

SECTION A. Project Title: High-Throughput Spark-Plasma Sintering of Compositional Arrays

SECTION B. Project Description and Purpose:

Many advanced nuclear reactor concepts require subjecting structural materials to higher temperatures and irradiation doses than most code-certified materials are capable of withstanding. To address this need, new materials, such as high-entropy alloys (HEAs), are being investigated and many have been found to exhibit promising resistance to irradiation damage. While several HEAs appear promising, only a handful of compositions have been used in irradiation studies and the mechanisms for irradiation damage resistance are HEAs is still unsettled. To expand the experimental knowledgebase of HEAs for nuclear applications, the proposed work will adapt spark-plasma sintering (SPS) into a high-throughput (HTP) synthesis technique to rapidly produce arrays of multiple alloy compositions on a single substrate. The compositional arrays will be irradiated using heavy ions, in a high-throughput fashion, to damage levels comparable to end-of-life conditions in proposed advanced reactors. The microstructure and thermal transport properties will be measured before and after irradiation using automated, HTP characterization techniques developed and deployed at Idaho National Laboratory (INL). Specifically, the thermal diffusivity of each alloy will be examined and compared against the volumetric void swelling after irradiation to examine whether this property can be used to predict irradiation-resistant HEAs over a broad range of alloy compositions, as has been posited in literature. From this work, irradiation-resistant HEA compositions will be experimentally identified for potential nuclear applications, thermal diffusivity will be examined as a potential predictor for irradiation tolerance in HEAs, and a new high-throughput synthesis technique will be developed at INL using already existing equipment.

To surpass the challenges of other HTP synthesis techniques, the approach proposed herein is to use a set of custom punches and dies to produce several compositional arrays of standard and novel alloys (e.g., HEAs) using the SPS systems already in use at INL. Compositional arrays of different alloys would then be subjected to ion irradiation and characterized before and after in parallel with one another. The results from the irradiation experiments will yield insight into the origins of the radiation tolerance of novel HEAs, and more broadly complex concentrated alloys (CCAs), which is not fully understood. Specifically, by examining the thermal diffusivity and irradiation response of each alloy produced, theories from literature, which suggest the thermal diffusivity can be used to predict the relative irradiation tolerance of HEAs and CCAs, can be validated over a large range of alloy compositions to determine if these theories apply universally or only to the limited number of alloys which have been examined thus far. If broadly applicable, the implications for designing new radiation-resistant materials are substantial, as lower thermal diffusivities are thought to limit the number of surviving defects in a material following interaction with energetic particles, which ultimately governs every aspect of irradiation damage evolution including void swelling, radiation-induced segregation (RIS), and radiation embrittlement. At the conclusion of the project, promising alloy compositions for advanced nuclear applications will be identified and the relationship between thermal diffusivity and irradiation damage accumulation will be better elucidated. More broadly, the experimental results could be used to inform modeling and alloy development efforts for advanced nuclear applications, while the process developed to produce compositional arrays using SPS constitute a new high-throughput synthesis technique that would have major implications for the materials science community. Additionally, this work can be easily coupled to produce sample arrays for other INL projects and more generally be used to support the Advanced Materials and Manufacturing for Extreme Environments (AMMEE) initiative and the Nuclear Materials Discovery and Qualification Initiative (NMDQI). There are multiple projects currently underway at INL dedicated to developing materials for advanced reactors which would benefit from the proposed research produces an opportunity for synergistic activities between different programs.

