Observations of defect structure evolution in proton and Ni ion irradiated Ni-Cr binary alloys

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HIGHLIGHTS
• Binary Ni-Cr alloys were irradiated with protons or Ni ions at 400 and 500 °C.
• Higher irradiation temperatures yield increased size, decreased density of defects.
• Hypothesize that varying Cr content affects interstitial binding energy.
• Fitting CD models for loop nucleation to data supports this hypothesis.

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ABSTRACT
Two binary Ni-Cr model alloys with 5 wt% Cr and 18 wt% Cr were irradiated using 2 MeV protons at 400 and 500 °C and 20 MeV Ni 4+ ions at 500 °C to investigate microstructural evolution as a function of composition, irradiation temperature, and irradiating ion species. Transmission electron microscopy (TEM) was applied to study irradiation-induced void and faulted Frank loops microstructures. Irradiations at 500 °C were shown to generate decreased densities of larger defects, likely due to increased barriers to defect nucleation as compared to 400 °C irradiations. Heavy ion irradiation resulted in a larger density of smaller voids when compared to proton irradiations, indicating in-cascade clustering of point defects. Cluster dynamics simulations were in good agreement with the experimental findings, suggesting that increases in Cr content lead to an increase in interstitial binding energy, leading to higher densities of smaller dislocation loops in the Ni-18Cr alloy as compared to the Ni-5Cr alloy.

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1. Introduction
Ni-based alloys are commonly used in high-temperature applications due to their superior high temperature creep strength and were considered for nuclear reactor systems during fast reactor development programs in the '70s and '80s [1–6]. High-Cr Ni-based alloys are currently used primarily in systems in which there is no neutron flux, such as steam generators, as they have been found to be susceptible to irradiation-induced embrittlement [6]. However, there is a renewed interest in radiation damage effects in Ni-based alloys due to their excellent corrosion resistance, especially in molten salt reactor environments [7,8]. In these environments Cr-content, usually added to increase oxidation resistance, is considered detrimental as it is preferentially leached by the fluoride salts [9]. As such, an understanding of radiation damage effects in low-Cr Ni-based alloys is desired.

Many prior radiation effects studies on Ni-based alloys focused on the Nimonic PE16 Ni-Fe-Cr alloy [1–5] and there is considerable literature on composition effects in austenitic stainless steels and ternary model alloy systems [3,10–13]. However, only a few fundamental studies have been performed to study Cr content effects on the radiation response of Ni-based alloys. Hudson and Ashby showed that increases in Cr content tended to reduce swelling in Ni-irradiated Ni-Cr binary systems and swelling rates for Ni-Cr continued to increase for higher damage doses, rather
than saturate as for pure Ni [14]. Garner has postulated that atomic ordering effects may influence void swelling [15], and Robinson and Jenkins have demonstrated weak dependence of dislocation loop formation on Cr content [16]. Finally, Barr et al. investigated the effects of grain boundary character on the radiation-induced segregation response in a Ni-5Cr alloy [17]. Extrapolation of data from these analogous systems can help to develop Ni-based alloys for the next generation reactor applications. However, more work is required to understand the fundamentals of the radiation response of these alloys.

Ion irradiation experiments have long been used to simulate neutron radiation damage in reactor environments; comparable damage levels are achieved much more rapidly and the resulting samples are typically non-radioactive, making the logistics of sample handling post-irradiation much easier. In this study both protons and Ni ions have been used to induce damage with the purpose of comparing the effect of dose rate on the induced microstructure, though other factors such as the efficiency of producing mobile point defects and gradients in induced damage must be considered in the context of the presented results. While no neutron irradiation experiments have been performed in the current work, the insights gained can be extrapolated to predict in-core radiation response, though the best way to reconcile the

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**Table 1**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>Si</th>
<th>Co</th>
<th>P</th>
<th>S</th>
<th>Other minors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-5Cr</td>
<td>5.00</td>
<td>94.94</td>
<td>0.007</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.005</td>
<td>0.005</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Ni-18Cr</td>
<td>17.90</td>
<td>82.02</td>
<td>0.016</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.005</td>
<td>0.006</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

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Fig. 1. (a) Damage profile for 2 MeV proton irradiations in both Ni-Cr alloys. Damage profiles are extremely similar and are assumed to be equivalent for the purpose of this experiment (studied region from 0 to 10 μm). (b) Damage profile for 20 MeV Ni$^{4+}$ irradiations in Ni-5Cr. Microstructural investigation took place at a target depth of 1 μm, corresponding to a nominal damage dose of 3.4 dpa. Damage profiles generated using the SRIM-2008 software [27].
differences in the resulting microstructures induced by neutrons and different types of ions is a topic of debate and has been the focus of several studies [18–23].

