DIRECTION DES ÉTUDES ET RECHERCHES
SERVICE RÉACTEURS NUCLÉAIRES ET ECHANGEURS
DÉPARTEMENT ETUDE DES MATÉRIAUX

EDF
Electricité de France

FR9702034

Juillet 1996

AUGER P.
PAREIGE P.
AKAMATSU M.
BLAVETTE D.

ETUDE A LA SONDE ATOMIQUE DE LA FORMATION D'AMAS D'ATOMES DANS DES ALLIAGES FE-CU ET DES ACIERS DE CUVES IRRADIES AUX NEUTRONS

APFIM INVESTIGATION OF CLUSTERING IN NEUTRON-IRRADIATED FE-CU ALLOYS AND PRESSURE VESSEL STEELS

Pages : 10

96NB00193

Diffusion : J.-M. Lecœuvre
EDF-DER
Service IPN. Département PROVAL
1, avenue du Général-de-Gaulle
92141 Clamart Cedex

ISSN 1161-0611

VOL 28 № 22

SYNTHÈSE :

Les aciers de cuve des REP se durcissent et se fragilisent sous l'effet de l'irradiation neutronique. Il est couramment admis que l'évolution des propriétés mécaniques résulte de la formation de défauts ponctuels, de boucles de dislocation, de microvides et de précipités riches en cuivre. Cependant, la nature exacte du dommage d'irradiation, dans ces aciers à très bas cuivre (< 0,1 % pds), n'a pas encore été clairement identifiée.

Un travail expérimental a été mené en sonde atomique et microscopie ionique, et plus particulièrement avec une nouvelle génération de sonde atomique développée récemment : la sonde atomique tomographique. Cette technique a permis d'améliorer la compréhension du comportement complexe de la précipitation du cuivre rencontré lorsque des alliages Fe-Cu à faible teneur en cuivre sont irradiés aux neutrons, et la caractérisation microstructurale de l'acier de cuve du réacteur de CHOOZ A à différentes fluences (programme de surveillance français).

Ces travaux mettent clairement en évidence la précipitation d'amas riches en cuivre dans les alliages Fe-Cu irradiés, alors que l'on observe que des "nuages" d'atomes de Si, Ni, Mn et Cu plus complexes se sont formés dans la solution solide ferritique de l'acier de cuve à bas cuivre.

AUGER P., PAREIGE P., BLAVETTE D. : Laboratoire de Microscopie Ionique, URA CNRS 808, Université de Rouen.

AKAMATSU M.

EXECUTIVE SUMMARY :

Pressure vessel steels used in PWRs are known to be prone to hardening and embrittlement under neutron irradiation. The changes in mechanical properties are commonly supposed to result from the formation of point defects, dislocation loops, voids and copper-rich precipitates. However, the real nature of the irradiation induced damage, in these particularly low copper steels (> 0,1 wt%), has not been clearly identified yet.

A new experimental work has been carried out thanks to atom probe and field ion microscopy (APFIM) facilities and, more particularly with a new generation of atom probe recently developed, namely the tomographic atom probe (TAP), in order to improve :

- the understanding of the complex behavior of copper precipitation which occurs when low-alloyed Fe-Cu model alloys are irradiated with neutrons ;
- the microstructural characterization of the pressure vessel steel of the CHOOZ A reactor under various fluences (French Surveillance Programme).

The investigations clearly reveal the precipitation of copper-rich clusters in irradiated Fe-Cu alloys while more complicated Si, Ni, Mn and Cu-solute "clouds" were observed to develop in the low-copper ferritic solid solution of the pressure vessel steel.

NEXT PAGE(S) left BLANK

APFIM investigation of clustering in neutron-irradiated Fe–Cu alloys and pressure vessel steels

P. Auger [a], P. Pareige [a], M. Akamatsu [b], D. Blavette [a]

[a] *Laboratoire de Microscopie Ionique, URA CNRS 808, Université de Rouen, 76821 Mont Saint Aignan Cedex, France*
[b] *EDF, Centre de Recherche des Renardières, Ecuelles, 77 250 Moret / Loing, France*

1. Introduction

This paper presents some new experimental results in the investigation of the nanoscale clustering which occurs during neutron irradiation of a French pressure vessel steel and two Fe–Cu model alloys. Previous results obtained on these materials by means of transmission electron microscopy (TEM), small angle neutron scattering (SANS) as well as conventional APFIM were already reported [1,2].

