**Microstructure, chemistry and mechanical properties of Ni-based superalloy Rene N4
under irradiation at room temperature**

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Abstract:

Nickel superalloys with cubic $L1_2$ structured γ' ($\text{Ni}_3(\text{Al}, \text{Ti})$) precipitates exhibit high strength at high temperatures and excellent corrosion resistance when exposed to water. Unlike prior studies on irradiation damage of other Ni-based superalloys, our study on Rene N4 involves much larger γ' precipitates, ~ 450 nm in size, a size regime where the irradiation-induced disordering and dissolution kinetics and the corresponding mechanical property evolution are unknown. We report that under heavy ion irradiation at room temperature, the submicron-sized γ' precipitates were fully disordered at ~ 0.3 dpa and only later partially dissolved after 75 dpa irradiation. Nanoindentation experiments indicate that the mechanical properties of the alloy change significantly, with a dramatic decrease in hardness, with irradiation dose. Three contributions to the change in hardness are examined: defect clusters, disordering and dissolution. The generation of defect clusters in the matrix and precipitates slightly increased the indentation hardness, while disordering of the submicron-sized γ' precipitates resulted in a dramatic decrease in the total hardness, which decreased further during the early stages of the intermixing between γ' precipitates and matrix (<18 dpa). Controlling the long-range-ordering and chemical intermixing can be used to tailor the mechanical properties of Ni-based superalloys under irradiation.

Keywords: Ni-based superalloy, ion irradiation, order-disorder transition, dissolution, mechanical properties.

1. Introduction

Ni-based alloys have been proposed as structural materials in next generation nuclear reactors due to their superior high temperature mechanical properties and corrosion resistance [1-4]. For instance, solid solution strengthened Inconel 617 is considered as a candidate material for the components in high temperature gas-cooled fast reactors (GFR), such as in the heat exchangers and turbine blades [1]. The precipitation-hardened Nimonic PE 16 alloy has been tested as a cladding material in fast breeder reactors (FBR) [5]. In addition, Ni-based superalloys are often used for spallation target and window applications, where the materials have to withstand low-temperature irradiation with high-energy protons and spallation neutrons [6-8].

The high temperature strength of Ni-based superalloys mainly originates from the long-range ordered (LRO) γ' ($\text{Ni}_3(\text{Al}, \text{Ti})$) precipitates, possessing the cubic L1_2 structure, and γ'' (Ni_3Nb) precipitates, possessing the hexagonal D0_{22} structure [9, 10]. However, these precipitates are susceptible to phase instability under irradiation environment. Several radiation damage studies have focused on the behavior of these precipitates under irradiation. Examples include a study using separately neutron and proton irradiation at low temperatures (32-55°C), where it was shown that the precipitate phases, γ' and γ'' with a size of 10-20 nm, in Inconel 718 became disordered by 0.6 dpa [11]. In another study on Nimonic PE16 with ~20 nm γ' (Ni_3Al and Ni_3Ti) precipitates, it was shown that the precipitates were fully dissolved after Ni ion irradiation to a dose of 10 dpa at room temperature [12, 13].

Irradiation-induced disordering of LRO precipitates is attributed to the creation of vacancies, interstitials and anti-site defects, which can disrupt the chemical and structural ordering of the precipitates [14-18]. However, as diffusion is enhanced, for example, by irradiation or thermal annealing, the disordered atoms tend to return to the equilibrium sites and

the annihilation of defects can be promoted [12, 19, 20]. Müller et al. [21] reported that the disordering kinetics below room temperature are mainly based on the thermal spike model, while at elevated temperatures, the disordering and reordering processes occur simultaneously. Ewert et al.[20] studied the reordering kinetics of irradiation-disordered Ni_3Al and found that reordering at high temperatures is dominated by the motion of non-equilibrium vacancies. Liou et al.[22] proposed a model to calculate the steady state of these two opposing processes (disordering and reordering) and concluded that the increased free energy of partially or fully disordered phases are sufficient to cause phase instability and modify the phase diagrams.

