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Heterogeneous irradiation-induced copper precipitation in ferritic iron–copper model alloys

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Abstract

The mechanism at the origin of the formation of nano-copper-enriched clusters in the ferritic matrix of nuclear reactor pressure vessel steel is not yet fully understood. In this work, specific irradiation experiments were carried out using 3 MeV electron and 150 keV Fe^+ ions in order to point out the effect of (i) free migrating point defects (produced as Frenkel pairs with 3 MeV electron) and (ii) the ballistic mixing and partial recombination of atoms due to displacement cascades (produced with ions). In both cases the irradiation-induced phase transformation were characterized using the 3D atom probe technique. The time-dependant evolution of the point defect population was computed using the cluster dynamic code (MFPVIC) developed at CEA. The combination of experiment and simulation shows that, in low copper (<0.1 at.% Cu) FeCu alloys, heterogeneous irradiation-induced copper precipitation is taking place on point defects clusters generated by 20–30 keV displacement cascades.

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1. Introduction

The reactor pressure vessel (RPV) of nuclear power plant is the most important barrier between the reactor core and the outside. It must stay reliable during the reactor's life. However, during operation the vessel undergoes energetic neutron irradiation resulting in an embrittlement of the vessel steel, characterized by an upward shift in the ductile to brittle transition temperature and a drop in the upper shelf toughness of impact energy in Charpy impact tests. Irradiation also results in a hardening of the vessel. The deterioration of the mechanical properties is due to different changes of the microstructure under irradiation. One of these changes is the formation of ultra-fine (2–3 nm in diameter) copper-rich solute atom clusters (other solutes being Ni, Mn, Si and P) [1]. In order to be able to predict the evolution of this irradiation induced phase transformation, the understanding of the basic mechanism allowing their formation is needed. Indeed, in ferritic alloys and steels containing 0.2 at.% Cu, the precipitation of rich copper clusters at 573 K under irradiation can be explained by a simple radiation enhanced

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homogeneous precipitation mechanism due to the supersaturation of point defects. However, in low copper content alloys and steels (at.% Cu < 0.1 at.%, as in modern RPVs), the mechanism is less clear. The main goal of this work is to study experimentally and theoretically the formation of copper rich clusters under specific irradiation condition in a FeCu model alloy (the effect of others will be published in detail in an other paper).

In order to clarify this important point, a binary FeCu alloy containing 0.08 at.% Cu and 80 appm. C was irradiated with 3 MeV electrons and with 150 keV Fe^+ ions. These two irradiation conditions allow to determine the effect of the supersaturation of free migrating point defects and the effect of a point defect production in the form of displacement cascades. The phase transformation occurring under these irradiation conditions were characterized using the 3D Atom Probe (3D AP) technique [2]. In parallel to this, the time dependant evolution of the population of point defects (isolated (interstitial (i) or vacancy (v)) or in clusters) is computed using the cluster dynamic code (MFPVIC) developed at CEA [3,4].

The results reported in this paper show that point defects clusters, formed in displacement cascades, play a determinant role in the phase transformation of low copper FeCu alloys under ion irradiation.

2. Experimental

A binary FeCu (0.088 at.% Cu) alloy was manufactured at the Centre d'Etudes Nucléaires de Grenoble. The samples were cold rolled down to a thickness of 800 μm. Plates of a few square centimeters were cut and subjected to recrystallisation and homogenization annealing: 1073 K under argon atmosphere for 2 h. followed by a quench under argon jet ($\sim$10 K s^{-1}). This ensure a homogeneous distribution of the copper-solute atoms in the matrix [5].

The electron irradiation was performed in a van de Graaff (at the Centre d'Etudes Nucléaires de Grenoble) using 3 MeV electrons. A surface of 2 cm in diameter in the center of the sample is exposed to the electron beam. The irradiation temperature is close to 573 K (similar to irradiation temperature of RPV steels). The sample is heated by the electron flux with thermal exchanges being ensured by a helium atmosphere. The electron flux was 10^{17} m^{-2} s^{-1} and the fluence 10^{23} m^{-2}. In terms of displacement per atom (dpa), a damage of 5.6×10^{-9} was reached with a damage rate (dpa s^{-1}) of 3×10^{-3}. This number is calculated using the table of Oen [6] with a displacement threshold of 40 eV for iron [7]. After irradiation, the microhardness (50 g load) is measured along the plate to verify the effectiveness of irradiation and estimate the hardening due to irradiation.

