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Exploring radiation induced segregation mechanisms at grain boundaries in equiatomic CoCrFeNiMn high entropy alloy under heavy ion irradiation

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ABSTRACT

High entropy alloys have gained significant interest due to several unique properties including enhanced radiation resistance. In this work, radiation induced segregation, a key phenomenon observed in alloys under irradiation, is examined for the first time at high angle grain boundaries under Ni heavy ion irradiation in the CoCrFeNiMn alloy. Our experimental study indicates significant Mn depletion and Co and Ni enrichment at grain boundaries. The segregation is discussed in the context of a proposed vacancy dominated radiation induced segregation mechanism and compared to existing models in conventional single core component alloys including stainless steels.

Single-phase and multi-phase alloys of multiple core principle elements broadly classified as high entropy alloys (HEAs) have recently garnered extensive interests [1–4] due to numerous improved or unique properties in comparison to conventional alloys. These multi-principle element alloys, for example, have shown excellent room temperature and cryogenic fracture toughness [5], high ductility [6,7], increased corrosion resistance [8], and improved wear properties [9]. Researchers have explored the potential of particular single-phase concentrated solid solution alloys (SP-CSAs) and HEAs for nuclear energy applications by examining their response under irradiation [10–14]. Early experimental and computational studies of SP-CSA such as equiatomic FeNi, CoFeNi, CoCrFeNi, and CoCrFeNiMn under ion and electron irradiation environments have indicated reduced swelling, delayed void formation, slower irradiation induced defect cluster migration, and reduced dislocation size and density in comparison to pure Ni.

The improved radiation response of SP-CSAs have been attributed to proposed compositional complexity and high configurational entropy leading to slower point defect diffusion and delayed defect evolution in comparison to conventional alloys or pure metals [12,15,16]. In addition to the defect evolution during irradiation, two recent studies have explored radiation induced segregation (RIS) at dislocations in SP-CSA alloys. Lu et al. [17] reports that the magnitude of RIS at irradiation induced dislocation loops is minimized in CoCrFeNiMn at 500 °C under 3 MeV Ni^{2+} irradiation conditions. In contrast, He et al. [18] shows notable Co enrichment and Mn depletion with negligible Cr, Fe, Ni segregation at irradiation induced dislocation loops under 1.25 MeV electron irradiation. While these studies provide an early indication of solute segregation under irradiation, to date, no experimental efforts have been undertaken to characterize RIS at grain boundaries (GBs) in the most commonly studied CoCrFeNiMn HEA. Solute segregation to GBs is known to be a key microstructural feature in irradiated assisted stress corrosion cracking and localized intergranular corrosion resistance in several conventional alloys including Fe-Ni-Cr austenitic alloys [19]. Therefore, a fundamental understanding of experimentally observed GB segregation behavior and potential GB RIS mechanisms are critical for possible radiation environment applications.

In this study, we explore GB RIS in CoCrFeNiMn under heavy ion irradiation. The experimental observations indicate substantial segregation of constituent elements at GBs. The solute segregation at 2 and 3 dpa was compared to conventional alloys; we observed significant segregation of Mn, Ni, and Co to random high angle GBs (RHAGBs). The segregation is discussed in the context of a proposed vacancy

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dominated RIS GB mechanisms in multi-component alloys and compared to conventional single component alloys including commercial and model austenitic Fe- and Ni-based alloys.

Equiatomic CoCrFeNiMn ingots were produced by vacuum induction levitation melting in high purity Ar atmosphere. The samples were further homogenized for 20 h at 1100 °C in Ar atmosphere, followed by straining via a 25% rolling reduction and annealed at 1100 °C for 2 h and water quenched. Fig. 1a illustrates the inverse pole figure colored orientation map of the alloy prior to irradiation which has an average grain size with twin boundaries included of 87 ± 44 μm. Heavy ion irradiations were completed with 3 MeV Ni^{2+} ions to a total fluence of 3 × 10^{15} at 500 °C (dose rate of 3 × 10^{-3} dpa/s). The corresponding displacements per atom (dpa) as a function of cross-sectional depth, shown in Fig. 1b, was determined using SRIM-2008 with the quick Kinchin-Pease calculation (40 eV displacement threshold energy for all elements) [20]. Fig. 1b also indicates the estimated level of implanted Ni as a function of cross-sectional depth. RIS was characterized at RHAGBs by Scanning Transmission Electron Microscopy (STEM) – energy dispersive x-ray spectroscopy (EDS) on cross-sectional focused ion beam (FIB) lift-out specimens [21]. All EDS measurements were taken at cross-sectional depths of 0.5 μm and 1 μm which corresponded to approximately 2 and 3 dpa, respectively. STEM-EDS was completed using a FEI F200X Talos S/TEM operated at 200 kV; FIB-prepared samples were approximately 80 nm in thickness while all GBs regions reported were edge-on to the electron beam. In addition to the RIS measurements, STEM-annular dark field (ADF) taken with a JEOL 2100F S/TEM, shown in Fig. 1c, indicates there are no irradiation induced voids at this relatively low to intermediate dose regime. The lack or reduction of void swelling in comparison to Ni and particular Ni binary alloys is consistent with previous literature [10,22–25].

