Investigation of defect clusters in ion-irradiated Ni and NiCo using diffuse X-ray scattering and electron microscopy

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Abstract

The nature of defect clusters in Ni and Ni₅₀Co₅₀ (NiCo) irradiated at room temperature with 2–16 MeV Ni ions is studied using asymptotic diffuse X-ray scattering and transmission electron microscopy (TEM). Analysis of the scattering data provides separate size distributions for vacancy and interstitial type defect clusters, showing that both types of defect clusters have smaller sizes and higher densities in NiCo than in Ni. Diffuse scattering results show good quantitative agreement with TEM size distributions for cluster sizes greater than **2 nm in diameter, but we find that TEM underrepresents the number of defect clusters ≤ 2 nm, which comprise the majority of vacancy clusters in NiCo.** Interstitial dislocation loops and stacking fault tetrahedra are identified by TEM. Comparison of diffuse scattering lineshapes to those calculated for dislocation loops and SFTs indicates that most of the vacancy clusters are SFTs.

Keywords: irradiation damage, asymptotic diffuse X-ray scattering, stacking fault tetrahedra, nickel, alloy

1. Introduction

The search for radiation-tolerant structural materials has largely focused on evolution-ary changes to existing alloys, seeking variations in the type and concentration of the solute species which may improve the properties.¹ Recently, the search has been expanded

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to single-phase concentrated solid solution alloys (SP-CSAs) with multiple principle components, from two to five elements in equal or near-equal concentrations. Experimental studies have shown that certain SP-CSAs are more resistant to radiation damage than pure metals [1, 2, 3, 4], but the detailed reasons why are still not understood. In SP-CSAs, the increased chemical complexity can have many different effects, such as reducing the mean free paths of the energy carriers in the system (phonons, electrons, and magnons) and thus reducing the thermal conductivity, and creating complex energy landscapes for defect formation and migration. Radiation tolerance in metals is determined by damage accumulation, which involves a competition between the processes of defect creation, defect aggregation, and defect annihilation. Chemical complexity may influence the overall radiation tolerance of the material by affecting any or all of these processes and thereby changing the balance between them. Assessing the effect of alloying requires quantitative measurement of accumulated damage, including the defect density and distributions of defect size and type. In particular, it is important to be able to separate the properties of vacancy type defects from those of interstitial type defects.

One common technique used to study vacancy type defects is to irradiate thin foils at room temperature with ions having energies in the keV range and then study the defects with TEM. Under these conditions, the surfaces act as strong sinks for interstitials **which are mobile, while vacancies are less mobile since the onset of Stage III is just above room temperature [5].** Thus the remaining defects are mostly of vacancy type [6, 7, 8]. However, because of the resolution limit of transmission electron microscopy (TEM), small vacancy defects may be missed. Accordingly, comparisons of size distributions are impacted, and size differences may be missed entirely if the average defect size is small enough. These size limitations may result in misleading inferences about the effects of alloying on damage accumulation. **Additionally, previous work has shown that defects within a ~ 50 nm range from the surface are affected by its presence, with the size and density of vacancy type defects significantly changed [9, 10, 11], and thus the damage observed in irradiated thin films is not representative of the damage created in bulk materials.**

Asymptotic diffuse X-ray scattering is a diffraction technique which detects the presence of defect clusters by measuring the change in lattice spacing in the strain field around the defect [12]. Because interstitial and vacancy type defect clusters produce compressive or tensile strain respectively, they produce diffuse scattering on opposite sides of the

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Bragg peak, allowing them to be easily distinguished from one another. This means that both interstitial and vacancy defect clusters may be studied at the same time, without the need of separating vacancies from interstitials by using a thin foil sample. The diffuse scattering technique is also most sensitive to small defects (0.3-10 nm diameter), **making diffuse scattering an ideal complementary technique to TEM, which has a resolution limit of ~ 2 nm.** Moreover, because X-rays **penetrate several micrometers into the sample where defects are unaffected by the presence of the surface**, diffuse X-ray scattering is a bulk technique and provides excellent statistics when sufficiently high numbers of defects are present.

In this work we study defect clusters in **bulk samples of** pure Ni and the equiatomic solid solution alloy, NiCo, irradiated at room temperature with Ni ions. By comparing the results of diffuse scattering measurements to TEM measurements, we are able to show the consistency of these two methods for determining defect type and density over the range within which the two methods overlap, while also showing that neglecting accurate measurement of small defects using diffuse scattering would lead to opposite conclusions about the effect of alloying on defect accumulation in this system. As with a previous study of NiCu [13], the nickel-cobalt system was chosen because the two elements have very similar masses and sizes, thus the kinematics of the alloy are similar to the pure metal. But unlike the NiCu system, both the melting temperature [14] of NiCo and the elastic constants [15] do not change appreciably with concentration. The most significant differences in materials properties between Ni and NiCo are the stacking fault energy [16] and the thermal conductivity [17, 18], thus this study allows us to probe the importance of these parameters to defect accumulation.