In addition to disordering, the displacement of atoms induced by irradiation can cause the atoms in precipitates to migrate into the surrounding matrix, resulting in the dissolution of precipitates [14, 23, 24]. Nelson et al.[25] pointed out that the occurrence of disordering can destabilize the precipitates and promote dissolution. The chemical dissolution can be controlled by cascade-induced ballistic displacements and thermal spikes. Sigmund et al.[26] concluded that ballistic displacements have a dominating influence on the mixing behaviors during the low-energy ion bombardment. Rossum et al.[27] explained the ion mixing rate of metallic bilayers at temperature of liquid nitrogen by using a model based on thermal spikes. Molecular dynamics (MD) simulations on radiation-induced mixing of Cu/Nb interface showed that the atoms undergo ballistic displacement within first 0.3 ps. After 0.3 ps, thermal spikes start to shrink and last ~ 10 ps [28].

Ordered intermetallic compounds normally have high strength and poor ductility at ambient temperature, whereas their disordered counterparts tend to be softer and more ductile. For example, disordered fcc Ni_3Al exhibited almost twice the critical strain to fracture, more than three times the fracture toughness and $\sim 20\%$ lower hardness than ordered L1_2 structured Ni_3Al

[29]. Ni-based superalloys with γ and γ' phases generally possess a good combination of strength and ductility, while the buildup of interstitials and vacancy clusters, radiation-induced disordering and dissolution of γ' precipitates can cause a significant degradation of mechanical properties. Maloy et al.[30] reported that, for Alloy 718 strengthened by γ' and γ'' precipitates ~ 20 nm in diameter, the uniform elongation decreased to less than 2% after 0.5 dpa of neutron exposure, and the yield strength increased slightly at low doses up to 1 dpa due to the generation of dislocation loops and then decreased at higher doses because of the disordering and dissolution of the precipitates.

Ni-based superalloy Rene N4 is the first generation single crystal turbine airfoil alloy with enhanced oxidation resistance and superior long-time rupture strength [31, 32]. Compared to the other precipitation hardening Ni-based superalloy, like Inconel 718 and Nimonic PE 16, the size of the γ' precipitates of Rene N4 in this study is much larger, ~ 450 nm. Irradiation-induced disordering, dissolution and the corresponding mechanical response of submicron-sized γ' precipitates are still unknown. Here we performed *in situ* ion irradiation experiments to directly observe the order-disorder transformation of γ' precipitates and *ex situ* irradiation experiments to explore the kinetics of chemical intermixing between γ' precipitates and matrix under high dose irradiation. Nanoindentation testing was employed to examine the evolution of mechanical properties of irradiated Rene N4 with respect to the disordering and dissolution of γ' precipitates.

2. Methodologies

2.1 Materials and ion irradiations

The chemical composition of the single crystal Ni-based superalloy Rene N4 is Ni-9.8Cr-7.5Co-6W-4.8Ta-4.2Al-3.5Ti-1.5Mo-0.15Hf (wt.%), and the details of the heat treatment have been reported [33]. *In situ* Kr²⁺ ion irradiations with an energy of 1 MeV at room temperature were performed under IVEM at Argonne National Laboratory [34] to study the microstructure evolution at a low fluence, 1×10^{14} ions/cm². The average flux of Kr ions was 2×10^{11} /cm²·s. Ni³⁺ ion irradiations with an energy of 3 MeV at room temperature were performed at different fluences. *Ex situ* Ni³⁺ ion irradiation experiments were performed in the Ion Beam Materials Laboratory in Los Alamos National Laboratory on a Tandem accelerator using fluences of 1×10^{15} , 2.4×10^{16} and 1×10^{17} /cm² with a flux of 6×10^{12} /cm²·s, and *in situ* irradiation facility at Sandia National Laboratories [35] were used to examine the order-disordering transition under Ni³⁺ ion irradiation. SRIM simulations were used to predict the profile of damage and Kr and Ni ion concentration distribution by using Kinchin-Peace method [36]. The displacement energy, 25eV, was used in the calculations. The results in Figure 1 show that the Kr ions with an energy of 1 MeV and Ni³⁺ ions with an energy of 3 MeV penetrate deep into the material, leaving behind a relatively uniform damage region over the first 100 nm of the sample. Transmission electron microscopy (TEM) sample foils were used in irradiation experiments for microstructure characterization, and disks with 3mm diameter were irradiated for mechanical testing.

