|---|
| **% CE** | **b** | **950°C** | **960°C** | **970°C** | **980°C** |
| 100 | 0.01440 | 1213.98 | 1215.59 | 1216.93 | 1218.41 |
| 95 | 0.01135 | 1166.68 | 1168.25 | 1169.50 | 1171.08 |
| 90 | 0.00798 | 1119.48 | 1120.83 | 1122.17 | 1123.52 |
| 85 | 0.00423 | 1072.01 | 1073.33 | 1074.57 | 1075.85 |

Table III. Enthalpy Increase Per Equation 15, Soderberg anode with Boudouard Reaction

| **100(x) =** | | **ΔH° in kJ for 6 Faradays Current** | | | |
|---|---|---|---|---|---|
| **% CE** | **b** | **950°C** | **960°C** | **970°C** | **980°C** |
| 100 | 0.2164 | 1251.40 | 1252.75 | 1254.25 | 1255.75 |
| 95 | 0.2129 | 1204.05 | 1205.48 | 1206.92 | 1208.33 |
| 90 | 0.2091 | 1156.60 | 1157.95 | 1159.32 | 1160.69 |
| 85 | 0.2048 | 1109.12 | 1110.42 | 1111.72 | 1113.02 |

Table IV. Enthalpy Increase Per Equation 22, Inert Anodes

| **100(x) =** | **ΔH° in kJ for 6 Faradays Current** | | | |
|---|---|---|---|---|
| **% CE** | **950°C** | **960°C** | **970°C** | **980°C** |
| 100 | 1779.06 | 1780.23 | 1781.39 | 1782.56 |
| 95 | 1690.11 | 1691.21 | 1692.32 | 1693.43 |
| 90 | 1601.15 | 1602.20 | 1603.25 | 1604.30 |
| 85 | 1512.20 | 1513.19 | 1514.19 | 1515.18 |

The ΔH° values in tables I, II, III, and IV were converted to voltages by dividing by 6F, or 578.91 kJ / Volt equivalent, giving $E_{Al}$ values per equation 16. Multiple regression analysis of these values produced equations 23 and 24. $T_b$ is in °C.

$$E_{Al} = 0.23706 + 4.6757e\text{-}4(T_b) - 2.25e\text{-}7(T_b)^2 + x[1.4024 + 2.23e\text{-}4(Tb)] + b[0.3086 - 1.97e\text{-}5(T_b)] \qquad 23.$$

For inert anodes:

$$E_{Al} = x\,(2.881 + 0.0002016\,T_b) \qquad 24.$$

Equations 23 and 24 are valid for steady state operation. They neglect the minor heat content of electrolyte fume. Also, in equation 23, the heat generated by air burning of the anodes is neglected as well as the heat content of the spent prebaked anode. An ambient temperature of 25°C was assumed.

$E_{Al}$ is useful in calculating both steady state heat loss and energy efficiency.

$$\text{Heat loss (kW)} = I\,(E_{cl} - E_{Al}) \qquad 25.$$

Energy efficiency is often based upon the heat loss and considers as productive all electrical power input that does not become heat loss. On this basis,

$$\text{Energy efficiency} = 1 - [(\text{Heat loss})/(\text{power input})] \qquad 26.$$

Substituting values,

$$\text{Energy efficiency} = 1-[(I\,E_{cell} - IE_{Al}/I\,E_{cell})]$$

Which simplifies to

$$\text{Energy efficiency} = E_{Al}/E_{cell} \qquad 27.$$

Using equation 27, the power efficiencies would be 48.1% for carbon anode cell and 69.6% for an inert anode cell if both operated at 960°C, 4.2 volts, and 95% current efficiency.

# Tables

Assume:

Hall Heroult Reaction: Al2O3+ (1.5/(1-n))C ---> 2Al + (1.5(1-2n)/(1-n))CO2 + (3n)CO (1-n) = CE

Al2O3 + (1.5/(CE))C ---> 2Al + (3-(1.5/(CE)))CO2 +( 3(1-(CE))/(CE))CO

Inert Anode Reaction Al2O3 ----> 2Al + 1.5O2

Operating temperature = 960 C = 1233 K

Current Efficiency between 94% and 100%

State of the Art Hall Heroult Cell Performance, 4.1 Volts, 94% CE or 5.90 Kwh/lb Al