2. Methods

2.1. Sample preparation

Single crystal Ni and NiCo samples were prepared using ingots of elemental Ni and equiatomic NiCo, which were formed by arc melting the **99.98%** pure nickel and cobalt starting materials, remelting and remixing five times, and drop casting into a copper mold. Single crystals were then grown from the polycrystalline ingots in an optical floating zone furnace [19]. The diameter of the molten zone was controlled during crystal growth to create a neck that prevented slower growing grains from propagating [20, 21]. **Incorporation of impurities during sample preparation is limited by the use of vacuum arc melting and by not using a crucible during single crystal growth.** X-ray diffraction and metallographic examination was used to confirm that the samples were single crystal and to orient the [001] direction. Disks of ~ 1 mm thickness and ~ 15 mm diameter were cut parallel to the (001) plane using electro-discharge machining, and electrochemically polished to remove surface damage originating from the cutting process.

The ion irradiations were performed at the Ion Beam Materials Laboratory (IBML) at the University of Tennessee in partnership with Oak Ridge National Laboratory [22]. In order to generate a deep and uniform region of damage for high quality X-ray measurements with a high signal-to-noise ratio, samples were irradiated with Ni ions having several different energies. An analogous method was also used by Maeta et al. [23] to produce a deep region of damage for diffuse X-ray measurements. The Ni ion energies and the corresponding fluences are 16 MeV Ni⁶⁺ to $5.8 \times 10^{14} \text{ cm}^{-2}$, 8 MeV Ni³⁺ to $2.9 \times 10^{14} \text{ cm}^{-2}$, 4 MeV Ni⁺ to $2.5 \times 10^{14} \text{ cm}^{-2}$, and 2 MeV Ni⁺ to $2.5 \times 10^{14} \text{ cm}^{-2}$. The irradiation sequence was from higher energies to lower energies in order to avoid annealing of defects created by the low energy ions at shallower depths. Irradiations were performed at room temperature, and the samples were tilted $\sim 7^\circ$ to minimize channeling effects. Half of each sample was irradiated, leaving the other half to use as a comparison. The Stopping and Range of Ions in Matter, (SRIM, or TRIM) code [24] was used to estimate the displacements per atom (dpa) as a function of depth. “Full cascade mode” was used in the simulation, and 40 eV was assumed as the threshold displacement energy. (As explained by Stoller et al. [25], full cascade mode overestimates dpa by up to a factor of two, but it was used to produce a more accurate shape of the damage profiles.) The results of the simulation for the Ni sample are shown in Figure 1, showing a region of approximately uniform damage to 1.2 dpa to a depth of $l_0=3500 \text{ nm}$. **(The value of the more standard NRT-dpa is 0.6.) Because this depth is several order of magnitude larger than the depth to which the surface affects damage cascades, we neglect the effect of the surface in analysis.**

2.2. X-ray scattering measurements

Unpolarized X-rays were generated by a Rigaku RU300 rotating anode operating at 50 keV and 100 mA with a Cu anode. Cu K $_{\alpha}$ X-rays were selected with a sagittally-focusing graphite (0002) monochromator. A pair of slits defined a $1 \times 1 \text{ mm}$ incident beam. Sample orientation was controlled using a Huber 4-circle diffractometer. X-rays were counted using a Pilatus 200K pixel-array detector with 487×407 pixels, with each pixel $0.172 \times 0.172 \text{ mm}$ in size. The sample-detector distance was 270 mm. For the NiCo sample, the scattering intensity produced by fluorescence was reduced by setting the threshold energy of the Pilatus detector to 7.6 keV.

Scans were made in the radial reciprocal-space direction through the (002) Bragg reflection of each sample, with 121 images collected between $L=1.7\text{--}2.3$ reciprocal lattice units (rlu), using a step size of 5×10^{-3} rlu. The data were reduced to HKL space and averaged over the H and K directions with $\Delta H = \Delta K = 25 \times 10^{-3}$ rlu. Data are plotted as a function of $q = (L-2) \times 2\pi/a_0 \text{ \AA}^{-1} = Q - 4\pi/a_0$ where a_0 is the lattice spacing, which was measured to be $3.524 \text{ \AA}$ for the Ni sample and $3.549 \text{ \AA}$ for the NiCo sample. Scattering

Figure 1: Simulated damage profile for the Ni sample irradiated with multiple energies of Ni ions, calculated by SRIM (TRIM).

intensities were corrected for the polarization reduction factor and transformed from counts into electron units using the measured direct beam signal and tabulated values for the linear absorption coefficient μ .

