

Effect of irradiation on the precipitate stability in Zr alloys

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Zirconium alloys undergo structural changes under various types of irradiation. This is particularly the case for intermetallic precipitates such as $Zr_2(Fe,Ni)$, $Zr(Fe,Cr)_2$ in Zircalloys and $Zr(Fe,V)_2$ in Zr–Fe–V alloy: under irradiation those phases are subject to a crystalline-to-amorphous transformation. Experimental results obtained with electron and ion irradiations are presented. With both types of irradiations, the dose to amorphization increases with the irradiation temperature and diverges when a critical temperature is reached. The relative stabilities of the four types of precipitates studied appear to be reversed for low and high irradiation temperatures.

1. Introduction

Zirconium alloys such as the Zircalloys or Zr–Fe–V alloy, contain intermetallic precipitates which undergo a crystalline-to-amorphous transformation (amorphization) under irradiation. Several results have been reported on the amorphization of the precipitates of those alloys under neutron [1–4], ion [5,6] and electron [7] irradiations. Recent reviews [8,9] have presented the experimental and modeling work done on the amorphization of precipitates in the Zircalloys and discussed general amorphization mechanisms under irradiation.

The aim of the present paper is to complement previous high temperature electron and ion irradiations made in the laboratory with low-temperature irradiations, to allow a direct comparison of the different behaviors over a large temperature range. The results obtained on $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$ precipitates are, in addition, extended to $Zr(Fe,V)_2$ precipitates to compare their relative stability under irradiation.

2. Experimental procedure

2.1. Materials

The materials used in this work are recrystallized sheets of Zircaloy-4, Zircaloy-2 and Zr–Fe–V alloy

furnished by CEZUS, Ugine, France. Their chemical compositions are presented in table 1.

2.2. Irradiations

The behavior of the precipitates present in these three Zr alloys has been studied under electron and ion irradiations:

– Electron irradiations have been performed using the high voltage transmission electron microscope of the Centre d'Etudes Nucléaires de Grenoble (CENG). As the irradiation and observation were simultaneous, the irradiation-induced crystalline-to-amorphous transformation of the precipitates has been followed continuously from the beginning until complete amorphization. A temperature control system allowed the irradiation to be performed down to 7 K. The electron energy and the flux were respectively 800 keV and $4 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$. The temperatures reported in this work are not corrected for the heating due to the electron beam, which is estimated to be about 10 K in our conditions.

Table 1
Chemical composition (wt%) of the alloys used in this study

	Sn	Fe	Cr	Ni	V	O
Zircaloy-4	1.48	0.22	0.11	0	0	0.10
Zircaloy-2	1.52	0.17	0.10	0.07	0	0.12
Zr–Fe–V	0	0.25	0	0	0.25	0.10

– Ion irradiations have been performed with 127 MeV Ar ions between 273 and 373 K on the three Zr alloys to complement the first irradiations performed with Ar ions (127 MeV, 323 K) and Kr ions (97.5 MeV, 873 K) [5,6]. The three Zr alloys have also been irradiated in the Van de Graaff of the CENG with 1.5 MeV He ions between 77 and 123 K.

2.3. Evaluation of irradiation damage and characterization

In the case of electron irradiation, the displacement damage (expressed in dpa) has been calculated with the fluence received by the sample and with the displacement cross section given by Oen's tables. For an electron energy of 800 keV and a critical displacement energy of 25 eV, the displacement cross section is 14.5 barns. In the nominal irradiation conditions, the damage rate was about 5×10^{-4} dpa s⁻¹.

The damage profiles induced in the sample by the incident He, Ar and Kr ions have been calculated using the software TRIM86 [10]. The displacement damage is mainly localized in the nuclear stopping area, which is a few microns thick. In the case of Ar and Kr-ion irradiations, precipitates have been observed in this area and then the damage was taken as the average value over the nuclear stopping area. In the case of He-ion irradiations, precipitates have been observed directly on the surface of the irradiated specimens and

then, the value reported was the average over the electronic stopping area, before the collision peak. Thus for He, Ar and Kr ions, the flux and damage rates were respectively equal to 8×10^{16} , 2.3×10^{15} and 4.4×10^{15} (ions m⁻² s⁻¹) and 1.5×10^{-5} , 1.4×10^{-4} and 6×10^{-4} (dpa s⁻¹).

