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Advanced Steels for Accident Tolerant Fuel Claddings

Ferritic Martensitic Alloys as Accident Tolerant Fuel (ATF) Cladding Material for Light Water Reactors

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GE Project Team

GE Global Research

Michigan**Engineering**

Los Alamos
NATIONAL LABORATORY

GNF
Global Nuclear Fuel
A Joint Venture of GE, Toshiba, & Hitachi

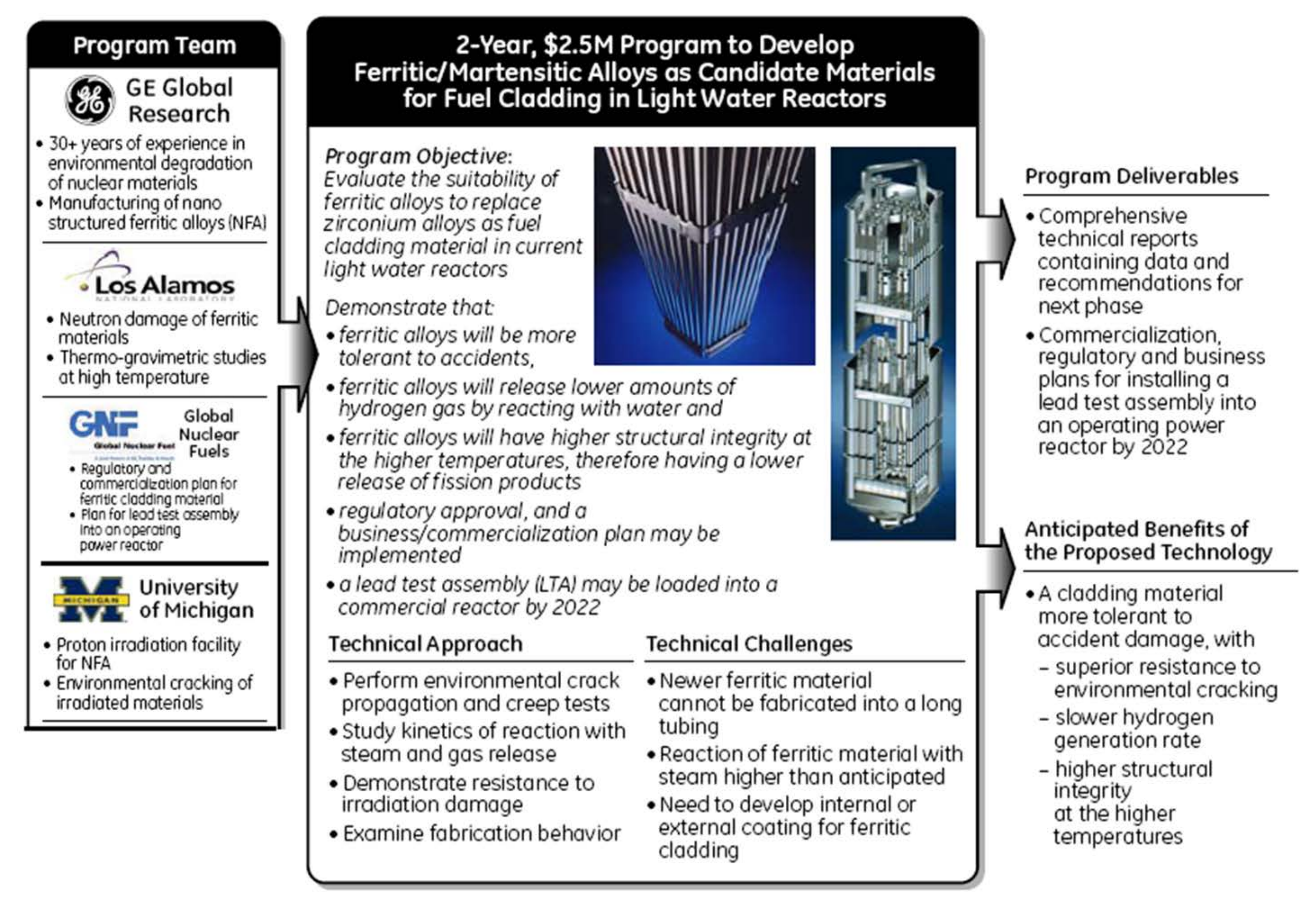
Approach of GE Research Proposal

- Demonstrate that stainless iron based bulk alloys or Advanced Steels can be used as fuel cladding materials in commercial nuclear reactors
- The proposed material should be as good as Zr alloys (or better than Zr alloys) under normal operation conditions
  1. Resistant to general corrosion and environmental cracking under normal operation conditions
  2. Resistant to radiation damage up to 10-20 dpa

Approach of GE Research Proposal

- The proposed Advanced Steels should be able to outperform the containment the fuel in the case of an accident scenario (e.g. LOCA) as compared to the current Zr alloys
  1. Better mechanical strength at higher temperature
  2. Enhanced retention of fission products (no cracking)
  3. Improved reaction kinetics with steam
  4. Lower generation of hydrogen gas when reacting with steam

Initial Proposal



Program Team

GE Global Research

- 30+ years of experience in environmental degradation of nuclear materials
- Manufacturing of nano structured ferritic alloys (NFA)

Los Alamos NATIONAL LABORATORY

- Neutron damage of ferritic materials
- Thermo-gravimetric studies at high temperature

GNF Global Nuclear Fuels

- Regulatory and commercialization plan for ferritic cladding material
- Plan for lead test assembly into an operating power reactor

University of Michigan

- Proton irradiation facility for NFA
- Environmental cracking of irradiated materials

2-Year, $2.5M Program to Develop Ferritic/Martensitic Alloys as Candidate Materials for Fuel Cladding in Light Water Reactors

Program Objective:
Evaluate the suitability of ferritic alloys to replace zirconium alloys as fuel cladding material in current light water reactors

Demonstrate that:

- *ferritic alloys will be more tolerant to accidents,*
- *ferritic alloys will release lower amounts of hydrogen gas by reacting with water and*
- *ferritic alloys will have higher structural integrity at the higher temperatures, therefore having a lower release of fission products*
- *regulatory approval, and a business/commercialization plan may be implemented*
- *a lead test assembly (LTA) may be loaded into a commercial reactor by 2022*

Technical Approach

- Perform environmental crack propagation and creep tests
- Study kinetics of reaction with steam and gas release
- Demonstrate resistance to irradiation damage
- Examine fabrication behavior

Technical Challenges

- Newer ferritic material cannot be fabricated into a long tubing
- Reaction of ferritic material with steam higher than anticipated
- Need to develop internal or external coating for ferritic cladding

Program Deliverables

- Comprehensive technical reports containing data and recommendations for next phase
- Commercialization, regulatory and business plans for installing a lead test assembly into an operating power reactor by 2022

Anticipated Benefits of the Proposed Technology

- A cladding material more tolerant to accident damage, with
  - superior resistance to environmental cracking
  - slower hydrogen generation rate
  - higher structural integrity at the higher temperatures

Justification for the Proposal

Advanced Steels

- Ferritic Steels have Low Coefficient of Thermal Expansion and High Thermal Conductivity
- Orders of Magnitude More Resistant to Environmental Cracking than Austenitic Steels
- Good Mechanical Properties even Above Operation Conditions
- Resistant to Radiation Damage such as Swelling
- Ferritic Steels have Reduced Nickel for Activation and Lower Cost
- Combination of Chromium and Aluminum Provide Protection Against Attack by Steam

Steels Selected to Study

Original Materials in Proposal	**ID**	**Composition**
Zircaloy-2	A	Zr + 1.2-1.7 Sn + 0.07-0.2 Fe + 0.05-0.15 Cr + 0.03-0.08 Ni
Ferritic steel T91	B	Fe + 9 Cr + 1 Mo + 0.2 V
Ferritic steel HT9	C	Fe + 12 Cr + 1 Mo + 0.5 Ni + 0.5 W + 0.3 V
Nanostructured ferritic alloys - 14YWT	D	Fe + 14 Cr + 0.4 Ti + 3 W + 0.25 Y2O3
Newer Identified Candidates		
MA956	E	Fe + 18.5-21.5 Cr + 3.75-5.75 Al + 0.2-0.6 Ti + 0.3-0.7 Y2O3
APMT	G	Fe + 22 Cr + 5 Al + 3 Mo
E brite	H	Fe + 25-27.5 Cr + 1 Mo + 0.17 (Ni + Cu)
Alloy 33	J	33 Cr + 32 Fe + 31 Ni + 1.6 Mo + 0.6Cu + 0.4 N
8 Newer Alloys (4 NFA and 4 Traditional)	X	Fe-Cr-Al alloys (X9, X12, X16, X20)

