

Arthur T. Motta,¹ Florence Lefebvre,¹ and Clément Lemaignan¹

Amorphization of Precipitates in Zircaloy under Neutron and Charged-Particle Irradiation

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ABSTRACT: The crystalline-amorphous transformation of the intermetallic precipitates $Zr(Cr,Fe)_2$ and $Zr_2(Ni,Fe)$ in Zircaloy under charged-particle and neutron irradiation is studied.

In the first section, the experimental results in the literature are reviewed for the three types of irradiation: neutron, electron, and ion. It is found that the dose to amorphization in all three types of irradiation exhibits roughly the same exponential dependence with temperature but that there are important differences. The critical temperatures, above which amorphization is not practically attainable, are different for each type of irradiation, indicating the presence of different damage accumulation and annealing mechanisms in each case. Further evidence of this are the different amorphization morphologies observed under neutron and electron irradiation, and the shift in the relative susceptibility to amorphization between the two types of precipitate under high (neutron and ion) and low (electron and ion) temperature irradiation.

In the next section, the theoretical models for amorphization are reviewed and applied to the problem in an effort to obtain a coherent picture of amorphization induced by all types of irradiation in the precipitate/zirconium system. Amorphization mechanisms are proposed for each type of irradiation, based on the experimental results.

A brief conclusion indicates that different mechanisms are operative for amorphization induced by each type of irradiation and points out future areas that in our view deserve further investigation.

KEY WORDS: intermetallic precipitates, neutron irradiation, charged-particle irradiation, Zircaloy

Zircaloy-2 and -4 are used widely in the nuclear industry as cladding and structural material for fuel rods because of good thermal, nuclear, and mechanical properties, as well as good resistance to corrosion [1]. The intermetallic precipitates $Zr_2(Ni,Fe)$ and $Zr(Cr,Fe)_2$ are present in as-fabricated Zircaloy-2. $Zr(Cr,Fe)_2$, with a generally lower Cr/Fe ratio, is present in Zircaloy-4. The morphology and distribution of these precipitates may be correlated to the corrosion resistance of Zircaloy. Recently, however, observations of amorphization and dissolution of those precipitates under irradiation [2,3] have caused concern that those good properties might be vitiated at the end of extended burnup, especially since a previous study has found that corrosion rates in Zircaloy increase with decreasing precipitate diameter below a critical value of $\approx 0.18 \mu m$ [4]. Amorphization under irradiation leads to precipitate dissolution, as reported by several researchers. The resulting higher content of alloying

¹Research Fellow, Research Engineer, and Head of Laboratory, respectively, CEA/DRN/SECC, Centre d'Etudes Nucleaires de Grenoble/SECC, 85x, 38041 Grenoble CEDEX, France.

elements in the matrix as well as the absence of precipitates could then influence corrosion rates. Also, the advancement of the oxidation front, and particularly the incorporation of precipitates in the oxide layer, might be different for amorphous precipitates than for crystalline precipitates.

Studies have been done of amorphization of these precipitates under electron [5] and ion irradiation [6] in order to better understand the phenomenon under controlled conditions. The experiments with charged particles have the advantage of delivering a much higher dose rate, so that a number of displacements per atom (dpa) equivalent to three reactor years can be obtained in hours (ions) or minutes (electrons). Also the temperature and dose rate are controllable parameters that can be varied to study their impact on the phenomenon.

Theoretical understanding of irradiation-induced amorphization in the literature has centered on two models for energy storage in the lattice: point defect increase [7–10] and chemical disordering [11–13]. The precipitate/zirconium system is a useful system to investigate amorphization, since extensive data are available on the amorphous transformation of the intermetallic precipitates induced by the three types of irradiation: neutron, ion, and electron.

It is the purpose of this paper to review the experimental results, present some new results, discuss prospective mechanisms for the transformation in terms of those experimental results, and point out some areas that need additional research.

Review of Experimental Data

General Remarks

The amorphous transformation has been verified in the case of neutron and ion irradiation by post-irradiation examination in the transmission electron microscope (TEM) [2,3,6]. For electron irradiation the transformation was verified *in situ* during irradiation in the high voltage electron microscope (HVEM) [5].