2.2 Material characterization

Electron microscopy analysis was performed to study the evolution of long-range ordering, defect clusters and chemical stoichiometry before and after irradiation. Field emission scanning electron microscopy (FESEM), using an FEI Inspect, was used to observe the overall microstructure of pristine Rene N4. TEM measurements were performed to examine the

irradiation-induced microstructure using both a FEI Tecnai F30 and JEOL 3000F operating at 300 keV. Scanning transmission electron microscopy (STEM) equipped with energy dispersion spectrum (EDS) was used to identify the chemical dissolution of precipitates under irradiation. TEM sample foils were prepared by twin-jet polishing in 5% perchloric acid ethanol solution at temperature of -30°C.

2.3 Nanoindentation testing

To investigate the effect of irradiation-induced disordering, dissolution and defect clusters on the mechanical strength, nanoindentation hardness measurements were performed on samples with different radiation damage levels. A Nano Indenter XPTM from Materials Testing System Corporation installed with a Berkovich indenter tip was used to test the indentation hardness at room temperature. The indentation measurements were operated in continuous stiffness mode (CSM) at a constant nominal strain rate of 0.05 s⁻¹. Twenty-five indentations were made on the surface of each sample. Indentation hardness as a function of indentation depth were determined by using Oliver and Pharr analysis[37].

3. Results

3.1 Microstructure of pristine Rene N4

The microstructure obtained using both SEM and TEM of pristine Rene N4 is shown in Figure 2. Figure 2a is a SEM micrograph showing a regular cuboidal structure with average size of ~ 450 nm. Figure 2b shows the TEM micrograph of the pristine Rene N4; the inset selected area diffraction (SAD) pattern in this figure indicates that the pristine Rene 4 alloy is single crystalline. The superlattice reflections shown in the SAD pattern originate from γ' precipitates,

implying a chemically ordered $L1_2$ structure within the precipitates. Figure 2c shows a bright field TEM image obtained under a two-beam condition with diffraction vector $g=[100]$ and the corresponding dark field image is shown in Figure 2d. The cuboidal γ' precipitates with bright contrast and the fcc structured matrix with dark contrast are easily distinguished from one another in Figure 2d.

3.2 *In situ* Kr^{2+} ion irradiation under low fluences

Figure 3 shows the microstructural evolution of Rene N4 under *in situ* Kr^{2+} ion irradiation at room temperature. Dark field imaging with reflection vector $g=[200]$ was used to view the dislocation loops. Figures 3a-b show the dark field image and corresponding diffraction pattern of the pristine sample, respectively. Again, the weaker superlattice reflections indicate the presence of $L1_2$ structured γ' precipitates. After irradiation to a dose of 0.2 dpa, shown in Figure 3c, dislocation loops were generated and the diffraction pattern in Figure 3d reveals that the intensity of the superlattice reflections has decreased, suggesting the occurrence of a disordering process. By 0.3 dpa, the density and average size of the dislocation loops increased to $\sim 1.8 \times 10^{22}/m^3$ and ~ 5 nm, respectively, as shown in Figure 3e. No superlattice reflections were detected in the diffraction pattern in Figure 3f, implying that the ordered γ' precipitates became fully disordered by 0.3 dpa. We also observed that the precipitate starts to expand immediately under irradiation. A representative example in Figure 3 shows that two phase boundaries migrate towards each other and the distance between them decreased from 45 to 30 nm by a dose of 0.3 dpa. The supplementary video #1 shows dark field TEM imaging of the evolution of the material under *in situ* irradiation from 5.2×10^{-3} to 12.5×10^{-3} dpa; during this irradiation, the generation of defect clusters and expanding of precipitate were observed.

