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Title: Additive Manufacturing of Hierarchical Multi-Phase High-Entropy Alloys for Nuclear Component

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Abstract

In recent years, high entropy alloys (HEAs), composed of four or more metallic elements mixed in equal or near equal atomic percent, have attracted significant attention due to their excellent mechanical properties and good corrosion resistance. They show significant promise as candidates for high temperature fission and fusion structural applications. However, the conventional synthesis methods are unlikely to present an industrially suitable route for the production and use of HEAs. Recognizing rapidly evolving additive manufacturing (AM) techniques, the goal of this proposal is to optimize the AM process to fabricate HEAs with pre-designed chemical compositions and phase morphologies for nuclear components. For this project, two HEAs FeCrNiMn and FeCrNiMnAl have been successfully synthesized. Correlated mechanical response has been systematically characterized under a variety of laser processing and ion irradiations. Both high entropy alloys are found to present comparable swelling and extraordinary irradiation tolerance (limited voids and stabilized phase structure under high irradiation dose). In addition, the microstructure and radiation-induced hardening can be tailored by laser processing under additive manufacturing. And we have assembled at LANL a unique database of HEAs containing a total of 674 compositions with Phase Stability information. Based on this, the machine learning and Artificial Intelligence capability now are established to predict the microstructure of casted HEAs by given chemical compositions. This unique integration will lead to an optimal AM recipe for fabricating radiation tolerant HEAs. The development of both modeling models and experimental capability will also benefit other programs at LANL.

Background and Research Objectives

The U.S. Department of Energy Global Nuclear Energy Partnership and Generation IV have proclaimed the need for new and clean sources of energy and for the urgent development of fusion power. In the recently published DOE report "Next Generation Materials: Technology Assessment" [1], innovative irradiation-resistant steels with lifespans up to 80 years by 2020 have been identified as a critical need. To accomplish this requirement is extremely challenging. It requires us to explore both the materials and the corresponding manufacturing processes. In recent years, high entropy alloys (HEAs), composed of four or more metallic elements mixed in equal or near equal atomic percent, have attracted significant attention due to their excellent mechanical properties and good corrosion resistance [2, 3]. They show significant promise as candidates for high temperature fission and fusion structural applications [4]. Due to high configuration entropy, the mutual solubility limits become extended, decreasing the chance to form the deleterious Cr-rich precipitates under irradiation [2]. Severe lattice distortion, as a consequence of the random distribution of several different sized atoms in the crystal lattice, successfully suppresses the diffusion process. In addition, the intense local strain is assumed to escalate the formation energy barrier of both interstitials and vacancies, and enhances the vacancy-interstitial spontaneous recombination radii. Consequently, the density of nucleated Frenkel pairs under radiation is expected to be low. Recent work on the quaternary FeNiMnCr alloy has uncovered high radiation damage tolerance of single fcc phase HEAs as compared to austenitic stainless steels [4].

However, the conventional synthesis methods are unlikely to present an industrially suitable route for the production and use of HEAs. Most of the HEAs are synthesized by arc melting or casting. However, during the melting process, the evaporation rate is different for chemical elements with different melting points, and thus the chemical composition cannot be precisely controlled. Limited fabrication variables, such as cooling rate and ensuing thermal treatment, are knobs to tailor the consequent phase morphology. On the other hand, recently emergent AM techniques provide a unique capability to build parts with novel geometries from high quality metal alloys, and opens a door for the production of breakthrough in products[5]. Especially, in comparison to the conventional arc melting or casting methods, laser processing is particularly advantageous in synthesizing HEAs due to its ability to reach the high instantaneous temperatures and associated high quench rates that lead to stabilizing the HEAs chemical composition and phase morphology. The rapid quenching becomes particularly important as HEAs undergo various phase transformations. Furthermore, rapid quenching restricts diffusion of the elements and inhibits nucleation and growth of the brittle intermetallic compounds. Another advantage of direct laser deposition is that the sample piece is created layer-by-layer, which eliminates the influence of the substrate and allows gradual chemical compositional changes through the growth[6].

Generally, the quality and properties of AM products are influenced by multiple manufacturing parameters, such as beam energy and shape, scanning trajectory and speed, powder shape, grain size & size distribution, and impurities. In this project, in order to avoid complicated manufacture processing variables, we simulate the synthesis process in AM by surface laser scanning on bulk alloys. As shown in Fig. 1, this project is focusing on the influence of laser processing variables on material microstructural evolution and how the resulting mechanical/irradiation response.

