MICROSTRUCTURAL CHARACTERIZATION OF ATOM CLUSTERS IN IRRADIATED PRESSURE VESSEL STEELS AND MODEL ALLOYS

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ABSTRACT. In order to characterize the microstructural evolution of the iron solid solution under irradiation, two pressure vessel steels irradiated in service conditions and, for comparison, low copper model alloys irradiated with neutrons and electrons have been studied. The characterization has been carried out mainly thanks to small angle neutron scattering and atom probe experiments. Both techniques lead to the conclusion that clusters develop with irradiations. In Fe-Cu model alloys, copper clusters are formed containing uncertain proportions of iron. In the low copper industrial steels, the feature is more complex. Solute atoms like Ni, Mn and Si, sometimes associated with Cu, segregate as "clouds" more or less condensed in the iron solid solution. These silicides, or at least Si, Ni, Mn association, may facilitate the copper segregation although the initial iron matrix contains a low copper concentration.

Keywords: pressure vessel steel, FeCu alloys, neutron and electron irradiations, microstructural characterization, small angle neutron scattering, atom probe, copper precipitates, copper-iron clusters, Si-Ni-Mn-Cu rich clouds.

I INTRODUCTION

Pressure vessel steels used in pressurized water reactors are low alloyed ferritic steels. They may be prone to hardening and embrittlement under neutron irradiation. The changes in mechanical properties are generally supposed to result from the formation of point defects, dislocation loops, voids and/or copper rich clusters. However, the real nature of the irradiation induced-damage in these steels has not been clearly identified yet.

In order to improve our vision of this damage, we have characterized the microstructure of steels irradiated in the French surveillance programme, i. e. materials having a chemical composition, a structure and irradiation conditions very similar to those of the vessel core zone. We present here the results obtained on two steels irradiated in CHOOZ A and DAMPIERRE 2.

Since copper is known to play an important role in the irradiation embrittlement, we have also studied some Fe-Cu model alloys irradiated with neutrons or with electrons. For comparison, a model alloy has also been characterized after thermal ageing.

The microstructural characterization has been carried out by Transmission Electron Microscopy (TEM), Positron Annihilation (PA), Small Angle Neutron Scattering (SANS) and Atom Probe Field Ion Microscopy (APFIM).

II STUDIED MATERIALS

a) Steels from surveillance programmes

Both steels from surveillance programmes are 16 MND 5 type ; they are representative of the C shells of the two reactors. Their chemical compositions are given in table 1.

The steel from CHOOZ has a ferrito-bainitic structure. The samples used in the study were irradiated during up to 13 years with a fluence of 1.4 10^{20} n.cm^{-2} (all the fluences are given for neutrons with energy higher than 1 MeV), which corresponds to a dose of about 0.2 dpa. The irradiation temperature was 255°C until 1970 and then 265°C (1).

The steel from DAMPIERRE is entirely bainitic. It has been irradiated during 9 years to a fluence of 4.6 10^{19} n.cm^{-2} (≈ 0.08 dpa) at a temperature of 290°C.

Table 1. Chemical compositions (wt%) of the CHOOZ A and of the DAMPIERRE 2 pressure vessel steels

	C	S	P	Si	Cr	Mo	Mn	Ni	V	Al	Co	Cu
CHOOZ	0.16	0.006	0.012	0.32	0.16	0.39	1.26	0.57	0.020	0.024	0.02	0.09
DAMPIERRE	0.16	0.008	0.008	0.19	0.24	0.55	1.25	0.74	-	0.009	0.01	0.07

It is noticeable that the concentrations of reputed embrittling elements (P, Ni, Cu) are rather low in both steels. Nevertheless, the CHOOZ A steel is subject to an increase in the Charpy transition temperature as high as 145°C for a fluence of about 10 10^{19} n.cm^{-2}. With a fluence 4.6 10^{19} n.cm^{-2}, the same parameter rises of only 40°C for the DAMPIERRE 2 steel.

b) Binary Fe-Cu alloys

Three Fe-Cu alloys have been prepared with the following copper contents : 0.1 ; 0.7 ; 1.4 wt%. They have been irradiated in the OSIRIS pool test reactor of CEA/Saclay. The fluence received in the centre of the specimens is about 5.5 10^{19} n.cm^{-2} (≈ 0.1 dpa) with a rather high flux of 3 10^{13} n.cm^{-2}. s^{-1}. The irradiation temperature was close to 290°C.