3.3 Ni³⁺ ion irradiation to high fluences

The order-disorder transition of the γ' precipitates under *in situ* Ni ion irradiation at room temperature is shown in Figure 4. SAD patterns were taken from the same area successively starting from the pristine case up to a dose of 0.3 dpa. The region monitored during the irradiation contained both γ' precipitates and the matrix. Figure 4a shows the SAD pattern of the pristine sample and Figure 2b-d show the SAD patterns after irradiation to doses of 0.1, 0.2, and 0.3 dpa, respectively. The SAD patterns reveal that the intensity of reflections from γ' precipitates decreases with increasing dose. By 0.3 dpa, no superlattice reflections were observed, suggesting that the γ' precipitates lost the long-range-ordering under Ni ion irradiation. Supplementary video #2 shows the evolution of SAD pattern under Ni ion irradiation. Decrease of the intensity of the superlattice spots was clearly observed.

Dislocation loops were formed in γ' precipitates and matrix of Rene N4 under irradiation as shown in Figure 5. Bright field TEM images were obtained under a two-beam condition, with the diffraction vector $g=[110]$, and the corresponding dark field images were used to image the irradiation-induced dislocation loops which appear as classic black spots. By a dose of 0.75 dpa, individual dislocation loops were formed in the cuboids as well as at the γ'/γ phase boundaries. The dislocation loop density in the cuboids was $\sim 1.5 \times 10^{22}/\text{m}^3$ and the average size of the loops was ~ 6 nm. At 75 dpa, the density and the size of dislocation loops increased to $\sim 2.8 \times 10^{22}/\text{m}^3$ and ~ 10 nm, respectively. Figure 6 shows the evolution of the loop density and size under irradiation up to a dose of 75 dpa. The density and size of the loops increased for doses lower than 18 dpa and then saturated to a steady state level for doses from ~ 18 dpa up to 75 dpa. The

SEM images in Figure 7 show the size of cuboids increased from an initial 0.45 μm to 0.50 and 0.65 μm after irradiation to doses of 0.75 and 75 dpa, respectively.

The evolution of selected chemical constituents in Rene N4 under irradiation was shown in the EDS mapping measurements in Figure 8. In the pristine sample, cuboids with clear phase boundaries were observed. Al, Ti and Ni were enriched in the cuboidal γ' precipitates, while Co, Cr and Mo were enriched in the fcc structured matrix phase. Under irradiation, chemical intermixing occurred and the phase boundaries diminished. By 75 dpa, most of the large aggregates were still visible, although partially dissolved. However, even by this large dose, the precipitates, for the most part, retained their chemistry. Figures 9a-b show the evolution of the measured chemical profile across a phase boundary using the EDS line scan technique. λ denotes the broadness of the phase boundaries, which was measured as the distance from the maximum/minimum concentration to the minimum/maximum concentration of the elements. Before irradiation, the broadness of phase boundary (λ_0) is ~ 20 nm. After 75 dpa, the broadness (λ) increased to ~ 100 nm. Figure 9c is a plot comparing the broadness of the phase boundary with irradiation dose and Figure 9d shows the intermixing length squared $[(\lambda - \lambda_0) / 2]^2$ as a function of irradiation dose. By using $D_{\text{mix}} = \frac{[(\lambda - \lambda_0) / 2]^2}{6(\text{dose})}$ (considering 3 dimensional diffusion), the effective intermixing diffusion coefficient D_{mix} was estimated to be $\sim 3.1 \text{ nm}^2/\text{dpa}$, which was used to determine the mixing parameter in the discussion section.