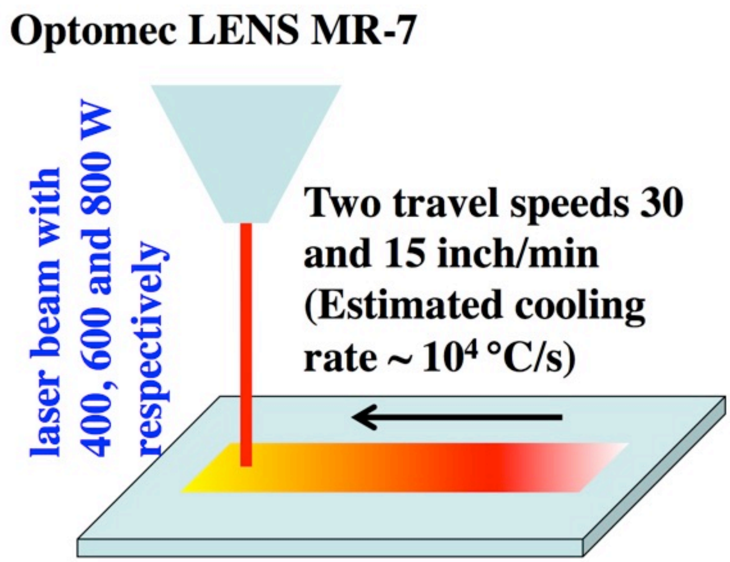

Figure 1. Schematic illustration of the laser processing.

Scientific Approach and Results

1. Both FCC FeCrNiMn and BCC FeCrNiMnAl HEAs have been investigated and found to present comparable swelling and extraordinary irradiation tolerance (limited voids and stabilized phase structure under high irradiation dose).

This observation provides scientific underpinning of investigating the irradiation response of dual-phase HEAs. Because if the swelling is dramatically different between fcc and bcc HEAs, internal strain will be accumulated due to incompatible swelling between two different phases and the fcc/bcc heterophase boundary will become unstable under irradiation. However, our Phase I work, shown in Fig. 2, has uncovered that the swelling is about 0.01% in fcc FeCrNiMn and about 0.03% in bcc FeCrNiMnAl after 5 MeV Fe ion irradiation at 500 °C with a dose of 50 dpa. Such observation makes the ensuing investigation meaningful.

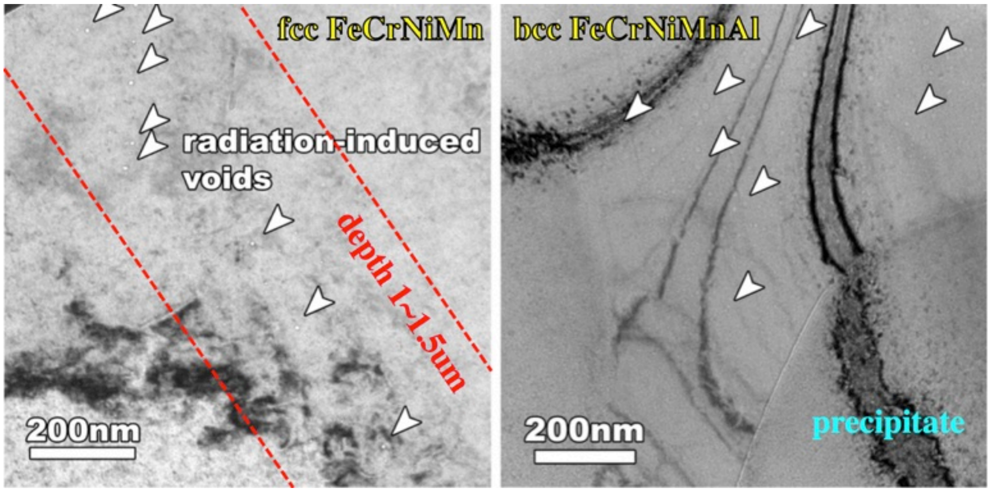

Figure 2. Transmission electron microscopy (TEM) micrographs of FCC FeCrNiMn and BCC FeCrNiMnAl HEAs after Fe ion irradiation at 500 °C. Radiation-induced voids are captured and labeled.

