Evolution dependence of vanadium nitride nanoprecipitates on directionality of ion irradiation

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1. Introduction

Accelerated ion irradiation has been used to emulate reactor irradiation damage in structural materials because of its economic advantages and capability of emulating neutron irradiation-induced features to some extent [1]. There are extensive examples of the similarities between proton irradiation and reactor irradiation, in terms of induced microstructures and some properties, but far fewer examples of the comparability of self-ion irradiation and reactor irradiation with regard to radiation-produced defects or defect-solute clusters such as loops, voids, and precipitates [2]. However, the advantages of very high damage rates, minimal activation, and excellent controllability of irradiation conditions make self-ion irradiation a good option for emulating radiation effects in a reactor environment.

Evolution of precipitates is an essential phenomenon that may directly influence the mechanical properties and even corrosion-related properties of alloys. Radiation-induced or -enhanced precipitates, together with some radiation-modified precipitates, have been reported in austenitic stainless or ferritic steels [1,3–5]. Reports on the evolution—in shape, size, and density—of radiation-modified precipitates are limited. This paper presents the effects of self-ion irradiation on the evolution of pre-existing precipitates.

2. Experimental

Samples of a model ferritic alloy (Fe–1.11Cr–0.44W–0.09Mn–0.18Si–0.22V–0.0964N–0.0089C–0.0046O in atomic percentages or at%), characterized by dispersed vanadium nitride (VN) nanoprecipitates with a density of (8.02 ± 2.86) × 10^{20} m^{−3} and an average particle length of 20.1 ± 4.1 nm [6,7], were used in this study because of the prevalence of VN precipitates in both ferritic-martensitic and austenitic stainless steels. The face-centered cubic VN nanoprecipitates were formed in ferrite with a body-centered cubic (bcc) structure in the wake of the migrating austenite-ferrite boundary during thermo-mechanical processing and heat treatment [8]. The model alloy facilitates this analytical study because it has a simple homogeneous microstructure of VN nanoprecipitates dispersed in ferrite grains, in contrast to the complex heterogeneous microstructures of ferritic-martensitic steels with their high densities of subgrains.
and dislocations and variety of precipitates of carbides and nitrides.

Two batches of samples were separately irradiated to relatively low and high damage levels with fluences of $2.45 \times 10^{16}$ and $2.47 \times 10^{17}$ ions/cm$^2$, respectively, at 500°C using a raster-scanned beam of Fe$^{2+}$ ions at 5 MeV with damage rates on the order of $10^{-4}$ displacements per atom per second (dpa/s). The low-dpa and high-dpa irradiations took 17.9 and 106.7 h, respectively. The thermal aging effect on particle growth at 500°C for such short periods of time is expected to be negligible, considering the minor effect at 600°C for 200–5000 h [7]. The depth–dependent irradiation dose and implanted Fe profiles are shown in Fig. 1 for the two damage levels. They were simulated using the stopping and range of ions in matter (SRIM) software with the recommended Quick Kichin–Pease option and parameters of lattice binding energy (set to zero) and atomic displacement energy such as 40 eV for Fe/Cr/Mn/V, 90 eV for W, 31 eV for C, and 25 eV for Si/N/O [9,10]. The peak damages of ~24 and ~243 dpa occur at ~1.3 μm depth from surface. The high dpa does not influence the irradiation depth, but significantly increases the implanted Fe to a peak value of ~5.69 at% from ~0.59 at% of the low-dpa situation at ~1.5 μm depth. The implanted ~5.69 at% Fe would increase the local Fe concentration to a normalized value of ~97.96 at% from initial ~97.84 at%, which would not significantly alter the local species’ chemical potential. The simulation was conducted on the ferritic steel composition, rather than on the VN particles, because the primary knock-on atom on the embedded particles in the steel is totally different from that in the particles. The damage depth profiles should reflect a reasonable estimation and trend for the particles, owing to the small volume fraction of the dispersed ultrafine particles.

Transmission electron microscopy (TEM: FEI CM200 field-emission-gun [FEG] and JEOL 2100F FEG) was used to characterize the particle evolution after the Fe$^{2+}$ ion irradiations. Focused ion beam milling (FIB: Hitachi NB5000) was used to lift out and thin the TEM specimens parallel to the ion irradiation direction. A low voltage (e.g., 2 keV) ion-beam cleaning process was applied to the specimens as a final step to mitigate FIB-induced artifacts. The local TEM specimen thickness was estimated using the convergent beam electron diffraction method.