Approach to Study and Rate the Steels

Environmental Degradation Under Normal Operation Conditions

Environmental Degradation Under Accident Scenarios

Fabrication Capabilities

Regulatory Analysis, Fuel Economy

Resistance to Stress Corrosion Cracking Under Normal Operation Conditions

Selected Current Tests at GE GRC

Currently Under Testing Crack Propagation under Normal Operation Condition

1) HT9 neutron irradiated material from PNNL
2) Non-irradiated Candidate Materials
    - 14YWT (NFA)
    - Alloy 33
    - T91
    - HT9
    - APMT

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Testing Procedure

Resistance to environmental crack propagation is determined by using compact specimens

The specimens contain a notch and an air or hot water fatigue pre-crack

Crack advance is continuously monitored in situ by using the potential drop technique

The conductivity of the solution and the open circuit potential of the specimens are also monitored

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Standard Testing Conditions BWR

- Autoclave, water board, pumps, meters
- 288°C (550°F)
- 2 ppm dissolved oxygen – NWC
- 63 ppb dissolved hydrogen - HWC
- 30 ppb sulfate contamination (to increase aggressiveness of the environment)
- Load applied is generally 25-50 ksi√in
- Initially the load is cyclic to establish a crack growth and it is later transitioned to static load

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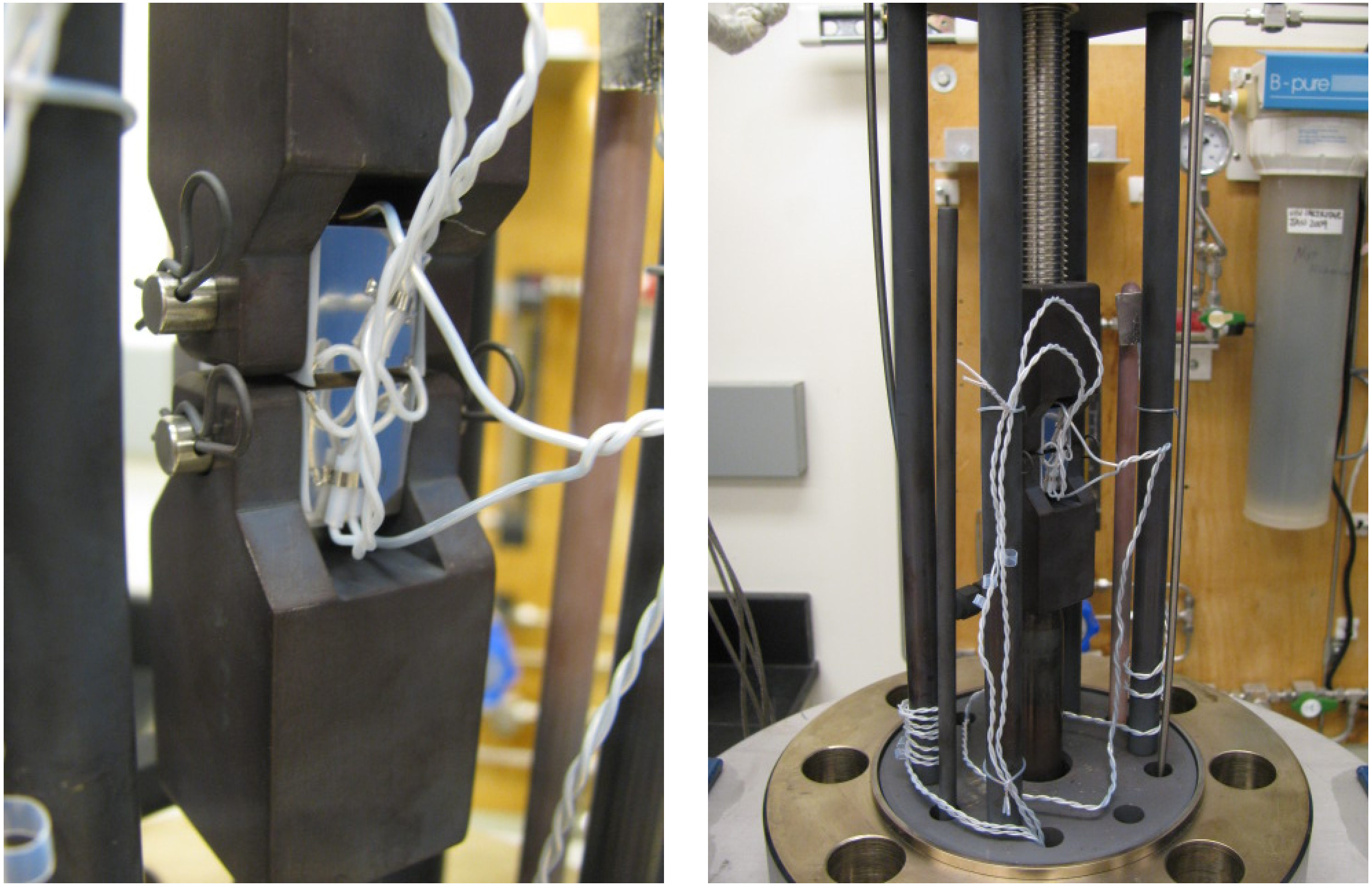
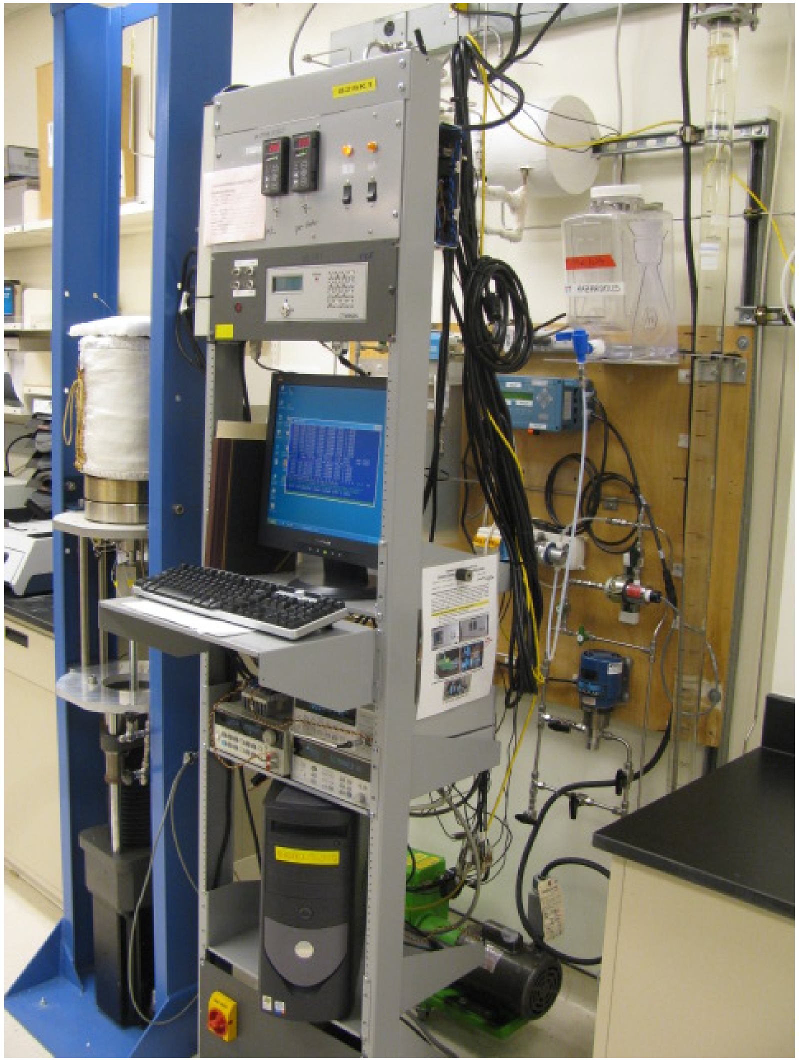
Specimen mounted for testing in the autoclave frame