The present study investigates the effects of Cr content, irradiation temperature, and irradiating species on the resulting microstructure of ion irradiated Ni-based alloys with a focus on the formation of dislocation loops and voids. The dislocation loop structures seen in this system are faulted Frank loops commonly seen in other irradiated austenitic steels [24,25] and are the primary contributors to radiation-induced hardening and embrittlement effects. Voids are responsible for radiation-induced void swelling, and both are typically considered to be detrimental to materials performance.

2. Experimental details

Two binary model Ni-Cr alloys of nominal composition 5 wt% Cr and 18 wt% Cr (referred to henceforth as Ni-5Cr and Ni-18Cr, respectively) were vacuum arc melted and cast in a water-cooled copper hearth and recrystallized by cold-rolling to 50% of their original thickness followed by annealing for one hour at 1050 °C. These two compositions were selected because they represent binary analogs to a broader family of Ni-based alloys that contain Cr primarily for high-temperature oxidation resistance and creep strength. Their relatively pure compositions allow us to eliminate the effects of minor alloying elements from this study. The composition of these materials was verified using inductively coupled plasma optical emission spectroscopy (ICP-OES). The results of this analysis are shown in Table 1. Observed impurities are dilute enough such that differences in their concentration between the two materials are not expected to significantly affect radiation response behavior.

After recrystallization, the samples were examined using electron backscatter diffraction (EBSD). Defect-free sample surfaces were prepared by mechanical polishing with SiC paper to 800 grit before electropolishing with an electrolyte solution of 30% nitric acid, 10% sulfuric acid, 10% orthophosphoric acid and 50% glacial acetic acid [26].

Proton irradiations were conducted at the University of Wisconsin Ion Beam Lab (UW-IBL) on a 3.4 MV Pelletron tandem accelerator with 2 MeV ions for approximately 100 h until a final fluence of $2.58 \times 10^{19}$ ions/cm$^2$ was achieved at a nominal flux of $3.9 \times 10^6$ dpa/s.

![Fig. 2. Representative inverse pole figure (IPF) of (a) Ni-5Cr and (b) Ni-18Cr sample materials prior to irradiation. IPF key is shown in (c).](image-url)
Target temperatures of 400 and 500 ± 15 °C were monitored using two thermocouples mounted on either end of the sample stage and was controlled primarily by optimizing beam current through minimal adjustments. Ni ion irradiations were performed at the Sandia National Laboratories Ion Beam Laboratory on the 6 MV tandem Van de Graaff accelerator using 20 MeV ions for approximately 4 h until a final fluence of $1.9 \times 10^{16}$ ions/cm² was achieved at a nominal flux of $1.32 \times 10^{12}$ ions/cm² s. Temperature was controlled using a button heater coupled with LabVIEW software and was monitored using spot-welded thermocouples and maintained at 500 ± 10 °C.

Damage profiles for both the proton and Ni ion irradiations were computed using the SRIM-2008 code [27]. The parameters were selected to comply with the methodology established by Stoller...
Fig. 4. Comparison of Frank loop densities and size distributions for the different material conditions investigated. Reported error represents one standard deviation for calculated number densities of individual TEM micrographs.
et al. [28]. The resulting damage profiles for the proton and Ni-ion irradiations are shown in Fig. 1. A nominal dose of approximately 1.6 displacements per atom (dpa) was achieved in the region examined for the proton-irradiated materials, which extended to a maximum depth of 10 μm, at an average damage rate of 4.2 \times 10^{-9} \text{ dpa/s}.