Observations were carried out in a JEOL 1200EX scanning transmission electron microscope and chemical composition data were obtained by energy dispersive X-ray spectroscopy.

To follow the structural evolution of the precipitates before and in the ion stopping area, cross sectional thin foils have been prepared in a plane containing the ion beam. This special sample preparation has been described in detail elsewhere [6].

3. Results

3.1. Reference materials

The three Zr alloys studied exhibit four types of precipitates:

– Zircaloy-4 contains mainly Zr(Fe, Cr)₂ intermetallic precipitates, with a C14 hexagonal and C15 cubic Laves phase structure, and both have an Fe/Cr ratio equal to 1.7.

– Zircaloy-2 contains mainly two kinds of precipitates: Zr(Fe, Cr)₂ similar to those observed in



Fig. 1. Reference Zr(Fe, V)₂ precipitate in the Zr–Fe–V alloy. The stacking faults contrast typical of Laves phase is clearly seen.

Zircaloy-4 but with an Fe/Cr ratio equal to 0.7 and $Zr_2(Fe, Ni)$ precipitates with a C16 tetragonal Zintl phase structure and an Fe/Ni ratio equal to 1.

- In the Zr-Fe-V alloy, the $Zr(Fe, V)_2$ precipitates have the same Laves phase structure as $Zr(Fe, Cr)_2$ precipitates, with a Fe/V ratio equal to 1 (fig. 1) [11].

3.2. Irradiation effects on precipitates

For both types of irradiations (electron and ion), at low temperatures (< 230 K), the same observations have been made on the different precipitates studied: $Zr(Fe, Cr)_2$ in Zircaloy-4, $Zr(Fe, Cr)_2$ and $Zr_2(Fe, Ni)$ in Zircaloy-2, $Zr(Fe, V)_2$ in Zr-Fe-V alloy. The amorphous transformation is homogeneously distributed in the precipitate and no alloying element depletion is detected (fig. 2).

The temperature dependence of the dose to amorphization has been determined for $Zr(Fe, V)_2$ precipitates using electron irradiation between 7 and 213 K and for $Zr(Fe, Cr)_2$ precipitates in Zircaloy-4 between 77 and 873 K, using He, Ar and Kr-ion irradiation data. In each case, the dose necessary to amorphize the precipitates increases exponentially with the irradiation temperature (fig. 3).

The relative stability of the four types of precipitates has been studied at three different temperatures using electron irradiations (7 K), He-ion irradiations (123 K) and Ar-ion irradiations (333 K).

- At 7 K, under electron irradiations, $Zr_2(Fe, Ni)$ precipitates are the first to become amorphous followed by $Zr(Fe, V)_2$, $Zr(Fe, Cr)_2$ in Zircaloy-4 and then $Zr(Fe, Cr)_2$ in Zircaloy-2.
- At 123 K, after He-ion irradiations, a similar behavior was observed. This is illustrated on fig. 4, where a $Zr_2(Fe, Ni)$ precipitate is amorphous close to a $Zr(Fe, Cr)_2$ precipitate that remains crystalline, as indicated by the presence of stacking faults.
- At 333 K, after Ar-ion irradiations, the relative stability of $Zr_2(Fe, Ni)$ and $Zr(Fe, Cr)_2$ precipitates was observed to be reversed: at 2.8 dpa, $Zr(Fe, Cr)_2$ precipitate in Zircaloy-2 and -4 is amorphous whereas $Zr_2(Fe, Ni)$ precipitate remains crystalline. At 3.8 dpa, they are all observed to be amorphous.

These results are summarized in fig. 5.

4. Discussion

4.1. Effects of the three different incident particles

The observations made on electron-irradiated $Zr(Fe, V)_2$ precipitates and on ion-irradiated $Zr(Fe, Cr)_2$ precipitates, over a large range of temperatures, are in good agreement with those previously reported [5-7].