Standard Type of CGR Testing



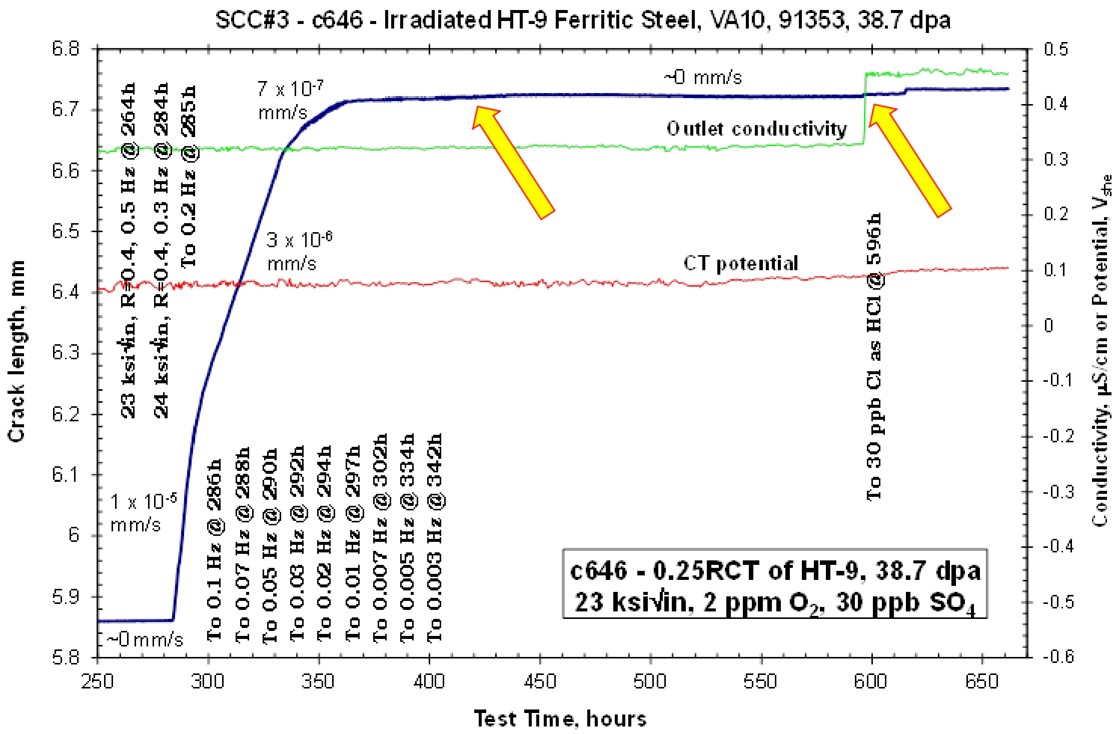
Specimens Cut from Plate in the S-L Direction

For example, plates may be initially 2.0 inch thick.
Reduced in thickness (cold forging) by 20% at ambient temperature

Testing Protocol

- Start with 25 ksi√in (27.5 MPa √m) stress intensity
  - R = 0.6, f = 0.001 Hz, h = 0
  - R = 0.6, f = 0.001 Hz, h = 9000 sec
  - R = 1, Constant Load
- Increase K = 30 ksi√in, repeat series
- Increase K = 35 ksi√in
- Increase K = 40 ksi√in
- Increase K = 45 ksi √ in (49.5 MPa √ m)
- Increase K = 50 ksi √ in (55 MPa √ m)

Highly Irradiated HT9 (38.7 dpa) Extremely Resistant to Environmental Cracking



Under 23 ksi√in, R = 0.4 and high frequency the crack may grow; however, as the frequency is continuously reduced the crack stops growing.

Replacing the Sulfate with Chloride at 596 h does not reactivate the crack

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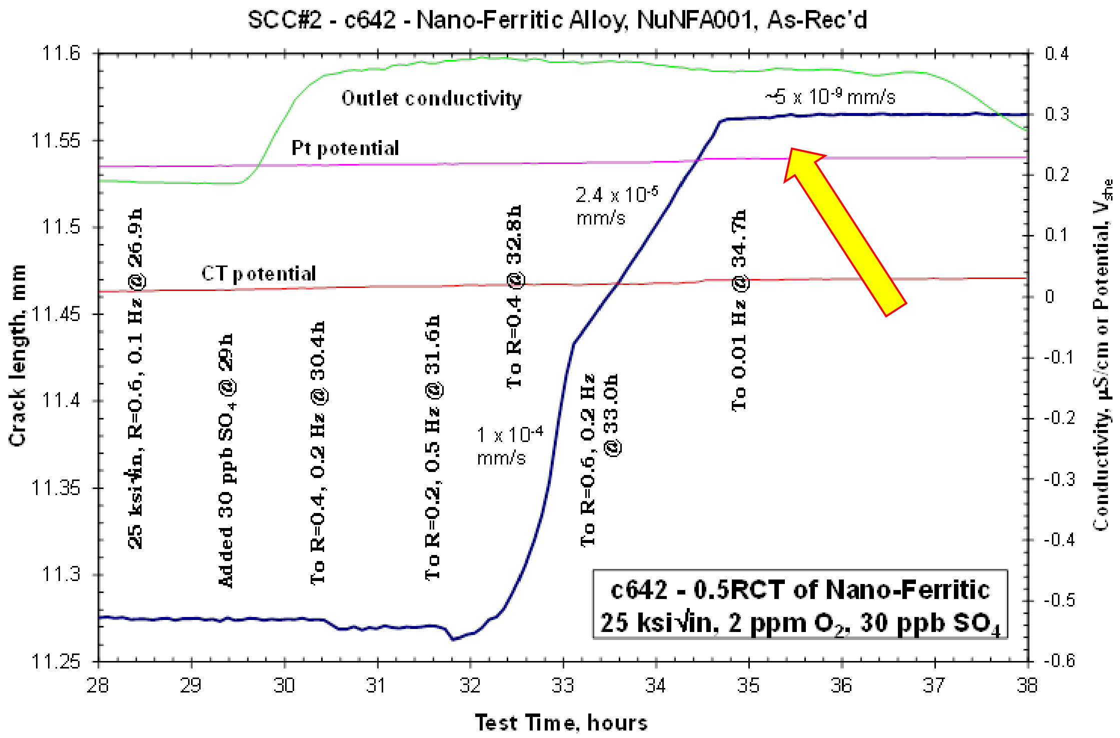
Testing of Alloys Under Non-Irradiated Conditions

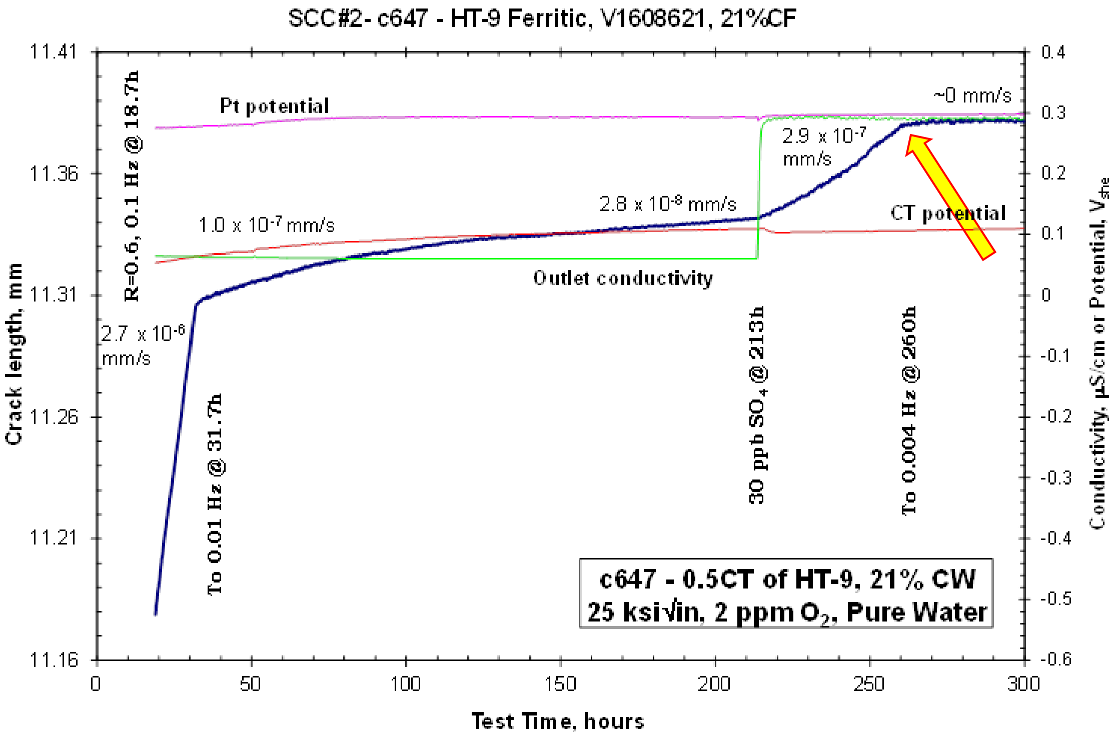
Specimen ID	Specimen, Condition	Alloy, Heat	Testing System	Comments
c642	0.5TCT, As-Fabricated	Nuclear NFA, Experimental	84SK9	In testing
c647	0.5TCT 21% CF	HT-9 V1608621	82SK1	In testing
c648	0.5TCT 23.2% CF	APMT, melt 241975	84S3	In testing
c649	0.5TCT 22.6% CF	T91, A122133	84SK11	In testing

