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Clustering Effects Under Irradiation in Fe-0.1% Cu Alloy: An Atomic Scale Investigation with the Tomographic Atom Probe

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Abstract: In order to understand the effect of displacement cascades on the evolution of the microstructure of ferritic low copper supersaturated materials, analyses by 3D atomic tomography of neutron, electron and self ion irradiated Fe-0.1%Cu, were performed. This alloy was chosen because of its low copper concentration, close to that of french pressure vessel steels. The comparison of the microstructure evolutions in these irradiated specimens reveals the appearance of tiny copper "clusters" or "aggregates" only when displacement cascades are involved, namely under ion or neutron irradiation. These results lead to the conclusion that displacement cascades or mixing of atoms (instead of enhanced diffusion) have a specific role on the behavior and the evolution of the solid solution of this binary alloy. 3D observation of these clusters was achieved using the tomographic atom probe.

1. INTRODUCTION

Ferritic steels of nuclear power water reactors are materials subjected to irradiation with energetic neutrons. It is well-known that, in these materials, the irradiation disrupts the crystalline lattice and atoms are displaced, creating pairs of point defects, vacant lattice sites and atoms occupying interstitial positions. A consequence of these transformations is changes in the microstructure and microchemistry of the material, which, unfortunately, are responsible for changes in macroscopic properties. In these ferritic steels the irradiation causes the ductile-to-brittle transition temperature to be shifted towards higher temperatures. The progress in understanding the microstructural evolution that occurs in the material under irradiation has been largely the consequence of the development and application of advanced characterization tools such as the atom probe field ion microscopes (APFIM) and more recently 3D atom probes. Thus, in these nuclear materials, the microstructural changes were identified as being copper enriched "nano-precipitates" or "nano-clusters" associated with other solutes such as Ni, Mn, Si and P. These were observed and accurately characterized in weld metals (Mn-Mo-Ni-weld wire/Linde 80 flux submerged arc welds) [1-3] and in French steels (Chooz and Dampierre vessel steels) [4].

Given the complexity of pressure vessel steels and in order to improve our understanding of the neutron-induced formation of these undesirable features, studies of model alloys were performed. In order to identify the specific role of isolated point defects and displacement cascades, experiments were carried out using electron (creation of isolated point defects: Frenkel pairs) and neutron (which produces isolated point defects and displacement cascades) irradiations[5-15]. Also, to easily create displacement cascades in materials and to try to explain their proper effects, self ion irradiation is frequently used [16]. Indeed, this type of irradiation is often used to simulate the energetic neutron irradiation because it causes similar damage. In addition, the easiest availability of ion beams, the non-activity of samples after irradiation and the better understanding of the characteristics of the irradiation (energy, flux,...) are also convenient

factors for such studies. In this paper, we report experimental results related to investigations that we have conducted on a Fe-0.1%Cu model alloy. This low supersaturated binary alloy was chosen for its copper content close to that specified for French reactor pressure vessel steels (<0.09 wt%). In the first part, we will focus on recent results related to the binary alloy irradiated by Fe⁺ ions (300 keV) at room temperature. Because of the extremely small size of the microstructural changes involved during this kind of ion irradiation, experiments were performed using the recently developed Tomographic Atom Probe (TAP). In the discussion part, we compare the results observed under different irradiation conditions (electron, neutron, ion) and point out that displacement cascades, as generated during neutron or ion irradiation, have a specific effect on the clustering of copper atoms.

2. EXPERIMENTAL

The alloy used for this study was prepared by the CECM-Vitry (Centre d'Etudes de Chimie Metallurgique, France) from a high purity iron ingot (Si<25 wtppm, C<15 wtppm, N, O, Al < 10 wtppm). After an austenitisation heat treatment at 1000°C for 30 min., the alloy was treated in vacuum for 1h. at 850°C, then air quenched to produce a reference random solid solution. A grain size ranging from 2 to 4 μm was revealed by optical micrographies. EDX measurements revealed a copper level of 0.1±0.03 (wt%).