By using ions, the main experimental objective was to produce point defects through displacement cascades. With a controlled ion beam, it is possible to irradiate samples with Fe^+ ions, which act also as the primary knocked atoms (PKA) in RPV steel. As the maximum energy transferred to an iron atom (PKA) by an incident neutron (1 MeV) is about 70 keV and as PKAs with energy higher than 50 keV result in the formation of subcascades with an average energy of about 20–30 keV in each subcascade, our main goal was to reproduce these 20–30 keV displacements cascades in a sample that could be subsequently analyzed with 3D AP. The needle shape of the specimen for atom probe analyses is 100 nm thick and the probed volume is in the center of the specimen (50 nm in depth). This means that effects on the microstructure due to 150 keV Fe+ ion irradiation (mean range of 50 nm in iron, subcascades at 50 nm with energies between 10 and 40 keV), can be detected in 3D AP samples (see Fig. 1). Combining both techniques (ion implantation and 3D atom probe [8,9]) a large set of parameters (nature of incident ion, ion energy, dose, dose rate, specimen temperature, ...) may be controlled and the effect of each may be evaluated. The specimens for this work were irradiated in the ion accelerator of the Mass Spectroscopy and Nuclear Spectroscopy Centre (CSNSM) – Orsay France [8]. It must be noted that, due to the high value of fluxes (corresponding to a damage rate (dpa s^{-1}) of 1.26×10^{-4} in this work), available using ion implanters, the aging conditions are different from irradiation conditions for RPV steels (damage rate (dpa s^{-1}) of about 5×10^{-10}). The use of ions is here to identify the effect of displacement cascades.

The sample were irradiated at 573 K with an Fe^+ ion flux of 5×10^{14} m^{-2} s^{-1} i.e., a damage rate (dpa.s^{-1}) of 1.26×10^{-4} with ion fluences of 8.5×10^{15}, 5×10^{15}, 4.2×10^{17} and 1.25×10^{18} m^{-2}.

3. Results

The clustering of copper under these irradiation conditions was followed by 3D AP. No copper clusters is observed after electron irradiation to 3×10^{-3} dpa (with a dpa rate of 5.6×10^{-9}) (Fig. 2).

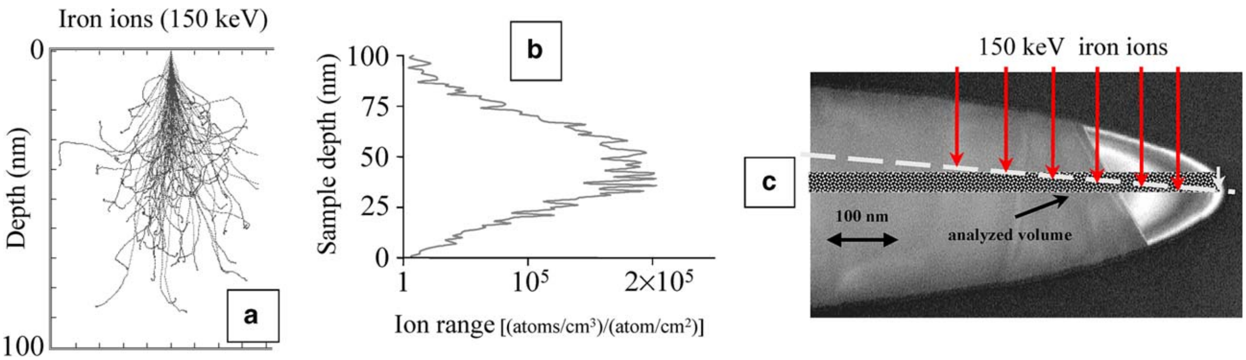

Fig. 1. Experimental procedure for ion irradiation of 3D AP samples (needle shape). (a) The energy of the iron ions is chosen with SRIM 2003 code [10] in order to have an ion penetration depth equal to the half of the thickness (b) of the atom probe sample (50 nm (c)). (b) The ion range distribution allows to calculate the number of ions that stopped in the different depths of the sample and the number of displacement cascades that affect the 3D AP analyzed volume. The number of point defects that are created in different depths of the sample is calculated. (c) TEM micrograph of typical atom probe specimen with computed 150 keV ion range and analysis volume superimposed.

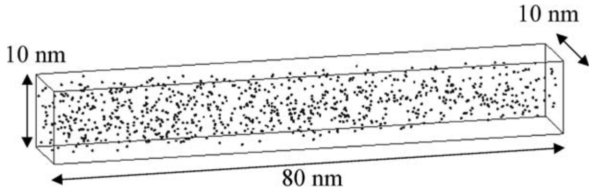

Fig. 2. 3D Atom Probe reconstruction of a small volume of Fe–0.1 at.% Cu ferritic alloy after electron irradiation ($T_{\mathrm{irrad}} = 573$ K and Fluence (in dpa) $= 3 \times 10^{-3}$). Only copper atom of the sample are shown for clarity of the image. No copper clusters are detected. The copper content in the matrix is equal to nominal copper content. The volume is: $10 \times 10 \times 80\ \mathrm{nm}^3$.