The binary alloys were also irradiated with electrons in a Van de Graaff accelerator (3 MeV). The maximal received fluence was 2 10^{19} e^{-}.cm^{-2} (≈ 1.8 10^{-3} dpa) at a temperature of 290°C. Electrons induce the formation of isolated point defects (interstitials and vacancies) and so can favour the clustering of solutes, as neutrons are supposed to do. However, after electron irradiation the materials are not radio-active, which makes the studies easier.

For both kinds of irradiations (electron and neutron), the induced-damage was characterized by Transmission Electron Microscopy (TEM) at EDF, Positron Annihilation (PA) at CEA/Grenoble, Small Angle Neutron Scattering (SANS) at Brookhaven National Laboratory or Laue Langevin Institute (in Grenoble) and Atom Probe Field Ion Microscopy (APFIM) with a energy - compensated instrument at University of Rouen (2).

The effects of electron and neutron irradiations on the mechanical properties were studied by hardness tests with a load of 5 N. In order to make some comparisons, hardness tests and APFIM experiments have also been performed on the Fe-0.7 wt%Cu alloy thermally aged 70 hours at 500°C.

III RESULTS

3.1 Steels from surveillance programmes

a) CHOOZ A pressure vessel steel

The results of TEM, PA and SANS experiments carried out on samples from CHOOZ have already been published elsewhere (3, 4, 5, 6) and can be summarized as follows : the steel has a ferrito-bainitic structure ; some regions are fully bainitic, whereas some others contain about 60% of bainite and 40% of ferrite. The observed carbides are of M_3C or M_2C types. Conventional TEM has not allowed to detect any irradiation induced-defect such as atom clusters, cavities or dislocation loops. However, the dislocation density seems to be slightly smaller after irradiation (3). Positron annihilation has shown that neutron irradiation had not induced the formation of microvoids containing more than 50 vacancies (4).

SANS experiments (3, 5) have revealed the presence of irradiation induced defects. It was observed that their volume fraction increases as the fluence rises ; however their radius (Guinier analysis) remains nearly constant ($R_g \approx 1.3$ nm), at least for fluences ranging between 2.4 and 14 10^{19} $n.cm^{-2}$. Complementary SANS measurements with magnetic field have shown that the ratio of the intensities scattered parallely and perpendicularly to the applied field (so called A ratio) is about 2 (± 1). Hence, it can be ruled out that the irradiation induced defects are pure copper clusters (A = 11). The unambiguous determination of the composition of the scattering centres required complementary studies by APFIM.

The APFIM investigations were carried out on the steel from CHOOZ in non irradiated and irradiated states (fluence : 1.10^{20} $n.cm^{-2}$). The first experimental evidence is the absence of particular contrast on FIM micrographs, even for the irradiated sample. For this reason, only atom probe analysis from random areas has been performed.

It was observed that the irradiation had induced the formation of a high density (1 10^{18} cm^{-3}) of local enrichments of the iron solid solution in solutes like Si, Mn, Ni and Cu. The apparent size of these clusters ranges from 3 to 8 nm. Their solute concentrations are very low and they can be regarded as "clouds" of solute atoms more or less condensed in the iron solid solution (7, 8). A mean chemical composition of the observed clusters is given in table 2. If nickel, manganese and silicon seem to be systematically associated all together in the clusters with a quasi M_2Si stoechiometry (M = Mn + Ni)(7), copper has not always been observed. Nevertheless, analysis of the matrix reveals that 60% of the total copper atoms have segregated.