As-Received Nano-Ferritic Alloy Extremely Resistant to Environmental Cracking



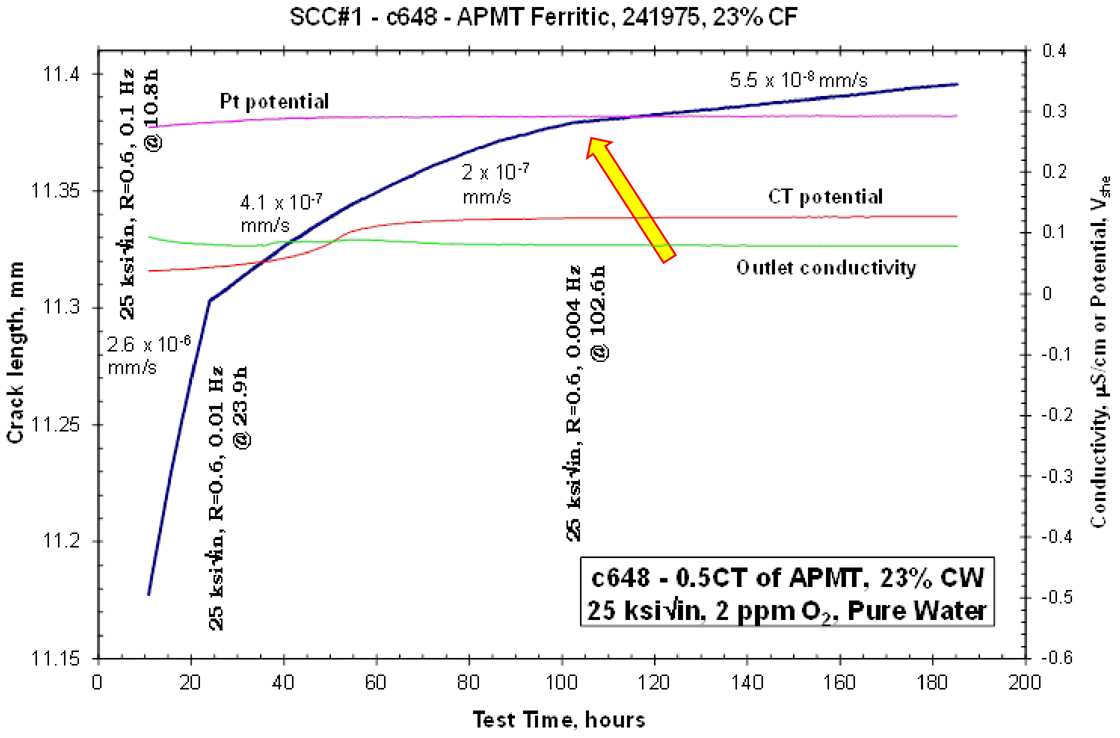
Under 25 ksi√in, R = 0.6 and high frequency the crack may grow at f = 0.2 Hz; however, as the frequency is reduced to 0.01 Hz the crack dramatically stops growing.

21% Cold Worked Ferritic HT9 Extremely Resistant to Environmental Cracking



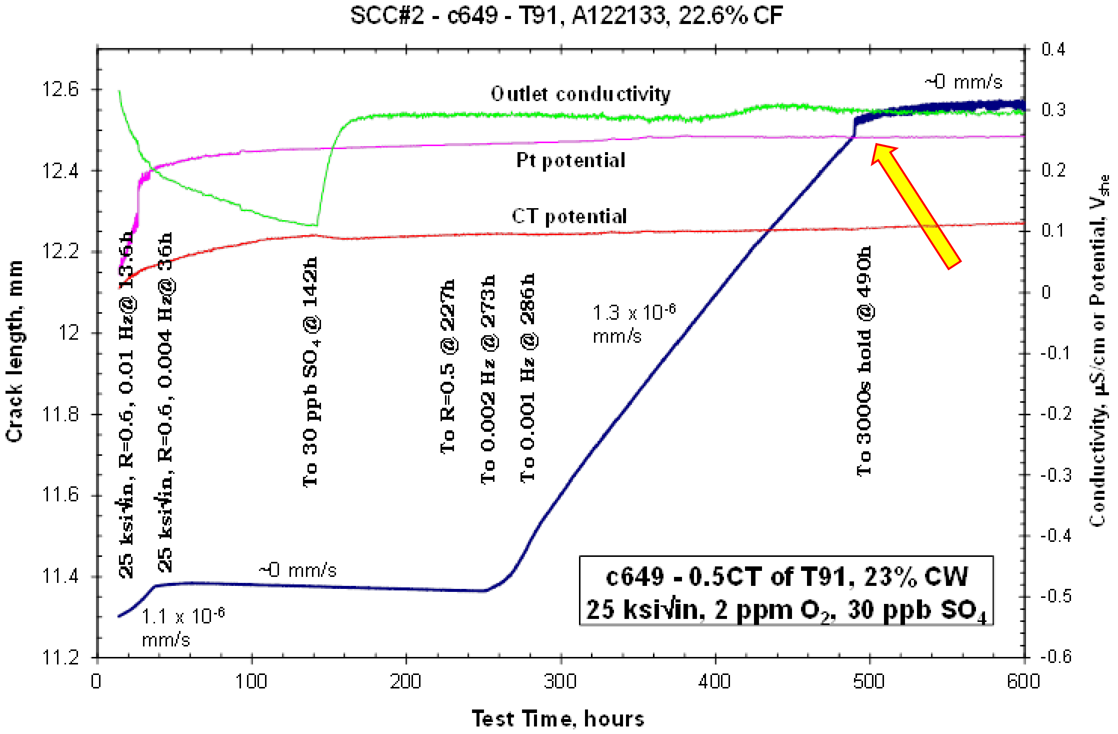
Under 25 ksi√in, R = 0.6 and high frequency the crack may grow at f = 0.01 Hz; however, as the frequency is reduced to 0.004 Hz the crack stops growing.

23% Cold Worked Fe-Cr-Al APMT Resistant to Environmental Cracking



Under 25 ksi√in, R = 0.6 the crack slows down at lower frequencies – This specimen was not transitioned to constant load yet.

23% Cold Worked 9Cr0.5Mo T91 Extremely Resistant to Environmental Cracking



Under 25 ksi√in, R = 0.5 the crack stops growing at lower frequencies

Resistance to General and Localized Corrosion Under Normal Operation Conditions

Immersion Corrosion Tests under Normal Operation Conditions

BWR, 288°C, Normal Water Chemistry

BWR, 288°C, Hydrogen Water Chemistry

PWR, 330°C, High Purity Water

- Zircaloy-2
- T91
- HT9
- 14YWT (NFA)
- Alloy 33
- MA956
- APMT

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Advanced Steels Reaction with Superheated Steam

1 - GE Global Research
2 – LANL – TGA
3 – ORNL – Severe Test Station

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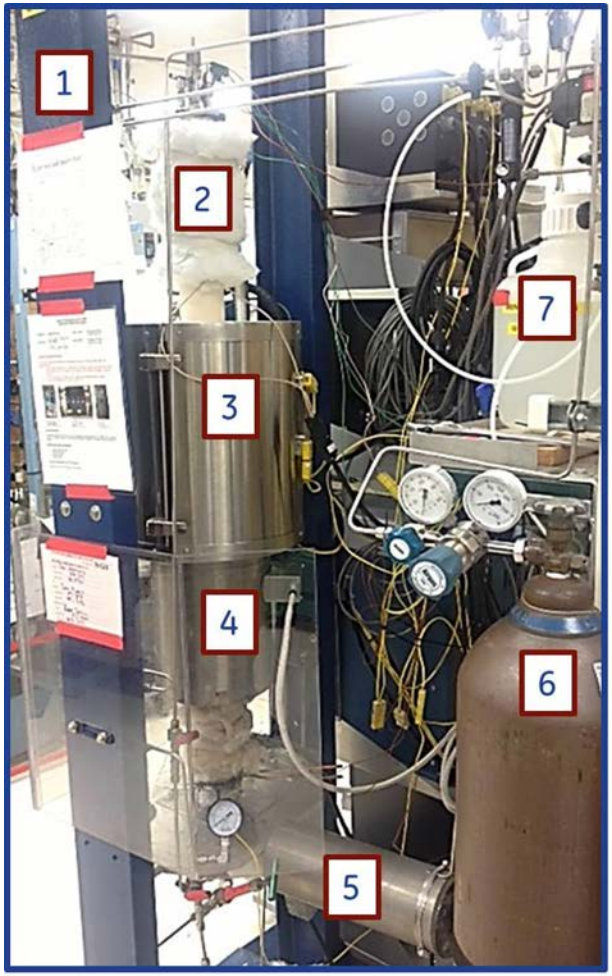
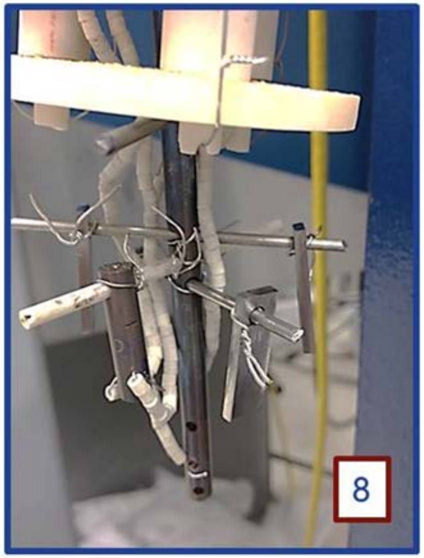
Testing Conditions at GE Global Research 400 to 1000°C