Theoretical Energy Requirements Based on Enthalpy Requirements for Heating Reactants, Chemical Reaction, and Withdrawing Products at Cell Temperature

| Curr. Eff. | 94% | 95% | 96% | 97% | 98% | 99% | 100% |
|---|---|---|---|---|---|---|---|
| **Hall Heroult Cell** | | | | | | | |
| Cal/gm m | 298,231 | 297,496 | 296,760 | 296,025 | 295,289 | 294,554 | 293,818 |
| Kwh/kg | 6.423 | 6.408 | 6.392 | 6.376 | 6.360 | 6.344 | 6.328 |
| Kwh/lb | 2.914 | 2.906 | 2.899 | 2.892 | 2.885 | 2.878 | 2.871 |
| Energy Eff at 5.9 kwh/# | 49.4% | 49.3% | 49.1% | 49.0% | 48.9% | 48.8% | 48.7% |
| **Inert Anode Cell** | | | | | | | |
| Cal/gm m | 429,223 | 429,223 | 429,223 | 429,223 | 429,223 | 429,223 | 429,223 |
| Kwh/kg | 9.245 | 9.245 | 9.245 | 9.245 | 9.245 | 9.245 | 9.245 |
| Kwh/lb | 4.193 | 4.193 | 4.193 | 4.193 | 4.193 | 4.193 | 4.193 |
| Needed Eng Eff for 5.9 Kwh/# | 71.1% | 71.1% | 71.1% | 71.1% | 71.1% | 71.1% | 71.1% |
| Comparison to K. Grjotheim and B. Welch, Aluminum Smelter Technology - A Pure and Applied Approach, Aluminum Verlag GMBH, Dusseldorf, 1980, p. 83. for Hall Heroult Cells<br>H(Total) = (1.43/(CE)) + 4.91 Kwh/kg Al (at 1250K) | | | | | | | |
| Kwh/kg | 6.431 | 6.415 | 6.400 | 6.384 | 6.369 | 6.354 | 6.340 |
| Kwh/lb | 2.917 | 2.910 | 2.903 | 2.896 | 2.889 | 2.882 | 2.876 |

Specific Energy Consumption = (2.98V/(CE)) kwh/kg

Hall Heroult Cell Energy Efficiency = (0.48 + (1.65CE))/V (at 1250K)

Hall Heroult Cell Energy Efficiency for various voltage and current efficiency levels

| | Current Efficiency | | | | | |
|---|---|---|---|---|---|---|
| Voltage | 90% | 92% | 94% | 96% | 98% | 100% |
| 2.2 | 89.3% | 90.8% | 92.3% | 93.8% | 95.3% | 96.8% |
| 2.4 | 81.9% | 83.3% | 84.6% | 86.0% | 87.4% | 88.8% |
| 2.6 | 75.6% | 76.8% | 78.1% | 79.4% | 80.7% | 81.9% |
| 2.8 | 70.2% | 71.4% | 72.5% | 73.7% | 74.9% | 76.1% |
| 3.0 | 65.5% | 66.6% | 67.7% | 68.8% | 69.9% | 71.0% |
| 3.2 | 61.4% | 62.4% | 63.5% | 64.5% | 65.5% | 66.6% |
| 3.4 | 57.8% | 58.8% | 59.7% | 60.7% | 61.7% | 62.6% |
| 3.6 | 54.6% | 55.5% | 56.4% | 57.3% | 58.3% | 59.2% |
| 3.8 | 51.7% | 52.6% | 53.4% | 54.3% | 55.2% | 56.1% |
| 4.0 | 49.1% | 50.0% | 50.8% | 51.6% | 52.4% | 53.3% |
| 4.2 | 46.8% | 47.6% | 48.4% | 49.1% | 49.9% | 50.7% |

Specific Energy Consumption = (2.98V/(CE)) kwh/kg
Inert Anode Cell Energy Efficiency = 3.093 (CE/V) kwh/kg
Inert Anode Cell Energy Efficiency for various voltage and current efficiency levels