As already proposed in ref. [8], the two different incident particles induce a similar temperature depen-

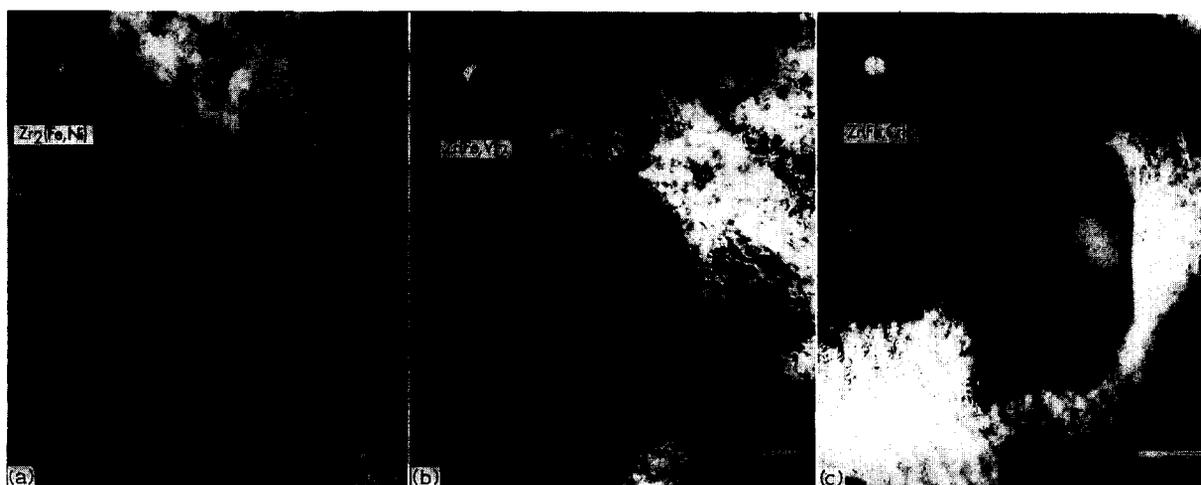


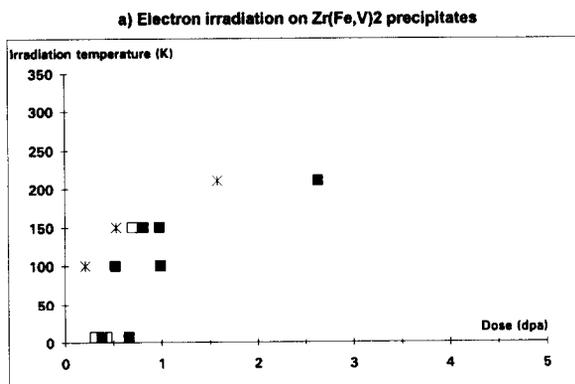
Fig. 2. Amorphous precipitates after He-ion irradiation at 77 K and 0.4 dpa; (a) in Zircaloy-2, (b) in Zr-Fe-V alloy, (c) in Zircaloy-4.

dence of the dose to amorphization: a progressive increase for low irradiation temperature followed by a drastic change when a critical temperature ($T_{crit.}$) is reached. This critical temperature depends on the irradiation damage (rate, nature, point-defect distribution) and on the nature of the intermetallic precipitate target.

According to the experimental conditions reported [7] and to ours on $Zr(Fe, Cr)_2$ precipitates, it is clear that $T_{crit.}(electrons) \ll T_{crit.}(ions)$. This large difference is in good agreement with the competition between thermal recovery and two kinds of irradiation damages. Electron irradiation produces Frenkel pairs and chemical disorder homogeneously distributed in the intermetallic precipitate, while ion irradiation produces point defects clustered in collision cascades. In the case of electron and ion irradiations, the critical tem-



Fig. 4. Precipitates at the surface of a Zircaloy-2 sample irradiated with He ions at 0.4 dpa and 77 K. The $Zr_2(Fe, Ni)$ precipitate is amorphous whereas the $Zr(Fe, Cr)_2$ precipitate is still crystalline. (The α -Zr matrix surface appears to be oxidized.)