3.4 Nanoindentation hardness evolution

The mechanical properties of the pristine and Ni ion irradiated Rene 4 were evaluated by performing nanoindentation measurements. Indentation hardness was measured instantaneously

when the indentation tip probed into the sample. Figure 10a shows the indentation hardness as a function of indentation depth for samples with different irradiation damage levels. In order to minimize artifacts of the surface and the nonirradiated region, the values of indentation hardness measured at a depth of 200-300 nm, which are reasonably far from each region, were compared. As shown in Figure 10b, the indentation hardness decreased dramatically from ~ 8.3 to ~ 6.5 GPa after irradiation to 0.75 dpa, further decreased to 5.9 GPa after 18 dpa, and eventually saturated at ~ 5.8 GPa for doses up to 75 dpa.

4. Discussion

4.1 Disorder of γ' precipitates

The γ' precipitates in Rene N4 start to disorder immediately after irradiation and become completely disordered by a very low dose of 0.3 dpa at room temperature. The order-disordering transformation occurs over three different timescales under irradiation. First, in the initial collision stage, disordering can be induced by mixing within displacement cascades with local molten cores. Second, the population of the cascade-induced point defect increases rapidly and defect clusters are created, as shown in Figure 3e. The generation and migration of point defects, defect clusters and anti-site defects disrupt the ordered sites and induce disorder. Third, the dissolution of the precipitates results in the instability of the stoichiometry and thus destabilizes the ordering of the precipitates. Destruction of LRO in precipitates and the chemical intermixing between precipitates and matrix occur simultaneously[12], while for our study at room temperature, disordering of the γ' precipitates in Rene N4 occurs at relatively low doses (<0.3 dpa), which do not allow for the full dissolution of submicron-sized γ' precipitates, as shown in Figure 8. MD simulations [38] also show that $L1_2$ crystalline LRO of Ni_3Al was lost under

irradiation at 10K within 1 ps, this time scale was too short to allow for a comparable loss of chemical short-range ordering (SRO). Thus, it is suggested that the effect of chemical interdiffusion on the disordering of submicron-sized γ' precipitates in Rene N4 is insignificant under irradiation at room temperature.

4.2 Dissolution of γ' precipitates

The chemical concentration profiles of phase boundaries in irradiated Rene N4 show that after irradiation at 75 dpa, the precipitates are only partially dissolved and the chemical aggregate domains can still be clearly observed in the sample, as shown in Figure 8. In Camus's work [12], the γ' precipitates in Nimonic PE16 were completely dissolved at room temperature under a much lower dose of ~ 10 dpa. This rapid rate of dissolution is due to the smaller size of the precipitates in Nimonic PE16, ~ 20 nm, than those in Rene N4, ~ 450 nm. Matsumura et al.[39] developed a kinetic model and suggested that the ordered precipitates could survive with longer life time before complete dissolution through increasing their volume fraction. The chemical intermixing associated with the displacement cascades are attributed to collision and thermal spike processes. The mixing parameter (k) of γ/γ' interface can be described as[40]:

$$k = \frac{D_{mix} t}{\Phi F_D} = \left(\frac{\langle Dt \rangle}{\Phi F_D} \right)_{collision} + \left(\frac{\langle Dt \rangle}{\Phi F_D} \right)_{thermalspike} \quad (1)$$

where t is the irradiation time, Φ is the ion fluence and F_D is the damage energy deposited per unit length normal to the specimen surface, as calculated from nuclear stopping by SRIM. D_{mix} is the effective intermixing diffusion coefficient. By using $t=16200$ s, $\Phi = 10/\text{\AA}^2$, $F_D = 75$ eV/ $\text{\AA}$ /ions and $D_{mix} = \sim 1.4 \text{\AA}^2/\text{s}$, k is calculated to be $\sim 30 \text{\AA}^5/\text{eV}$. The value of k predicted by

