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Letter to the Editors

A comparison of the effect of electron irradiation and of thermal aging on the hardness of FeCu binary alloys

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Abstract

The hardening of binary *Fe*Cu alloys under 2.5 MeV electron irradiation between 175°C and 360°C was investigated. We show that an extra-hardening component which cannot be ascribed to copper precipitation is induced during irradiation with electrons. We discuss the possible nature of the objects responsible for this extra-hardening component. They have to be very small since they are not visible by transmission electron microscopy. We come to the conclusion that they most likely are very small interstitial clusters nucleated by random encounter of interstitials. An important issue from the technological point of view raised by this work is to know whether it is reasonable to totally ignore any hardening component of the pressure vessel steels attributed to the clustering of freely migrating point defect escaping from the core of the displacement cascades or created between them.

1. Introduction

We recently published a synthesis of our results concerning the copper precipitation in the binary *Fe*Cu alloys under electron irradiation [1]. We showed that the mechanisms of precipitation are identical under electron irradiation and under thermal aging: the sole effect of electron irradiation on the precipitation is to enhance the kinetics. The aim of this study is to report and discuss microhardness measurements carried out on the same samples.

2. Materials and techniques

Three binary *Fe*Cu alloys containing 1.34, 0.30 and 0.11 at.% Cu, respectively, together with base iron were cold-rolled. Samples ($1.2 \times 3 \times 0.04$ cm^3) were then cut for irradiation and ($1.5 \times 1.5 \times 0.08$ cm^3) for thermal aging. They were annealed 24 h at 820°C and quenched at ≈10°C/s. At this stage the carbon content is ≈100 appm. The irradiations were carried out with 2.5 MeV electrons in a van de Graaff accelerator at doses up to 5 C cm^{-2} (3.1×10^{19} e$^-$ cm^{-2} or 1.4×10^{-3} dpa using a cross section for point defects production of 50 barns). The dose rate was around 6×10^{-6} C cm^{-2} s^{-1} (4×10^{13} e$^-$ cm^{-2} s^{-1} or 2×10^{-9} dpa s^{-1}). The beam is scanned to ensure a good homogeneity of the flux in the irradiated area the radius of which is 10 mm. For details, see Ref. [1]. The thermal aging was performed at only 500°C up to 312 h. The Vickers microhardness measurements were carried out using a Shimadzu HVM 2000 device. The load was 50 g. For each sample the mean value of more than 20 measurements was obtained.

3. Results and analysis

3.1. Electron irradiation at 290°C and thermal aging at 500°C of FeCu1.34at.%

The evolution of the microhardness H_v with fluence or aging time is given in Tables 1 and 2, respectively.

We showed previously [1] that the evolutions of the microstructure of the precipitation are identical by using the following scaling law: *1 C/cm*^{2} *at 290°C under*

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Table 1
Measured and calculated microhardness change H_v and H_{vc}, respectively in the *Fe*1.34at.%Cu alloy during thermal aging at 500°C

Aging time (h)	H_v measured	R_m (nm) SANS	f_ρ	H_{vm}	H_{vp}	H_{vc}
0	125±5	(0)	(0)	125	0	125
2.5	200±5	0.9±0.2	1.01	91	95	186
4.5	243±3	2.3±0.3	1.20	84	158	242
8	237±4	2.9±0.3	1.28	81	153	234
25	220±3	3.0±0.3	1.28	81	151	232
142	187±5	6.3±0.4	1.29	81	107	188
312	178±5	8.0±0.4	1.29	81	94	175

R_m is the mean radius of the precipitates given by SANS, f_ρ the volume fraction of precipitates inferred from the electrical resistivity measurements, H_{vm} the hardening component of the matrix calculated by using f_ρ and relation (3) and H_{vp} the hardening component of precipitates calculated using f_ρ, R_m and relation(1).