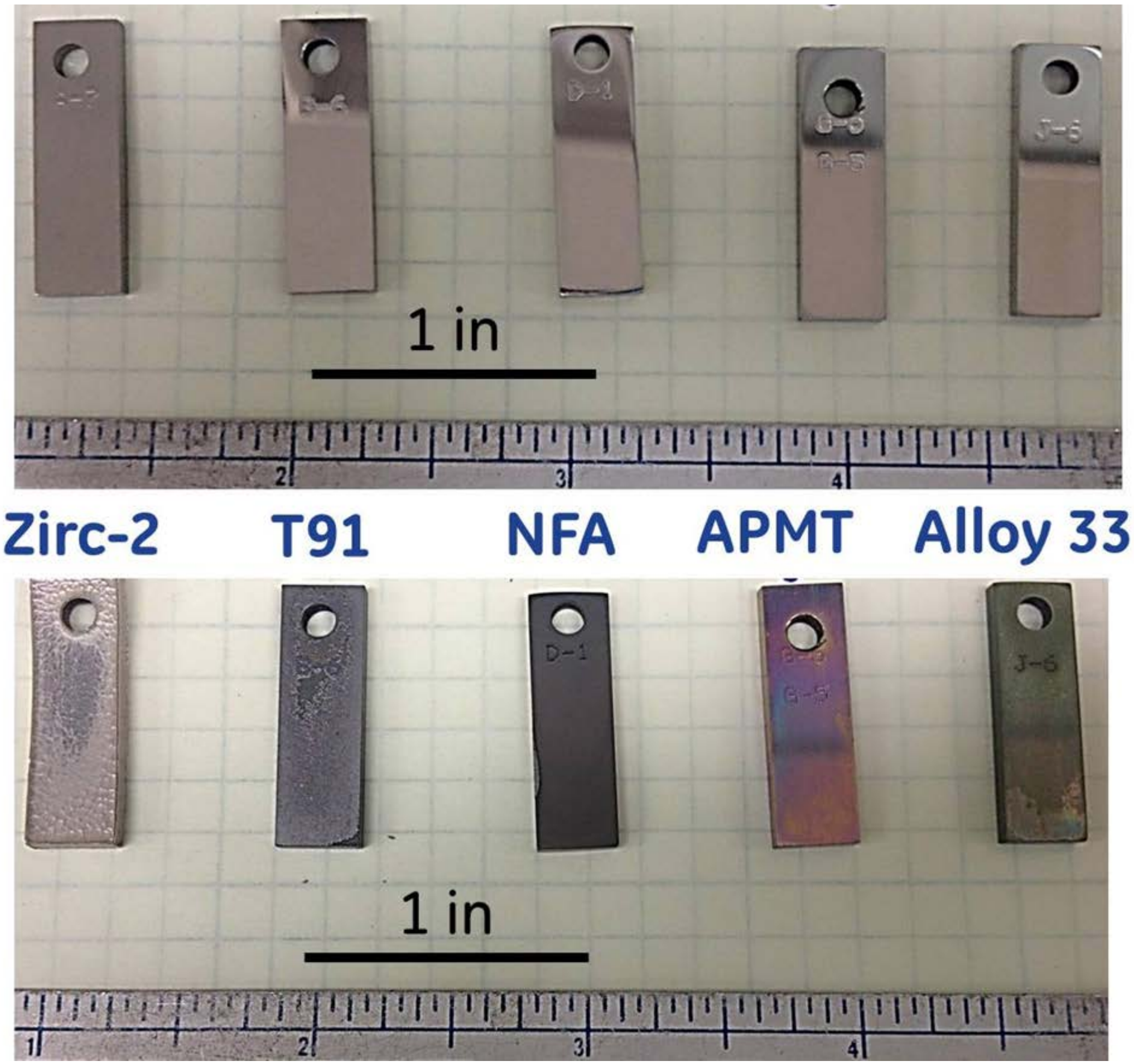
1. Operational instructions
2. Alumina retort
3. 3-heating zones furnace
4. Preheater
5. Steam generator
6. Testing gas
7. Water reservoirs
8. Specimens holder