No attempt was made to standardize the doses reported in previous works for different types of irradiation, except in the cases of ion irradiation to make the doses internally coherent, since in that case several references were used [6,14–18]. The reason for not imposing a standard is that displacement energies for the intermetallics are not well known and, depending on the value selected, the calculated values of the dose in dpa can vary by as much as a factor of three. Less emphasis should therefore be paid to the actual values of the dose to amorphization given here than to the dependence of the dose to amorphization on temperature. In the case of neutron irradiation, the data are reported as given in Refs 2, 3, 19, and 20. For electron irradiation, Oen's tables [21] were used to calculate the dose from the measured electron flux. For ion irradiation, the TRIM code [22] was used to calculate the displacement profile and the examination depth was measured or estimated, resulting in a more accurate dose reported for each specific precipitate examined than in Ref 14.

For neutron irradiations, in-pile temperature measurements are assumed to be accurate within ± 10 K. Temperature measurements in the HVEM are corrected in accordance with the calculated beam heating [23]. Corrections are on the order of a few tens of degrees Kelvin. This was not done for the case of ion irradiation, because the corrections are much smaller.

In the next sections the experimental results for the three different types of irradiation will be discussed. In all three, the transformation is dose-dependent, indicating that a certain amount of damage must be made to the crystalline lattice before it will amorphize. A critical temperature (T_c) can also be defined in each case as the temperature above which amor-

phization cannot be achieved under practical irradiation conditions. This definition links T_c to the type of irradiation, since conditions are different for each type of irradiation.

Neutron Irradiation

The experimental methods and results reviewed here have been described more extensively elsewhere [2,3,19,20]. Those results from several authors are summarized in Fig. 1 for both types of precipitates.

The results for $Zr(Cr,Fe)_2$ precipitates show a temperature dependence of the dose to amorphization that is similar to the exponential dependence found under electron irradiation. There is a large increase of the dose to amorphization around 580 K, which can be taken as the critical temperature for amorphization (T_c) of the $Zr(Cr,Fe)_2$ precipitates under neutron irradiation. This temperature agrees with Naguib and Kelly's criterion of $T_c \approx 0.3 T_m$ [24], suggesting that the mechanism of neutron-irradiation-induced amorphization is related to the occurrence of cascades.

The examination of specimens irradiated at different doses showed that the C-A transformation starts heterogeneously at the precipitate-matrix interface (Figs. 2 and 3). An amorphous layer is formed first at the interface and moves inwards at a velocity of 10 nm per 10^{25} n/m² [2] until, at a fluence of $\approx 10^{26}$ n/m², a 0.2 to 0.3 μ m diameter precipitate is completely amorphous.

Concurrently, in the amorphous layer a depletion of Fe of 30% relative to the initial value has been observed [2]. The dissolved iron forms a depletion ring [6,25] around the precipitate. The ring diameter increases with time until it dissipates into the matrix. After amorphization, the Cr-type precipitates are observed to dissolve preferentially along the $10\bar{1}0$ direction of the Zr matrix [19].

For $Zr_2(Ni,Fe)$ precipitates there are comparatively less data available than there are for $Zr(Cr,Fe)_2$ precipitates. As shown in Fig. 1, they have been observed to be completely amorphous after 1 dpa irradiation at 330 K and completely crystalline after 18 dpa irradiation at 580 K [2]. No partially amorphous precipitates have been reported. If the criterion of $T_c \approx 0.3 T_m$ mentioned above is valid for the Ni-type precipitates as well, then they should be seen partially amorphized at doses between 1 and 10 dpa, delivered at about 420 K, a temperature range not commonly available in nuclear reactors.

Figure 4 [26] shows a cluster composed of an amorphous $Zr(Cr,Fe)_2$ precipitate and two crystalline $Zr_2(Ni,Fe)$ precipitates. This means that $Zr(Cr,Fe)_2$ precipitates are more susceptible to neutron irradiation-induced amorphization than are $Zr_2(Ni,Fe)$ precipitates.