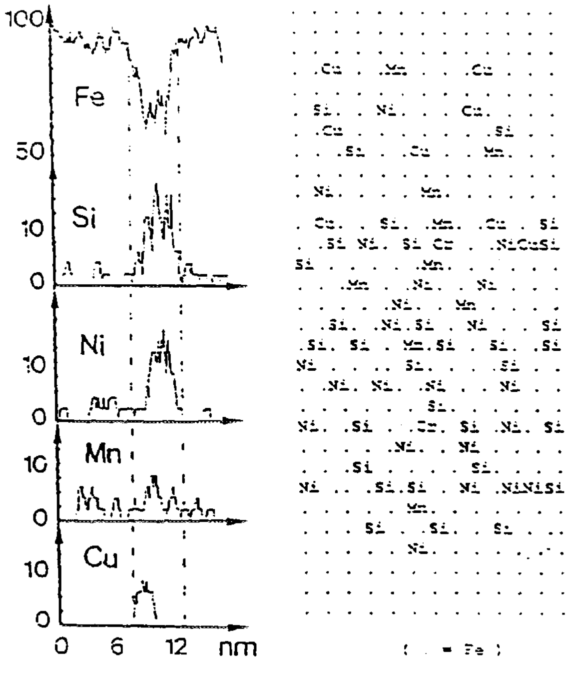
Table 2 : Mean concentrations of Ni, Mn, Si, Cu (at% ± 2 σ) in clusters and enrichment ratios (compared to the nominal composition of the ferrite)

	Ni	Mn	Si	Cu	Fe
average at%	3.6 ± 0.6	3.8 ± 0.7	4.8 ± 0.7	0.9 ± 0.3	balance
enrichment. ratio	up to 12	up to 6	up to 12	up to 45	-

The internal constitution of one cluster has been investigated thanks to a plane by plane evaporation process (figure 1). It has been shown that the core of the cluster is mainly constituted of Ni, Mn and Si atom enrichment, whereas copper atoms are systematically gathered on one border. Rather than a unique cluster, this suggests the existence of two types of symbiotic ones.

From the chemical composition given in table 1, it is possible to calculate the A ratio that such defects would give in SANS experiments. Assuming that the magnetic contrast in the clusters is proportional to their iron content (which is possible for high iron contents) we find a A ratio of 2.1. This value is consistent with the experimental one (cf 3.1.a), which indicates that the defects observed by APFIM could be the same as those revealed by SANS experiments. It is likely that only the core of the clusters is dense enough in solutes to induce a neutron scattering. This may explain why the radius of the defects appear smaller after SANS measurements than after APFIM ones.

Figure 1.
Composition profiles of Fe, Si, Ni, Mn and Cu obtained during a (100) plane by plane evaporation sequence of an irradiation induced "cloud".
30 successive atomic planes have been evaporated. The identified atoms have been positioned in their order of arrival, therefore, their actual disposition inside each plane is unknown.
The core of the "cloud" is Si, Ni, Mn rich, whereas copper is mainly gathered on the top border.



The results obtained by APFIM in the steel from CHOOZ give a picture of the irradiation induced-damage which is slightly different of the usually proposed scenarios (9-16). For this low copper highly irradiated steel, not only copper but also Ni, Mn and Si are concerned in the solid solution demixing process.

b) DAMPIERRE 2 pressure vessel steel

The DAMPIERRE 2 pressure vessel steel is slightly different from the previous one. More precisely, its copper and silicon concentrations are lower, conversely the nickel content is higher than for the CHOOZ A steel (table 1). The irradiation conditions are different too : the DAMPIERRE 2 steel has been submitted to a lower fluence with a weaker flux, but it has been irradiated at a higher temperature.

SANS examination (6) of the non irradiated and irradiated samples exhibit almost the same feature. In both cases, no apparent neutron scattering is observed.

Atom probe random analyses (8) of irradiated samples give no evidence of solute peaks on concentration profiles. However, small differences exist between solute distribution in irradiated and non irradiated samples. These differences can be revealed thanks to statistical tests like contingency tables (17) which allow to check the first stages of clustering. These tests show that after irradiation, solute atoms are no longer completely randomly distributed in the iron solid solution. There appears a trend to the formation of Si-Ni, Si-Mn or Si-Ni-Mn very small clusters of a few atoms of each species which do not exist in the non irradiated condition. The eventuality of copper segregating to these clusters is uncertain because of the high statistical error bar due to the tiny number of detected copper atoms.