X-ray scattering spectra were collected from both the un-irradiated and irradiated regions of each sample s , referred to respectively as S_0^s and S_r^s . The diffuse scattering (the part of the scattering caused by the large strain field around defects) is then given by $\tilde{S}_d^s(q) = S_r^s(q) - S_0^s(q)$. The asymptotic diffuse scattering intensity created by a defect cluster falls off as $\sim 1/q^4$, thus to emphasize the asymptotic diffuse scattering, spectra are scaled by q^4 for plotting, as shown in Figure 2. This scaling reveals details in the shape of the fall-off that provide direct information about defect size and shape [12]. Due to the multiplication by q^4 , statistical fluctuations are amplified far from the Bragg peak. Thus for $|q| > 0.23 \text{ \AA}^{-1}$, data were averaged over 5 points to reduce the noise.

In order to estimate defect densities from the diffuse scattering spectra, we must account for the fact that the X-rays penetrate more deeply than the region of damage, thus the measured spectra include information from both the damaged and undamaged regions. We corrected the diffuse scattering spectra using,

$$S_d^s(q) = \tilde{S}_d^s(q)/r^s(Q - 4\pi/a_0), \quad (1)$$

where $2\theta(Q)$ is the scattering angle at momentum transfer Q , r^s is the ratio of the

Figure 2: Experimental asymptotic diffuse X-ray scattering spectra.

scattering intensity coming from the damaged region to the total intensity,

$$r^s(Q) = \frac{\int_0^{l_0} e^{-2\mu^s l / \sin\theta(Q)} dl}{\int_0^\infty e^{-2\mu^s l / \sin\theta(Q)} dl}, \quad (2)$$

and μ^s is the average linear absorption coefficient of sample s averaged over the chemical composition of the sample. Using $l_0 = 3500$ nm from Figure 1, we find $r^{\text{Ni}} = 0.506$ and $r^{\text{NiCo}} = 0.929$.

2.3. Diffuse scattering cross sections

To calculate theoretical diffuse scattering cross sections for defects, the atomic configurations must first be calculated. Equilibrium atomic positions for circular Frank (faulted) loops of both vacancy and interstitial type were generated using the continuum elasticity method of Ohr [26]. For stacking fault tetrahedra (SFTs), the equilibrium atomic positions were generated by running a molecular dynamics (MD) simulation of the defect for 10 ps at 300 K, then quenching the temperature to 0 K over another 10 ps. The MD simulation was run using the LAMMPS MD package [27] and the Bonny et al. [28] Ni-Ni potential. Because the elastic constants for near-equiaxial NiCo have been found to vary by less than 5% from the elastic constants for pure Ni [15], the same atomic configurations were used for both Ni and NiCo. For a vacancy loop containing 45 vacancies, the diffuse scattering computed from the atomic positions generated by both the continuum and MD methods was compared, and found to have no significant difference for the parameters of interest in this study.

Numerical diffuse scattering spectra were calculated from the atomic positions using the methods described by Larson [12], where the asymptotic diffuse scattering intensity

can be written as,

$$S_d^i(q) = \left| f_s(Q) \left(\sum_j e^{i\vec{Q} \cdot \vec{r}_j^i} - \sum_j e^{i\vec{Q} \cdot \vec{r}_j^0} \right) \right|^2. \quad (3)$$

In this expression $\vec{Q} = [0, 0, 4\pi/a_0 + q]$ is the momentum transfer along the reciprocal lattice vector at the (002) Bragg reflection, $f_s(Q)$ is the atomic form factor in electron-units for sample s , $\vec{r}_j^i$ is the equilibrium position of the j th atom in the crystal containing defect i , and $\vec{r}_j^0$ is the equilibrium position of the j th atom in the perfect crystal. This formulation uses the single defect approximation [29], in which defects are assumed to be randomly distributed throughout the crystal. The total scattering from the sample is then given by,

$$S_d^s(q) = \sum_i c_i^s S_d^i(q) \quad (4)$$

where c_i^s is the concentration of defect i in sample s .