x Crystalline □ Partially amorphous ■ Fully amorphous

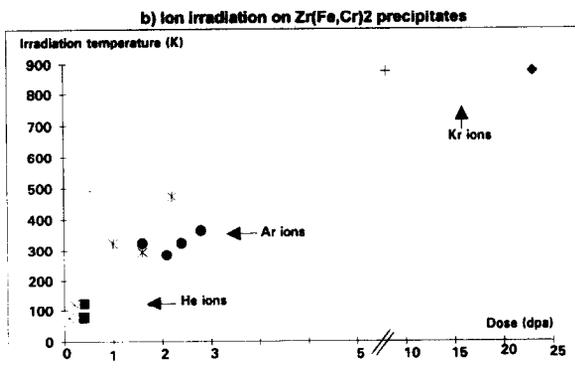


Fig. 3. Relation between dose to amorphization and irradiation temperature for (a) $Zr(Fe, V)_2$ precipitates in Zr-Fe-V alloy irradiated with electrons, (b) $Zr(Fe, Cr)_2$ precipitates in Zircaloy-4 irradiated with ions.

peratures are respectively 300 and 850 K although the calculated damage rates are similar: $\sim 5 \times 10^{-4}$ dpa s^{-1} .

The same kind of temperature dependance of the dose to amorphization obtained with electron and ion-irradiations has already been reported in the case of neutron irradiation on both $Zr_2(Fe, Ni)$ and $Zr(Fe, Cr)_2$ precipitates [2,8]. Moreover, when comparing ion irradiations with neutron irradiations, both of which induce collision cascades, damage rates and critical temperatures are in good accordance: the highest damage rate results in the highest critical temperature ($T_{crit.}(Kr) \approx 850$ K for about 6×10^{-4} dpa s^{-1} , while $T_{crit.}(neutrons) \approx 580$ K for about 10^{-7} dpa s^{-1}).

4.2. Relative stability of Zr intermetallic compounds

After electron and He ion irradiations at low temperatures (< 230 K), the four intermetallic precipitates

show the same relative susceptibility to amorphization. The $Zr_2(Fe, Ni)$ precipitate is the first to become amorphous followed by $Zr(Fe, V)_2$, $Zr(Fe, Cr)_2$

($Fe/Cr = 1.7$) and $Zr(Fe, Cr)_2$ ($Fe/Cr = 0.7$). Although the irradiation defects of electron and He-ion irradiations are different, it appears that at low tem-