the collisional model is less than $10 \text{ Å}^5/\text{eV}$ [41]. The magnitude of κ estimated in the current experiments is much greater than the range predicted by collision theory. MD simulations on the radiation-induced intermixing of Ni/Ni₃Al interface show that κ is $\sim 13\text{-}20 \text{ Å}^5/\text{eV}$ [42], which is close to our experimental value and also larger than the κ value estimated by collision process. Thus, we conclude that thermal spike is the major mechanism contributing to the chemical intermixing between γ' precipitates and matrix in Rene N4 under irradiation.

4.3 Evolution of nanoindentation hardness

Precipitates can impede the motion of mobile dislocations through a variety of interaction mechanisms, including ordering strengthening, coherency strengthening, modulus hardening, etc[43]. Here the evolution of the nanoindentation hardness of irradiated Rene N4 is determined by the combined effects of the formation of defect clusters, disordering and dissolution. Each has a different effect on the strength of the alloy: (1) Radiation-induced defect clusters, such as dislocation loops, produce resistance forces against dislocation glide and thus result in small obstacle hardening by the interaction of mobile dislocations with defect clusters, increasing the strength [44-46]. (2) During the interaction of dislocations with ordered precipitates, antiphase boundaries (APBs) can be created. The creation of APBs opposes the motion of dislocations that move into the ordered precipitates and thus enhance the strength of the alloy. Radiation-induced disordering can result in the loss of the ordering strengthening by antiphase boundaries. (3) The misfit of lattice parameters between precipitates and matrix gives rise to strain fields which interact with dislocations and can also impede the movement of dislocations. Chemical decomposition under irradiation mitigates the hardening effects of misfit strain and leads to a decrease in hardness. In our study, the order-disorder transformation occurs at low-dose region

and significant chemical intermixing arises at high-dose region, the change of the total strength

of Rene N4 under irradiation ($\Delta \tau_{cT}$) can be estimated by:

$$\Delta \tau_{cT} = \tau_{cL} - \tau_{cO} - \tau_{c\varepsilon} \quad (2)$$

The first term, τ_{cL} arises from the irradiation-induced dislocation loops and can be described as[47]:

$$\tau_{cL} = \alpha \mu b \sqrt{Nd} \quad (3)$$

where α is a parameter depending on average barrier strength of loops and is estimated to be 0.2 [48], μ is the shear modulus ($\mu = 90$ GPa for Rene N4), b is the Burgers vector ($b = 0.25$

for Rene N4). N and d are the density and size of dislocation loops, respectively. By using

$H = 2.7 \sigma_y$ [49] and $\sigma_y = M \tau_{cL}$, where M is the Taylor factor, 3.06 for fcc structured metals [50], the loop-induced hardness increase in the irradiated Rene N4 as a function of dose was plotted in Figure 10b. Clearly, the irradiation-induced hardness saturates after irradiation to 18 dpa. The second term in Equation (2) describes the loss of precipitate hardening due to

disordering. Assuming that during the deformation, the leading dislocation bows out between

precipitates and the trailing dislocation remains straight, the order strengthening (τ_{cO}) can be

calculated by[43]

$$\tau_{cO} = \frac{\gamma_{APB}}{2b} \left[\left(\frac{3\pi^2 \gamma_{APB} f l}{32 T} \right)^{1/2} - f \right] \quad (4)$$

where γ_{APB} is the antiphase boundary energy, 83 mJ/m² for (100) APBs[51]. l is the edge-to-

edge distance between the precipitates ($l = 50$ nm for the pristine Rene N4). f is the volume

fraction of the precipitates, $\sim 65\%$. Line energy of dislocation, $T = \mu b^2 / 2$ [52]. By using the parameters above, the hardness drop after irradiation to 0.75 dpa due to the loss of ordering is calculated to be ~ 1.8 GPa. The third term in Equation (2), $\tau_{c\varepsilon}$, describes the intermixing-induced softening due to the removal of misfit strain between the disordered precipitate and matrix[43].