| | Current Efficiency | | | | | |
|---|---|---|---|---|---|---|
| Voltage | 90% | 92% | 94% | 96% | 98% | 100% |
| 2.2 | --- | --- | --- | --- | --- | --- |
| 2.4 | --- | --- | --- | --- | --- | --- |
| 2.6 | --- | --- | --- | --- | --- | --- |
| 2.8 | 99.4% | --- | --- | --- | --- | --- |
| 3.0 | 92.8% | 94.9% | 96.9% | 99.0% | --- | --- |
| 3.2 | 87.0% | 88.9% | 90.9% | 92.8% | 94.7% | 96.7% |
| 3.4 | 81.9% | 83.7% | 85.5% | 87.3% | 89.2% | 91.0% |
| 3.6 | 77.3% | 79.0% | 80.8% | 82.5% | 84.2% | 85.9% |
| 3.8 | 73.3% | 74.9% | 76.5% | 78.1% | 79.8% | 81.4% |
| 4.0 | 69.6% | 71.1% | 72.7% | 74.2% | 75.8% | 77.3% |
| 4.2 | 66.3% | 67.8% | 69.2% | 70.7% | 72.2% | 73.6% |

Specific Energy Consumption = (2.98V/(CE)) kwh/kg Al

| | Current Efficiency | | | | | |
|---|---|---|---|---|---|---|
| Voltage | 90% | 92% | 94% | 96% | 98% | 100% |
| 2.2 | 7.284 | 7.126 | 6.974 | 6.829 | 6.690 | 6.556 |
| 2.4 | 7.947 | 7.774 | 7.609 | 7.450 | 7.298 | 7.152 |
| 2.6 | 8.609 | 8.422 | 8.243 | 8.071 | 7.906 | 7.748 |
| 2.8 | 9.271 | 9.070 | 8.877 | 8.692 | 8.514 | 8.344 |
| 3.0 | 9.933 | 9.717 | 9.511 | 9.313 | 9.122 | 8.940 |
| 3.2 | 10.596 | 10.365 | 10.145 | 9.933 | 9.731 | 9.536 |
| 3.4 | 11.258 | 11.013 | 10.779 | 10.554 | 10.339 | 10.132 |
| 3.6 | 11.920 | 11.661 | 11.413 | 11.175 | 10.947 | 10.728 |
| 3.8 | 12.582 | 12.309 | 12.047 | 11.796 | 11.555 | 11.324 |
| 4.0 | 13.244 | 12.957 | 12.681 | 12.417 | 12.163 | 11.920 |
| 4.2 | 13.907 | 13.604 | 13.315 | 13.038 | 12.771 | 12.516 |

Specific Energy Consumption = (1.34V/(CE)) kwh/lb Al

| | Current Efficiency | | | | | |
|---|---|---|---|---|---|---|
| Voltage | 90% | 92% | 94% | 96% | 98% | 100% |
| 2.2 | 3.278 | 3.207 | 3.139 | 3.073 | 3.011 | 2.950 |
| 2.4 | 3.576 | 3.499 | 3.424 | 3.353 | 3.284 | 3.219 |
| 2.6 | 3.874 | 3.790 | 3.709 | 3.632 | 3.558 | 3.487 |
| 2.8 | 4.172 | 4.082 | 3.995 | 3.912 | 3.832 | 3.755 |
| 3.0 | 4.470 | 4.373 | 4.280 | 4.191 | 4.105 | 4.023 |
| 3.2 | 4.768 | 4.665 | 4.565 | 4.470 | 4.379 | 4.292 |
| 3.4 | 5.066 | 4.956 | 4.851 | 4.750 | 4.653 | 4.560 |
| 3.6 | 5.364 | 5.248 | 5.136 | 5.029 | 4.927 | 4.828 |
| 3.8 | 5.662 | 5.539 | 5.421 | 5.309 | 5.200 | 5.096 |
| 4.0 | 5.960 | 5.831 | 5.707 | 5.588 | 5.474 | 5.364 |
| 4.2 | 6.258 | 6.122 | 5.992 | 5.867 | 5.748 | 5.633 |

All Data is from **Thermodynamic Properties of 65 Elements - Their Oxides, Halides, Carbides, and Nitrides**
C.E. Wicks and F.E. Block, Bulletin 605, Bureau of Mines, U.S. Government Printing Office, Washington, DC: 1963

| | **Calories per Gram Mole** | | | | | **100% CE, Enthalpy Requirement** | | |
|---|---|---|---|---|---|---|---|---|
| | H(T)-H298 | Heats of Formation | | | | | | |
| Temp. K | $Al_2O_3$ | C | $Al_2O_3$ | $CO_2$ | CO | **Normal**<br>**100%** | **Inert**<br>**100%** | **Ratio** |
| 298 | 0 | 0 | -400300 | -94050 | -26400 | **259225** | **400300** | **1.544** |
| 1000 | 18710 | 2310 | -404400 | -94400 | -26750 | **284975** | **423110** | **1.485** |
| 1100 | 21710 | 3320 | -404000 | -94250 | -26900 | **289315** | **425710** | **1.471** |
| 1200 | 24740 | 3850 | -403600 | -94300 | -27000 | **292665** | **428340** | **1.464** |
| 1300 | 27790 | 4390 | -403200 | -94300 | -27300 | **296125** | **430990** | **1.455** |
| 1400 | 30850 | 4930 | -402800 | -94300 | -27350 | **299595** | **433650** | **1.447** |