Testing Conditions at GE Global Research 400 to 1000°C

Before

8 hours pure steam test at 800°C and 2.5 g/min injection flow rate

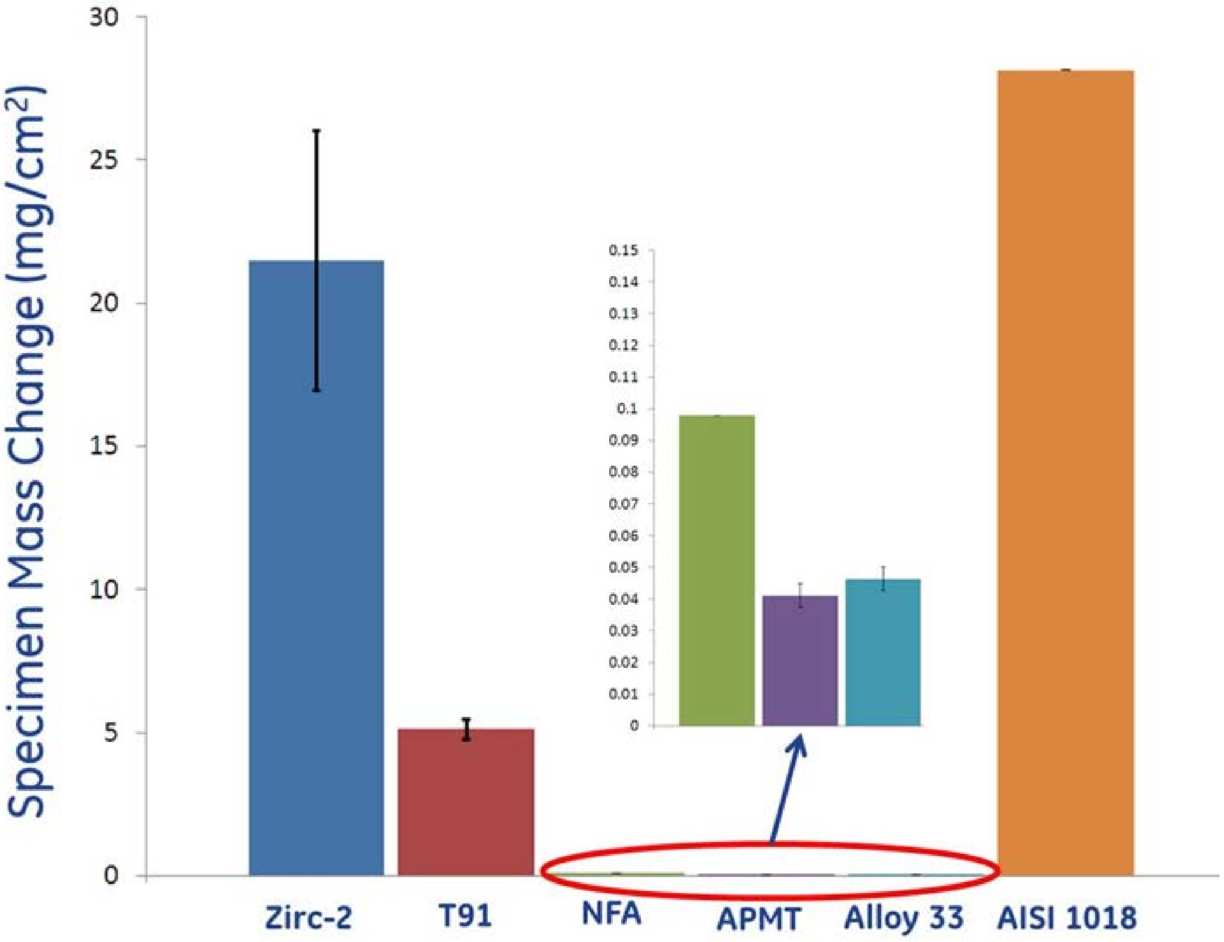
After



Testing Conditions at GE Global Research 400 to 1000°C

8 hours steam test at 800°C and 2.5 g/min

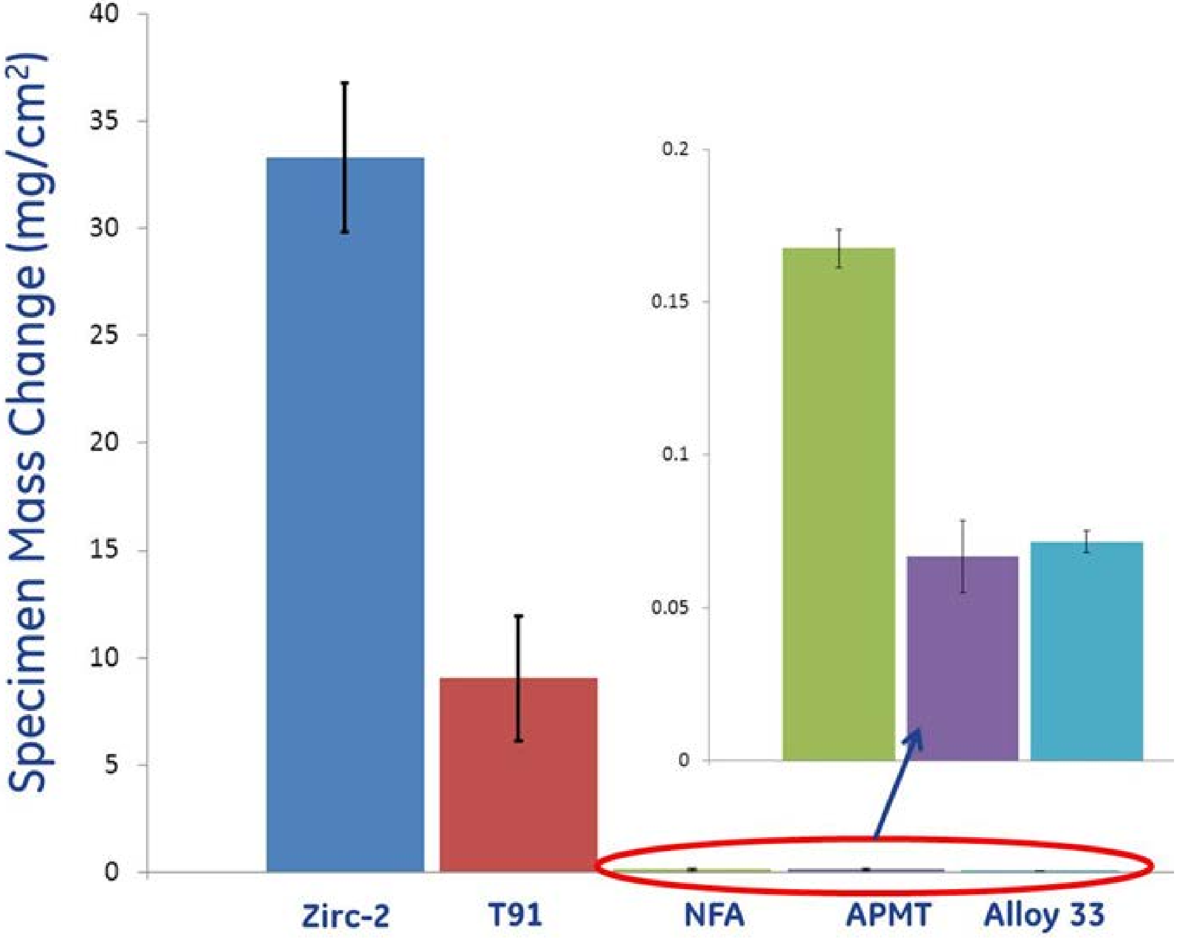
The lowest mass change was for APMT



Testing Conditions at GE Global Research 400 to 1000°C

24 hours steam test at 800°C and 2.5 g/min

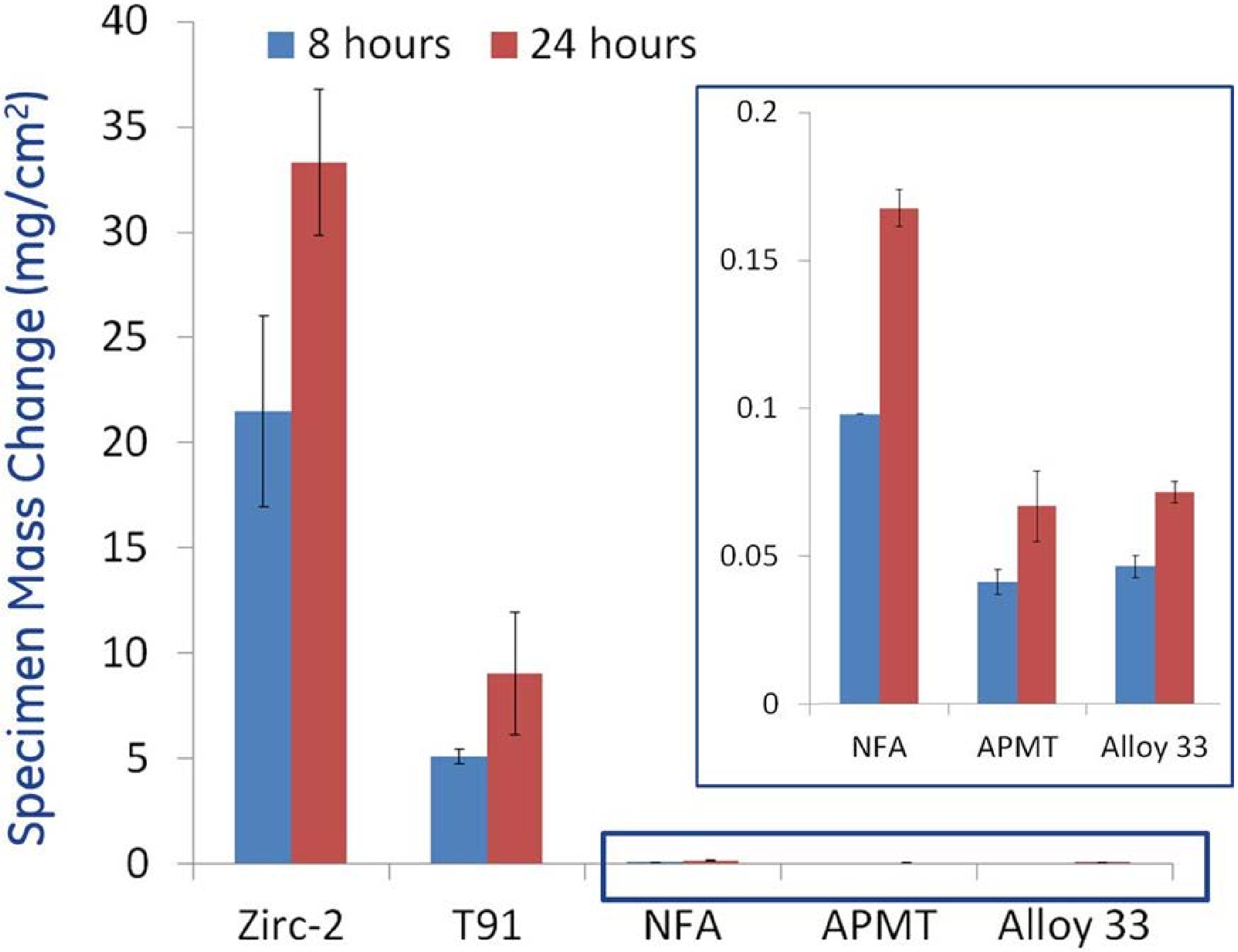
The lowest mass change was for APMT



Testing Conditions at GE Global Research 400 to 1000°C

8 & 24 hours steam test at 800°C and 2.5 g/min

The lowest mass change was for APMT & Alloy 33



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Tests at LANL in Steam at T > 1000°C

Thermal Gravimetric Analysis (TGA) tests to determine

- Reaction Rate with Steam
- Hydrogen Gas Generation Rate
- 7 alloys are being tested (140 coupons)
    1. Zirc-2
    2. T91
    3. NFA - 14YWT
    4. MA956
    5. APMT
    6. Ebrite
    7. Alloy 33