Table 2
Experimental microhardness H_v of the *Fe*1.34at.%Cu alloy as a function of the fluence under 2.5 MeV electron irradiation at 290°C

Dose (C cm^{-2})	H_v	R_m (nm) SANS	f_ρ	H_{vm}	H_{vp}	H_{vc}	δH_v
0	125±5						
0.05	170±5		0.34	113			
0.15	217±8	1.2±0.2	0.74	100	115	215	2
0.5	272±7	2.1±0.3	1.21	83	162	245	27
1.6	264±7	2.5±0.3	1.28	81	160	241	23
1.8	258±8	2.6±0.3	1.30	80	160	240	18
5	250±10	3.2±0.2	1.29	81	150	230	20

H_{vc} is the calculated hardening assuming that only precipitation occurs. The difference δH_v between H_v and H_{vc} represents the extra component of hardening under irradiation attributed to interstitial clustering.

electron irradiation corresponds to 9 h under thermal aging at 500°C (both quantities being referred to in the following as one unit of λ). Fig. 1 recalls the change of the mean radius R_m and the number density N_p of the precipitates with λ and shows the corresponding measured microhardness. The equivalence between irradiation and thermal aging observed for R_m and N_p are no more true for the microhardness which is larger under irradiation. The difference increases from 0 Vickers at $\lambda = 0$ to 31 Vickers at the peak hardening ($\lambda = 0.5$). For larger values of λ, the difference remains constant within the experimental error. This means that a hardness component exists under electron irradiations at low flux that cannot be attributed to copper precipitation.

Thanks to the scaling law between precipitation under thermal aging at 500°C and electron irradiation at 290°C, we can directly deduce from Fig. 1 the extra-hardening component under irradiation at 290°C. In contrast, for any other temperature or copper content we have to calculate the hardening component due only to the precipitates H_{vp} taking advantage of the values of R_m and N_p (or f the volume fraction of precipitate) previously obtained by small angle neutron scattering [1]. To do this we need a mathematical expression for $H_{vp}(R_m, f)$.

The analysis of the hardness change due to precipitation of copper in FeCu alloys is usually carried by using the Russell and Brown model [2]. It gives the shear stress due to a monodispersed distribution of precipitates of radius R. Assuming a linear relation between H_{vp} and the shear stress, the expression given by Russel and Brown [2] can be written

$$H_{vp} = \frac{G\,bf^{1/2}}{R} F(R), \tag{1}$$

where G is the shear modulus of the matrix (8.3×10^4 MPa), b the Burgers vector of the dislocation (2.48 Å) and F a function of the precipitate radius.

The calculated hardness of the alloy containing precipitates H_{vc} is then

$$H_{vc} = H_{vp} + H_{vm}, \tag{2}$$

where H_{vm} is the matrix contribution resulting only from the presence of isolated solute atoms in the matrix. To obtain H_{vm} versus the copper concentration we carried out microhardness measurements for the three supersaturated solutions and the base iron. We found