Fig. 2a illustrates the representative RIS microchemistry for the CoCrFeNiMn HEA at 2 dpa. The change in the matrix composition from the GB composition of the five elements is shown in Fig. 2b. At both 2 and 3 dpa there is nearly identical solute segregation behavior at RHAGBs. Substantial Co and Ni enrichment to approximately 27 at.% and Mn depletion to approximately 9 at.% were observed. The level of Cr and Fe at GBs is near the adjacent matrix compositions and within approximately 1 at.% depletion at both 2 and 3 dpa. Supplemental Fig. S1 shows a representative STEM-EDS elemental map collected at a RHAGB. The 3 dpa condition at 1 μm cross-sectional depth as shown in Fig. 1b is near the Ni ion irradiation end of range where the interstitial injected effects can modify the irradiation response [24,26]. In this case, slightly less Co and Ni enrichment and Mn depletion are observed in comparison to the 2 dpa depth. The segregation width of the elemental depletion and enrichment in Fig. 2 is approximately 5 nm on both sides of the GB. The segregation width is consistent with minor STEM-EDS beam broadening effects but is consistent with RIS segregation width in extensively studied austenitic [27,28] and ferritic steels [29,30] under similar 400 °C proton and 500 °C heavy ion irradiations.

The results presented above are the first reported analyses of GB RIS in CoCrFeNiMn. The experimental data can be compared to preceding studies that have explored dislocation RIS in the same alloy. Segregation profiles measured by STEM-EELS across edge-on dislocations in Lu et al. [17] indicate no clear solute segregation in CoCrFeNiMn irradiated to 38 dpa at 500 °C using 3 MeV Ni^{2+} heavy ions. Lu et al. [17] attribute the reduced and minimal dislocation RIS to high lattice distortion which they propose enhances vacancy/interstitial recombination and subsequently suppress the overall defect fluxes to point defect sinks. In the same HEA, He et al. [18] observed significant Mn depletion, Co enrichment, and no detectable segregation of Ni, Cr, or Fe at Frank partial dislocations at 1 dpa under 1.25 MeV electron irradiation at 400 °C using STEM-EDS. In their study, they attribute the observed segregation behavior in this and other compositionally complex HEA alloys through an interstitial binding mechanism [31] and associated atomic size difference. The smaller Co and Ni atomic size in comparison to larger Fe and Cr atoms are favored for preferentially coupling with interstitials and subsequently enrich at dislocations. The proposed dislocation solute segregation mechanism does not include vacancy-defect preferential interactions. While these two studies offer distinct perspective and varying observations of chemical segregation to dislocations under irradiation in CoCrFeNiMn, the mechanism for RIS at GBs have not been previously explored. Furthermore, while comparison to the existing dislocation RIS studies are valuable due to the limited existing studies, the overall segregation mechanism and sink strength can be quite different than GBs [32]. Specifically, dislocations, in comparison to a random general GB, are a biased defect for interstitials and so it is possible that the dominant solute segregation mechanisms of the core elements can differ.

As described above, there are very limited experimental segregation studies under irradiation in fcc based compositional complex alloys such as HEAs. However, there has been substantial effort over the past several decades to have a mechanistic understanding of irradiation induced GB segregation in conventional (i.e. single core element) Fe- and Ni-based fcc based commercial and model alloy systems such as 304 and 316 stainless steels. The modified inverse Kirkendall (MIK) model [33,34] has been successfully implemented to predict RIS trends in both model and commercial austenitic Fe-Ni-Cr alloys. The MIK model was built on the foundation of the Perks model [35] where RIS is dictated by differences in species dependent atomic-vacancy jump rates (i.e. inverse Kirkendall effect mechanism). The MIK model added to the Perks model by incorporating additional terms to account for localized short-range ordering and alloy composition. Importantly, both models rely exclusively on the coupling of the solute flux with the vacancy flux and make note that interstitial effects are not required to sufficiently describe the RIS behavior of the key core and alloying elements: Fe, Ni, and Cr. More recently, Yang et al. [36] and others [37–40] have indicated that incorporation of preferential atom-interstitial coupling via an interstitial binding mechanisms [31] can

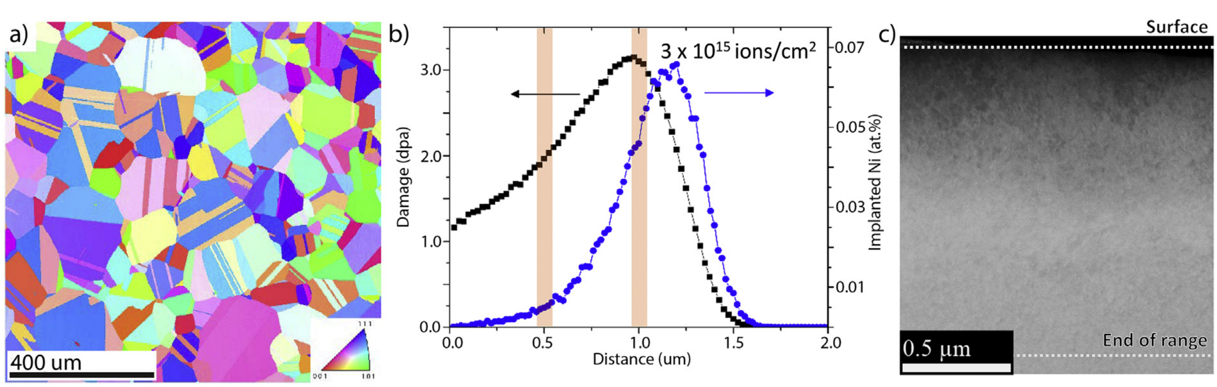

Fig. 1. (a) Inverse pole figure colored map of the coarse grain CoCrFeNiMn used for the ion irradiation; (b) SRIM calculated dpa as function of cross-sectional depth for 3 MeV Ni^{2+} irradiations; (c) STEM-ADF image of irradiated sample with implanted Ni end of range and surface highlighted.