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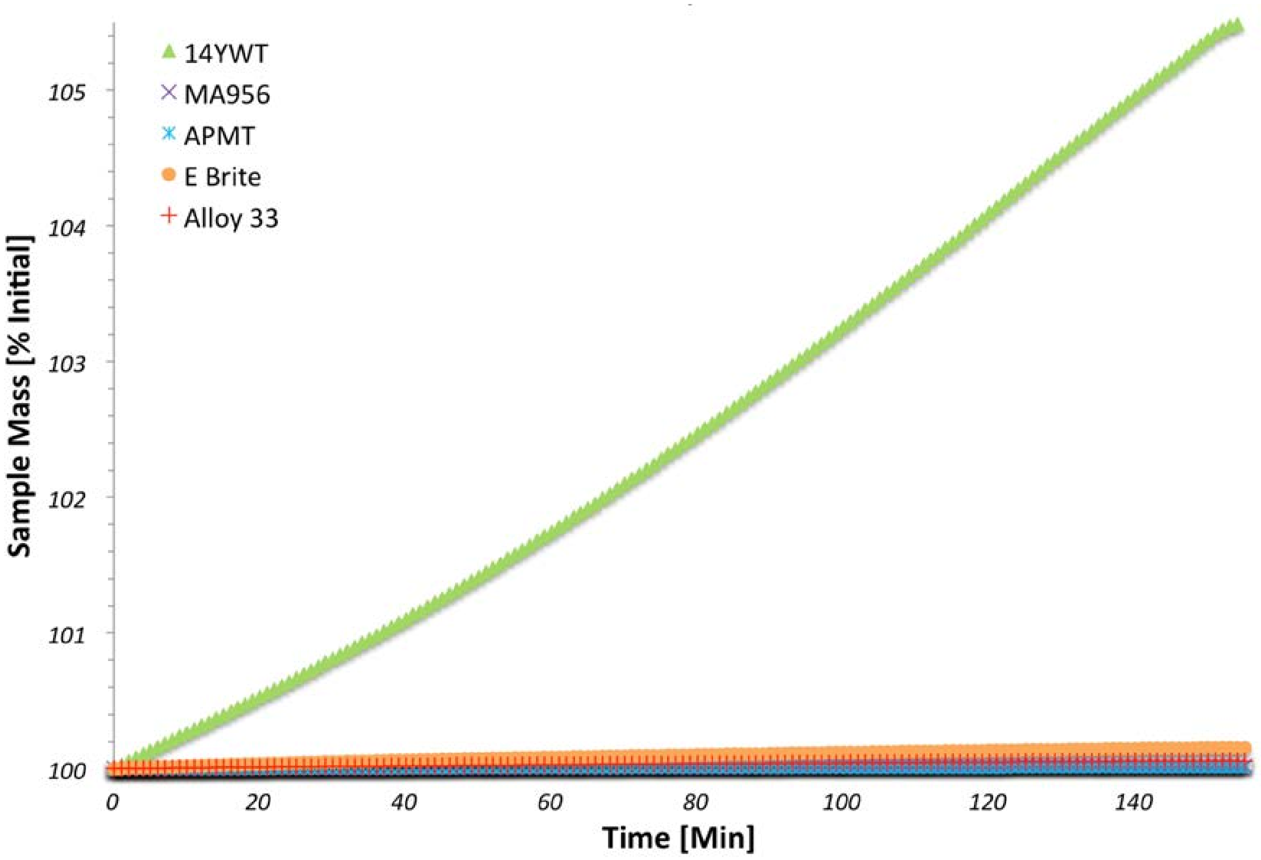
Testing Conditions at LANL, 1100°C

3 hours 100% steam test at 1100°C

T91 and Zirc-2 were not tested

14YWT is the only alloy showing weight gain due to oxidation at this scale

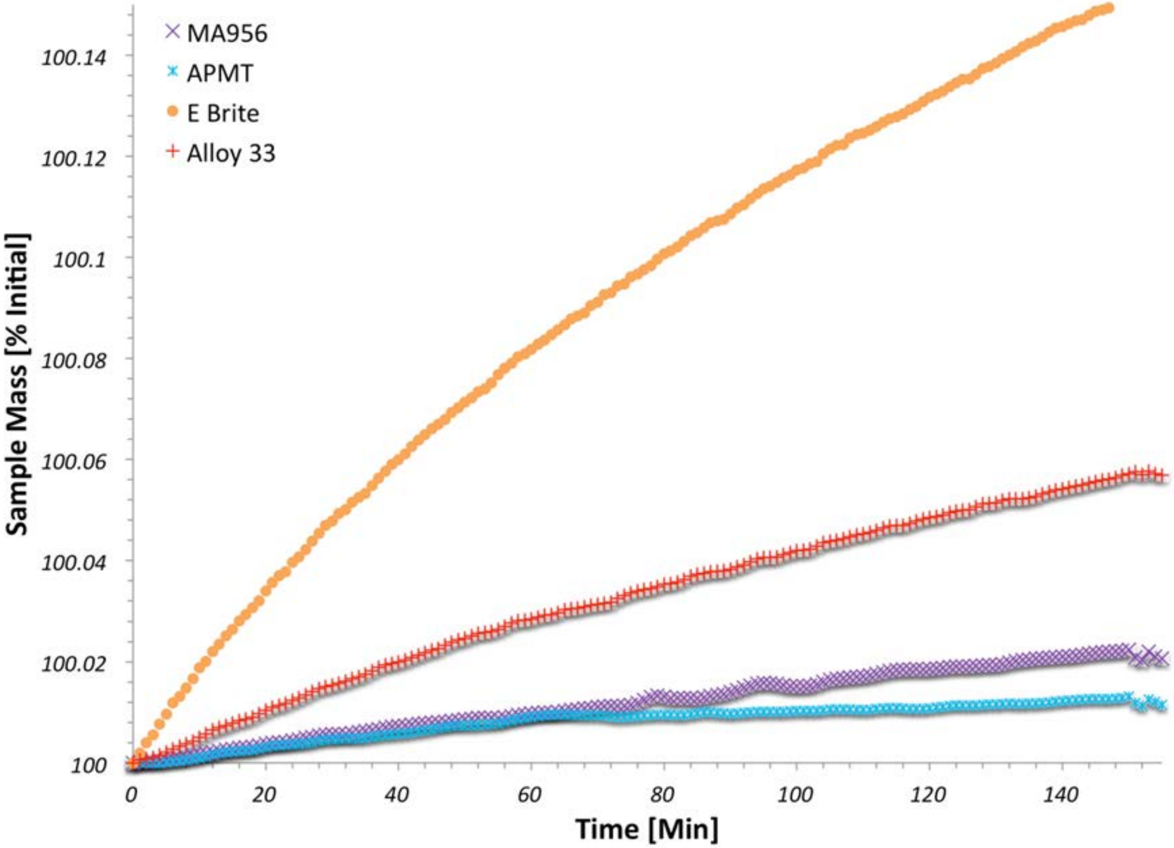


Testing Conditions at LANL, 1100°C

3 hours 100% steam test at 1100°C

Same as previous slide with 14YWT excluded

All four of the materials exhibit parabolic oxidation



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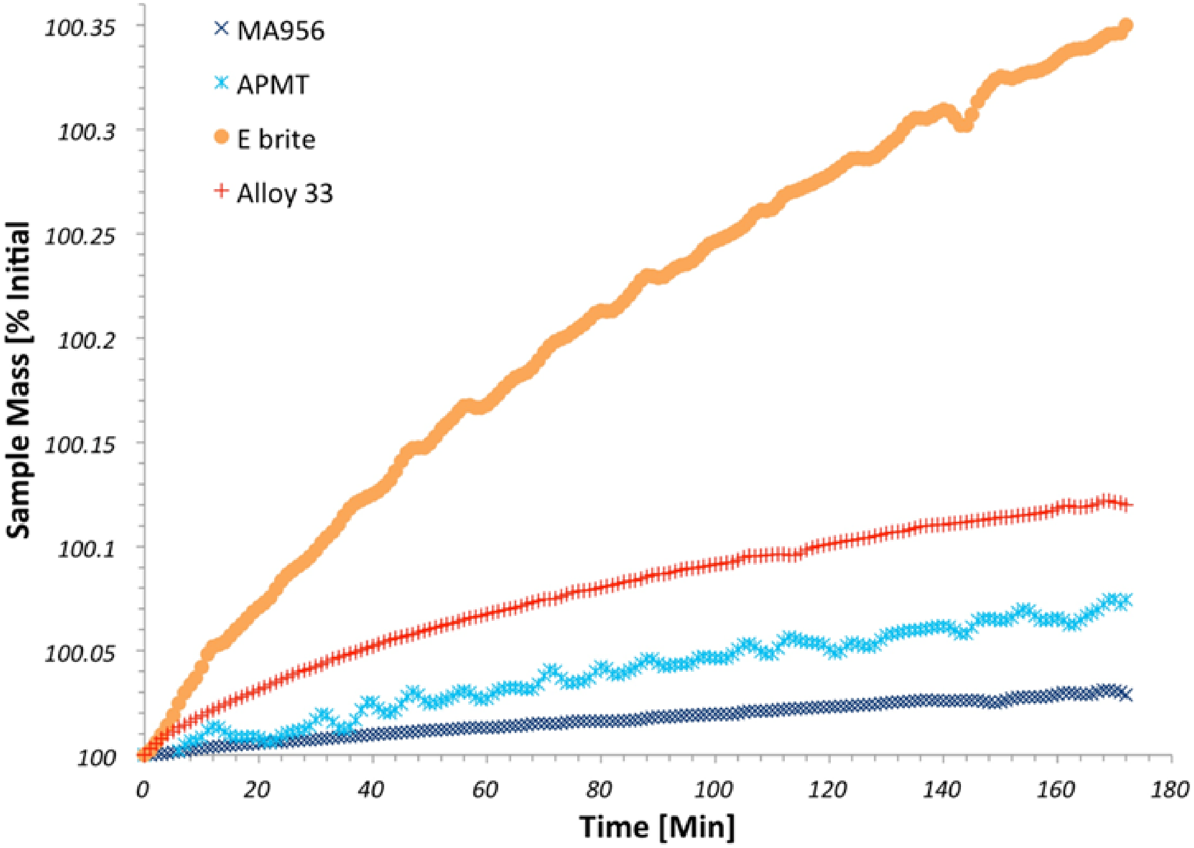
Testing Conditions at LANL, 1200°C

3 hours 100% steam test at 1200°C

APMT and MA956 had the slowest reactions with steam

All four of the materials exhibit parabolic oxidation



Tests at ORNL in Steam at T > 1200°C

The initial list of coupons included 5 for each alloy.

