**HIGH-RESOLUTION ELECTRON MICROSCOPY STUDIES OF
THE PRECIPITATION OF COPPER UNDER NEUTRON
IRRADIATION IN AN FE-1.3WT% CU ALLOY***

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HIGH-RESOLUTION ELECTRON MICROSCOPY STUDIES OF THE PRECIPITATION OF COPPER UNDER NEUTRON IRRADIATION IN AN Fe- 1.3WT%CU ALLOY

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ABSTRACT

We have studied by electron microscopy the copper-rich precipitates in an Fe-1.3wt%Cu model alloy irradiated with neutrons to doses of 8.61×10^{-3} dpa and 6.3×10^{-2} dpa at a temperature of $\sim 270^\circ\text{C}$. In the lower dose material a majority (ca. 60%) of the precipitates visible in high-resolution electron microscopy were twinned 9R precipitates of size $\sim 2\text{--}4$ nm, whilst ca. 40 % were untwinned. In the higher dose material, a majority (ca. 75%) of visible precipitates were untwinned although many still seemed to have a 9R structure. The average angle α between the herring-bone fringes in the twin variants was measured as 125° , not the 129° characteristic of precipitates in thermally-aged and electron-irradiated material immediately after the bcc $\rightarrow$ 9R martensitic transformation. We argue that these results imply that the bcc $\rightarrow$ 9R transformation of small (< 4 nm) precipitates under neutron irradiation takes place at the irradiation temperature of 270°C rather than after subsequent cooling. Preliminary measurements showed that precipitate sizes did not depend strongly on dose, with a mean diameter of 3.4 ± 0.7 nm for the lower dose material, and 3.0 ± 0.5 nm for the higher dose material. This result agrees with the previous assumption that the lack of coarsening in precipitates formed under neutron irradiation is a consequence of the partial dissolution of larger precipitates by high-energy cascades.

INTRODUCTION

It is well known that neutron-irradiated reactor pressure vessels can be embrittled by the radiation-enhanced formation of copper-rich clusters [1]. The precipitation of copper in ferrite matrices has therefore received much attention, with a good deal of the work focussed on thermally-aged model alloys for reasons of simplicity and convenience. Such studies have shown that very small (with diameters of $\sim 1\text{--}4$ nm) copper-rich precipitates are initially coherent with the ferrite matrix [2-4] but after reaching a critical size they lose their coherency [5, 6]. High resolution electron microscopy (HREM) of copper precipitates in Fe-Cu and Fe-Cu-Ni model alloys thermally-aged at 550°C has shown that the precipitate structures follow a complicated bcc $\rightarrow$ 9R $\rightarrow$ 3R $\rightarrow$ fcc sequence with increasing ageing time [7,8]. The size at which the bcc $\rightarrow$ 9R transformation occurs in thermally-aged Fe-Cu model alloys depends on temperature, and has been shown experimentally to be around 12 nm at 550°C and 4 nm at room temperature [9]. In thermally-aged Fe-1.3wt%Cu, precipitates continue to coarsen and the 9R $\rightarrow$ 3R transformation occurs at a size of about 17 nm in material aged at 550°C for 10 hours.

HREM has also been used to investigate copper precipitation in an Fe-1.5 wt % Cu alloy irradiated with 2.5 MeV electrons at 295°C to a dose of 1.4×10^{-3} dpa [10]. Again, precipitates in the size range 4-8 nm had a twinned 9R structure. Precipitates with sizes up to about 20 nm were observed and those larger than about 8 nm appeared to have transformed wholly or partially to 3R or fcc. The main effect of electron irradiation was to enhance the diffusion of copper and hence to accelerate the diffusion kinetics.

Previous investigations have indicated that the precipitate evolution in neutron irradiated materials may differ from that found in thermally-aged and electron irradiated specimens [11, 12]. Precipitates appear not to coarsen to sizes greater than about 2-4 nm. This difference may be related to the fact that in neutron irradiation most displacements occur in energetic displacement cascades, with cascade-induced precipitate dissolution playing a role. In the present work we describe studies of copper precipitates in an Fe-1.3wt%Cu model alloy irradiated with neutrons at a temperature of $\sim 270^\circ\text{C}$. We concentrate mostly on HREM studies of the precipitate morphologies, although we also show preliminary results from weak-beam microscopy.