![Fig. 1. SRIM calculated two sets of 5 MeV Fe$^{2+}$ damage depth profiles resulting from irradiation (solid and dashed black curves), together with implanted Fe profiles (solid and dashed red curves), in a VN-populated ferritic alloy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image)

3. Results and discussion

The overall distribution of VN nanoprecipitates in white features from surface (left) to unirradiated matrix (right) are shown in the dark-field images of Fig. 2, which were taken using the (200)$_{VN}$ reflection between the (200)$_{bcc}$ two-beam near [001] zone axis as illustrated in Fig. 2 a–c. The platelet-shaped VN nanoprecipitates appeared as short white streaks (in Fig. 2) under this imaging condition, with their length and width corresponding to the diameter and thickness of the platelets, respectively. The consistent imaging condition allows statistical analyses of the particles in the same edge-on situation. There is a noticeable difference between the ion beam direction (beam: dashed arrow perpendicular to sample surface) and the general length direction of the unirradiated nanoprecipitates (ppt: solid arrow). Compared with the $\langle$beam–ppt$\rangle$ angle of ~12° in the low-dpa case in Fig. 2a, two orientations of ~20° and ~82° are characterized in the high-dpa case in Fig. 2b and c, respectively, from two individual grains within the same irradiated sample. The nanoprecipitates in Fig. 2b retained a shape similar to those in Fig. 2a, but Fig. 2b has many more ultrafine (shorter) particles in lower contrast. After the same high-dpa irradiation illustrated in Fig. 2b and c shows noticeably fewer visible particles with notable nano-angles in particle shape, suggesting the significant influence of the $\langle$beam–ppt$\rangle$ angle.

The area fraction of the nanoprecipitates was analyzed using ImageJ with a depth-bin size of 200 nm, which was normalized to 100 nm specimen thickness according to the measured thicknesses in the characterized areas. The adjusted particle area fractions as a function of depth for the three experimental conditions are plotted in Fig. 3, with black circles, red triangles, and blue squares denoting low-dpa/12°, high-dpa/20°, and high-dpa/82°, respectively. Corresponding black, red, and blue lines approximately outline the evolution of the particle area fraction in the three conditions. The low-dpa case with ~12° $\langle$beam–ppt$\rangle$ angle resulted in a significantly increased particle area fraction to ~0.011 in the irradiated zone before the peak-dpa (at ~1.3 μm) from ~0.006 in the matrix (or unirradiated condition [7]). The peak-dpa and the implanted Fe with a peak concentration ~0.59 at% (~1.5 μm) did not result in noticeable effect on the particle area fraction evolution. In contrast, the high-dpa case with ~20° $\langle$beam–ppt$\rangle$ angle only slightly increased the particle area fraction with a larger variation in the irradiated zone before the peak-dpa (~1.3 μm). The particle area fraction increased to a peak fraction at a depth of ~1.7 μm, slightly beyond the calculated implanted Fe peak at ~1.5 μm. It suggests that the high-dpa implanted Fe with a peak concentration of ~5.69 at%, together with the high-dpa irradiation (and prolonged irradiation time at 500°C) in a synergistic effect, had a significant influence on the particle area fraction evolution by showing a peak particle area fraction. The high-dpa case with ~82° $\langle$beam–ppt$\rangle$ angle primarily resulted in some decreases in particle area fraction in the irradiated zone before the peak-dpa, which gradually increased with large variations to a peak particle area fraction at a depth beyond 2 μm, noticeably away from the calculated implanted Fe peak at ~1.5 μm. This phenomenon, together with the presence of large particles in parallelograms at ~1.8 μm from surface in Fig. 2c, may suggest the presence of ion channeling in the condition with ion beam deviated ~8° [i.e., ~82° $\langle$beam–ppt$\rangle$] from $\langle$200$\rangle$ of the matrix, which extended the ranges of irradiation damage and implanted Fe into deeper regions compared to the SRIM calculation without considering crystalline and temperature effects. The 5 MeV Fe$^{2+}$ ions provided more than enough energy to favor ion channeling at appropriate lattice orientations with the ion beam because the minimum energy for the occurrence of channeling is as low as 300 eV [11]. Ion-irradiation enhanced diffusion mainly results in the implanted ions diffusing outward toward the surface.
but not deeper into the sample [12]. The observed channeling effect is similar to the reported ion channeling effect in pure polycrystalline iron irradiated with 1.2 MeV yttrium ions at room temperature, which resulted in much deeper radiation defects at up to ~3.5 times of the SRIM-calculated damage depth [13].