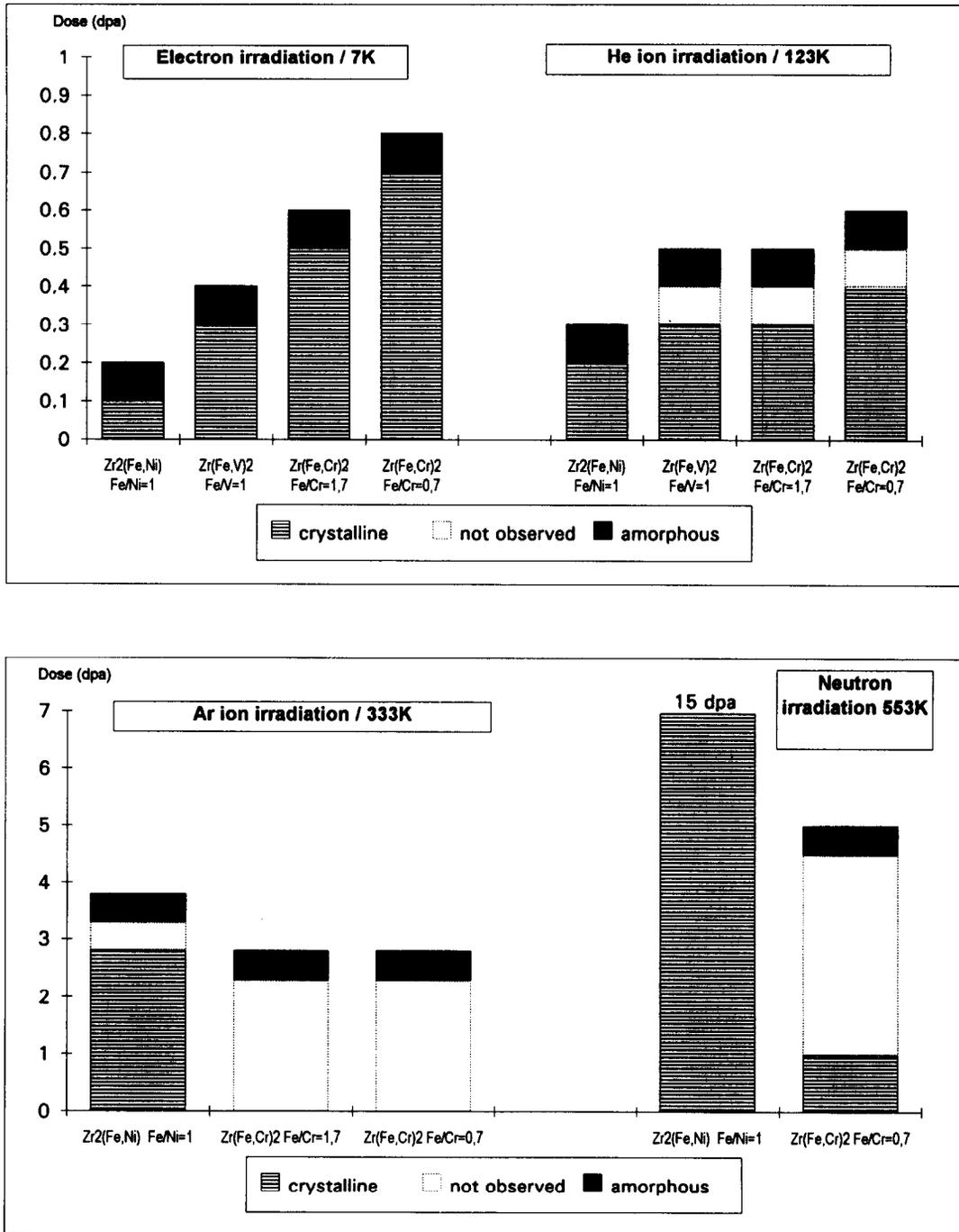


Fig. 5. Relative stability of the different precipitates; (a) after electron and ion irradiations at low temperature, (b) after ion irradiation at high temperature.

peratures the relative stability of these four precipitates is not affected.

After Ar ion irradiation at 333 K, i.e. at higher temperature, $Zr_2(Fe, Ni)$ precipitates are observed to be crystalline while $Zr(Fe, Cr)_2$ in Zircaloy-2 and -4 are completely amorphous. The relative behavior of the intermetallic phases under He-ion irradiation at 123 K and Ar-ion irradiation at 333 K appears to be reversed. Since the two ion irradiations induce similar damage, the temperature elevation seems sufficient to reverse the relative susceptibility to amorphization.

The observation made after ion irradiation at 333 K is consistent with what has been reported on the same intermetallic precipitates after 580–600 K neutron irradiations [2]: $Zr_2(Fe, Ni)$ precipitates remain crystalline up to 15 dpa while $Zr(Fe, Cr)_2$ precipitates undergo a crystalline-to-amorphous transformation for much lower doses. It is moreover observed that the center of the $Zr(Fe, Cr)_2$ precipitates in Zircaloy-4 ($Fe/Cr = 1.7$) becomes amorphous later than in Zircaloy-2 ($Fe/Cr = 0.7$), which is in good agreement with the postirradiation annealing results showing that the amorphous phase is more stable in the Cr-rich precipitates [2].

Various approaches have been proposed to discuss the relative stability of intermetallic compounds under irradiation or more generally of binary systems, and have been reviewed in refs. [8,9]. In the case of the intermetallic compounds studied, additional thermodynamical and kinetical considerations can also be proposed:

- The first involves the nature of atomic bondings in the irradiated intermetallic precipitates [2]. Two types of phases are involved: the Laves phases as $Zr(Fe, Cr)_2$ and the Zintl phases as $Zr_2(Fe, Ni)$. The relative strength of the atomic interactions in those compounds can be correlated to their melting temperatures (respectively 1410, 1570 and 1946/1950 K for Zr_2Ni , ZrV_2 and $ZrFe_2/ZrCr_2$), the stronger the bonding, the more resistant to amorphous transformation. In the case of $Zr(Fe, Cr)_2$, it was shown that a higher Cr concentration allows long range disorder [12], and thus gives a structure more resistant to irradiation damage. In addition, the Laves phases are known to accept larger composition ranges. In agreement with what has been observed at low temperature, a good correlation exists between the resistance to amorphous transformation under irradiation of an intermetallic phase, and its ability to accept stoichiometry variations [13].
- The second is based on the fact that, even at low temperature (e, He), the dose to amorphization is temperature-dependent. This stresses the existence of