Detailed studies have been performed on neutron-irradiated Fe–Cu model alloys and pressure vessel steels over the last 20 years [3–9]. Generally, these materials have higher Cu contents than the French steel under study. Some controversy subsists in literature about the Cu concentration in particles which are formed under irradiation process. This controversy comes from the fact that for small particles, only atom probe techniques can provide quantitative composition data. However, for very small sizes (< 3 nm), mixed analyses of clusters may lead to biased Cu-level measurements [10].

The tomographic atom probe (TAP) recently developed at the Université de Rouen is an attractive tool for the investigation of precipitation. This instrument allows the three-dimensional (3D) reconstruction of a small volume of the material to be obtained on a subnanometric scale. The spatial distribution of each chemical species may be directly observed with a spatial resolution better than 0.5 nm. The typical volume which is analyzed is about $10 \times 10 \times 100$ nm^3 (i.e. a hundred times larger than the volume explored with a conventional atom probe [11]). In contrast to conventional atom probe (AP), this new generation of instrument provides 3D compositional maps of the material in real space and can give direct and unbiased measurements of local concentrations.

Our previous studies [1,2] showed that neutron irradiation of Fe–Cu alloys (until maximum hardness is reached) leads to the formation of a high density of copper clusters which could contain a significant amount of iron. Conversely, for thermal aged samples (peak, hardness at 500°C), *quasi-pure copper precipitates* were observed with a lower number density.

The microstructure of the CHOOZ A low-copper pressure vessel steel reveals more complex features. Rather than copper enriched particles, local and diffuse Si, Ni, Mn and Cu-enriched 'clouds' within the ferrite solid solution were detected.

In this work, the TAP was used to study these irradiation induced effects in more details. A new approach of nanostructural features in the three dimensions of real space is undertaken. A particular attention has been paid to the study of a neutron-irradiated Fe–Cu alloy, the low Cu-content of which (0.1 wt%) is very close to that of the CHOOZ A pressure vessel steel. For comparison, TAP examinations of a thermally aged Fe–0.7 wt% Cu and of a neutron-irradiated Fe–1.4 wt% Cu alloys have been undertaken. Also, a study of the microstructural evolution with fluence in irradiated steels has been performed with APFIM techniques.

2. Studied materials

2.1. Surveillance programme steel

The chosen steel (CHOOZ A PW(R)eactor) irradiated in the framework of the French Surveillance Programme has a chemical composition and a structure very similar to those of the vessel core zone and was submitted to the same irradiation conditions. This steel is of 16 MND5 type with a ferrito–bainitic structure. Its chemical composition is given in Table 1. The samples under study were neutron irradiated ($\sim 260°C$, $E > 1$ MeV) up to a fluence of 16×10^{19} n cm^{-2} which corresponds to a dose close to 0.2 dpa. Though the concentrations of reputed embrittling residual elements (Cu, P) are rather low, the increase in the Charpy transition temperature reaches 145°C for a fluence close to 1×10^{20} n cm^{-2}. These materials are therefore subjected to a real embrittlement.

2.2. Binary Fe–Cu alloys

The experimental results for three Fe–Cu alloys are presented in this paper. These alloys were prepared with the following copper contents: 0.1, 0.7, 1.4 wt%. They were irradiated in the OSIRIS pool test reactor of CEA/Saclay. The fluence received in the center of the specimens was 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.

One of these alloys (0.7 wt%) was also thermally aged for 70 h at 500°C (close to the peak hardness) in order to compare the defects induced by irradiation with those formed via a classical volume diffusion controlled mechanism.

3. Results

3.1. Thermally aged Fe–0.7 wt% Cu alloy

Former work on this sample using field ion microscopy (FIM) and conventional atom probe techniques has already been published [2]. FIM revealed the existence of a low number density (0.3×10^{17} cm^{-3}) of spherical and elongated ellipsoidal precipitates whose spatial extensions are of a few nanometers (4 to 7). These precipitates were analyzed by atom probe via the so-called selected area analysis method [12]. They were unambiguously shown to be quasi-copper pure (95 to 100%), whereas the ferrite solid solution was Cu-depleted down to 0.14 at%.

Although the number density of these particles was rather low, some of them were encountered during the TAP analyses we undertook (Fig. 1). On the 3D reconstruction shown in Fig. 1, each dot represents a single copper atom. For the clarity of the image, iron atoms are not shown. One precipitate appears with a roughly spherical shape, its diameter is close to 5 nm. The blurred aspect of the particle contour may be due either to a true diffuse interface or more likely to the 3D/2D projection of the image. This last point is discussed later in more details.