Figure 3 shows numerical diffuse scattering cross sections for several sizes of circular Frank vacancy loops and full SFTs, scaled by the number of vacancies in the cluster. Analogous cross sections for interstitial loops are not shown because they look very similar to those of vacancy loops mirrored about $q = 0$ [12]. We considered only faulted loops because most work shows that they are more common than perfect loops in nickel [30, 31, 32, 33, 34]. Spectra are shown for different vacancy type defects of similar size. Some important differences between the loops and SFTs are apparent. Firstly, the cross sections for SFTs are in general, broader and shifted to higher $|q|$ compared to the spectra for loops of the same size. The reasons for these differences in scattering cross sections can be related to the different structures of the defects, but will be discussed in detail in future work. Secondly, the spectra for the SFTs have less scattering on the $+q$ side than the loops, corresponding to compressive strain. While a vacancy type defect generally produces tensile strain, there is also some compressive strain outside the edge of the loop [12, 26]. This can be understood by considering the defect structure of a large loop on a small scale near the edge of the loop. On this scale, the edge of a vacancy loop extending in one direction cannot be distinguished from the edge of an interstitial loop extending in the opposite direction, thus there must be both compressive and tensile strain in this region. But because a SFT does not have missing or extra planes, there is no compressive strain at its edge. In Section 3 we will show that the difference in the diffuse scattering cross sections on the $+q$ side between vacancy loops and SFTs can be used to determine vacancy cluster type in the system under consideration here.

Figure 3: Numerically calculated diffuse scattering cross sections for vacancy loops (top) and stacking fault tetrahedra (bottom) of several representative sizes. Each spectrum is scaled by N , the number of point vacancies in the defect. The sizes refer to the diameter of the loops and the edge length of the SFTs.

2.4. Electron microscopy

Microstructural characterization was performed on the Ni sample. Samples consisting of (110) cross sections for transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were prepared by a focused ion beam (FIB) lift-out technique using a FEI Helios Nanolab Dualbeam workstation. **The standard “lift-out” procedure for the cross-sectional TEM sample preparation was first conducted by FIB. The FIB-induced surface damage that may obscure the damage created by the primary ion irradiation was removed using a flash polishing technique developed using unirradiated samples of the same materials by increasing the degree of flash polishing until the observed damage did not change any further.** Initial polishing used a 30kV Ga^+ beam with a $\pm 1.5^\circ$ angle between the Ga^+ beam and the sample surface. Final thinning and cleaning was performed at 5 kV with an incident angle $\pm 7^\circ$ for 5 min. This FIB polished sample was then flash polished using an electropolishing apparatus, with an electrolytic solution of 4% perchloric acid in 96% ethanol. An electric potential of 6–14 volts was applied to the sample in a temperature range of -30°C to -50°C . An accurate timer was used to control the polishing period between 0.05 s to 0.2 s.

Bright field TEM images were taken with a JEOL 3100R05 operated at

Figure 4: Bright field TEM images of a cross section of the Ni sample lying parallel to the (110) plane. (Top) Image showing damage profile. The (001) surface can be seen on the left, and the scale gives the depth along the [001] direction. The sample is slightly thicker at the top than the bottom. (Bottom) Section from the top image at a higher magnification.

300keV. Images were taken under a two-beam condition with $g=[200]$ using an exposure time of 2 seconds. Sample thickness was measured by electron energy loss spectroscopy (EELS). A representative image of the entire damage profile is shown in Figure 4. Over 4000 defects were counted over the entire depth of the damaged region to create the histogram shown below in Figure 8. To better see the smallest defects in these nickel based materials [35, 36, 37], weak beam dark field (WBDF) TEM images with $g=[200]$ and diffraction condition $g(3g)$ were collected with a JEOL 3011 operated at 300keV. The image pixel size and exposure time per pixel was 1024×1024 and 960 ms, and a representative image is shown in Figure 5. Over 2000 defects were counted in 6 images collected over the entire depth of the damaged region to create the histogram shown below in Figure 8. The size reported in the histogram

Figure 5: Weak beam dark field TEM images of a cross section of the Ni sample lying parallel to the (110) plane.

is the image size, and may slightly underestimate the actual defect size for sizes under 5 nm[38] Double C_s -Corrected STEM using a JEOL 3100R05 was employed for high resolution STEM imaging with an inner angle of 59 mrad and camera length of 15 cm. The image pixel size and exposure time per pixel was 1024×1024 and $30 \mu s$, and two representative images is shown in Figure 6. Approximately 10 HRTEM images of individual defects were taken over a range of depths, none of which were within 200 nm of the surface.