3.2 Irradiated Fe-Cu MODEL ALLOYS

a) Results of hardness tests

The fluences of the neutron and electron irradiations are high enough for the hardness of each alloy to reach a plateau. For both irradiations, the evolution of the maximum hardness increase (ΔHv_e for electrons and ΔHv_n for neutrons) is plotted in figure 2 as a function of the initial copper content in the solid solutions. ΔHv_n and ΔHv_e evolve with the copper content according to parabolic laws. Whatever the copper content, it is noticeable that the hardening is higher after neutron than electron irradiation. This can be due to an effect of flux or to the difference of the primary damage induced by the particles : Frenkel pairs and cascades for neutrons and only Frenkel pairs for electrons.

b) Microstructural examinations

SANS experiments have been carried out on the alloys with 0.7 and 1.4% of copper after neutron irradiation (18). It was noticed that the intensity scattered at small angles clearly increases with the alloy copper content. The measured Guinier radii of the scattering centres are respectively 1.2 and 1.5 nm ; their A ratios are 2.2 and 4.1. These values show that the defects are not pure copper clusters (A = 11).

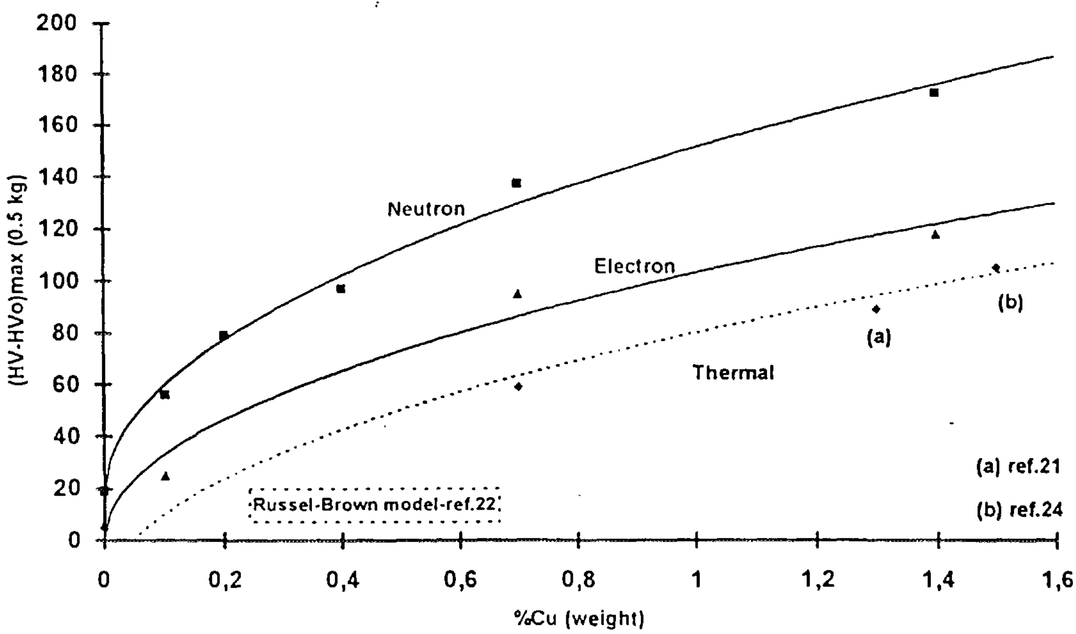


Figure 2. Maximum hardness increase after neutron irradiation, electron irradiation or thermal ageing as a function of initial solid solution copper content.

<u>On the APFIM micrographs</u> of neutron or electron irradiated specimens, no well defined contrast is detected. This precludes selected area analyses to be carried out. Thus, with the hope of a sufficient number density of particles, random analyses have been performed.

Random Atom Probe analyses of the neutron irradiated samples with 0.7 and 1.4 wt% copper contents, revealed copper rich clusters having a non unique distribution of apparent sizes, which can suggest the existence of several populations or, more probably, the simultaneous presence of different stages of development of the same population. 20% of the smallest clusters are particularly copper rich and considering the large uncertainties, they could be pure copper particles.

In the electron irradiated Fe-0.1%Cu, no special event was detected. In the Fe-0.7%Cu, electron irradiation has induced the formation of small copper clusters. Their density appears much lower than after neutron irradiation.