Fig. 2 provides concentration profiles through this latter particle. Elemental concentrations are measured by moving through the particle a small box whose extension is $1 \times 1 \times 1$ nm^3. The copper content inside the precipitate is shown to be 95 ± 5 at%. This procedure introduces some spatial convolution effects in

Table 1
Chemical composition (wt%) of the CHOOZ A pressure vessel steel

C	S	P	Si	Cr	Mo	Mn	Ni	V	Al	Co	Cu
0.16	0.006	0.012	0.32	0.16	0.39	1.26	0.57	0.020	0.024	0.02	0.09

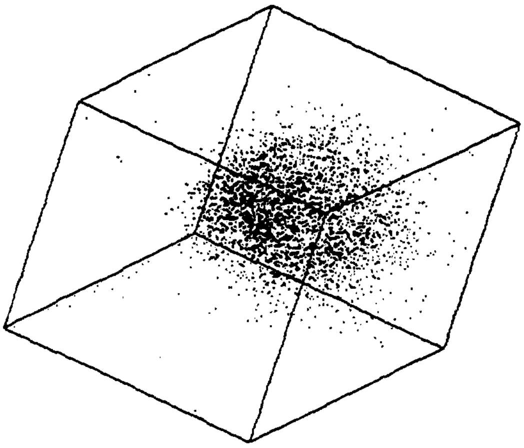

Fig. 1. 3D reconstruction showing the presence of a copper-rich particle in a thermally aged Fe–0.7 wt% Cu alloy (70 h at 500°C). Only a portion of the analyzed volume is represented here ($6\times6\times10$ nm^3). Each elemental dot represents a single copper atom.

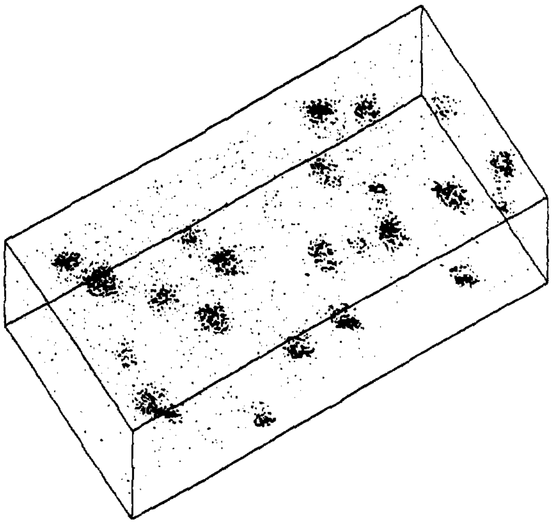

Fig. 3. Spatial distribution of copper atoms in a neutron irradiated Fe–1.4 wt% Cu alloy. The dimensions of the analyzed volume are $15\times15\times30$ nm^3. About 23 clusters can be distinguished.

concentration profiles, especially close to matrix–particle interfaces. The sampling box induces an extra enlargement of 1 nm at interfaces leading to an apparent diffuse transition (width ~ 1.5 nm). Taking into account these convolution effects, it can be assessed that the interface is abrupt (≤ 0.5 nm) in reality [13].

3.2. Fe–1.4 wt% Cu alloy irradiated with neutrons

Previous works on this sample [2] lead to the conclusion that a high number density ($\sim 7\times10^{17}$ cm^{-3}) of small (~ 5 nm) copper rich clusters formed during irradiation.

Fig. 3 clearly exhibits the presence of twenty clusters. Their number density was estimated to be on the order of 1×10^{18} cm^{-3}. The particle mean size (~ 2 nm) is slightly smaller than that previously reported from conventional AP results (~ 5 nm). The large uncertainties introduced in size measurements with conventional AP can explain this discrepancy (because of the small number of detected particles and size dispersion, in addition to spatial convolution effects). One of the major advantages of TAP is that one gets direct measurements of particle size and number density. More, as the observed volume is much larger, a better precision is obtained.