2. The microstructure and radiation-induced hardening can be tailored by laser processing under additive manufacturing.

As shown in Fig. 3, in terms of fcc FeCrNiMn, laser scanning correlated fast melt-fast solidification process leaves the microstructure unaffected, as well as the favorable radiation damage tolerance. In terms of bcc FeCrNiMnAl, laser processing significantly changes the correlated microstructure and leads to enhanced hardness. After irradiation, the hardening is negligible.

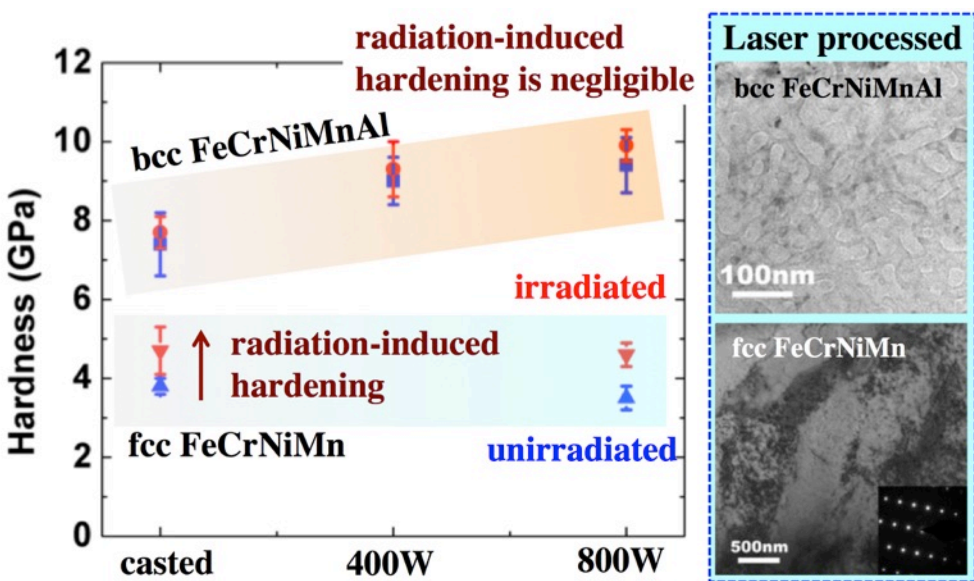

Figure 3. Hardness change and microstructure evolution after laser processing in FCC FeCrNiMn and BCC FeCrNiMnAl HEAs.

3. Machine learning model to predict the hardness of HEAs as a function of laser power and scan speed.

We have assembled at LANL a unique database of HEAs containing a total of 686 experimentally explored multicomponent HEA alloys. This space consists of 46 elements from the periodic table and the compositions assembled span a variety of mixtures. Thus, we now know from this data the probabilities of forming FCC, BCC, FCC+BCC, solid–solutions and amorphous materials. Our test data predicted 33 new BCC+FCC compounds followed by 12 BCC and 11 FCC. The arc melted LANL compositions did have intermetallics in the microstructure, confirming our ML predictions. However, after Additive Manufacturing we were able to obtain 100% solid solutions. In this step, the machine Learned (ML) models were not trained to predict the Additive Manufacturing processing. This was performed in the next step where we predicted the hardness of HEAs as a function of Laser Power and Scan speed. The training data came from the experimental work in MST for FeCrNiMn and FeCrNiMnAl alloys and consisted of the measured hardness at a laser power of 400W, 600W and 800W and scan speeds of 15 and 30 in/min. We thus currently have a capability to do an adaptive design feedback loop with hardness measurements to guide the synthesis of new alloys. As shown in Fig. 4, using machine learning, the hardness of HEAs as a function of laser power and scan speed is predictive.