1. NFA - 14YWT
2. MA956
3. APMT
4. Ebrite
5. Alloy 33

The first tests will be at 1200°C steam, for 4h.

Based on the results, the matrix at higher temperatures (1400°C and 1475°C) will be established.

Tests at the U. of Michigan

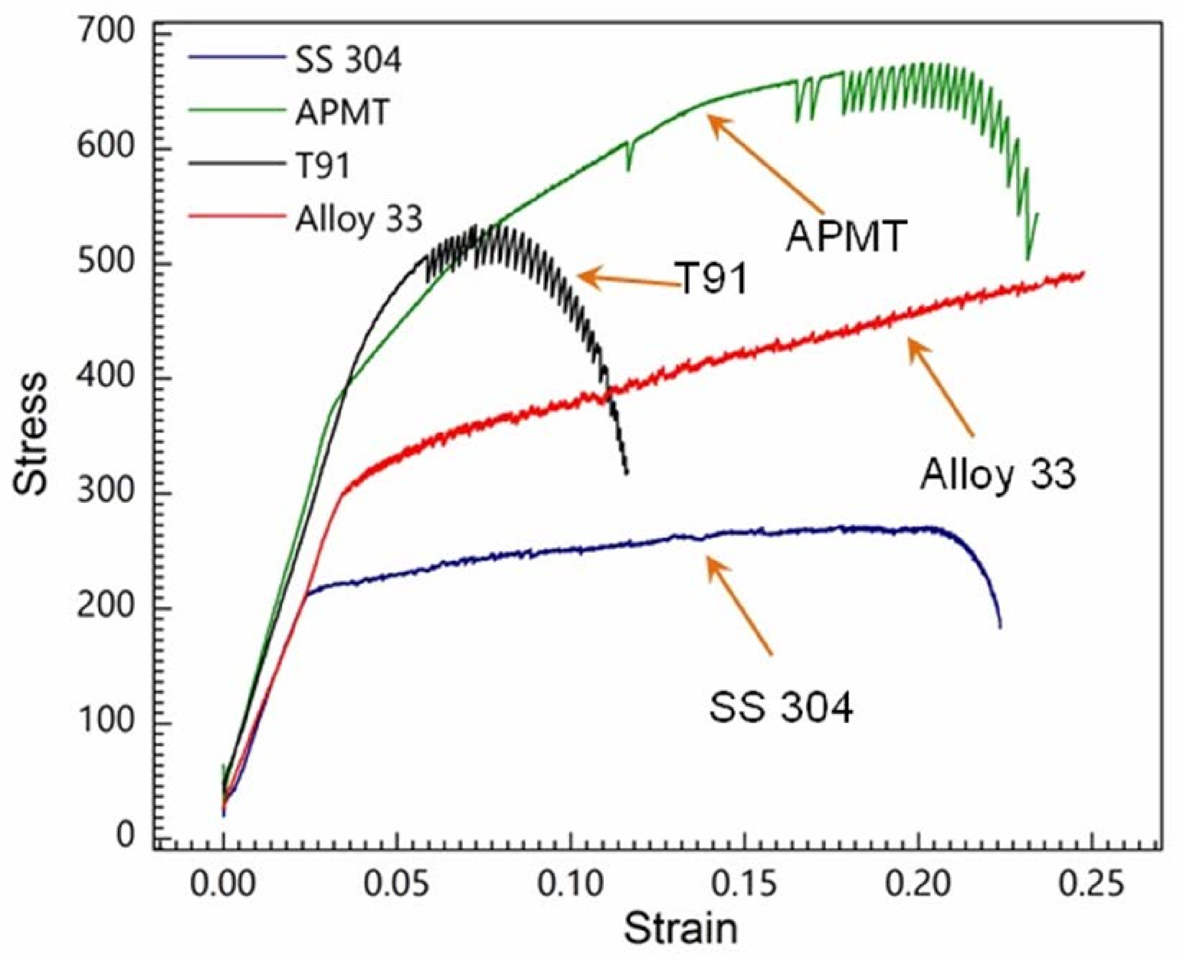
Selected Current Tests – U. of Michigan

1) Proton irradiation of candidate ferritic-martensitic alloys to a dose in the range 10 dpa and at a temperature near 400°C.
2) Microstructure characterization of the proton irradiated nano-ferritic alloy, including determination of the dislocation microstructure, void formation, precipitate formation and radiation-induced segregation. This task will also include measurement of hardness of all irradiated alloys
3) Constant extension rate tensile (CERT) testing on both non-irradiated and proton-irradiated samples in a water environments consistent with other SCC tests conducted at GE GRC
4) CERT testing of neutron irradiated tensile samples of comparable alloys to irradiation conditions relevant to LWR fuel cladding

Slow Strain Rate Testing at U. Michigan

Stress-strain curves for 4 alloys in argon atmosphere at 288°C with a strain rate of 3 × 10^{-7} s^{-1}

Higher strain-hardening rate for ferritic-martensitic (FM) alloys T91 and APMT as compared to austenitic Alloy 33 and SS 304



Fabrication Studies

Tubing Fabrication Experience of Candidate Alloys

Material	Commercial Availability	Commercial Experience
T91	Yes	Currently processed to manufacture boiler and heat exchanger tubing (0.75" OD and 0.083" wall thickness)
APMT	Yes	Tubing fabricated using extrusion and pilger process at Sandvik. Smallest OD and wall thickness of 2.95" and 0.18", respectively.
NFA	No	No commercial experience
Alloy 33	No	No commercial experience. Currently only offered in sheet and plate. Although, Alloy 33 should process similar to other austenitic, high Cr alloys, such as Alloy 690 which is offered as a commercial thin wall tubing product.

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Summary and Conclusions

Summary and Conclusions - 1

- The objective of the GE project is to demonstrate that advanced steels could be used as accident tolerant fuel cladding material in commercial nuclear reactors
- The advanced steels need to perform as good as zirconium alloys under reactor normal operation conditions and better than zirconium alloys under accident conditions such as LOCA
- GE GRC teamed with the University of Michigan, Los Alamos National Laboratory and Global Nuclear Fuels to study the environmental and mechanical behavior of the advanced steels and to offer recommendations based on the findings
- Main studies include the characterization of eight or more alloys under normal operation conditions of commercial nuclear reactors and under accident conditions in superheated steam

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Summary and Conclusions - 2

1) Under normal operation conditions the candidate alloys (such as MA956, APMT, Alloy 33) showed excellent resistance to general corrosion and to environmentally assisted cracking
2) Under accident conditions the selected candidate materials showed several orders of magnitude improvement in the reaction with superheated steam as compared with the current zirconium based alloys.
3) Tube fabrication viability of Fe-Cr-Al alloys is in progress
4) Based on the current outcome of the experimental characterization testing, it is likely that an iron based alloy containing Cr and Al may be the best candidate to replace the current zirconium based alloys.

Buck up Slides

Benefits of Ferritic Steels (compared with austenitic)

- Lower cost (No Ni, lower Cr)
- No Ni or Co activation in commercial nuclear reactors
- Resistant to swelling from radiation damage
- Low coefficient of thermal expansion (matching CTE of pressure vessel material)
- Higher thermal conductivity

Comparative Thermal Conductivity and Coefficient of Thermal Expansion

Steel	CTE (0-538°C) µm/m/°C	Thermal Conductivity at 100°C (W/m.K)
Ferritic type 430 (16% Cr)	11.4	23.9
Austenitic type 304L (18% Cr)	18.4	16.2

Preliminary comparison Austenitic (18%Cr) vs. Ferritic (17% Cr)

Type 304 or 316 SS Austenitic, 20% CW, K= 25 ksi√in, 288°C water, NWC	**~1 x 10^{-7} mm/s** **3 mm/year**
Type 430 17Cr ferritic steel Similar conditions	**<1 x 10^{-9} mm/s** **30 µm/year (two orders of magnitude lower)**

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Common Variables Studied

Susceptibility to SCC is assessed at GE GRC by measuring the crack growth rate = CGR in a compact specimen

e.g. CGR = 10^{-8} mm/sec = 315 µm/year

In general it is known that

CGR ↓ when Cr ↑ T ↓ K_I ↓ OCP ↓ CW ↓

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