$$H_{vm} = 79 + 34[\mathrm{Cu}], \tag{3}$$

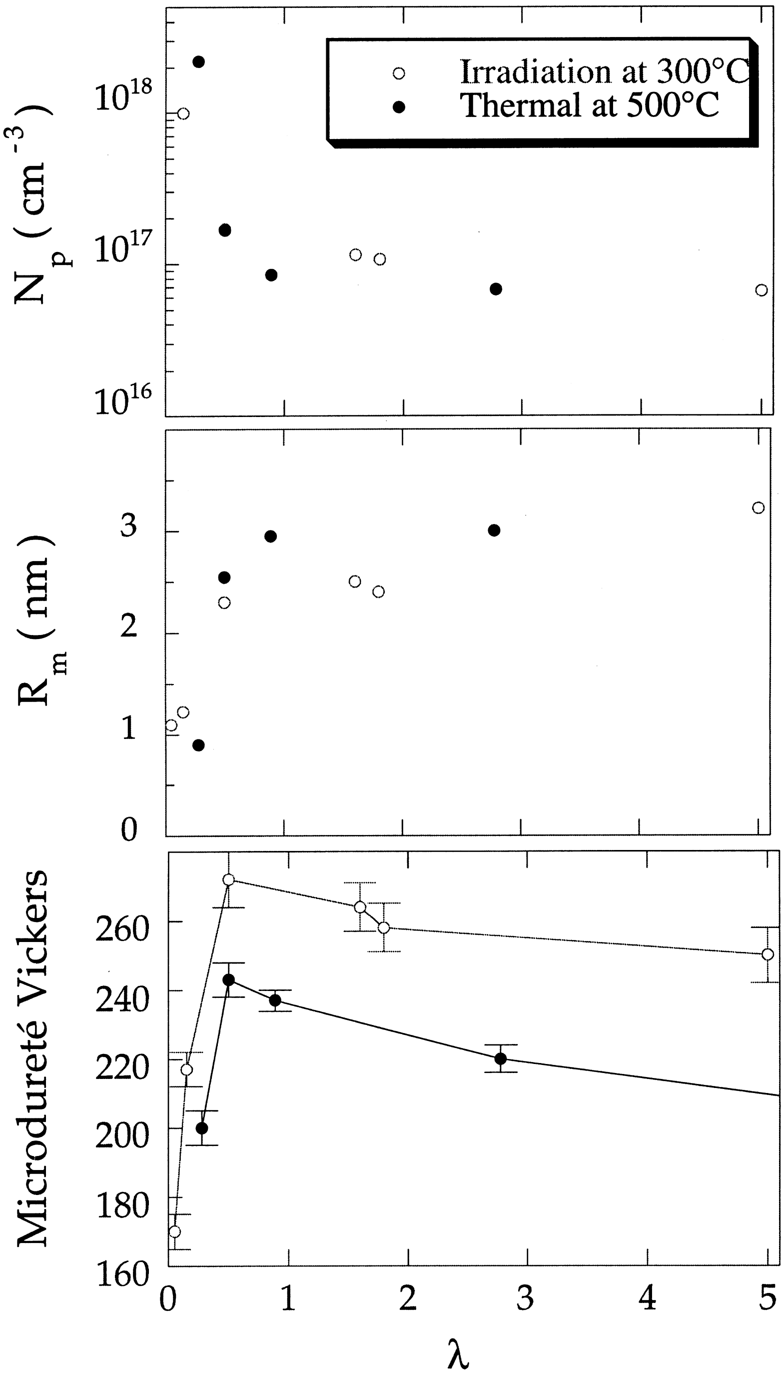

Fig. 1. Microhardness (bottom), precipitate radius (center) and precipitate number density (top) in *Fe*Cu1.34% either irradiated at 290°C or thermally treated at 500°C. One λ is 1 C/cm^2 under irradiation and is 9 h for the thermal aging.

where [Cu] is the copper concentration in atomic percent deduced from electrical resistivity measurements.

In fact, it has been showed [3] that the Russell model is certainly not well founded for the age-hardening of *Fe*Cu. Furthermore it is known to give the peak harness at too small a radius. For this reason, we will use formula (1) simply as a phenomenological one. $F(R)$ is obtained experimentally by fitting the hardness curve

Table 3
Effect of the temperature on the hardening for the *Fe*1.34at.%Cu alloy irradiated up to a fluence of 0.5 C/cm^2

T (°C)	H_v	R_m (nm) SANS	f_ρ	H_{vm}	H_{vp}	H_{vc}	δH_v
175	237±7	1.0±0.2	0.42	110	73	183	53
300	272±7	2.1±0.3	1.23	83	163	245	26
360	250±7	2.3±0.3	1.34	79	167	246	4

versus the radius R_m, measured after thermal aging at 500°C. Finally because of the too large uncertainties in the values of the volume fraction of precipitates f given by SANS, we preferred to use the volume fraction of precipitates f_ρ derived from the electrical resistivity taking into account the precipitate contribution (see Appendix A). Table 1 shows the experimental value H_v and the calculated one H_{vc} obtained by using the method described above.