Transmission electron microscopy (TEM) techniques were employed to investigate the irradiated microstructures. Samples for TEM analysis were prepared from the unirradiated specimens using electrolytic jet thinning utilizing the same electrolyte solution used for EBSD sample preparation. TEM specimens from irradiated materials were prepared using the focused ion beam (FIB) lift-out method on the FEI Quanta 3D FEG at the Microscopy and Characterization Suite located at the Center for Advanced Energy Studies (CAES) in Idaho. The specimens were prepared from random locations on the irradiated surface and sampled multiple grains. Lift-outs were mounted on copper Omniprobe FIB grids and cleaned with a 5 kV (Ga) FIB beam to minimize FIB-induced radiation damage. Frank loops residing on the four {111} planes of the face centered cubic (fcc) lattice with Burgers vector a/3{111} were imaged using a relrod dark field imaging technique with a 200 kV accelerating voltage on the FEI Tecnai TF-30 TEM/STEM and the JEOL JEM2100 TEM/STEM at the University of Wisconsin-Madison and Drexel University, respectively. The imaging conditions were set in selected area diffraction mode by tilting from the [011] zone axis until a two beam condition was met with the \{g\} = 3\{T\} reflection and then centering the smallest objective aperture between the \{200\} and \{11\} diffraction spots [24]. Voids were imaged using scanning transmission electron microscopy high-angle annular dark field (STEM-HAADF) imaging with 200 kV electrons on the FEI Titan Aberration-corrected (S)TEM at the University of Wisconsin-Madison. Areal defect densities were obtained through manual counting in the ImageJ software [29]. At least three separate micrographs from different sample regions were used for statistical analysis. Sample thicknesses for number density determination were calculated using the electron energy loss spectroscopy (EELS) log-ratio method with an assumed electron mean free path for pure Ni of 98 nm for 200 keV electrons [30]. EELS thickness measurements were taken at five different regions for each sample and averaged to determine the mean specimen thickness.

A cluster dynamics (CD) model was used for simulating loop evolution under proton irradiation to understand mechanisms for loop evolution behavior in Ni-5Cr and Ni-18Cr. The CD simulation technique predicts microstructure evolution in a system described as a gas of non-interacting clusters. The clusters are defined by a single parameter, their size or the number of atoms they contain. The evolution of clusters is deduced from reaction rate theory equations. A previously established CD model for defect evolution based on Duparc et al. and Pokor et al. [31,32] was used in this study. In this model only single interstitials and single vacancies are considered mobile. In-cascade clustering of defects [33,34] under proton irradiation based on Gan et al. is also included in the model [35]. The material parameters, cascade production properties, and environmental parameters (dose rate and temperature) for the CD model are listed in Table 2. In most cases the properties of pure Ni were considered due to lack of data for specific Ni-5Cr and Ni-18Cr alloys. The binding energy of dimer interstitials is used as fitting parameter, as discussed below.

### 3. Results and discussion

#### 3.1. Unirradiated microstructure

Inverse pole figure maps for each material obtained via EBSSD are shown in Fig. 2. It can be seen that the grains are equiaxed, with an area averaged grain size (including twin boundaries) of 163.9 and 106.6 μm for the Ni-5Cr and Ni-18Cr specimens, respectively. Due to these large grain sizes compared to implantation and analysis depths in these materials the presented results are expected to be representative of bulk material behavior.

TEM investigation on the unirradiated jet-polished specimens showed a clean microstructure with very few dislocation structures and a complete absence of voids. In addition, TEM examination of the Ni-irradiated foils in regions beyond the damage range showed minimal FIB damage artifacts. Based on these observations it is concluded that all obvious microstructural defects are a result of the ion irradiation treatment.