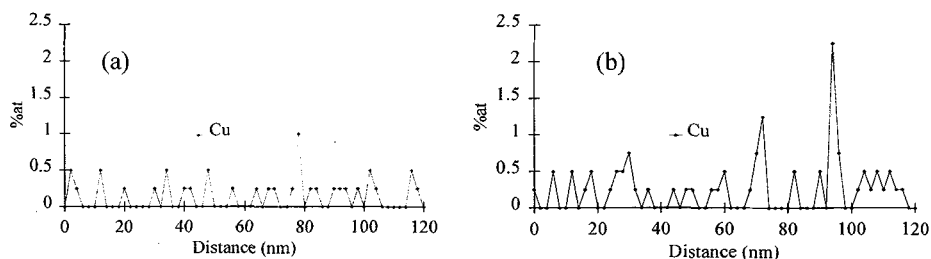
In order to produce the needle-like specimens required for TAP investigations, small bars (20 x 0.3 x 0.3 mm³) were cut out from the reference material. The field ion needles were electropolished using standard procedures [17]. The ready-prepared FIM specimen were irradiated in the ion accelerator of the Hahn-Meitner-Institut (Berlin). The irradiation was performed perpendicular to the tip axis with 300 keV Fe⁺ ions at room temperature. The current density on the tip was 100 nA/cm². The flux was $\Phi = 5 \times 10^{15}$ ion/m².s and the corresponding displacement rate $\kappa = \sigma_d \cdot \Phi$ (σ_d : displacement cross section, 2×10^{-19} m² [18]) was estimated to 10⁻³ dpa.s⁻¹ (displacements per atom per second). The irradiation was performed for 10 seconds in order to reach a fluence of 10⁻² dpa (the order of magnitude encountered in reactor pressure vessel steels).

The irradiated specimens were then analysed using the Tomographic Atom Probe (TAP) at the Laboratoire de Microscopies Ionique et Electronique, Université de Rouen (France). The principle of the TAP is described with full details in recently published papers [19,20]. The basic principle of the instrument lies in the use of a multi-impact spatial detector. For each evaporation pulse, the time of flight of field evaporated ions as well as the co-ordinates of ion impacts are measured (80 pulses/s). The position of atoms at the tip surface are thus deduced from the co-ordinates of ion impacts on the detector. A simple point projection is involved here. Layer after layer, a 3D-reconstruction of the material may thus be obtained. With the help of a graphics work-station and high level 3D software, it is possible to manipulate the analysed volume and various specific calculation treatments can be applied. The overall spatial resolution is close to 0.3 nm. Each atom being individually identified, a three-dimensional reconstruction related to a given chemical species can be obtained. The mass spectrum resolution ($M/\Delta M$) of the TAP is close to that of a conventional atom probe: the full width at half maximum is close to 200. This allows all the doubly charged Fe and Cu isotopes to be resolved. Copper is also detected in the single charge state.

Analyses were performed at 50K, in order to avoid the preferential evaporation of copper atoms [4], with a pulse fraction of 19%. Analyses of irradiated and unirradiated specimens were both performed along the tip axis in arbitrary crystallographic directions. For each material about one million atoms were collected. The average atomic concentrations for copper derived from these experiments are in both cases (irradiated and unirradiated): 0.11±0.01 at%Cu. These values are slightly above the average value of the given nominal concentration: 0.06≤Cu at%≤0.11.

3. RESULTS

In order to characterize the effect of the ion irradiation, unirradiated and irradiated samples were investigated. The observation of the 3D reconstructed volumes, for both materials, did not reveal clearly any significant qualitative difference. In order to compare these results on a more quantitative basis, statistical treatments were performed. In both cases, reconstructed volumes were divided into sub-volumes, along the analysis direction, with a 2 nm x 2 nm square section. Elemental concentration profiles related to each sub-volume were thus carefully examined. Sampling blocks of 400 ions were chosen. The related thickness of blocks was then close to their lateral extension. Figures 1.a and 1.b show two typical composition profiles obtained before and after irradiation. More than fifty of these composition profiles were obtained in each case. These are representative of the whole data set.



Figures 1(a) and 1(b): composition profiles of the copper solute obtained in samples analysed by 3D atomic tomography before (a) and after (b) Fe^+ irradiation (300 keV, room temperature).

These figures suggest that some tiny local copper enrichments were formed during the irradiation. However, the quantitative changes in the microstructure "before" and "after" the irradiation have to be ascertained. Statistics were applied in order to give a clearer tendency.

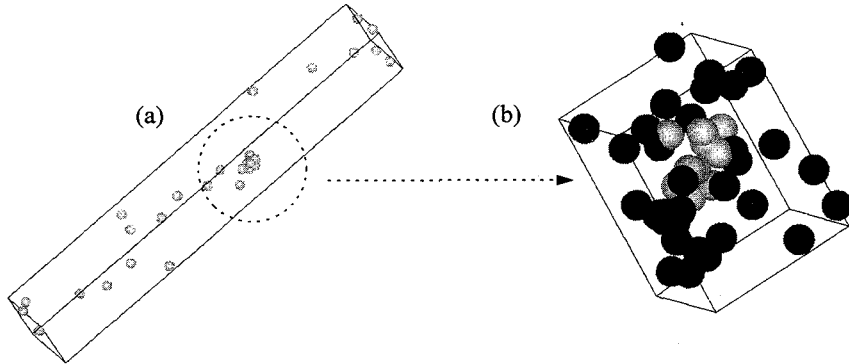
Table 1 reports the observation frequencies (or percentage) of a given number of copper atoms per blocks of 400 ions. The total number of blocks in each case is equivalent (~1000).