3. Results

Figure 2 shows the asymptotic diffuse scattering measurements scaled by q^4 , which represent the scattering from the defect clusters that were created by the irradiation process. For both the pure Ni and the NiCo alloy, there is far more scattering on the negative q side, corresponding to vacancy clusters, than the positive q side, corresponding to interstitial clusters. When the q^4 scaling is applied to diffuse scattering data, the scattering intensity is roughly proportional to the number of interstitials or vacancies in clusters rather than the number of defect clusters [12]. Thus the asymmetry of the spectra directly indicates that there are more vacancies than interstitials in clusters in the measurable size range. The NiCo spectrum is broader on the negative q side, and the peak is shifted toward larger values of $|q|$. On the positive q side, the NiCo spectrum has a higher intensity, and the diffuse peak is shifted toward larger values of $|q|$. Below we will show by fitting the measured spectra that these differences in the spectral shapes are

related to differences in the defect size distributions.

Figure 6: High resolution bright field STEM images of several defects taken from a (110) cross section of the Ni sample. (Top) Truncated stacking fault tetrahedron, with the inset to the right showing the calculated atomic positions for a full SFT. (Bottom) Interstitial loop, with the inset to the left showing the calculated atomic positions for a faulted interstitial loop.

TEM was used to identify the defect types that should be used in analysis of the diffuse scattering data. Figure 4 is a cross-section TEM micrograph showing the damage profile of the Ni sample. As predicted by the simulation (Fig. 1) the damage is fairly constant as a function of depth, then begins to fall off around 3500 nm. A defect size distribution was produced from this image (shown below in Fig. 8), but the defect types and their vacancy or interstitial nature were not identified. The defect types were, however, examined using high resolution TEM as shown in Figure 6. **Figure 6 also shows atomic positions calculated using MD for similar sized defects. The atom positions are shown as filled black circles for many (110) planes, thus the size and shape of the overlapping symbols represent the direction and degree of deviation in the displacements of atoms along the row, with the darker regions thus corresponding to larger strain. No attempt is made to simulate TEM images using these atom positions.** Both stacking fault tetrahedra

Figure 7: Fits of experimental spectra for (top) Ni and (bottom) NiCo.

(SFTs) and Frank interstitial loops were found, but no vacancy loops were identified. The top left corner of the SFT shown in Fig. 6 is difficult to identify, thus the SFT is likely truncated. Previous work has found both full and truncated SFTs in nickel with a ratio of 1.4 [39]. **While not enough defects (<10) were imaged using HR-TEM to be able to produce adequate statistics by defect type and make a firm conclusion about defect type, the fact that we saw only SFTs and no vacancy loops means we must consider SFTs when fitting our experimental diffuse scattering spectra.**

To evaluate the usefulness of diffuse scattering at distinguishing between loops and SFTs, we fit the experimental spectra using Equation 4, where i runs either over all possible sizes of both interstitial and vacancy loops, or over all sizes of both loops and SFTs. Figure 7 shows the results of the two types of fit for each sample. While both the loop fit and the loop/SFT fit are able to describe the $-q$ (vacancy) side of the experimental spectra quite well, only the loop/SFT fit is able to describe all of the data at once. When SFTs are included in the fit, they represent 90% of the total number of vacancy clusters in Ni and 95% in NiCo. However, the total number of vacancies and interstitials contained in the clusters does not change significantly. Unless otherwise indicated, numbers from the loop/SFT fit will be used in the following discussion.

Figure 8 shows the size distributions of both vacancy and interstitial type clusters resulting from the loop/SFT fit, as well as the size distribution from TEM for the Ni sample. In both samples, the vacancy clusters are much smaller than the interstitial

clusters, and both vacancy and interstitial clusters are smaller in NiCo than in Ni. Table 1 shows the diffuse scattering fit results along with the TEM results.

Sample	Ni			NiCo	
Method	Loop fit	Loop/ SFT fit	TEM	Loop fit	Loop/ SFT fit
vacancies ($\times 10^{17} \text{ cm}^{-3}$)	906	867		804	850
vacancy clusters	20.7	14.4		25.0	27.2
vacancy loops	20.7	1.5		25.0	1.3
SFTs	—	12.9		—	25.9
vacancy clusters < 4 nm	98.2%	93.6%		99.3%	98.5%
vacancy clusters < 2 nm	82.2%	34.4%		89.5%	81.3%
average cluster size (nm)	1.5	2.3		1.3	1.5
interstitials ($\times 10^{17} \text{ cm}^{-3}$)	279	283		372	387
interstitial clusters	0.33	0.35		0.84	0.98
average cluster size	6.8	6.7		5.1	4.6
defect clusters ($\times 10^{17} \text{ cm}^{-3}$)			1.35		
defects in clusters <20 nm			1463		
defects in clusters <10 nm			1026		