#### 3.2. Frank loops in irradiated Ni-Cr

Frank loops in irradiated Ni-Cr specimens showed distinct differences in density and size for different compositions and irradiation conditions. Representative TEM relrod micrographs showing these loop structures for the five investigated conditions are shown in Fig. 3 and plots illustrating the loop sizes and densities are shown in Fig. 4. As is evident from Fig. 5, irradiations at 400 °C tended to result in a higher density of Frank loops compared to irradiations at 500 °C and the higher irradiation temperature induced a slight increase in the loop size. Simulation of annealing effects in 304 L stainless steels by Busby et al. have illustrated that loop stability can be greatly affected by the temperature increase from 400 to 500 °C, especially over the course of a 100 h irradiation [40]. These observations imply that an increase in point defect recombination and annihilation due to enhanced mobility at 500 °C combined with increased thermal emission ultimately results in a reduced number of dislocation loops. Furthermore, the loops that do nucleate tend to absorb more point defects and increase in size. In addition, the lower density of Frank loops at 500 °C could be attributed to the unfaulting of Frank loops to network, perfect 1/2{111} dislocations. Zhang et al. recently indicated unfaulting of interstitial Frank loops at 500 °C during 1 MeV Kr₂⁺ irradiations of Inconel X-750 while also indicating a lower density of total loops observed at 500 °C than at 400 °C [41]. The growth and subsequent unfaulting of Frank loops at higher temperatures is consistent with the slightly larger loop size and small Frank loop density observed between 400 and 500 °C examined in the proton irradiations. These temperature trends are consistent with observed loop morphologies in Ni ion and neutron irradiated 316 L stainless steel systems [42–44]. Additionally, it was observed that the self-ion irradiated Ni-5Cr showed a higher density of larger loops than the proton-irradiated Ni-5Cr at 500 °C. Due to the differences in dose it is difficult to make one-to-one quantitative comparisons and extricate the effects of using a different irradiating ion species. However, Frank loop morphologies are known to eventually saturate with dose in similar irradiated systems [24,45], specifically in the 1–1.5 dpa range for ion-irradiated materials [41,46]. If it is assumed that saturation behavior is similar for the presently considered Ni-irradiated Ni-5Cr alloy, the higher density of observed loops would suggest that the immobile defect clusters generated during the more chaotic damage cascades can aid in loop nucleation. Additionally, the larger loop size distribution may indicate that a larger portion of the produced defects are being absorbed by this high density of nucleated loops instead of annihilating, or that nucleated loops may
interact with/absorb these defect clusters to grow at an increased rate.

While an increase in the irradiation temperature increased the loop size for the two compositions studied, changing the Cr content also had an effect on the loop density. For 400 °C irradiation, Ni-18Cr showed a higher loop density by approximately a factor of two when compared to Ni-5Cr. This higher density was accompanied with a slight decrease in average loop size. A similar trend is observed as a result of 500 °C irradiation but with a larger difference in the loop densities between the two compositions. This contradicts observations in a study of room temperature tungsten-irradiated Ni-8Cr and Ni-17Cr by Robinson et al. in which a lower Cr content resulted in a higher defect yield (defined as the fraction of displacement cascades which collapse to form point-defect clusters), though the differences in the densities was much less dramatic than observed here and within the reported error bars [16]. It is postulated here that the primary cause for the changes in defect morphologies with different compositions are due to the differences in the energetics of loop nucleation. This was investigated further by using cluster dynamics simulations discussed in the next section. It is noted that the Ni-5Cr specimen irradiated with protons at 500 °C appears to be an outlier in this study, due to the order of magnitude difference in the density of dislocation loops observed as compared to the other specimens. As such, the cluster dynamics simulations focus on the 400 °C proton-irradiated materials to study the composition effects, as variation of model parameters commensurate with what is expected for such a temperature shift did not yield good fits to this experimental data.

3.3. Cluster dynamics modeling results

It is hypothesized that the different loop behavior between Ni-5Cr and Ni-18Cr is due to changes in the initial energetics of the loop, which alters its nucleation. Ab initio calculations have reported strong binding energies between Cr and interstitials in Ni-Cr alloys, with differences between Ni-Ni and Cr-Cr dumbbell stability approaching 1 eV/dumbbell [47]. Therefore, it is expected that increases in Cr concentration would increase binding energy between dimer interstitials in Ni-Cr alloys, likely on the scale of approximately 0.1 eV for a 10 wt% change in Cr content. An increase in interstitial binding will increase loop nucleation, which in turn will increase number density and decrease size. This is exactly what is observed when increasing Cr content from 5 to 18 wt% Cr at 400 °C.

To further assess if this intuitive understanding is plausible, the aforementioned cluster dynamics (CD) model is used to explore if changes in the dimer interstitial binding energy (Eb), which is the decrease in energy of an interstitial pair relative to isolated interstitials) on the scale of 0.1 eV can yield the type of changes observed in the experiments. It should be noted that this is a highly approximate model and it is being used only to qualitatively assess if the arguments about Eb are plausible, not provide predictive accuracy. Therefore, Eb is used as a fitting parameter to explore what changes in this quantity are needed to explain the data. The fitted values are selected to best represent the loop size and number density. For Ni-5Cr the best fit value of Eb is 0.73 eV and for Ni-18Cr the best fit value of Eb is 0.9 eV at 400 °C. Fig. 5 shows the results of the current CD model compared with experimental data for both Ni-5Cr and Ni-18Cr at 400 °C. The good agreement for both size and number density suggests that the present simple model can provide useful qualitative guidance. The 0.17 eV change in Eb is fully consistent with our hypothesis that changes in the nucleation energetics, or equivalently, in Eb, on the scale of approximately 0.1 eV is responsible for the changes in loop properties with Cr concentration.