**Hall Heroult**
**Inert Anode**

$Al_2O_3 + (3/2x)C \dashrightarrow 2Al + 1.5((2x-1)/x)CO_2 + 3((1-x)/x)CO$

| x | $Al_2O_3$ | C | Al | $CO_2$ | CO | % Curr Eff |
|---|---|---|---|---|---|---|
| 1.00 | 1.00 | 1.50 | 1.00 | 1.50 | 0.00 | 100 |
| 0.90 | 1.00 | 1.67 | 1.00 | 1.33 | 0.33 | 90 |
| 0.80 | 1.00 | 1.88 | 1.00 | 1.13 | 0.75 | 80 |
| 0.70 | 1.00 | 2.14 | 1.00 | 0.86 | 1.29 | 70 |
| 0.60 | 1.00 | 2.50 | 1.00 | 0.50 | 2.00 | 60 |
| 0.50 | 1.00 | 3.00 | 1.00 | 0.00 | 3.00 | 50 |

Conversion Factor Derivation

Formula Basis, 1 gm mole $Al_2O_3$, or 2 gm mole Al

| | Example |
|---|---|
| Let H = Calories per gram mole $Al_2O_3$ | 259,225 |
| Calories per gm Al = J = H/(2 x 26.98) | 4,804.0 |
| Calories per kilogram Al = K = 1000 x J | 4,804,021 |
| kg Calories per kilogram Al = L = K/1000 | 4,804.0 |
| Kwh per kilogram Al = M = L x 0.00116222 | 5.583 |
| Kwh per pound Al = N = M/2.2046226 | 2.533 |

Overall Conversion Factor

| | |
|---|---|
| Calories/gm mole $Al_2O_3$ to Kwh/kg Al | 0.0000215 |
| Calories/gm mole $Al_2O_3$ to Kwh/lb Al | 0.0000098 |

# Production of Carbon Monoxide in Hall-Héroult Cells
# (Boudouard Reaction Effect)

There is good evidence that the anode reaction does not produce any carbon monoxide (CO) at normal current densities [11]. When oxygen (O) discharges onto carbon (C), it forms a stable C–O surface compound on the anode. At low oxygen evolution rates, the surface compound can slowly detach from the surface and produce CO. But at normal current densities (high oxygen activity), additional oxygen atoms react with the CO surface compound before it can detach from the surface as CO. This forms an unstable carbon dioxide ($CO_2$) surface compound that detaches rapidly from the surface as $CO_2$, and leaves fresh carbon for oxygen to deposit upon and form new C–O surface compound. Hence, the anode product is $CO_2$ [12].

Most of the CO in the off gas is produced by a redox reaction between $CO_2$ and metal, M, in the bath: either dissolved sodium, monovalent aluminum species, or impurities in the bath that were reduced to a lower valence state at the cathode. This results in a loss of current efficiency. One mole of $CO_2$ produces one mole of CO by this mechanism.

$$CO_2 + M \rightarrow CO + MO$$

CO can also be produced by the Boudouard reaction, whereby $CO_2$ reacts with carbon in pores of the anode or with carbon dust in the bath, forming two moles of CO for each mole of $CO_2$.

$$CO_2 + C \rightarrow 2CO$$

Production of CO is not part of the anode reaction and therefore does not affect the reversible potential. Production of CO does, however, enter into the enthalpy of the overall cell reaction and therefore affects the heat balance.

# APPENDIX A-10

# FURTHER PERSPECTIVES ON INERT ANODES

## Further Perspectives on Inert Anodes

Wear rate has been the most commonly used term for a quantitative measure of the susceptibility of anode material to dissolve during electrolytic production of aluminum metal. The convention for expressing wear rate is in thickness per time (usually millimeters per year or milli-inches per year [mpy]), and the rate is determined by measuring geometric changes in the anode directly or is calculated from metal purity measurements, assuming values for certain physical properties of the anode such as density.