Electron Irradiation

Both types of precipitates amorphize under electron irradiation. The experimental results for $Zr_2(Ni,Fe)$ precipitates are shown in Fig. 5 and those for $Zr(Cr,Fe)_2$ precipitates in Fig. 6. For an electron energy of 1.5 MeV, and a displacement energy of 25 eV, Oen's tables [21] give $\sigma_d = 25$ barns. A typical electron flux was 10^{19} e cm⁻² s⁻¹. The dose to amorphization increases exponentially with irradiation temperature [5,27], as previously observed during electron irradiation-induced amorphization of other intermetallic compounds [8,12]. For $Zr_2(Ni,Fe)$ precipitates, the dose to amorphization is lower for higher dose rates [5], an effect subsequently confirmed in Cu-Ti by Xu et al. [28]. For $Zr(Cr,Fe)_2$ precipitates, no such effect is apparent (Fig. 6). The fact that the $Zr(Cr,Fe)_2$ precipitates do not show the same dose rate effect is not surprising in view of the fact that the composition of the ternary compound varied widely, especially between Zircaloy-2 and Zircaloy-4 samples. Griffiths [2] reported that under neutron irradiation, precipitates with low Cr/Fe ratio were

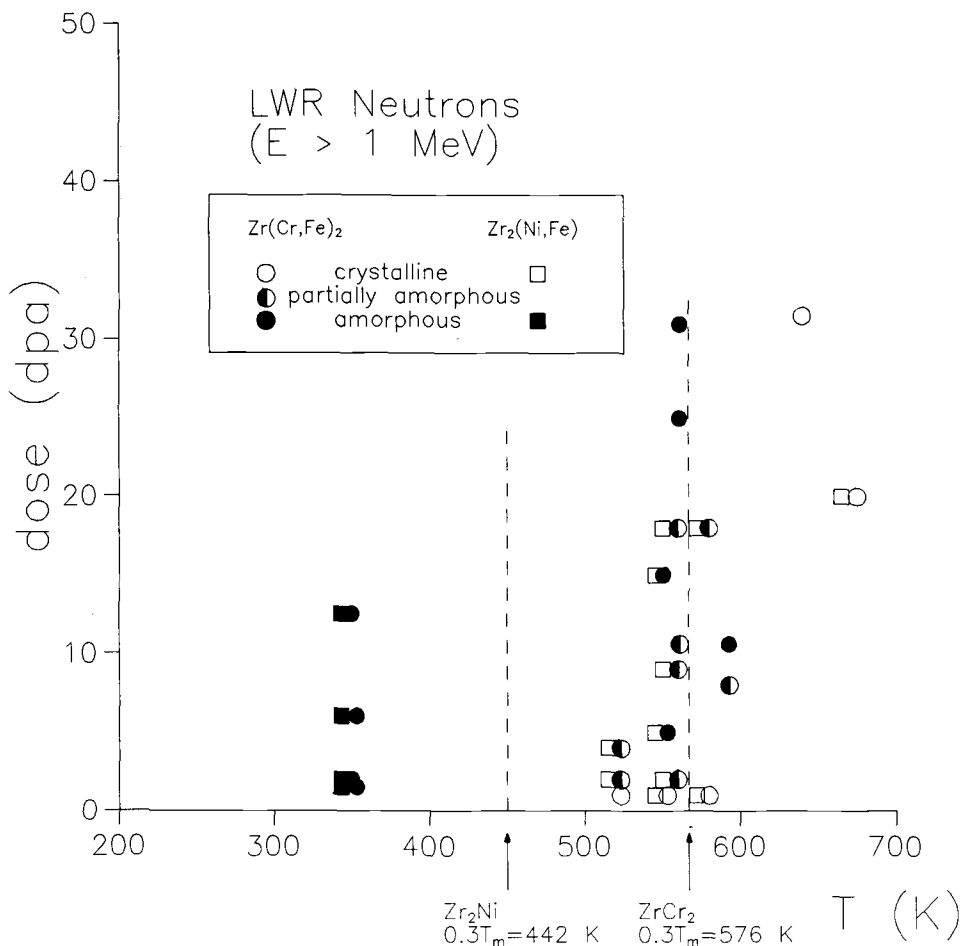


FIG. 1—Dose to amorphization under neutron irradiation versus temperature for $Zr_2(Ni,Fe)$ and $Zr(Cr,Fe)_2$ precipitates in Zircaloy [2,3,19,20]. The critical temperatures are indicated as well as the amorphization state.

harder to amorphize than those with high Cr/Fe ratio. This could be due either to a kinetical effect such as, for example, a higher mobility of Fe atoms than Cr atoms, or to a higher susceptibility to amorphization of the precipitates with high Cr, as indicated by their higher crystallization temperature on post-irradiation annealing [2]. In either cases, the dose rate effect could be masked in the $Zr(Cr,Fe)_2$ precipitates by chemical composition variations.