$$\tau_{c\varepsilon} = 1.2 f^{1/2} \left(\frac{T^3 \mu \varepsilon}{b^3 r^3} \right)^{1/4} \quad (5)$$

where mismatch strain $\varepsilon = \Delta a / a$, $\sim 1.4\%$, r is the size of the precipitates, ~ 225 nm. The intermixing-induced hardness drop is calculated to be ~ 0.9 GPa. Irradiation-induced chemical decomposition results in the removal of misfit strain. The total hardness change estimated by Equation (2) was compared with the experimental results, shown in Figure 10b. In Figure 10b, after irradiation at 0.75 dpa, disordering-induced softening completes. After 18 dpa, the dislocation loop-induced hardening reaches a steady state. Although the chemical intermixing still expands and increase the broadness of the boundaries, the total indentation hardness saturates at ~ 5.8 GPa, suggesting that chemical intermixing has negligible impact on the strength under high dose irradiation (>18 dpa). **A good agreement between the theoretical analysis and our experiment results indicate the softening of Rene N4 under irradiation at room temperature mainly originates from the disordering of precipitates and the chemical intermixing between precipitates and matrix.**

At room temperature, thermal diffusion is limited and the effect of recovery on the disordering and chemical intermixing is not considerable. Hardness starts decreasing at relatively low doses. We predict that increasing the irradiation temperature promotes the recombination of defects and facilitates the disordered constituent precipitate atoms back to the

thermodynamically stable sites, thus the effect of reordering is enhanced and the disordering-induced softening can be mitigated. In addition, under irradiation at high temperatures, the re-precipitation of γ' precipitates might result in the regaining of the hardness. Further studies are needed to understand how the mechanical properties correspondingly change with irradiation damage evolution at elevated temperatures in this alloy.

5. Conclusions

We performed *in situ* and *ex situ* heavy ion irradiations at room temperature on Ni-based superalloy Rene N4 with submicron-sized γ' precipitates. Irradiation-induced order-disorder transition, dissolution and the corresponding mechanical property evolution were studied. The γ' precipitates become fully disordered at a dose of 0.3 dpa, and after irradiation up to 75 dpa, the γ' precipitates are only partially dissolved due to the thermal spike effects. The combined effects of defect clusters, order-disordering transition and dissolution determine the evolution of hardness under irradiation. Irradiation-induced defect clusters slightly harden the alloy, while disordering of γ' precipitates result in a dramatic drop in the total hardness due to the loss of precipitation hardening. Chemical intermixing of γ' precipitates softens the alloy only in the early stages of dissolution (<18 dpa). This study sheds light on the degradation mechanisms of Ni-based superalloys under extreme irradiation environments.

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Figures

Figure 1 SRIM simulations of damage and ion concentration profiles in Rene N4 calculated by Kinchin-Peace method. (a) Kr ion irradiation at energy of 1 MeV to a fluence of $1 \times 10^{14} \text{ ions/cm}^2$. (b) Ni ion irradiation with ion energy of 3 MeV to a fluence of $1 \times 10^{17} \text{ ions/cm}^2$.

Figure 2 Microstructure of pristine Rene N4. (a) SEM image showing the cuboidal structure of the precipitates. (b) Bright field TEM image with zone axes of $[001]$. The γ'/γ phase boundaries were on $\{100\}$ planes. (c) Bright field TEM image under two-beam condition with diffraction vector $g=[100]$. (d) Dark field TEM micrograph. The bright cuboidal structure originates from the γ' precipitates.