Table 2 gives the experimental value H_v measured under electron irradiation at 290°C, H_{vc} and the difference $\delta H_v = H_v - H_{vc}$. We obviously arrive at the same conclusion as by comparing directly the experimental results under irradiation at 290°C and under thermal aging at 500°C.

3.2. Effect of the temperature

Table 3 gives H_v, for the FeCu1.34at.% alloy irradiated at a fluence of 0.5 C/cm^2 and three temperatures: 175°C, 290°C and 360°C. At 175°C, we are not sure to be beyond the peak hardening. However it is clear that the smaller the temperature, the larger the extra-hardening δH_v. At 360°C, there is no extra hardening.

3.3. Effect of the copper concentration at 290°C

Table 4 shows that in the 0.3 at.% Cu alloy, H_v increases from 90 to 170 Vickers at 2.5 C/cm^2. However, for this less concentrated alloy we do not have resistivity measurement above 0.3 C/cm^2 and the error on R_m and f measured by SANS are too large to calculate δH_v with any accuracy.

In the 0.1 at.% Cu alloy irradiated up to 5 C/cm^2, no SANS signal is obtained but a significant hardening of 31 Vickers is observed.

Table 4
Microhardness as a function of the fluence ot the 0.30 at.% Cu alloy irradiated at 290°C

Doses (C cm^{-2})	H_v
0	90
0.5	138
1.5	145
2.5	170

Finally a base iron sample irradiated at 290°C up to 1.5 C/cm^2 does not show any hardness increase.

4. Discussion

The results clearly show that in the copper rich *Fe*Cu alloy, a hardening component which cannot be ascribed to precipitation is induced by 2.5 MeV electron irradiations. Concerning the 0.1 at.% Cu alloys, the problem is to know whether the absence of precipitation detected by SANS [1] is real or is due to the very small sensitivity of this technique when the precipitates are very small. If it is not an artefact, the small decrease of the electrical resistivity observed up to 5 C/cm^2 [1] would suggest that some copper precipitation does take place. Unfortunately we did not have the opportunity to study this sample by tomographic atom probe, certainly the best method to get some insight under such conditions. Fortunately, Auger et al. [4] carried out an atom probe study of a *Fe*Cu0.08at.% sample irradiated with electrons up to 1.2 C/cm^2 and Akamatsu [5] measured its hardness. They showed that no precipitation occurs (the copper content in the matrix does not change) and found an increase of the hardness of 30 Vickers for a 200 g load. Although the loads are not the same, the value of hardness increase can be considered as equal for both studies. This implies that for electron irradiated 0.1% Cu samples, the contribution of the precipitates to the hardness is negligible.

As the hardening observed in binary *Fe*Cu alloys for [Cu] $\leqslant$ 0.1% cannot be explained by copper precipitation, the only possibility is that it is due to point defect clusters induced by electron irradiation. Since almost all interstitials and vacancies are created as freely migrating defects under 2.5 MeV electron irradiation, the clusters can only be created by random encountering of point defects or by the encounter of a freely migrating defect with a trapped one. These clusters have to be smaller than 1.5 nm since they are not visible by transmission electron microscopy. Several possibilities about their nature a priori exist: vacancy clusters such as nanovoids or dislocation loops and interstitial dislocation loops. They can be associated with solute atoms (here copper) or impurities (if the coupling between point defect flux and solute or impurity flux is positive). Let us now consider the various possibilities.