In neither of the two types of precipitates were any variations in chemical composition and/or precipitate dissolution observed either during or after amorphization. No influence of precipitate size on the amorphization process was detected.

The transformation occurred homogeneously throughout the precipitates; no heterogeneous nucleation points were evident. In particular, no preferential amorphization occurred at the precipitate-matrix interface and, for $Zr(Cr,Fe)_2$ precipitates, no preferential amorphization was detected at either twin boundaries or stacking faults. No dislocations were present inside the precipitates, so the observations of Fujita and co-workers of preferential amorphization at dislocations on Ni-Ti [29] could not be duplicated.

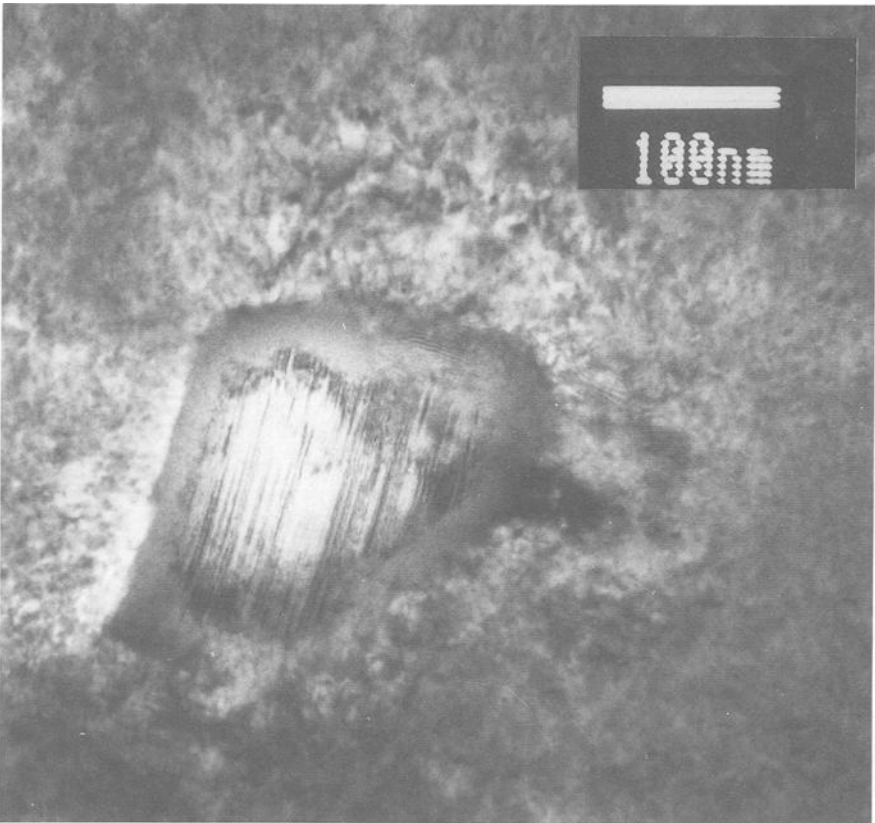


FIG. 2— $Zr(Cr,Fe)_2$ precipitate neutron irradiated at BR-3 at a temperature of 510 K to a fluence of 8 dpa, showing formation of amorphous layer.

The transformation kinetics were studied by measuring the ratio Φ , defined as:

$$\Phi = \frac{(I_D/I_T) \text{ at } t = t_{\text{irr}}}{(I_D/I_T) \text{ at } t = 0} \quad (1)$$

where I_T is the transmitted beam intensity and I_D is the intensity at one of the precipitate Bragg-diffracted spots. Φ goes from 1 to 0 as the material goes from crystalline to amorphous. For the cases studied in Ref 5, Φ remained close to 1 throughout the irradiation, dropping precipitously to zero at the end of the irradiation time. This suggests that the kinetics of the transformation are fast compared to the irradiation time. The rate-limiting-step for amorphization is, then, the development of the necessary conditions for the transformation. The transformation takes place relatively quickly once conditions are ripe.