EXPERIMENTAL

Neutron-irradiated Fe-1.3wt%Cu alloy was supplied by Magnox Electric. The start of life material was solution treated at 825°C for 6 hours, then water-quenched. The irradiations were carried out in the Trawsfynydd reactor to doses of 8.61×10^{-3} dpa (displacements per atom: 1.5 dpa is roughly equivalent to 10^{25} neutrons m^{-2} , $E > 1\text{MeV}$) and 6.3×10^{-2} dpa at a temperature of $\sim 270^\circ\text{C}$. Discs of diameter 3 mm were punched from the original Charpy test pieces and then ground to a thickness of $\leq 50 \mu\text{m}$. The discs were electropolished in a Struers twin-jet electropolisher, using a solution of 5% perchloric acid in methanol cooled at -60°C , and with an applied potential of 20-25V. Specimens were examined in a high-resolution JEOL 4000EX transmission electron microscope operating at 400 kV (or at 200 kV for the weak beam experiment). All HREM images were obtained with the beam direction closely parallel to a $\langle 111 \rangle$ direction in the matrix. The micrographs were recorded with the objective lens at or near to Scherzer defocus and in thin regions of the foil, close to the edge of the hole. Thermally-aged specimens (10 h at 550°C) were prepared and examined in the same way.

RESULTS

Figures 1 and 2 show HREM micrographs of typical copper-rich precipitates in neutron irradiated Fe-1.3wt%Cu irradiated to doses of 8.61×10^{-3} dpa and 6.3×10^{-2} dpa. The sizes of the precipitates shown in Fig. 1(a) through (c) are 4.0 nm, 3.1 nm and 3.0 nm respectively. Precipitates were found to range in size from 1.9 nm to 4.4 nm. Most precipitates were close to spherical in shape, with very small precipitates being slightly elongated.

Figure 1. High-resolution electron micrographs taken along $\langle 111 \rangle_{\text{Fe}}$ showing twinned 9R precipitates in neutron-irradiated Fe-1.3wt% at a temperature $\sim 270^\circ\text{C}$: (a) and (b) dose 8.61×10^{-3} dpa ; (c) 6.3×10^{-2} dpa.

Figure 2. High-resolution electron micrographs taken along $\langle 111 \rangle_{\text{Fe}}$ showing untwinned copper precipitates in neutron-irradiated Fe-1.3wt%Cu at a temperature $\sim 270^\circ\text{C}$: (a) dose 8.61×10^{-3} dpa; (b) dose 6.3×10^{-2} dpa.

The copper precipitates seen in Fig. 1 have a twinned 9R structure. They are similar to those found previously in thermally-aged and electron-irradiated Fe-1.3wt%Cu alloy [8,10]. The structure of these precipitates is easily recognised from the characteristic herring-bone fringes. The boundary between adjacent twin bands lies parallel to a set of matrix $\{110\}_{\text{Fe}}$ fringes. This boundary plane is the $(\bar{1}\bar{1}4)_{9\text{R}}$ plane of mirror symmetry. The orientation relation between the bcc matrix and 9R particle is $(011)_{\text{Fe}}//(\bar{1}\bar{1}4)_{9\text{R}}$ and $[1\bar{1}1]_{\text{Fe}}//[1\bar{1}10]_{9\text{R}}$. The fringe periodicity, measured over several fringes, is approximately 0.6 nm. This is equal to three times the 9R close-packed plane spacing. The thicknesses of twin segments varied. Often one twin segment was larger than the other. In some cases the three-layer spacing was replaced locally by two-layer spacing (see the region arrowed in precipitate (b) of Fig. 1). This indicates that random stacking faults are present within the 9R particles following the transformation from bcc. Such stacking faults were also seen within precipitates in thermally-aged and electron irradiated alloys, and are attributed to the martensitic transformation mechanism. The mean angle α between fringes in adjacent twin segments was measured as approximately 125° to 126° at both doses. This value is smaller than the angle of 129° characteristic of the orientation relationship found in precipitates immediately after the bcc $\rightarrow$ 9R martensitic transformation in thermally-aged alloys, and suggests that rotations of the $(009)_{9\text{R}}$ planes have occurred.