We can certainly rule out nanovoids since a positron annihilation experiment performed on a *Fe*0.08at.% Cu alloy containing the same carbon content as our alloys, irradiated with 3 MeV electrons at 288°C up to 4×10^{19} e^-/cm^2, did not show three dimension vacancy clusters [6]. Vacancy nanoloops can likely also be eliminated since they are known to be unstable under electron irradiation. Only small interstitial clusters hereafter called dislocation loops, although clusters containing only a few interstitials are certainly not two-dimensional, can seriously be envisaged. The fact that, under electron irradiation carried out on alloys of cubic crystallographic structure in a high voltage electron microscope (HVEM), the interstitial loops appear at very short fluence compared to voids, is also in favour of interstitial clusters even if, with such an irradiation, the electron flux is considerably larger than the one given by a van de Graaff accelerator and the sink strength of the surface (thin foils for HVEM irradiation) is significantly larger than grain boundary strength (bulk samples for van de Graaff irradiations).

It is worth noticing that the extra hardening observed in the alloy containing 1.34 at.% Cu is also near 30 Vickers. The simplest interpretation is that small interstitial clusters appear between precipitates in a matrix the composition of which remains above 0.04 at.% [7]. However an association of the point defect cluster with precipitates cannot be totally ruled out.

Finally as no hardening was observed in the base iron irradiated with 2.5 MeV electrons at 290°C up to 1.0 C/cm^2, we must admit that the presence of copper, even at very low concentration, is necessary for point defect clustering. The copper atoms can change the nucleation rate of interstitial clusters either by trapping interstitial and/or by stabilising the cluster. The former assumption is certainly not likely since Maury et al. [8] has shown that mixed Fe–Cu interstitials are formed in *Fe*Cu alloys but are as mobile as Fe–Fe interstitials, a behaviour which likely results of the absence of caging effect in bcc alloys.

5. Conclusion

We have shown that:

- Irradiations with 2.5 MeV electron, particles which almost create only freely migrating point defects, induce in *Fe*Cu alloys an hardening component which cannot be attributed to Cu precipitates.
- This extra hardening certainly stems from the presence of small interstitial cluster.
- The clustering of point defects does not occur in the absence of copper.

An important issue from the technological point of view raised by this work is to know whether it is reasonable to totally ignore any hardening component of the pressure vessel steels attributed to the clustering of freely migrating point defects escaping from the core of the displacement cascades or created between them.

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Appendix A

The matrix copper contents cannot be derived directly from the resistivity because of a precipitate contribution which is not negligible [1]. To evaluate this contribution we studied the 30°C electrical resistivity change during aging at 500°C of a *Fe*Cu0.7at.% because tomographic atom probe data are only available for various aging times at this composition [9]. The resistivity was obtained through the same procedure as under irradiation except that now the sample (a ribbon of 80 μm thick) is heated by Joule effect with a alternative current source. Assuming that the contributions of the matrix and of the precipitates are additive we write

$$\rho = \rho_0 + \rho_m[\mathrm{Cu}]_m + ([\mathrm{Cu}]_0 - [\mathrm{Cu}]_m)\rho_p(R), \qquad \text{(A.1)}$$

where $[\mathrm{Cu}]_0$ is the nominal copper concentration of the alloy, $[\mathrm{Cu}]_m$ the actual copper concentration in the matrix, ρ_0 the resistivity for $[\mathrm{Cu}]_m = 0$, ρ_m the resistivity per copper atom in the matrix and $\rho_p(R)$ the resistivity per copper atom in the precipitates of radius R. Using the values of $[\mathrm{Cu}]_m$ and R given by the tomographic atom probe study on the *Fe*Cu0.7at.% alloy and the values of $\rho_0 = 10.4$ μΩ cm and $\rho_m = 3.9$ μΩ cm/at.% [1], we found that $\rho_p(R)$ is given by

$$\rho_p(R) = 1.5R^{-1/2}$$

with R in nm.

As no tomographic atom probe analysis was carried out on the irradiated samples or on the 1.34 at.%Cu sample aged at 500°C considered in the body of this paper and considering the large incertainties on the volume fraction of precipitates f obtained by SANS, we prefered to get f from $[\mathrm{Cu}]_m$ given by Eq. (A.1) by taking advantage of the electrical resistivity and of the radius of the precipitates given by SANS [1].

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