Table 1: Observation frequencies of a given number of copper atoms per block of 400 ions.

Copper atoms per block	0	1	2	3	4	5	6	7	8	9
Unirradiated	43.6	35.8	14.3	4.6	1.6	0.1	-	-	-	-
Irradiated	52.0	28.0	12.6	5.2	1.6	0.3	0.1	-	-	0.2

These values indicate that blocks containing 5 or more copper atoms are detected mainly in the irradiated samples. The appearance of these local enrichments in the irradiated samples are consistent with the higher number of empty blocks (0 copper atoms) and the lower number of blocks containing 1 or 2 atoms. For each analysis the block distributions were compared to a Poisson law and the χ^2 test was performed. The large experimental χ^2 value ($\chi^2 = 52.5$) determined in the irradiated material, compared to the tabulated χ^2 values for a confidential interval of 95% (with 4 degrees of freedom): $\chi^2(0.05) = 9.49$, allows to assess that the hypothesis of a random distributed solid solution can be rejected. As far as the unirradiated material is concerned, the low χ^2 value ($\chi^2 = 2.3$) allows to describe the solid solution as randomly distributed. However, the concept of an ideal solid solution randomly distributed cannot be experimentally achieved at this ultimate observation scale. The strong tendency for copper solutes to cluster in α Fe may leads to a redistribution (or migration) of the solutes during the quench after annealing at 850°C. This is illustrated by the presence of some small local concentration fluctuations, as observed on the composition profile of the unirradiated material (Figure 1.a).

A close examination of the "large" aggregates detected in the irradiated material was performed. The figure 2(a) shows a 3D reconstruction of a portion of the analysed volume where a copper segregation was detected. For clarity, only copper atoms are represented. Figure 2(b) is a magnified view of the copper cluster. The 54 isotope atoms of iron (dark spheres) is also represented in this magnified view.



Figures 2(a) and 2(b): 3D atomic tomography images of a copper cluster in the Fe^+ irradiated specimen (300 keV, room temperature). Volume (a) : $2.8 \times 3.1 \times 25.9 \text{ nm}^3$. Magnified view of the copper cluster (white spheres) with Fe^{54} isotope atoms (dark spheres), volume : $2.8 \times 1.5 \times 2.2 \text{ nm}^3$.

The detected atoms in this cluster were ionised under the two common copper charge states: 3 ions Cu^{2+} (31.5 u), 3 ions Cu^{2+} (32.5 u), 2 ions Cu^+ (63 u) and 1 ion Cu^+ (65 u). This information demonstrates the actual nature of these clusters, no possible experimental artefacts could have generated them. Also, we have to keep in mind that the detector efficiency being on the order of 50%, all the observed features may be (in the actual analysed sample) constituted by a larger number of atoms (twice at most). In addition, the lateral resolution of the TAP (0.3-0.5 nm) may slightly distort the lateral position distribution of the atoms within the clusters. However the very close spatial location of atoms (9 atoms in a depth smaller than 2 nm) seems to indicate that these solutes were close (or even first) neighbours. A close examination of the whole set of experiments indicates that the number density of clusters is close to 10^{17} cm^{-3} . As far as the copper level in the matrix is concerned, no copper depletion was observed. The small size of clusters and the small amount of involved solutes easily explains this result.

4. DISCUSSION

In this section, the microstructural changes in ion irradiated materials, as reported above, will be compared to those observed in neutron and electron irradiated alloys. Fe-0.1%Cu alloys were studied after neutron irradiation in the pool test reactor of CEA Saclay. The irradiation temperature was close to 290°C, representative of the service temperature of the nuclear pressure vessels [14]. Analyses were also performed on this same material after electron irradiation [13]. The irradiation was performed in a 3 MeV Van de Graaff accelerator (CEN-Grenoble) at 290°C. Table 2 summarizes the main characteristics of these irradiations.