For all irradiation conditions and copper contents, it appears that the iron solid solution is copper depleted down to about 0.1 at%. This concentration seems to be a limit under which irradation (neutron or electron) cannot induce the clustering of copper atoms. This is likely why the Fe-0.1%Cu sample does not decompose after electron irradiation.

c) Analysis of the measurements

In order to study the effects of the copper content and to compare the two kinds of irradiations, we have treated all the experimental results through a same geometrical model (19) which assumes a random distribution of identical spherical precipitates.

Taking into account the uncertainties of the experimental measurements, this analysis has led to determine possible intervals of values for the copper content, the size, the density and the volume fraction of the "mean cluster" in each irradiated sample (8). The results are given in table 2.

Table 2. Atom probe results on thermally aged and neutron or electron irradiated Fe-Cu model alloys.

Material	State	Cu in the matrix (at%)	Cu in clusters (at%)	Diameter of clusters (nm)	Density of clusters ($10^{17}.cm^{-3}$)	Volume fraction of clusters (%)
Fe-0.7wt%Cu	Thermally aged	0.14±0.02	100	7±1	0.30-0.35	0.5-0.6
	Electron irradiated	0.10±0.02	20-60	4.5-11.0	0.3-0.9	0.8-2.5
	Neutron irradiated	0.08±0.02	15-30	4-6	3-7	1.8-3.6
Fe-0.1wt%Cu	Electron irradiated	0.09±0.02	*	*	*	*
Fe-1.4wt%Cu	Neutron irradiated	0.08±0.02	20-40	4-6	4-9	3.0-5.8

* No defect has been observed

From this analysis, it appears that the "mean clusters" may have rather high iron contents. We notice also that their volume fraction seems to increase with the copper content of the alloys.

The uncertainties are too high to observe any influence of the kind of irradiation (electron or neutron) on the chemical composition and size of the "mean clusters". However, the density and volume fraction of these latter appear higher after electron than neutron irradiations

3.3 Thermally aged Fe-0.7 wt%Cu model alloy

In order to compare the clusters induced by electron or neutron irradiations with those due to thermal ageing, some analysis have been carried out on the Fe-0.7%Cu alloys aged at 500°C. At this temperature, copper has an extremely low solubility in iron and precipitates via a diffusion controlled mechanism. The samples were treated during 70 h so as to reach the maximum increase in hardness (ΔHv_{th}). The latter is plotted in figure 2 with two other values of peak hardness measured in iron copper alloys and given in the literature (21, 24). ΔHv_{th} also follows a parabolic law according to the Russel - Brown model (22). Whatever the copper content, we notice (18) that $\Delta Hv_{th} < \Delta Hv_e < \Delta Hv_n$

Field Ion Microscopy (FIM) reveals the existence of the precipitates induced by the thermal treatment. They appear as well defined but scarce dark contrasts in the bright pole figure of the iron solid solution (figure 3). They have been analysed by the selected area analysis method. These techniques allow a higher precision on shape and chemical measurements than the random analyses carried out on the irradiated samples. The analysis on the selected areas has been done with a constant lateral resolution of 0.5 nm. The results are given in table 2.

In this case, the precipitates are unambiguously composed of pure copper. Like after irradiation, the solid solution is copper depleted down to about 0.1 at%. By evaporating atomic planes one after one, we noted that the precipitates have a spherical or slightly ellipsoïdal shape with a mean diameter of 7 nm and a number density of $3\ 10^{16}\ cm^{-3}$ (6). Thus, they are slightly larger and less numerous than the defects observed in the same alloys after electron or neutron irradiation.