The target for the wear rate of inert anode materials, as specified in the *Inert Anode Roadmap,* is less than 10 mm per year. As previously mentioned, however, a target for this parameter that does not incorporate some aspects of the corrosion mechanism may not be a good predictor for the most important metrics in aluminum production, kWh/lb and cost/lb.

There are two principal shortcomings in using wear rates to gauge the performance of inert anodes. First, *it is assumed that the failure of the anode is equivalent to excess dimensional loss.* This is correct if the anode material simply dissolves similarly to the following reaction of the hypothetical metal oxide $M_xO_y$:

$$M_xO_y + 2yF^- = M_xF_{2y} + yO^{2-} \qquad (1)$$

It is acknowledged that

- the oxide $M_xO_y$ may be more complicated than a simple oxide,
- fluoride may exist in the melt as complexes involving $Al^{3+}$ and $O^{2-}$,
- the metal fluorides that form may contain $O^{2-}$ ions as well (i.e., aluminates),
- the $O^{2-}$ ions that form are most likely in the form of complexes,
- bath chemistry at the anode may be different than in the bulk electrolyte and that this will complicate matters, and
- wear may well not be uniform over an entire anode surface.

Nevertheless, the equation is a general representation of a solubility reaction and the size of its equilibrium constant will indicate the solubility of the oxide. Oxides that dissolve according to these general "rules" are plentiful and include the well-studied $SnO_2$, NiO, and various copper and iron oxides.

Components of inert anode materials may also oxidize and then dissolve as illustrated by the following reactions for the hypothetical (non-noble) metal M and metal oxide $M_xO_y$, respectively:

$$M + xF^- = MF_x + xe \qquad (2)$$

$$M_xO_y + (2y+w)F^- = M_xF_{2y+w} + yO^{2-} + we \qquad (3)$$

Oxidation of a lower-valence-state oxide prior to or during dissolution (Equation 2) has been observed for the nickel ferrite phase, nominally $NiFe_2O_4$, of some cermet anodes because the ferrite was non-stoichiometric, i.e., contained $Fe^{2+}$ ions. The $Fe^{2+}$ readily oxidized under anodic polarization and the subsequent chemical changes involved dissolution. In the above cases (Equations 1 through 3), collectively termed *uniform dissolution*, oxide and metal convert to ions and these diffuse away from the electrode, so that wear (provided it is uniform) can be accurately equated with a dimensional loss. Equations 1 through 3 do not frequently illustrate the reaction mechanism of inert anodes, however. If anode materials form solid phases according to the following reaction for the hypothetical metal M:

$$xM + yO^{2-} = M_xO_y + 2ye, \qquad (4)$$

the dimensions of the anode may increase as solid corrosion products form and expand its volume. The anode may deteriorate, that is, its important properties like conductivity may change, but its volume can increase or remain the same. (Of course, if this type of corrosion is not linear, the discrepancy between dimensional changes and chemical stability could be less even after the passage of a large amount of time, after some steady-state oxide layer thickness is obtained.)

The second problem with using wear rates to indicate the stability of inert anodes is that *wear rates do not describe how dissolution varies in three dimensions across the surface or throughout the volume of the anode material.* Many of the mechanisms of corrosion, especially those involving polycrystalline materials, involve localized phenomena. Anodes can degrade by localized corrosion as a result of ion migration along grain boundaries and through pores. Both of these types of failure modes might not be "sensed" using a simple wear-rate measurement. The anode's mechanical and electrical properties could be changed dramatically, however, as electrolyte migrated through the material and further reacted at the grain boundary surfaces or within pores. Several cases have been noted where ceramic anodes with very fine grain structure (of 1 µm) visibly swelled over very short exposure times due to "grain-boundary uptake" and the subsequent reaction of electrolyte with the anode material.

Inert-anode wear can also be attributed to de-alloying or selective oxidative dissolution of one component of metal or metal-containing anodes. This generally occurs because one part of the anode is inherently more reactive than another. A cermet, for example, may fail because the metal phase oxidizes and subsequently dissolves faster than do the original oxide phases. This was observed for nickel metal-containing cermets that were under development at Alcoa in the early 1980s. The resulting morphology of this type of failure is a surface devoid of the more reactive phase. Sometimes solid reaction products form in the vicinity of the voided regions but the products are not protective and the reactive phase is continually reacted preferentially through the balance of the material as long as mass transport is not limiting.