Figure 3 *In situ* Kr ion irradiation of Rene N4 at room temperature. (a) (c) (e) show the dark field images of the microstructure after irradiation to 0, 0.2 and 0.3 dpa, respectively. Kinematic imaging condition with diffraction vector $g=[200]$ were selected. (b) (d) (f) show the corresponding diffraction patterns. After Kr ion irradiation to a dose of 0.3 dpa, a high density of dislocation loops was generated and the γ' precipitates became fully disordered. The precipitates expanded, manifested as the decrease in the distance between two phase boundaries from 45 to 30 nm.

Figure 4 Disordering of the γ' precipitate phase under *in situ* Ni ion irradiation at room temperature. (a) Selected area diffraction (SAD) pattern of pristine Rene N4. The superlattice spots correspond to the γ' precipitate phase. (b) After 0.1 dpa irradiation, the intensities of the superlattice reflections were weakened. (c) After irradiation to 0.2 dpa, the intensities of superlattice spots decreased further. (d) By a dose of 0.3 dpa, the ordered γ' precipitate became fully disordered.

Figure 5 Generation of defect clusters in Rene N4 under *ex situ* Ni ion irradiation at 0.75 dpa (a-c) and 75 dpa (d-f). (a) Bright field TEM image under two-beam condition with diffraction vector $g=[110]$. As shown, dislocation loops were generated under irradiation. (b) Dark field TEM image showing the dislocation loops were generated in the precipitates, matrix and at the γ'/γ phase boundaries. (c) Magnified region A in (a). The phase boundary was still well-defined and dislocation loops preferentially formed on the phase boundaries. (d) Bright field TEM image of Rene N4 after irradiation up to 75 dpa. (e) Dark field TEM image showing a high density of dislocation loops were formed. (f) Magnified region B in (d). By this dose, the phase boundaries became vague.

Figure 6 Evolution of loop size and loop density in Rene N4 under Ni ion irradiation at room temperature. The size of radiation-induced loops increased with irradiation dose and then saturated at a size of ~ 10 nm by a dose of ~ 18 dpa. The density of irradiation-induced loops also saturated by ~ 18 dpa, reaching a value of $2.8 \times 10^{22}/\text{m}^3$ at 75 dpa.

Figure 7 SEM images of the cuboids in irradiated Rene N4. (a) After irradiation at 0.75 dpa, the phase boundaries were clearly observed and the average size of the cuboids was 0.5 μm . (b) After 75 dpa, the boundaries became indistinct, with some cuboids coalescing, and the average cuboid size increased to 0.65 μm .

Figure 8 EDS mapping of selected elements in Rene N4 after irradiation to 0.75, 18 and 75 dpa. In the pristine sample (0 dpa), clear phase boundaries were observed. Al, Ti and Ni were depleted, while Co, Cr and Mo were enriched in matrix. Under irradiation, chemical intermixing occurred. At 75 dpa, some phase boundaries became discontinuous due to the chemical intermixing.

Figure 9 Chemical profiles across the phase boundary in Rene N4 under irradiation. (a) Pristine sample, the broadness (λ_0) of the phase boundary is measured to be 20 nm. (b) After irradiation to a dose of 75 dpa, broadness (λ) increased to ~ 100 nm. (c) Broadness of the phase boundary as a function of irradiation dose. (d) The intermixing diffusion length squared versus irradiation dose. The effective intermixing diffusion coefficient was estimated to be $3.1 \pm 0.3 \text{ nm}^2/\text{dpa}$.

Figure10 (a) Hardness as a function of penetration depth for different irradiation doses. The hardness at a depth between 200-300 nm (shaded region) was considered to avoid contributions from surface and unirradiated regions. (b) Total hardness change (ΔH_{total}) and loop-induced hardening (ΔH_{loop}) vs irradiation dose. The total hardness decreased significantly after irradiation to a dose of 0.75 dpa, further decreased after 18 dpa and saturated under higher dose irradiation.

The calculated total hardness change (open squares) is compared with experimental data (solid squares).

Supplementary Video

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