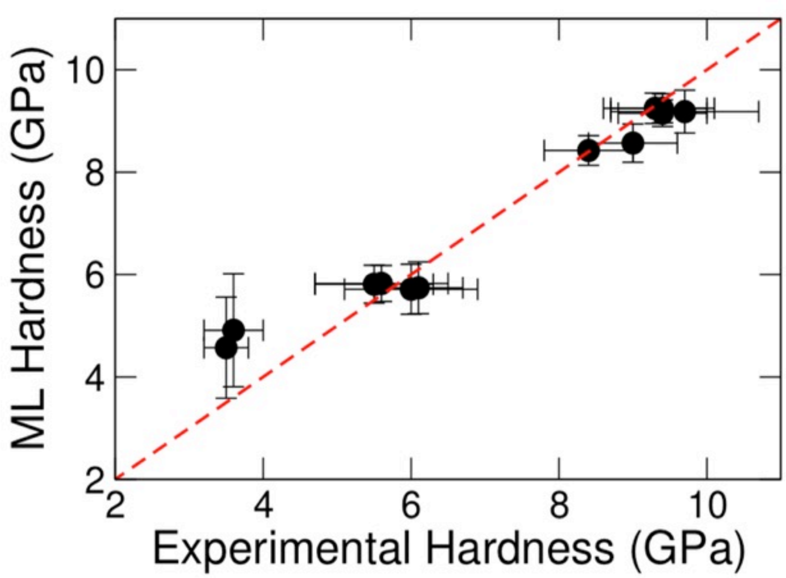

Figure 4. Predict hardness of HEAs as a function of laser power and scan speed using machine learning.

Anticipated Impact on Mission

The proposed work is strategically important to the mission of "Exploiting Additive Manufacturing for Fabricating Radiation-Tolerant Nuclear Components" and has the potential to benefit the other mission of "Manufacturing Process Agility and Innovation". Our project will fundamentally transform the manufacturing of the next generation nuclear components. This ER program notably fulfills all three pillars of LANL's Materials Strategy: (i) Defects and Interfaces. Our innovation tunes interfaces to suppress defect generation and accelerate their annihilation. (ii) Emergent Phenomena. Unlike conventional alloys, which contain one or two base elements, HEAs comprise multiple principal elements. Hence, new behaviors and properties are expected. (iii) Extreme Environments. This LDRD-ER project has developed a new materials modeling tool and provide insights into the roles of interfaces/grain boundaries under radiation extremes, which is of great significance to programmatic work at LANL.

Conclusion

In this project, FeCrNiMn based HEAs, either in FCC or BCC (with additional Al) phase, have been found to present comparable swelling and extraordinary irradiation tolerance. **Multiple journal papers are in preparation.** In the next step, two main tasks are foreseen.

- The swelling behavior of dual phase FeCrNiMnAl0.3 HEAs: In Phase I, through adjusting Al concentration[7], we have successfully synthesized dual-phase FeCrNiMnAl0.3 HEAs (33% bcc + 66% fcc) with a high density of heterophase boundaries (in Fig. 5). Our former EFRC has uncovered that fcc/bcc heterophase boundary provides much higher sink efficiency than homophase boundaries [8]. *We hypothesize that a hierarchical arrangement of fcc/bcc interphase boundaries that are stable under irradiation can be good defect sinks*: radiation-induced vacancies and interstitials preferentially aggregate on the misfit dislocation lines at interfaces, which are naturally effective channels for point defect annihilation [9]. The same irradiation conditions will be applied to investigate the swelling behavior of dual-phase HEAs.

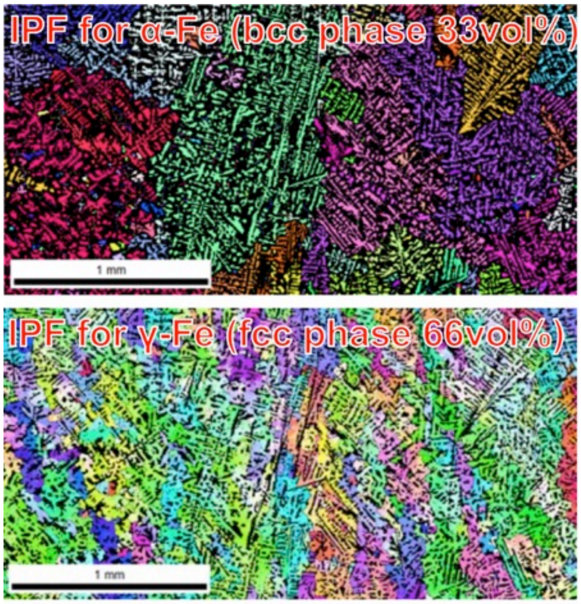

Figure 5. Microstructure of successfully synthesized dual-phase $FeCrNiMnAl_{0.3}$ HEAs (33% bcc + 66% fcc).

- Artificial Intelligence: We will further improve and refine our machine learning model with data for more alloys, including a more extensive literature search to enhance the LANL database which we have created on multicomponent alloys. The model needs to be tested further for robustness so that it generalizes well to new unsynthesized compositions. Additionally, we will start to incorporate the changes observed in microstructure, which are currently not implemented. Our focus will be largely on learning and guiding experiments, however, depending on funding, we will start to integrate our phase field models of alloys and steels with this work on HEAs.

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