The clusters formed in these conditions are not copper pure. Fig. 4 provides the Cu concentration profile drawn through one of these clusters. The maximum Cu content is reached in the core of the cluster and rises nearly to 60 at%. The bar-chart represented in Fig. 5 reveals the wide Cu concentration distribution as measured in the core of particles. Again, the advantage of TAP is that a much larger amount of ions can be collected so that the precision in the concentration measurements is higher. This is especially important

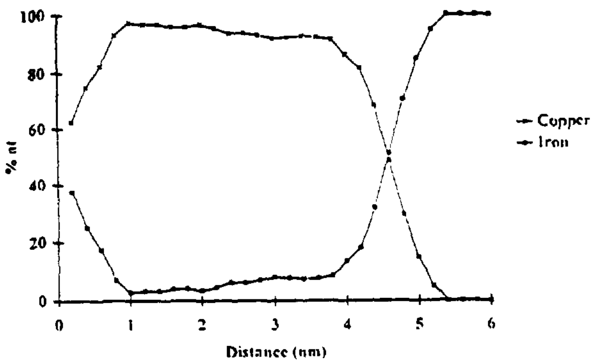

Fig. 2. Iron and copper concentration profiles through the copper particle displayed in Fig. 1.

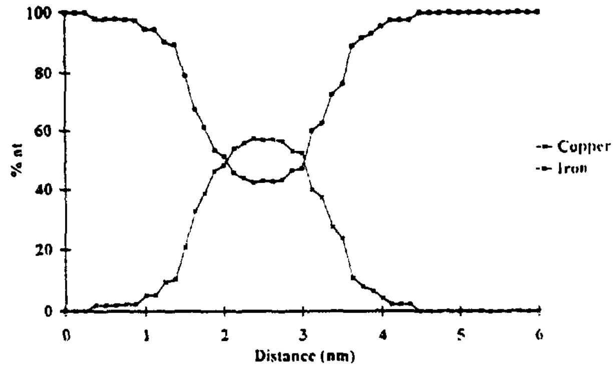

Fig. 4. Iron and copper concentration profiles through one of the clusters displayed in Fig. 3.

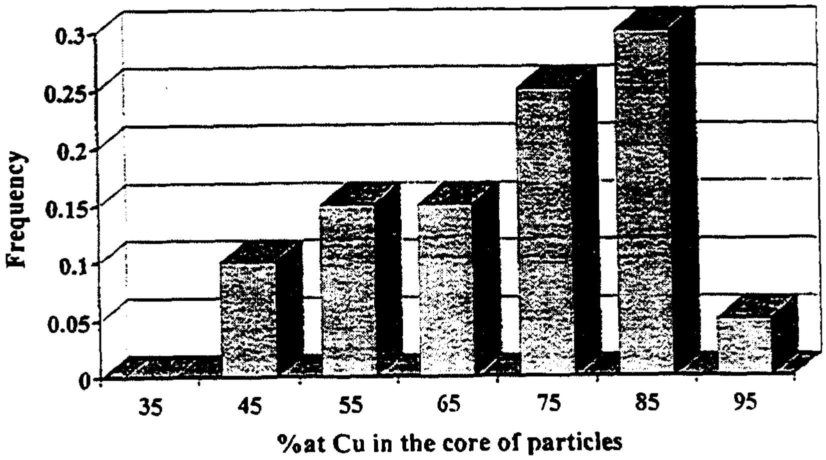

Fig. 5. Frequency distribution of copper levels measured in the core of clusters displayed in Fig. 3. The radius of the sampling sphere used in these measurements is 0.5 nm.

for such very small clusters. Also, direct measurements of core levels can be achieved for each individual particle.

It is noteworthy that the matrix/particle interface is not so abrupt as it was observed for the thermally aged specimen. This is true even if the convolution effects introduced by the sampling box are taken into account.

3.3. Fe–0.1 wt% Cu alloy irradiated with neutrons

This alloy was previously studied with conventional atom probe [2] after electron irradiation (290°C, 3×10^{-3} dpa). No microstructural evolution was detected after this treatment. This observation raises one question. Is this Cu content, in spite of what could be deduced from Salje et al. extrapolations [14], the solubility limit at this temperature? It must be kept in mind that this value may be overestimated if the thermodynamics equilibrium is not reached.