Figure 2 shows examples of precipitates that appear to be untwinned. Such precipitates were observed at both neutron doses, although they were more common at the higher dose where they made up a high proportion (ca. 75 %) of the total. Some precipitates show fringes of 9R spacing (e.g see Fig. 2(a)). Together with the observation of 9R precipitates with unequal twin segments, this suggests that these precipitates were originally twinned 9R precipitates which have untwinned by the preferential growth of one twin segment at the expense of the other, as proposed by Othen et al [8]. The sizes of the precipitates in Fig. 2 are (a) 4.4 nm and (b) 3.7 nm. In thermally-aged and electron irradiated alloys the minimum size of untwinned precipitates was ≈ 8 nm [10].

Figures 3 and 4 show that plane rotations and untwinning, such as seen in the neutron-irradiated material, can be induced in thermally-aged specimens by *in-situ* electron irradiation with 400 kV electrons. Initially $\alpha \sim 129^\circ$ in the typical precipitate shown in Fig. 3(a). After 7 minutes under the electron beam, the planes appear to have rotated, reducing α to about 126° , and the appearance of the precipitate is now similar to that found in the neutron irradiated material. Figure 3 shows that the rotations can occur without the precipitate first untwinning. However, untwinning can also be induced by electron irradiation. Figure 4 shows one 9R twin variant growing at the expense of the other, confirming directly the untwinning mechanism proposed.

Figure 3. *In-situ* 400kV electron irradiation of a twinned 9R precipitate in Fe- 1.3wt%Cu in thermally-aged at 550°C for 10 hours, showing rotation of the (009)_{9R} planes: (a) at start of observation; (b) after 7 mins.

Figure 4. *In-situ* 400kV electron irradiation of a twinned 9R precipitate in Fe- 1.3wt%Cu in thermally-aged at 550°C for 10 hours, showing one twin variant growing at the expense of the other: (a) at start of observation; (b) after 10 mins.

Figure 5. Weak beam micrographs taken in $g = 110$ with deviation parameter $s_g \approx 2 \times 10^{-1} \text{ nm}^{-1}$ of Fe-1.3wt%Cu alloy neutron irradiated at a temperature $\sim 270^\circ\text{C}$ to (a) dose $8.61 \times 10^{-3} \text{ dpa}$; (b) dose $6.3 \times 10^{-2} \text{ dpa}$.

Figure 5 shows weak beam images at both doses. A comparison with the corresponding bright-field images suggested that most, if not all, of the white dots are copper-rich precipitates and not dislocation loops or voids. Most precipitates appear spherical in shape. Full analyses of precipitate sizes and number densities have yet to be made. However, preliminary measurements of HREM micrographs indicate that precipitate sizes do not depend strongly on dose with a mean of 3.4 ± 0.7 nm for the lower dose material and 3.0 ± 0.5 nm for the higher dose material. There was no obvious change in number density.

DISCUSSION

This is the first direct observation of copper precipitates with a 9R structure in neutron-irradiated Fe-1.3wt%Cu alloys. Of course, we cannot exclude the possibility that the specimens also contain small coherent precipitates, which would have low visibility under HREM conditions, and indeed rough estimates of number densities indicate this might be the case. The 9R precipitates generally have a relaxed structure, with an angle between the fringes in adjacent twin segments $\alpha \approx 125^\circ$. It has been demonstrated that such plane rotations can be induced by electron irradiation at 400 kV. Monzen et al [9] have shown that the plane rotations are associated with a decrease in the magnitude of the strain contrast of the precipitates, and have also shown that similar plane rotations can be induced by thermal annealing at 400°C. It is thought that the $(009)_{9R}$ close packed planes in each twin band rotate to align more closely with the $\{110\}_{Fe}$ planes in order to reduce strain energy produced on transformation. Also notable in the neutron-irradiated material was the presence of a considerable number of untwinned precipitates, some apparently still with a 9R structure.