3.4. Voids in irradiated Ni-Cr

Voids were imaged using STEM-HAADF imaging and differences in the void structures were apparent. Representative images of void structures in the various irradiated Ni-Cr conditions are shown in Fig. 6 and histograms comparing the void sizes and densities are shown in Fig. 7. Void swelling was calculated from the ratio of the volume of the observed voids (assuming spherical geometries) to the total volume analyzed.

Increase in temperature resulted in similar effects for void morphologies as for dislocation loops. Higher temperature irradiations induced a lower density of larger voids. However, this change in morphology with temperature was much more pronounced for voids, with approximately 50% and 3x decrease in the observed densities going from 400 °C to 500 °C irradiations for Ni-5Cr and Ni-18Cr, respectively. Upon high temperature irradiation some voids showed double the diameter of those seen in the lower-temperature irradiated specimens. These results are consistent with observations made in similar systems, and likely originate from increased void nucleation at lower temperatures and from more favorable driving forces for void growth at high temperatures.
For the 400 °C irradiation, the void size distributions are similar and the error associated with the calculated densities overlap for the Ni-5Cr and Ni-18Cr, whereas the 500 °C irradiated materials show dramatically different size distributions and an order of magnitude difference in the void densities. The 400 °C proton-irradiated materials are likely more indicative of composition dependence, in which case Cr additions suppress swelling, likely by changing void nucleation behavior. This conclusion is consistent with results from earlier studies on void swelling binary and ternary Ni-based alloys in which initial swelling is suppressed by Cr additions but steady-state swelling rates are more or less unaffected [12,14,15].

The differences in void microstructure resulting from Ni-ion
irradiation is also dramatic with a higher density of much smaller voids observed when compared to proton-irradiated materials. This result is consistent with the hypothesis that lower dose rates incur more swelling and larger voids for the same dose, which has been well supported in austenitic steel systems [49]. In this case there is likely a large effect just due to time held at temperature - the Ni-ion irradiations took approximately 4 h whereas the proton irradiation took a little over 100 h, giving much more time for point defect diffusion and void agglomeration. The higher density of voids generated in the shorter Ni-irradiation may be indicative that higher disorder caused by in-cascade clustering effects aid in the void nucleation process.

Fig. 7. Comparison of void densities and size distributions for the different material conditions investigated. Reported error represents one standard deviation for calculated number densities for individual STEM micrographs.
4. Conclusions

In this study, the irradiation microstructures of Ni-5Cr and Ni-18Cr model alloys were investigated using analytical transmission electron microscopy techniques. A summary of this analysis is provided in Table 3. Most notably, our results indicate that the irradiation temperature has a distinct effect on the damage morphology. By increasing the proton irradiation temperature from 400 °C to 500 °C, an increase in size and a decrease in density was observed for dislocation loop and voids. This effect is proposed to originate from increased thermal motion of point defects, which results in more defects finding and combining with existing clusters than nucleating new clusters. Cluster dynamics simulations were in good agreement with the most robust experimental observations, and suggested that Cr content might be enhancing dislocation loop nucleation behavior through increasing the stability of the smallest clusters. Assigning interstitial binding energies of 0.73 eV–0.9 eV for 5 wt% Cr and 18 wt% Cr alloys, respectively, resulted in a good fit to the experimental data.

Ni-irradiated Ni-Cr specimens showed higher densities of much smaller voids than the proton-irradiated samples, which is likely a consequence of the much higher dose rate coupled with less time at temperature for defect structures to organize over the shorter course of the Ni irradiation (4 h) as compared to proton irradiation (100 h). However, the higher density of voids upon Ni-irradiation may be indicative of in-cascade clustering effects aiding in void nucleation. While comparing the effects of proton and heavy ion irradiations is valuable, further study on neutron irradiated Ni-Cr alloys is required, as the ultimate goal of ion irradiations is to emulate neutron damage in the best possible way. Additionally, the alloys that will be employed in nuclear components such as, for example, in molten salt reactor systems will likely not be binary systems. However, this fundamental study of radiation tolerance in binary Ni-Cr alloys gives insight into the mechanisms of defect formation and serves as a basis of comparison for future studies.

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