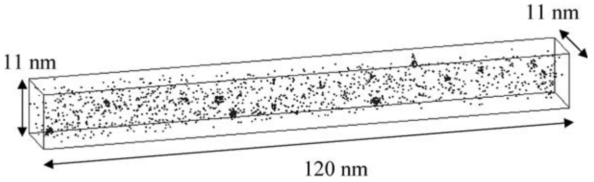

Fig. 3. 3D Atom probe reconstruction of a small volume of Fe–0.1 at.% Cu ferritic alloy after Fe^+ ions irradiation ($T_{\mathrm{irrad}} = 573$ K and Fluence (in dpa) $= 3.3 \times 10^{-2}$). Only copper atoms of the sample are shown for clarity of the image. The copper content in the matrix is 0.055 at.%. The number density of copper clusters is $10^{24}\ \mathrm{m}^{-3}$ and the radius 1 nm. The volume is: $11 \times 11 \times 120\ \mathrm{nm}^3$.

With Fe^+ ion irradiation, copper clustering starts after 100 s. irradiation. After 840 s irradiation the copper content in the matrix has significantly decreased (0.055 at.% Cu) and the number density of copper cluster is close to $10^{24}\ \mathrm{m}^{-3}$ with a mean radius of 1 nm (Fig. 3). The number of copper atoms associated to clusters varies from 5 to 70 (corresponding to sizes of 0.7–1.2 nm in diameter). These copper atoms give cluster composition ranging from 20 to 70 at.% Cu (balance is iron).

Between 100 and 2500 s of irradiation the copper content in the matrix continue to decrease and the mean size of the precipitates to increase.

Within the framework of the classical radiation enhanced homogeneous precipitation mechanism, these observations cannot be understood. Indeed, the homogeneous precipitation under electron as well as under ion irradiations were simulated using the cluster dynamic code MFPVIC. This code gives the evolution of the point defect cluster distribution as well as the precipitates distribution assuming that precipitation is homogeneous. It has been previously showed that this code is able to reproduce the precipitation in high copper content binary alloys observed experimentally [3]. In the case of the 0.08 at.% Cu alloys the calculated number densities of copper precipitates given by MFPVIC are about six orders of magnitude lower (i.e., $5 \times 10^{16}\ \mathrm{m}^{-3}$ for 5×10^5 s in this electron irradiation condition and $1 \times 10^{16}\ \mathrm{m}^{-3}$ for 2500 s in this ion irradiation condition) than the minimum observable value by 3D AP. Thus, precipitation may occur under this electron irradiation but the volume fraction is so small that it is not detectable.

Considering the output given by MFPVIC, it appears that the supersaturation of isolated point defects have the same order of magnitude for both kind of irradiation. In order to accurately determine the isolated point defect concentration, the large surface of the specimen (as it is for ion irradiation) is taken into account for the calculation. The high damage rate for ion irradiation is thus compensated by the efficiency of surface as sinks. Also the calculated concentrations of isolated point defects (mono-interstitial and mono-vacancy) are taking into account the recombination of point defects and their agglomeration in the form of point defect clusters. Thus a one to one comparison of the irradiation damage defects (in terms of mono-interstitial and mono-vacancy concentrations) is possible between electron and ion irradiations. The atomic fraction of (i)–(v) are respectively 5×10^{-13} and 2×10^{-7} after 5×10^{5} s of electron irradiation. In the case of ion irradiation, after 840 s the atomic fraction of (i) and (v) are respectively 5×10^{-13} and 10^{-7}. Thus, copper supersaturation, temperature and isolated point defects supersaturation are similar in both materials, as well as copper diffusion coefficient. The only parameters that differ from both microstructures are the number densities of interstitial and vacancy clusters. These numbers are totally negligible under electron irradiation (Fig. 4) and extremely important under ion irradiation (Fig. 5).

Thus, even if it is difficult to prove it, it is very tempting to consider that heterogeneous precipitation on point defect clusters play an important role in copper clustering in ion irradiated low copper binary alloys. The fact that the number density of copper-clusters detected with the atom probe is of the same order of the number density of point defects clusters (interstitials or vacancies) of size 10 interstitials or vacancies support this hypothesis. An important question must now be clarified: what is the role of these point defect clusters on the formation of copper precipitates. Indeed, it can simply lower the free energy of precipitate nucleus (the classical mechanism of heterogeneous nucleation) but, as under irradiation the material is far from equilibrium, it may develop a mechanism of radiation induced-segregation of copper. The point defect clusters is acting as sinks for point defects [11]. In that case a strong coupling between fluxes of solutes and point defects may be at the origin of the kinetic. The near future work will be devoted to this question.