Table 2: Characteristics of the neutron and electron irradiations of the Fe-0.1%Cu.

	flux	Fluence	dpa.s ⁻¹	dpa
Neutron (E > 1 MeV)	$2.8 \times 10^{13} \text{ n.cm}^{-2}.\text{s}^{-1}$	$5.5 \times 10^{19} \text{ n.cm}^{-2}$	4.2×10^{-8}	7.5×10^{-2}
Electron (3 MeV)	$9.4 \times 10^{13} \text{ e}^{-}.\text{cm}^{-2}.\text{s}^{-1}$	$2 \times 10^{19} \text{ e}^{-}.\text{cm}^{-2}$	5.6×10^{-9}	1.2×10^{-3}

As regards the electron irradiation, no microstructural evolution was detected after the treatment [12,13]. It must be noted that experiments on the electron irradiated samples were performed with a conventional energy compensated atom probe [21]. It implies that 10 times fewer ions were collected in comparison to the other experiments performed with the TAP and that the detection of small copper clusters could have been missed if their number density was lower or of the order of 10^{16} cm^{-3} .

The features observed after the neutron irradiation were found to be significantly different from those occurring in electron irradiated materials. As shown in figure 3, Cu clusters develop.

The main results of these experiments performed under various irradiation conditions are summarized in table 3.

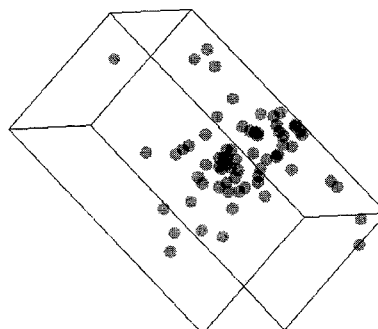


Figure 3: Spatial distribution of copper atoms in a neutron irradiated Fe-0.1%Cu alloy. The dimensions of the represented volume are $3 \times 2.5 \times 5 \text{ nm}^3$. Each grey circle is a single copper atom, black reinforcements give an idea of the local density inside the cluster.

Table 3: Atom probe results (APFIM and TAP) on the Fe-0.1wt%Cu alloy irradiated under various conditions: electron, neutron, ion.

Irradiation	Copper clusters	Diameter (nm)	Number density (cm^{-3})	Matrix copper content
Electron	no	-	-	0.09 ± 0.03
Neutron	yes	2-3	$\sim 10^{17}$	0.025 ± 0.01
Ion	yes	<1	$\sim 10^{17}$	0.11 ± 0.01

The comparison of these results, keeping in mind that the irradiation conditions were different from one case to the other (temperature and dpa), shows that, when displacement cascades are involved (neutron and ion irradiations), copper segregation is observed. This observation seems to indicate that, in the Fe-0.1%Cu, the mechanism of production of defects strongly influences the behavior and the evolution of the solid solution. It is of great importance to note that the irradiation efficiency (defined as the proportion of free defects compared to the total defect production (dpa estimated by the Kinchin and Pease formula [22])) varies from one for high energy electron irradiations to a few percent for heavy ions or neutron irradiations [23]. The free defects (isolated Frenkel pairs and small point defect clusters) concentration is therefore probably, in our case, higher under electron irradiation (1.2×10^{-3} dpa) than under neutron irradiation ($\sim 7.5 \times 10^{-4}$ dpa). This means that free defects are not at the origin of this clustering process. This observation leads to the important conclusion that displacement cascades have a very specific effect on the microstructural evolution of this ferritic model alloy with low copper content. This would indicate that the atomic transport, by forced atomic mixing, induces the agglomeration of copper atoms. This result is reinforced by our last experiment which demonstrates that copper aggregates were also observed in the self ion irradiated samples (performed at room temperature and for a short irradiation duration). These clusters could also be associated with vacancies, microvoids or very small dislocation loops. Unfortunately, FIM images could not give any evidence for the presence of such defects in these materials. This is due to the very small size of the induced features and their low contrast quality in FIM images.

5. CONCLUSION

In this work, previous and recent atom probe (ECAP and TAP) investigations of neutron, electron and ion irradiated Fe-0.1%Cu alloys are reported. A close examination and comparison of the results obtained in irradiated and unirradiated materials leads to the important conclusion that copper clustering is observed when the type of irradiation promotes displacement cascades (namely neutron and ion irradiation).

It must be noted that these radiation-induced clusters are also produced in the low copper reactor pressure vessel steels, like French ones (Cu<0.09%). However, the atom probe studies that we have conducted [12] on these steels show that the phenomena are far more complicated in this case. Indeed, the clusters, observed and characterized, contain not only copper but also other solutes such as silicon, manganese, nickel and phosphorus.

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