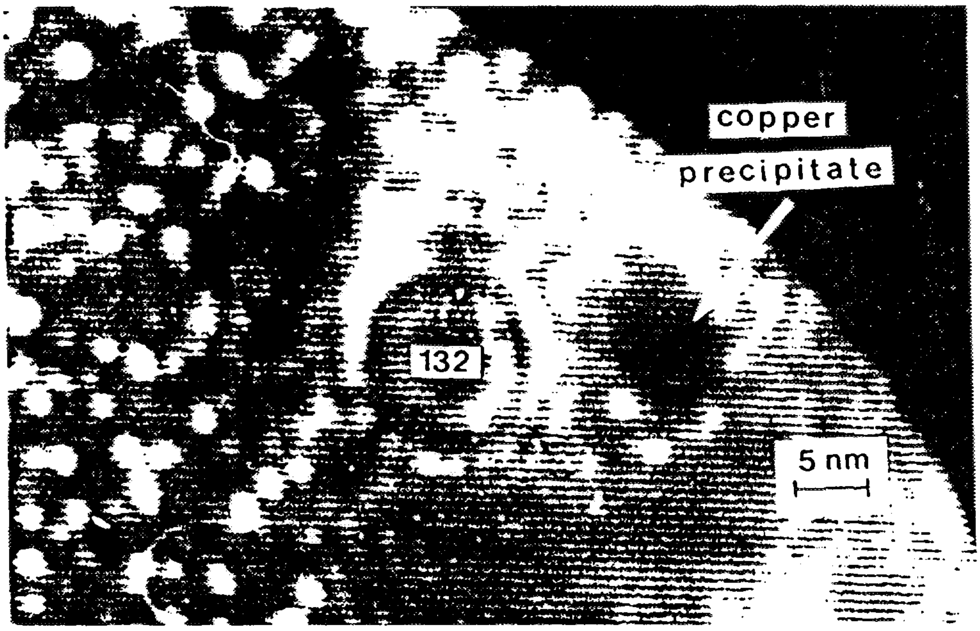


Figure 3. Video recording field ion micrograph of the thermally aged Fe-0.7 wt%Cu sample. The dark area near the (132) pole of the bcc structure of the brightly imaged iron matrix is the image of the copper precipitate.

IV DISCUSSION

The results obtained in the steels irradiated in CHOOZ and DAMPIERRE are consistent. For these low copper steels, it appears that neutron irradiation induces a clustering of elements like Ni, Mn and Si (maybe accompanied by Cu ?). The features detected in the steel from DAMPIERRE may be considered as the first stage of this process and the "clouds" encountered in the highly irradiated CHOOZ A steel can be regarded as a more developed one. New experiments on DAMPIERRE 2 samples have to be carried out in order to increase the statistical confidence. In addition, a kinetics study is in progress on CHOOZ A samples irradiated with different fluences in order to establish the successive stages of the clustering process.

In the irradiated Fe-Cu model alloys, we have shown that the irradiation-induced clusters present a non unique distribution of size. We have noticed that the smallest ones were copper rich, but we were not able to decide if they were pure copper or not. However, the following results tend to show that most of the clusters (at least the largest ones) are not made of pure copper :

- the A ratio measured by SANS (A = 2.2 and 4.1) is lower than the value expected for pure copper defects (A ≈ 11) ;
- the clusters do not exhibit any contrast on the FIM micrographs while pure copper precipitates obtained by thermal ageing have one ;
- a geometrical analysis of the AP measurements revealed that the "mean cluster" in each sample contains an uncertain iron content.

This study shows that most of the particles induced by irradiation in a ferritic matrix (at least with damage lower than 0.2 dpa) look like clouds of solutes rather than real precipitates. The presence of defects composed of iron, copper atoms and vacancies has already been envisaged (for example ref. 24) in order to justify the values of A ratios obtained with SANS experiments on FeCu alloys.

It still has to be determined if the hardening and the embrittlement of steels under irradiation is mainly due to the presence of such clouds or if there is an other component due to point defects. An unambiguous answer to this question will need further heavy work. In order to test the hypothesis of vacancy clusters, eventually associated with copper, SANS measurements with an applied magnetic field, as well as PA experiments are in progress.

V CONCLUSION

We have shown that in ferritic industrial or model alloys most of the irradiation induced-particles look more like clouds of solutes than real precipitates. These clouds can be more or less condensed. In low copper steels irradiated in service conditions, they are composed of Ni, Mn, Si, and sometimes Cu. The segregation of this latter may be facilitated by Si, Ni, Mn associations formed in early stages of the irradiation.

The presence of vacancies or microvoids isolated or related to these atom clusters cannot be ruled out. In order to conclude on the existence of these features, SANS measurements with an applied magnetic field as well as positron annihilation experiments are in progress.

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