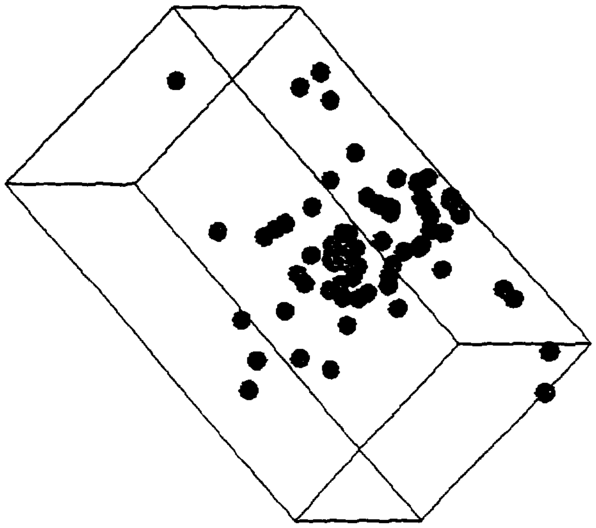

Fig. 6. Spatial distribution of copper atoms in a neutron irradiated Fe–0.1 wt% Cu alloy. The dimensions of the represented volume are $3 \times 2.5 \times 5$ nm^3. Each grey circle is a single copper atom, black reinforcements give an idea of the local density inside the cluster.

The feature which is obtained after neutron irradiation is somewhat different from that occurring in electron irradiated materials. As shown in Fig. 6, Cu clusters develop. Concentration measurements of the residual amount of copper in the ferrite matrix gives 0.03 ± 0.01 at% of Cu. A high number density ($\sim 1 \times 10^{18}$ cm^{-3}) of these clusters is observed. A similar Cu level in the ferrite was obtained in a Fe–0.2 wt% Cu alloy but with a higher cluster number density.

Neutron irradiation appears therefore to have a higher efficiency than electrons in the decomposition process. Nevertheless, since the solubility limit is unknown in theses conditions, it is premature to conclude on the nature of the solid solution decomposition process: enhanced or induced precipitation.

This discussion about the behavior of low-copper Fe–Cu alloys under neutron irradiation is not only of academic interest because their Cu contents are similar to those of pressure vessel steels.

Table 2
Evolution of the number density of Si, Ni, Mn and Cu clusters (CHOOZ A pressure vessel steel) measured by atom probe techniques as a function of the neutron fluence

Fluence (10^{19} n cm^{-2})	2.5	7	12	16
Number density (10^{17} cm^{-3})	3.3	5.7	8.9	11

3.4. CHOOZ A pressure vessel steel

Further atom probe analyses of samples submitted to various fluences were carried out. The clusters which were previously detected in a highly irradiated specimen (12×10^{19} n cm^{-2}) [1] exist even for lower irradiation conditions (3×10^{19} n cm^{-2}). On the one hand, surprisingly, the size and the microstructure of these clusters do not evolve when increasing the fluence, although this structure is obviously out of equilibrium; on the other hand, the cluster number density increases with fluence (Table 2). These conclusions are fully consistent with already reported SANS data [2,15]. This behavior which could be considered as a "stationary nucleation" appears to be a direct consequence of neutron-irradiation-induced defects and replacement cascades.

Fig. 7 depicts a TAP 3D reconstruction of a highly irradiated specimen. Although enriched zones are weakly concentrated in solutes (Si, Mn, Ni, Cu), precluding a good contrast to be obtained, at least two of these clusters can be distinguished in the analyzed volume ($11 \times 11 \times 50$ nm^3).

Concentration profiles associated with these clusters (Fig. 8), clearly show the low solute level in these clusters. The very low Cu concentration (≤ 3 at%) is not represented. Despite this low level, copper remains a very important element. Indeed, the relative enrichment ratio for copper (r_{Cu}) is the largest one ($r_{Si} \leq 12$, $r_{Ni} \leq 12$, $r_{Mn} \leq 6$, $r_{Cu} \leq 45$).

4. Conclusions

As far as Fe–Cu alloys are concerned, it has been shown that, for a thermally aged alloy (up to the peak hardness), precipitates were copper quasi-pure particles (95 ± 5 at%). In contrast, neutron irradiation (5.5×10^{19} n cm^{-2}, 290°C) has been proven to generate a large number density of copper-rich clusters exhibiting more diffuse interfaces and containing a significant amount of iron.

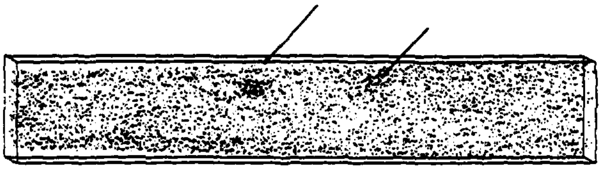

Fig. 7. Spatial distribution of silicon, nickel and manganese atoms in a highly neutron-irradiated (1.2×10^{20} n cm^{-2}) CHOOZ A sample. At least two local solute enrichments of the ferrite solid solution can be distinguished (arrows). The diffuse aspect of solute enriched atmospheres is in part due to the thickness of the displayed volume. In proportion as the amount of atoms represented get larger, the reconstructed volume gets obviously more opaque and small diffuse clusters may even disappear.