The project will have two major objectives to be completed in series. Firstly, over fiscal year 2022 (FY2022), the high-throughput SPS process will be developed, validated, and used to produce sets of chromium-iron-nickel-based (Cr-Fe-Ni-based) compositional arrays with additional transition and refractory element additions. Once a complete set of ~100 unique alloy compositions has been produced, each alloy will be irradiated using heavy ions to simulate end-of-life damage levels in an advanced fast-neutron reactor environment in fiscal year 2023 (FY2023). The microstructure and thermal properties of each sample will be characterized before and after irradiation using high-throughput characterization techniques at INL during FY2022 and FY2023. Specific details are given below:

Development of HTP SPS process (FY2022). Adapting the already existing SPS systems at INL to be able to produce many different alloys in parallel (and thus a high-throughput synthesis technique) is thought to be achievable by customizing the consumable tooling rather than needing to modify the base equipment at all. To produce compositional arrays using SPS, a custom set of graphite punches and dies that has been designed, featuring an array of cavities to contain each alloy mixture, will be machined with a conventional mill on-site. Powder mixtures for each custom alloy will be produced by weighing different combinations of elemental powders and mechanically mixing them in parallel using the Turbula three-dimensional (3D) powder mixer at the INL Research Center (IRC). The machined cavities in the custom graphite punch will each be manually loaded with a unique alloy powder mixture and a filler metal will be added to transfer pressure and electrical current during the SPS process as well as form the substrate of the compositional arrays. Small-scale trials using "well-behaved" elements (e.g., Cr, Fe, Ni) will be performed using the Thermal Technologies DCS-5 SPS system at IRC. Once initial synthesis parameters are determined (e.g., time, pressure, current density), additional elements will be added including more volatile species (e.g., aluminum, manganese) and refractory metals (e.g., molybdenum, tungsten) to determine the range of compositions which can be produced at once using a single set of SPS parameters. After the SPS processing parameter window has been determined, a batch of ~100 unique alloys, spanning the Cr-Fe-Ni-(additional element) composition space, will be produced as multiple sample arrays of a standardized geometry.

HTP ion irradiation experiments (FY2023). To perform the ion irradiations in a high-throughput manner which supports the goal of accelerating every step of the experimental process, the University of Wisconsin-Madison will be subcontracted to irradiate each of the ~100 alloys. With the newly developed Chronos system, the University of Wisconsin-Madison Ion Beam Laboratory (IBL) is uniquely equipped to perform high-throughput, high-temperature ion irradiations while minimizing damage annealing challenges which are posed by irradiating large arrays of samples in close proximity to one another. Utilization of the Chronos system will allow the SPS sample arrays to be irradiated without requiring additional machining following synthesis and will allow sample preparation to be reduced to a single polishing procedure where each of the samples in the array can be polished simultaneously while they remain attached to their shared substrate. The top surface of each sample will be irradiated using 4-MeV Ni²⁺ ions to a peak dose of 200 dpa at 600°C, near the peak swelling temperature for most alloys in the Cr-Fe-Ni at the dose rates used at the IBL, to promote void swelling. The irradiated alloys will then be sent back to INL for post-irradiation examination (PIE).

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HTP thermal property and microstructural characterization (FY2022/FY 2023). Thermal property and microstructural characterization both before and after irradiation is necessary to determine how the material properties and features evolve under irradiation. Additionally, by comparing the thermal diffusivity before irradiation to the microstructural evolution after irradiation for each alloy, it should be possible to assess whether a low thermal diffusivity can be universally used as a predictor for improved irradiation resistance in multicomponent alloys. Prior to ion irradiation, samples in the compositional arrays will be mechanically polished in parallel by placing the compositional array (pictured in Figure 1b) with the sample facing downward in a vibratory polisher. Each polished compositional array will be loaded into a scanning electron microscope (SEM) to measure the initial porosity, grain size, overall composition, and phase composition for every samples. X-ray diffraction (XRD) then be used to determine the crystal structure of the phases in each sample. Using the laser-based transient-grating spectroscopy (TGS) technique, the thermal diffusivity of each alloy will be measured non-destructively prior to irradiation. After irradiation, XRD and TGS will be reperformed to determine if any additional phases have formed as a result of irradiation and to examine how the thermal diffusivity, which can be affected by the presence of point defects, is impacted by the irradiation. Use of the TGS technique is particularly well suited for ion-irradiated materials as the probing depth in on the order of microns (similar to the ion implantation depth), which allows for measurements to be taken from the ion irradiated region without being washed out by signal from the unirradiated material beneath it. To determine the extent of void swelling in each sample, the irradiated arrays will be characterized using the state-of-the-art G4 plasma focused-ion beam (PFIB) located in the Irradiated Materials Characterization Laboratory The high-throughput SPS process will be developed, validated, and used to produce sets of chromium-iron-nickel-based (Cr-Fe-Ni-based) compositional arrays with additional transition and refractory element additions. Once a complete set of ~100 unique alloy compositions has been produced, each alloy will be irradiated using heavy ions to simulate end-of-life damage levels in an advanced fast-neutron reactor environment. The microstructure and thermal properties of each sample will be characterized before and after irradiation using high-throughput characterization techniques at INL. (IMCL). Using the PFIB, small trenches will be milled away on the surface of each sample using Xe ions to carve a window into the irradiation damage layer, produced by heavy ion irradiation, and image the voids that are present. Both the trenching and the imaging of each irradiated sample will be done in a completely automated fashion to support the high-throughput nature of this work. By measuring the void distributions in each sample, 1) promising irradiation-resistant HEA compositions can be identified from the batch of ~100 alloy compositions and 2) the hypothesis that a lower thermal diffusivity can retard irradiation damage accumulation can be tested by comparing the void swelling of each alloy with the thermal diffusivities measured via TGS previously.