Table 1: Density of point defects and defect clusters. **Unless otherwise indicated, units are in 10^{17} defects/cm³. TEM statistics are calculated using the WBDF histogram for defects under 10 nm, and the BF histogram for defects above 10 nm.**

4. Discussion

4.1. Separation of vacancies and interstitials

Because interstitials are much more mobile at room temperature than vacancies, vacancy clusters must form directly from displacement cascades, while interstitial clusters may continue to evolve and aggregate after the cascade. The formation of vacancy clusters directly from cascades has been demonstrated by *in situ* TEM observation of vacancy clusters after irradiation of Ni at a temperature of 30 K [34]. Because the density and size of vacancy and interstitial type defects are affected by different processes, measurements of the density and size distribution of each type can help to understand the different ways that alloying affects irradiation damage. One of the ways in which diffuse scattering represents a valuable complementary tool to TEM is its inherent ability to distinguish between vacancy and interstitial type defects.

Making use of this capability, we found that there are more vacancies in vacancy clusters than interstitials in interstitial clusters in both samples, by a factor of 3.1 in Ni, and a factor of 2.2 in NiCo. We also found the vacancy clusters to be smaller than the interstitial clusters in both samples (Table 1), and that both types of clusters are smaller in the alloy than they are in the pure metal.

Figure 8: Semi-log plot of the absolute defect size distribution as a function of size for Ni (top) and NiCo (bottom). For Ni, the size distribution from **both BF and WBDF** TEM is also shown for comparison. Data are scaled so that the area under the curve is proportional to the total density of defect clusters.

Because vacancies and interstitials are generated simultaneously as Frenkel pairs, there are an equal number of each created. **While diffuse scattering has no inherent size limit, practically speaking the technique is not** very sensitive to point defects and very small defect clusters under ~ 0.3 nm in size because their diffuse scattering is at such a large $|q|$ that the noise overwhelms the signal. Our diffuse scattering measurements are also not sensitive to defects >30 nm because they occur at a $|q|$ that is so small that it is on the order of our instrumental resolution. Thus the ‘missing’ interstitials may be in either very large or very small clusters, or they may have migrated to the surface or existing defects in the starting material. **In TEM images, we did not observe any dislocation lines in these materials that could act as sinks.** Given the larger average size of the interstitial clusters compared to the vacancy clusters, it is unlikely that there are many interstitials in very small clusters. However, TEM does find that 1.3% of the defect clusters are above 20 nm in the Ni sample, and it is almost certain that these are of interstitial type. While there are not adequate statistics on these large clusters, since the number of interstitials in a cluster grows quadratically with size, the average size of these large defect clusters need be only ~ 45 nm to balance the number of vacancies and interstitials. This hypothesis is consistent with the smaller number of ‘missing’ interstitials in NiCo and the smaller average interstitial size, meaning fewer

interstitials are likely to be in defect clusters too large for diffuse scattering to detect.

4.2. Comparison of TEM and diffuse scattering size distributions

In addition to the ability to separate vacancy and interstitial clusters, a second advantage of the diffuse scattering technique is its sensitivity to small defect clusters, **from 0.3-2 nm in diameter**, which are more difficult to detect with TEM. This leads to more accurate defect cluster concentrations and size distributions which give a more complete picture of the damage in the material and the effects of alloying.

This sensitivity to small defects is particularly important for accurate assessments of vacancy type defects in the materials studied here. Table 1 shows that the average vacancy cluster diameters are quite small, 2.3 nm in Ni and 1.5 nm in NiCo, while the interstitial clusters have broader distributions with average diameters of 6.8 nm for Ni and 4.6 nm for NiCo. For Ni, the size distribution determined by diffuse scattering for both types of clusters is in good agreement with the TEM result for defects >4 nm. **Below 2 nm, the defect density calculated by diffuse scattering continues to rise exponentially with decreasing size, while the defect density determined by WBDF TEM begins to level off and then decrease with size. This discrepancy between TEM and diffuse scattering results for small defects** has also been reported by other authors, [30, 12] and indeed TEM imaging resolution limits are well studied with respect to radiation damage [38, 40].

While our finding that TEM imaging misses an important fraction of the smallest defects detected by diffuse scattering is certainly not new, our results comparing these two Ni and NiCo samples underscores the importance in radiation damage investigations of obtaining accurate measurements in the smallest size range. We find that the number of vacancy clusters increases by 90% in the alloy as compared to the pure metal, but that 81% of the vacancy clusters in NiCo are under 2 nm while only 34% are <2 nm in Ni. If we measured only defects with diameters above 2 nm, we would conclude incorrectly that the vacancy cluster concentration decreases by 54% in the alloy; this leading to incorrect conclusions about the effect of alloying on defect agglomeration.