**A side note.** The formation of solid oxide corrosion products that do not readily dissolve in the fluoride melt would appear to be desirable under some circumstances. First, the tendency for the oxide to form generally means the fluoride is not as favored (Equation 1). Second, many oxides that form during corrosion are passive. They serve as kinetic barriers to further corrosion by severely retarding both electronic and ionic transport. Usually, passive oxide films are thin and very dense (without pores to allow solution ingress). Unfortunately, solid oxide corrosion products have a potentially important disadvantage for inert anodes. They are generally resistive, with the resistance depending on the thickness of the corrosion layer and its resistivity. A resistive element placed in series with the anode itself will add a potentially significant voltage penalty to cell operation. The layer may also contribute to catastrophic anode failure during operation if it is either too resistive or too thick to support the electrolysis current. The resulting voltage developed across the film may be high enough to cause physiochemical changes in the film including rupture and/or promotion of ion migration through defects that would normally be inaccessible. Variations in temperature could also cause mechanical failure when the oxide and metal have thermal expansivities that are poorly matched. Similar failures of passivated anodes have been observed in chlorine electrolysis cells that employ passivated titanium electrodes. These failures may also be responsible for why pure copper has not been used successfully as a material for inert anodes. Copper forms copper oxides that have low solubility in molten fluorides, but the oxides spall, probably for one or more of the reasons discussed above.

Selective oxidative dissolution has also been observed for metal alloys. Copper-nickel alloy anodes, for example, have shown preferential oxidation of the nickel component during electrolysis in fluoride melts. The resulting morphology was porous near the surface, indicating loss of nickel, with a surrounding region enriched in copper. A similar behavior was observed in the metallic phase of the $NiFe_2O_4$-NiO-Cu cermet material tested by ALCOA and the Pacific Northwest National Laboratory. The metallic phase in this cermet is actually a copper-nickel alloy containing about 15 percent nickel. After testing, the metallic phase of the anodes was depleted near the surface to a depth that varied depending on test conditions. Under the metal-depleted zone, the metallic phase in the cermet exhibited an enrichment of copper, again to a depth that depended on the conditions. In some cases, a layer of cermet was observed containing almost pure copper metal.

To complicate matters, selective oxidation of a metal alloy may be advantageous if the selectively oxidized component forms a solid, protective, oxide phase. Copper-aluminum bronzes investigated at MIT showed this type of behavior. Under certain conditions, the aluminum component oxidized selectively and a protective layer of alumina formed on the anode. More recently, alloy systems that contained up to five metal components have been studied by Eltech/Moltech to try to optimize both the protective and conductive properties of the passivating layer.

Other localized reactions that would be overlooked in a simple dimensional measurement of stability include reactions at "hot spots" or "cold spots" where current density is significantly higher or lower than average because of geometric non-uniformities in the reduction cell, reactions of fluoride vapors with the anode material above the liquid electrolyte level, localized erosion of the anode material by bubbles under conditions where the bubble flow is non-uniform, the formation of cracks from thermal shock or other sources, and the reactions of electrolyte with anode material exposed as a result of this cracking.

Finally, reactions of the anode material with aluminum, in dissolved or droplet form, or with other reductants in the melt, may occur under open circuit conditions. Cermet anodes left in the molten electrolyte without polarization have showed accelerated wear (compared to polarized anodes) even after a few hours. Passivated metals will also be susceptible to this mode of failure because, under open circuit conditions, the passive layer will tend to reductively dissolve. Consequently, any development work on inert anodes should consider reactions under open circuit conditions or a strategy for minimizing time in the unpolarized state in the electrolyte.

**Recommendations Regarding Wear Rates.** Considering the foregoing discussion, it is strongly recommended that researchers use wear rates to evaluate potential inert anode materials only in conjunction with metal quality measurements. This would help eliminate from consideration anodes with low wear rates that corrode according to mechanisms not equivalent to uniform dissolution (Equations 1 through 3). Another way to accomplish this objective would be to establish additional performance targets related to corrosion layer thickness and properties, microstructure and composition, and corrosion uniformity. Although this task would be very difficult, anode performance could, in principle, be determined by taking cross-sections of anode components after testing was completed and analyzing their microstructure and microchemistry. This would also provide a more mechanistic understanding of the failure modes of anode materials, and allow reviewers and the aluminum industry to make a more informed decision on whether to pursue future development of a particular material or cell design.