Bright-field images at high magnifications were used to characterize the detailed microstructures of the VN particles. Fig. 4 exhibits typical shapes of the particles at ~650 nm from the sample surface, corresponding to the ~11 dpa of Fig. 4a and ~110 dpa of Fig. 4b and c per the SRIM calculations. The platelet–shaped VN particles retained nice lattice fringes, approximately perpendicular to \( g_{200} \) after the low-dose (~11 dpa) irradiation. According to the Moiré fringe spacing (\( D \)) relationship with the interplanar spacings of matrix (\( d_1 \)) and particles (\( d_2 \)), i.e., \( D = d_1 d_2 / (d_1 - d_2) \) [14], the \( d_2 \) was calculated to be ~0.108 nm for the particles using the \( d_{200} \) of the matrix with a lattice parameter of 0.286 nm (measured by x-ray diffractometry) and \( D \) of ~0.435 nm (measured from the TEM images). The interplanar spacing \( d_2 \) was close to the \{400\} planes of VN with a lattice parameter of ~0.430 nm. It is slightly greater than the calculated lattice parameter of 0.419 nm for VN [15], which may be attributable to the irradiation, possible carbon contamination introduced by the Fe\(^{2+}\) ion irradiation process, and experimental error. The analytical result is consistent with the selected area diffraction (e.g., Fig. 2 a’), suggesting the relationship of \([400]_{\text{ppt}}\parallel[200]_{\text{bcc}}\). The high-dose (~110 dpa) irradiation with a slightly larger \( \angle (\text{beam–ppt}) \) angle of ~20° (Fig. 4b) did not result in significant changes to the shapes of the particles, other than introduced some dislocations, reduced particle length (L), and somewhat increased particle width (W). In contrast, the high-dose (~110 dpa) irradiation with a large \( \angle (\text{beam–ppt}) \) angle of ~82° (Fig. 4c) significantly transformed the shapes of the particles into parallelograms, with disordered lattice fringes approximately aligned with \( g_{\{110\}} \).

To prevent the influence of surface effects [16] and implanted Fe...
on the evolution of the VN nanoprecipitates, the volume number density of the particles was statistically analyzed within every 100-nm-depth bin size in the depth range of 200–800 nm from the surface. The analyzed density is plotted as a function of dose in Fig. 5a according to the dose–depth relationship shown in Fig. 1. The lower and upper bounds of the three sets of data for low-dpa irradiation with an ~12° ⟨beam–ppt⟩ angle (Fig. 2a), high-dpa irradiation with ~20° (Fig. 2b), and high-dpa irradiation with ~82° (Fig. 2c) were approximately in good agreement with their respective data sets within the depth range of 200–800 nm from the surface. In contrast to the increased particle density with increasing dose when the ⟨beam–ppt⟩ angle was low (e.g., 12° and 20°), the higher dose resulted in noticeable decreases in particle density when the ⟨beam–ppt⟩ angle was high (e.g., 82°). With the particle length and width schematically defined in Fig. 4, the aspect ratio (length/width: L/W) of the particles within the depth of 200–800 nm compared with that in the unirradiated region is shown in Fig. 5b. The data indicate that the low-dpa/12° irradiation primarily increased the length with minor increases in width. In contrast, the high-dpa/20° irradiation primarily increased the width with minor increases or significant decreases in length. The increased ⟨beam–ppt⟩ angle to 82° of the high-dpa significantly increased the width without much effect on length. The fitted solid (irradiated) and dashed (unirradiated) lines indicate the average L/W ratios of the particles. Compared with the high L/W ratio (~7.27) of the particles in the unirradiated region, the L/W ratio was slightly reduced to ~6.75 after the low-dpa irradiation and significantly reduced to ~2.44 after the high-dpa irradiation, both of which were at low ⟨beam–ppt⟩ angles of 12° and 20°. The higher ⟨beam–ppt⟩ angle of 82° further decreased the L/W ratio to ~1.07 after the high-dpa irradiation.