4.3. Changes in defect properties with alloying

The sensitivity of X-ray diffuse scattering to both small and relatively large defect clusters in combination with the inherent ability of diffuse scattering measurements to generate separate size distributions for vacancy and interstitial type clusters makes it possible to assess aspects of the impact of alloying on radiation induced defect clusters. As both of the starting materials have similar impurity levels (0.02%), alloying with cobalt is the primary difference

between these materials. The vacancy and interstitial cluster size distribution information in Fig. 8 can be used in combination with the associated numerical data in Table 1 to determine information on the impact of alloying Ni with Co (NiCo) on the characteristics of radiation induced defects and gain insight into the physical processes determining their character.

As discussed in Section 3, the average sizes of both the vacancy clusters and the interstitial clusters are reduced by $\sim 30\%$ in NiCo compared to the cluster sizes in pure Ni. For the case here of ambient temperature and a 1.2 DPA radiation dose in Ni and NiCo, these results provide accurate, quantitative measurements for comparison with theory and MD simulations. Although MD simulations are presently not available for such times and doses, the experimental observation of smaller interstitial cluster sizes for NiCo compared to Ni can be understood qualitatively in terms of the decreased mobility of point defects in concentrated alloys. That is, the higher (or lower) the mobility of interstitials, the larger (or smaller) the average size of point defect agglomerates.

The mobility of vacancies is expected to be small, since the annealing stage-III activation of long-range vacancy migration is slightly above ambient temperature (~ 340 K) for Ni [5]. However, the $\sim 30\%$ reduction for the sizes of vacancy as well as interstitial clusters observed by the diffuse scattering measurements in NiCo suggests that a reduction of either single vacancy or small vacancy cluster mobility impacts the damage accumulation. In copper, clusters of a few vacancies have been found to be much more mobile than either single vacancies or larger vacancy clusters [41] at room temperature. Thus if very small vacancy clusters are solidified into the crystal as the liquid-like core cools, they may still aggregate into larger clusters. Likewise, after the system solidifies but is still hotter than the surrounding crystal, stage III mobility of single vacancies may still lead to vacancy aggregation. Thus a reduction in vacancy mobility in NiCo is the likely explanation for the reduced vacancy cluster size.

It has been proposed [6, 7, 13] that a longer lifetime of the liquid-like core during the thermal spike phase increases the probability of vacancy cluster densities and sizes by giving atoms more time to rearrange and cluster at the center of the cascade. However, the observation of smaller cluster sizes in NiCo than in Ni suggests that the impact of the lower thermal transport in NiCo and, hence, less rapid dissipation of heat from cascades in the alloy is not the dominant factor determining the vacancy cluster sizes. That is, since the thermal conductivity [17] is reduced in NiCo while the melting

temperature changes very little [14], cascade thermal spike temperatures and the duration of the thermal spike phase will be enhanced. This would tend to increase thermal diffusion of point vacancies and argue for larger vacancy cluster sizes in NiCo. Accordingly, the effect of the alloy-induced decrease in defect mobility appears to be a larger factor than increased cascade temperature and longevity. It will be of interest in subsequent investigations to perform measurements at lower irradiation doses to determine if the cluster size changes observed here are intrinsic to individual cascade processes or if they are influenced by cascade overlap in the moderate dose 1.2 dpa in this work.

4.4. Defect type

While the fact that diffuse scattering cross sections for defects of a particular size vary with defect type makes it possible to determine defect type, the presence of a distribution of sizes makes the determination of defect type somewhat more difficult. We have shown here that SFTs represent most of the vacancy type defects in these samples, 90% of the vacancy clusters in Ni and 95% in NiCo, and that this result is consistent with the high-resolution TEM results in Ni, which found SFTs but no vacancy loops. This conclusion relies on the fact that the SFTs produce less scattering than vacancy type Frank loops on the $+q$ (interstitial) side and that the experimental spectra have few small interstitial loops. Perfect loops have even more scattering on the opposite side of the main peak than Frank loops [30], thus diffuse scattering would be even better at identifying the difference between SFTs and perfect vacancy loops. But if there were more small interstitials which also produced scattering on the $+q$ side in our samples, our conclusion that vacancy clusters are mostly SFTs would be less reliable. In future work, the scattering of SFTs and vacancy loops will be studied in three-dimensional reciprocal space to see if a more reliable determination of defect type may be made by more extensive measurements.