SECTION C. Environmental Aspects or Potential Sources of Impact:

Air Emissions

N/A

Discharging to Surface-, Storm-, or Ground Water

N/A

Disturbing Cultural or Biological Resources

N/A

Generating and Managing Waste

Generation of waste includes mixed metal powders (Cr, Fe, Mn, Ni, Al, W, and Mo (no nanopowders)). The amount of waste generated amounts to less than 1 liter in total waste over the course of the project lifetime. Some of the waste may be hazardous due to the presence of chromium. This waste will be characterized and disposed of according to INL procedures.

Releasing Contaminants

N/A

Using, Reusing, and Conserving Natural Resources

All materials will be reused and recycled where economically practicable. All applicable waste will be diverted from disposal in the landfill where conditions allow.

SECTION D. Determine Recommended Level of Environmental Review, Identify Reference(s), and State Justification: Identify the applicable categorical exclusion from 10 Code of Federal Regulation (CFR) 1021, Appendix B, give the appropriate justification, and the approval date.

For Categorical Exclusions (CXs), the proposed action must not: (1) threaten a violation of applicable statutory, regulatory, or permit requirements for environmental, safety, and health, or similar requirements of Department of Energy (DOE) or Executive Orders; (2)

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require siting and construction or major expansion of waste storage, disposal, recovery, or treatment or facilities; (3) disturb hazardous substances, pollutants, contaminants, or Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)-excluded petroleum and natural gas products that pre-exist in the environment such that there would be uncontrolled or unpermitted releases; (4) have the potential to cause significant impacts on environmentally sensitive resources (see 10 CFR 1021). In addition, no extraordinary circumstances related to the proposal exist that would affect the significance of the action. In addition, the action is not "connected" to other action actions (40 CFR 1508.25(a)(1) and is not related to other actions with individually insignificant but cumulatively significant impacts (40 CFR 1608.27(b)(7)).

References: 10 CFR 1021, Appendix B to subpart D, items B3.6, "Small-scale research and development, laboratory operations, and pilot projects."

Justification: The proposed R&D activities are consistent with CX B3.6 "Siting, construction, modification, operation, and decommissioning of facilities for small-scale research and development projects; conventional laboratory operations (such as preparation of chemical standards and sample analysis); small-scale pilot projects (generally less than 2 years) frequently conducted to verify a concept before demonstration actions, provided that construction or modification would be within or contiguous to a previously disturbed area (where active utilities and currently used roads are readily accessible). Not included in this category are demonstration actions, meaning actions that are undertaken at a scale to show whether a technology would be viable on a larger scale and suitable for commercial deployment."

Is the project funded by the American Recovery and Reinvestment Act of 2009 (Recovery Act) Yes No

Approved by Jason L. Anderson, DOE-ID NEPA Compliance Officer on: 03/17/2022