Monzen et al [9] have shown that during ageing of Fe-1.3wt%Cu at 550°C, precipitates retain the coherent bcc structure to a size of about 12 nm, but the bcc $\rightarrow$ 9R transformation of smaller precipitates may be induced by subsequent cooling. The question therefore arises whether the 9R precipitates seen in the present work transformed during the irradiation at 270°C, or only after the specimen was removed from the reactor and cooled to room temperature (or to -60°C during electropolishing). In the latter case, we would expect precipitates to have a structure typical of that found immediately after the martensitic transformation, i.e. with $\alpha \approx 129^\circ$. The observation of relaxed precipitates with $\alpha \approx 125^\circ$ shows that this is not the case. The observation of a population of untwinned precipitates, of a size considerably smaller than is seen under thermal ageing or electron-irradiation conditions and probably produced by the untwining of twinned 9R precipitates, provides further support that the bcc $\rightarrow$ 9R transformation in the reactor occurred at small (≤ 4 nm) precipitate size. Hardouin-Duparc et al [10] speculated that the smaller size at which the 9R $\rightarrow$ 3R $\rightarrow$ fcc transformations seemed to have occurred under electron irradiation was due to the incorporation of vacancies in the precipitates, or to nucleation of small dislocation loops at the precipitate-matrix interface. A similar argument may apply in the present case. The high-energy cascades produced by fast neutrons may also play a role.

The stable precipitate size of ~ 2 –4 nm at both doses is consistent with results from Buswell et al [3]. These authors found by TEM a mean precipitate size of 3.4 ± 0.7 nm in Fe-1.3wt%Cu irradiated to a somewhat higher dose of about 0.1 dpa (6.95×10^{23} neutrons m^{-2} ($E > 1$ MeV)) at 290°C. Buswell et al's SANS data also indicated that the mean precipitate size was independent of dose, with a mean of about 3.7 nm at 0.02 dpa and 4nm at 0.1 dpa. Note that we made size measurements from HREM micrographs of 9R twinned and untwinned precipitates. We do not see any coherent bcc precipitates which may be present, whereas such precipitates would be included in Buswell et al's data. The mean sizes we measure are however similar to

those obtained by Buswell et al, and so are representative of the population as a whole.

The lack of coarsening in precipitates formed under neutron irradiation may be a consequence of the partial dissolution of larger precipitates by high-energy cascades. Our results do however suggest that the bcc→9R→fcc transformations may occur over time. If the same is true of precipitates in pressure-vessel steels, this may have important consequences for understanding the hardening behaviour.

CONCLUSIONS

HREM was carried out on Fe-1.3wt%Cu neutron irradiated to doses of 8.61×10^{-3} dpa and 6.3×10^{-2} dpa at 270°C. In the lower dose material a majority of the visible precipitates have a twinned 9R structure, although a minority were untwinned 9R. In the higher dose material twinned and untwinned 9R precipitates were again identified, but untwinned precipitates were more numerous. All precipitates had similar sizes in the range ~ 2-4 nm. These observations are thought to imply that the bcc → 9R transformation of small (< 4 nm) precipitates under neutron irradiation takes place at the irradiation temperature of 270°C rather than after subsequent cooling. The lack of coarsening may be due to the partial dissolution of precipitates by high-energy cascades.

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Figure 1. High-resolution electron micrographs taken along $\langle 111 \rangle_{Fe}$ showing twinned 9R precipitates in neutron-irradiated Fe-1.5wt% at a temperature $-270^{\circ}C$: (a) and (b) dose 8.61×10^{-3} dpa ; (c) 6.3×10^{-2} dpa.

Figure 2 High-resolution electron micrographs taken along $\langle 111 \rangle_{Fe}$ showing untwinned copper precipitates in neutron-irradiated Fe-1.3wt%Cu at a temperature $-270^{\circ}C$: (a) dose 8.61×10^{-3} dpa, (b) dose 6.3×10^{-2} dpa.

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