Because the SFT is larger than a vacancy loop with the same number of point defects, it creates a lower strain in the surrounding material and acts as a weaker sink for interstitials, likely contributing the higher density of SFTs than vacancy loops in these materials. Previous work has found that both the shear modulus and the stacking fault energy are important for the formation and stability of SFTs [39], and that hexagonal Frank loops and SFTs have the smallest formation energies in Ni, with the SFT becoming slightly less energetically favorable than the Frank loops at larger sizes. The elastic constants in NiCo change little with alloying [15], but the stacking fault energy (SFE) decreases in fcc NiCo with increasing cobalt concentration, by approximately a factor of 2–4 for the equiatomic alloy compared to the pure metal [16]. Thus SFTs should be even more favorable in NiCo. This is consistent with our

finding that there are more SFTs in NiCo, though the difference is relatively small and more samples should be studied to test whether this conclusion is statistically significant.

Published estimates of the fraction of vacancy clusters that are SFTs in room temperature irradiated Ni measured by TEM vary significantly, both from our result and from one another. Robinson and Jenkins [33] reported seeing only faulted loops in Ni irradiated Ni, but only analyzed $\sim 10\%$ of the population, while Kitagawa et al. [42] reported that the vast majority, $>90\%$, of the vacancy type clusters were SFTs in Ar irradiated Ni. A more precise analysis by Robertson et al. [34] of the vacancy type loops in Kr^+ irradiated Ni found that 7.8% were SFTs, 61.8% were faulted or perfect loops, and the remaining 31.4% were unassigned. **These large variations are likely due to differences in TEM imaging conditions, which significantly change the lower size limit of detectability as demonstrated by the contrast between BF TEM and WBTEM histograms shown in Fig. 8. This variation in the SFT fraction could be also related to the smaller Burgers vectors of SFTs which makes their contrast fainter than loops of the same size [39].** Schäublin et al. [39] also compared the size distributions of SFTs, loops, and unidentified defects in Ni, finding that the average size of SFTs is smaller than the average size of loops, and the average size of uncatagorized defects to be smaller still. Thus more of the SFTs are likely to be missed by TEM due to their smaller size and fainter contrast and could easily result in large differences in the fraction of SFTs when different TEM methods are used.

5. Conclusions

Diffuse X-ray scattering has been used with TEM to investigate the density, size, and types of defect clusters generated in Ni and NiCo irradiated with MeV Ni ions to a dose of 1.2 dpa. The inherent sensitivity of diffuse X-ray scattering to small defects and its capability to provide separate size distributions for vacancy and interstitial type defect clusters has been coupled with the complementary abilities of TEM to determine the type of individual defect clusters together with defect cluster concentrations and size distributions to form a more complete picture of radiation damage in these materials.

The results show that both NiCo and pure Ni contain high concentrations of small vacancy type defects with average sizes of 1.5 nm in NiCo and 2.3 nm in Ni. In both samples, the interstitial defect clusters were found to be larger with average diameters of 6.8 nm in Ni and 4.6 nm in NiCo. The diffuse scattering and TEM results are in agreement that most of the vacancy clusters are SFTs. Moreover, the absolute concentrations and size distributions for both vacancy and interstitial clusters measured by diffuse X-ray scattering agree

well with TEM for the larger clusters. Albeit to a much smaller extent in the weak-beam case, both weak-beam and bright field TEM determined concentrations were found to fall appreciably below the X-ray results for cluster sizes below the 2 nm diameter range where TEM spatial resolution begins to be an issue. This demonstrates the important complementary use of direct imaging of defects by TEM compared with the diffuse scattering detection of small clusters without an inherent lower size limit for obtaining the most complete information.

The diffuse scattering measurements demonstrated that NiCo retains nearly twice as many vacancy clusters as Ni, but also that the significantly smaller sizes found in NiCo resulted in a nearly equal total number of vacancies in the two cases.

Thus we have exploited the complementarity of TEM and X-ray diffuse scattering measurements to study radiation induced defect clusters in a model system of pure Ni and binary Ni alloy NiCo. Comparison of the size distributions for vacancy and interstitial clusters in NiCo and pure Ni suggest that the decreased mobility of defects in the alloy is responsible for the significant reduction in the sizes of both vacancy and interstitial clusters in NiCo.

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We study defects in ion irradiated Ni and NiCo using diffuse X-ray scattering and TEM

We exploit the complementarity of these two methods for a complete picture of damage

Defect clusters in NiCo are smaller and more numerous than defect clusters in Ni

Both methods find that most vacancy clusters are small stacking fault tetrahedra