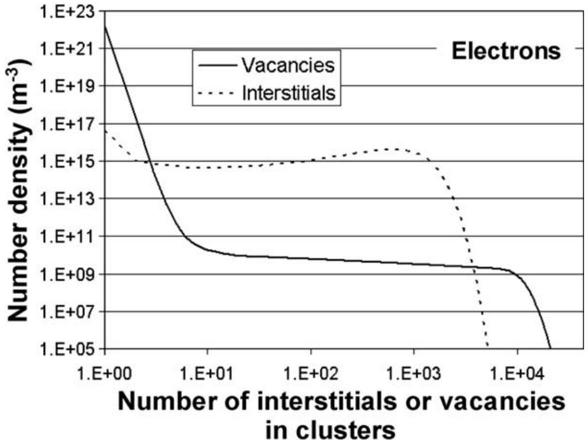

Fig. 4. Calculated (with MFPVIC code [3,4]) clusters number densities (for interstitials and vacancies) as a function of their size. The size is given by the number of interstitials or vacancies in the clusters. The material was irradiated with 3 MeV electron at 573 K.

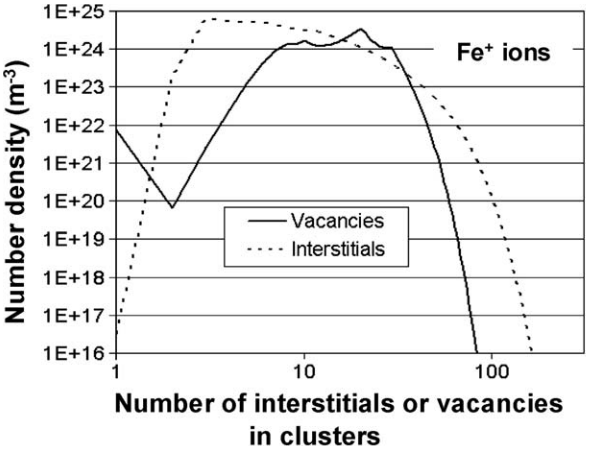

Fig. 5. Calculated (with MFPVIC code [3,4]) clusters number densities (for interstitials and vacancies) as a function of their size. The size is given by the number of interstitials or vacancies in the clusters. The material was irradiated with 150 keV Fe^{+} ions at 573 K.

4. Conclusion

Progress in the understanding of the formation of nano-copper-enriched clusters in the irradiated ferritic matrix of low alloyed FeCu alloy (Cu < 0.1 at.%) has been achieved. In this work, specific irradiation experiments were carried out using 3 MeV electrons and 150 keV Fe^{+} ions in order to point out the effect of: (i) free migrating point defects (produced as Frenkel pairs with 3 MeV electron) and (ii) free migrating point defects and high point defects clusters number density due to displacement cascades (produced with 150 keV Fe^{+} ions). The time-dependant evolution of the point defect population was computed using the cluster dynamic code (MFPVIC) developed at CEA. It is shown that at 573 K with a low supersaturation of copper (i.e., low driving force and slow kinetic), the precipitation of copper-clusters is only obtained via an heterogeneous precipitation mechanism of copper nucleus on the point defects clusters (interstitials or vacancies?) generated by 20–30 keV displacement cascades.

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References

[1] M.K. Miller, P. Pareige, M.G. Burke, Mater. Charact. 44 (2000) 235.
[2] P. Pareige, B. Radiguet, R. Krummeich-Brangier, A. Barbu, O. Zabusov, M. Kozodaev, Philos. Mag. 85 (2005) 429.
[3] F. Christien, A. Barbu, J. Nucl. Mater. 324 (2004) 90.
[4] A. Hardouin Duparc, C. Moingeon, N. Smetniansky-de-Grande, A. Barbu, J. Nucl. Mater. 302 (2002) 143.
[5] B. Radiguet, P. Pareige, A. Barbu, Surf. Interf. Anal. 36 (2004) 515.
[6] O.S. Oen, report ORNL-4897, Oak Ridge National Laboratory, Oak Ridge, TN, (1973).
[7] ASTM E521, Annual Book of ASTM Standards, 12.02. (1993).
[8] J. Chaumont, H. Bernas, F. Lalu, M. Salomé, A.M. Lamoise, Nucl. Instr. and Meth. 189 (1981) 193.
[9] P. Pareige, F. Pérocheau, P. Auger, S. Jumel, H. Bernas, Nucl. Instr. and Meth. 178 (2001) 233.
[10] J.F. Ziegler, J.P. Biersack, U. Littmark, Stopping and Range of Ions in Matter, Pergamon, New York, 1985.
[11] B. Radiguet, PhD thesis, Rouen University (2004).