some recovery during irradiation. Assuming a fast diffusion of Fe and Ni atoms in the precipitates, as in the Zr matrix [14], and a contribution of their mobilities to this recovery process, an increasing Cr concentration would slow the recovery and, thus, favour the destabilization of the microstructure (i.e. the stabilization of the amorphous phase). This consideration is in agreement with the relative stabilities observed after the high-temperature ion and neutron irradiations. For both irradiations, $Zr_2(Fe, Ni)$ intermetallic precipitates resist amorphization longer than $Zr(Fe, Cr)_2$ precipitates and an increase of Cr with respect to Fe favours the amorphous transformation of the $Zr(Fe, Cr)_2$ precipitates.

At low temperature, the relative stabilities of Zircaloy intermetallic precipitates are inverted. At the irradiation temperatures used (< 230 K), the diffusion rate of Cr, Fe and Ni atoms is probably too low to contribute to the recovery process by long-range migration. So, the presumed faster recovery of irradiation defects due to the larger Fe and Ni atomic mobilities compared with Cr is not valid.

Even if this analysis gives a general explanation of the behavior observed on the precipitates studied, the relative stability of the different types of precipitates, with respect to irradiation conditions, is still open for discussion.

5. Conclusion

The amorphization of four different precipitates [$Zr_2(Fe, Ni)$ and $Zr(Fe, Cr)_2$ in Zircaloy-2, $Zr(Fe, Cr)_2$ in Zircaloy-4 and $Zr(Fe, V)_2$ in Zr-Fe-V alloy] has been studied using electron and ion irradiations. The main results are that the dose to amorphization increases with increasing irradiation temperature and diverges when a critical temperature is reached. The relative stabilities of the precipitates appear to be reversed for low and high irradiation temperatures. The high-temperature results are in good agreement with those reported after neutron irradiations.

Acknowledgements

The authors would like to thank J. Pelissier, M. Dubus and M. Fruneau (CENG) for their help with electron, He-ion and Ar-ion irradiations.

References

- [1] R.W. Gilbert, M. Griffiths and G.J.C. Carpenter, *J. Nucl. Mater.* 135 (1985) 265.
- [2] M. Griffiths, R.W. Gilbert and G.J.C. Carpenter, *J. Nucl. Mater.* 150 (1987) 53.
- [3] M. Griffiths, *J. Nucl. Mater.* 159 (1988) 190.
- [4] W.J.S. Yang, R.P. Tucker, B. Cheng and R.B. Adamson, *J. Nucl. Mater.* 138 (1986) 185.
- [5] F. Lefebvre and C. Lemaignan, *J. Nucl. Mater.* 165 (1989) 122.
- [6] F. Lefebvre and C. Lemaignan, *J. Nucl. Mater.* 171 (1990) 223.
- [7] A.T. Motta and D.R. Olander, *Acta Metall. Mater.* 38 (1990) 2175–2185.
- [8] A.T. Motta, F. Lefebvre and C. Lemaignan, *Proc. 9th Int. Symp. on Zirconium in Nuclear Industry, ASTM-STP* 1132, eds. C.M. Eucken and A.M. Garde (ASTM, Philadelphia, 1991) pp. 718–739.
- [9] A.T. Motta and C. Lemaignan, *Mechanisms of Radiation-Induced Amorphization Ordering and Disordering in Alloys*, ed. A.R. Yavari (Elsevier, Amsterdam, 1992) pp. 255–275.
- [10] J.F. Ziegler, J.P. Biersack and U. Littmark, *The Stopping and Range of Ions in Matter*, vol. 1, ed. J.F. Ziegler (Pergamon, New York, 1985).
- [11] D. Charquet, J.P. Gros and J.F. Wadier, *Proc. Int. Topical Meeting on LWR Fuel Performance*, Avignon, France, April 21–24, 1991, pp. 143–153.
- [12] X. Meng Bungary and D.O. Northwood, *J. Less-Comm. Metals* 170 (1991) 27.
- [13] J.L. Brimhall, H.E. Kissinger and L.A. Charlot, *Radiat. Eff.* 77 (1983) 237.
- [14] G.M. Hood, *J. Nucl. Mater.* 159 (1988) 149.