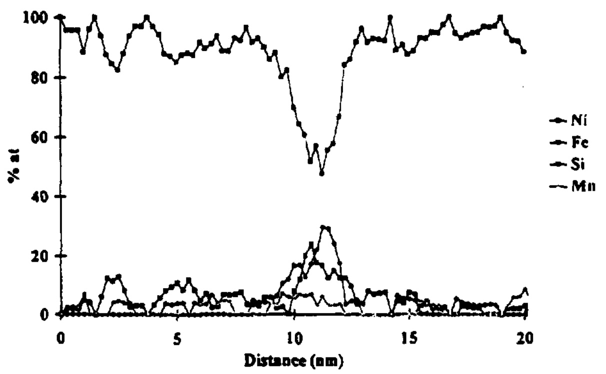

Fig. 8. Iron, silicon, nickel and manganese concentration profiles related to one of the clusters displayed in Fig. 7. Note the rather diffuse aspect of interfaces.

These new APFIM experiments, especially those carried out with TAP clearly indicate that, for low-copper steels (< 0.1 wt%), neutron irradiation does not give rise to pure copper precipitates. Instead, diffuse enriched 'clouds' containing Si, Ni, Mn, Cu ... were observed in the ferritic solid solution. The nature of these diffuse 'clouds' (composition, interfaces ...) is clearly different from that of quasi-pure copper precipitates (with well defined interfaces) observed in thermally aged model binary alloys. The size and structure of these solute enrichments do not seem to evolve with increasing fluences. In contrast, their number density increases with fluence.

It is thought that these 'clouds' could 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 complex materials. This is due to the rather low contrast quality of FIM images in such alloys. Positron annihilation experiments could give valuable complementary information on this subject.

As a conclusion, it appears that prediction laws used to foresee the material evolution, founded on the presence of pure copper precipitates in neutron irradiated pressure vessel steels should be revised, at least for low-Cu steels.

Acknowledgements

The authors would like to thank Dr. J.C. Van Duysen, Dr. A. Barbu, Dr. G. Martin and Dr. M. Guttmann for fruitful discussions. This research was financially supported by EDF, Département des Matériaux, under contract EDF/CNRS no. 508914.

References

[1] P. Pareige, J.C. Van Duysen and P. Auger, Appl. Surf. Sci. 67 (1993) 342.

[2] P. Auger, P. Pareige, M. Akamatsu, and J.C. Van Duysen, J. Nucl. Mater. 211 (1994) 194.

[3] M.K. Miller and S.S. Brenner, Res. Mech. 10 (1984) 161.

[4] G.R. Odette and G.E. Lucas, ASTM-STP 909 (1986) 206.

[5] P.A. Beaven, F. Frisius, R. Kampmann and R. Wagner, Proc. 2nd Int. Symp. on Environmental Degradation of Materials in Power Systems–Water Reactors, eds. J.T.A. Robert, J.R. Weeks and G. Theus (American Nuclear Society, La Grange Park, IL 1986) p. 385.

[6] M.K. Miller, M.G. Hetherington and M.G. Burke, Metall. Trans. A 20 (1989) 2651.

[7] J.T. Buswell, C.A. English, M.G. Hetherington, W.J. Phythian, G.D.W. Smith and G.M. Worall, ASTM-STP 1046 (1990) 127.

[8] W.J. Phythian, A.J.E. Foreman, C.A. English, J.T. Buswell, M.G. Hetherington, K. Roberts and S. Pizzini, ASTM-STP 1125 (1992) 131.

[9] M.K. Miller and M.G. Burke, J. Nucl. Mater. 195 (1992) 68.

[10] D. Blavette and S. Chambreland, J. Phys. 47 (1986) C7-503.

[11] D. Blavette, B. Deconihout, A. Bostel, J.M. Sarrau, M. Bouet, and A. Menand, Rev. Sci. Instr. 64 (1993) 2911.

[12] M.K. Miller and G.D.W. Smith eds., Atom Probe Microanalysis, MRS

[13] P. Pareige, Doctoral Thesis, Université de Rouen, October 1994.

[14] G. Salje and M. Feller-Kniepmeier, J. Appl. Phys. 48 (1977) 1833.

[15] M. Akamatsu, Doctoral Thesis, Université de Paris XI, Orsay, January 1994.