The SRIM-calculated ion trajectories were analyzed and plotted in Fig. 6, showing depth-dependent ion distributions within different deviations (δ) from the ion beam direction of 0%, 5%, 10%, and 50%. The fraction of ions close to the ion beam direction becomes significantly larger when the depth is away from the peak damage. For the statistical analysis of the precipitates within the depth of 200–800 nm in Fig. 5 and 90%–30% of the ions were in the ion beam direction (δ = 0%), together with 10%–67% of the ions within 5% deviation from ion beam direction (0% < δ ≤ 5%). It suggests that the evolution of the precipitates within the depth of 200–800 nm was primarily influenced by the forward momentum of the ions close to the ion beam direction. The low ⟨beam–ppt⟩ angle (e.g., 12° and 20°) irradiation resulted in particle growth in length, as indicated in Fig. 5b, during the low-dpa irradiation, which is approximately along the irradiation direction. The phenomenon of particle growth aligned with incident beam direction was also observed in ion beam synthesized elemental metal nanoparticles (nickel, copper, or bismuth) embedded in amorphous SiO₂ [17]. It was deduced that >85% of the incident energy is deposited within 5 nm of the ion-track center, which resulted in a threshold diameter to determine the evolution.
of the particles. The nanoparticles grew along the beam direction when the diameters were above the threshold. However, the mechanisms for the particle evolution, involving melting, flow, elongation and vaporization, are likely to be not applicable to the radiation-induced VN evolution in this work because of the lower ion energy in this study vs. that (185 MeV) in Ref. [17]. Unlike amorphous SiO2, additionally, the crystalline ferritic matrix favored a specific precipitate-matrix orientation relationship of \( \{400\}_{\text{VN}} \parallel \{200\}_{\text{bcc}} \). When the forward ion beam is approximately parallel to the lattice fringes of the particles as schematically shown in Fig. 7a, the particles tended to be elongated. Some of them became unstable and split into short sections when the L/W ratio was larger than a threshold, but the others survived by minor increases in width to keep the L/W ratio smaller than the threshold. This situation led to increased particle number density as shown in Fig. 5a for the high-dpa/20\(^{\circ}\). When the forward ion beam is approximately perpendicular to the lattice fringes of the particles as schematically shown in Fig. 7b, the particles were primarily broken apart into small sections, resulting in dissolution of some of the finer sections, and consequently decreased particle number density as shown in Fig. 5a for the high-dpa/82\(^{\circ}\). The few survived particles evolved by progressive dislocation-assisted orientation rotation, which have the lattice fringes approximately aligned with \( \{110\}_{\text{bcc}} \) (see Fig. 4c), corresponding to \( \{220\}_{\text{VN}} \parallel \{110\}_{\text{bcc}} \). The new orientation relationship resulted in the noticeable reduction in the reflection intensity of \( (020)_{\text{VN}} \) in Fig. 2c.  

This scenario favor the growth of the case-I particles and the shrinkage of the case-II particles. The stress-oriented particle growth mechanism appears to explain the presence of some long (grown) vertical particles in the irradiated layer, following the “b1” route in Fig. 7b, and short (shrunk) vertical particles beneath (slightly right from the dashed line) in Fig. 2c. However, it does not explain the “b2” routes in Fig. 7b for vertical particles evolved into short and parallelogram particles in Fig. 2c. Furthermore, it does not elucidate the increased density of short particles in the irradiated layer and short particles beneath in Fig. 2b, which deviated ~20\(^{\circ}\) from the beam (horizontal) direction. The results indicate that the evolution of the VN nanoprecipitates is primarily dependent on the particle orientation with the directionality of the ion beam because the forward momentum of the ions played a primary role at a depth up to 800 nm according to the SRIM calculation in Fig. 6. It is expected that the depth having the primary forward ions was extended into deeper areas, facilitated by

![Image](image-url)
the ion channeling effect as shown in Fig. 3 and the lateral tensile state beneath the irradiated layer (Fig. 7c), in which the VN nanoparticles evolved. Other than the generation of dislocations and other types of defects, the effect of cascades on the particle evolution is not clear yet.

4. Conclusions

Self-ion (Fe$^{2+}$) irradiation experiments were conducted at 500 °C on a ferritic steel with dispersed VN nanoparticles. TEM characterization illustrated a strong evolution dependence of the VN particles on the orientation between the particles and ion beam direction. The forward momentum of the ions played an important role on the particle evolution. The particles grew in length approximately aligned with the forward ion beam when the ion beam was approximately parallel to the particle length, which caused some of the particles split into shorter sections, and consequently increased particle number density and reduced particle aspect ratio (L/W) after the high-dpa irradiation. In contrast, the particles were primarily sectioned into short particles when the ion beam was approximately perpendicular to the particle length, leading to the dissolution of some of the finer particles, consequently decreased particle number density and reduced particle aspect ratio after the high-dpa irradiation. Some of the survived particles were transformed into parallelograms, further decreased particle aspect ratio, which have a [220]_{VN}[][][110]_{bcc} orientation relationship evolved from the initial platelet shape with a (400)_{VN}[(200)]_{bcc} orientation relationship. Additionally, ion channeling, manifested by particle evolution at noticeably deeper area, was observed in the condition with ion beam approximately parallel to $h(200)_{bcc}$. This study suggests that statistical quantitative analysis of the stability of ultrafine particles in heavy ion irradiation experiments may not be able to represent their stability in neutron reactor irradiation situations.

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