It is worth noting that the relative phase stabilities of $Zr(Cr,Fe)_2$ and $Zr_2(Ni,Fe)$ precipitates under electron irradiation are reversed with respect to their relative stabilities under neutron irradiation. Figure 7 is a video series from an amorphization experiment done at 800 keV in the HVEM at the CEN-Grenoble. At the start of irradiation, both precipitates in the cluster shown in Fig. 7a are crystalline. The dark fields (b, d, e, f) are taken with the aperture around crystalline spots from both precipitates, while dark field c is taken

Fluence

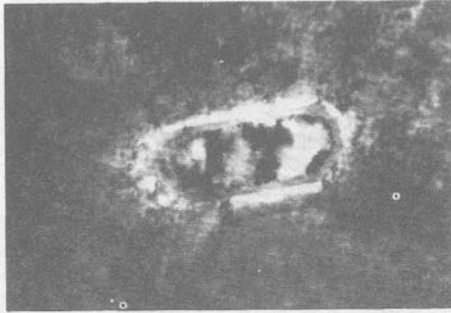
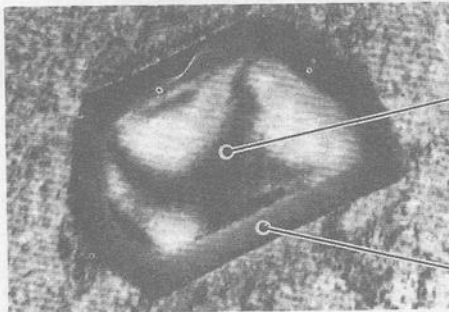
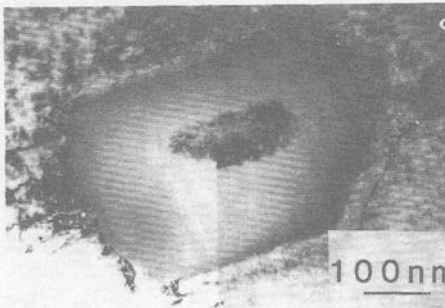
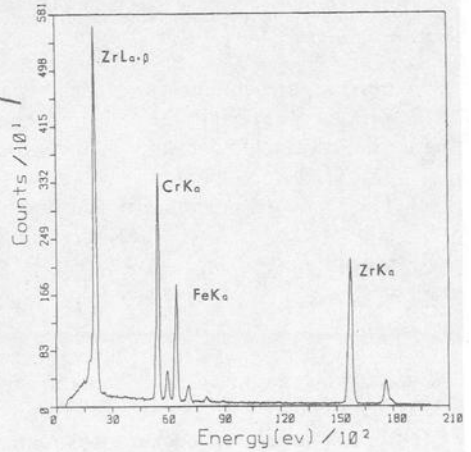
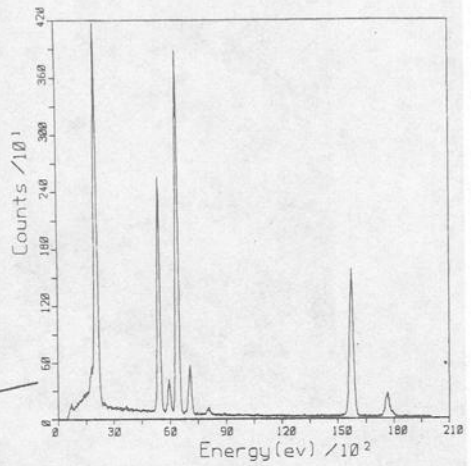
 $1.0 \times 10^{25} \text{ n/m}^2$  $3.5 \times 10^{25} \text{ n/m}^2$  $8.5 \times 10^{25} \text{ n/m}^2$ 

FIG. 3—Evolution of the amorphous layer with fluence for a $\text{Zr}(\text{Cr},\text{Fe})_2$ precipitate neutron irradiated at 560 K to 18 dpa [2]. The Fe depletion in the amorphous layer is also indicated.

utilizing the amorphous ring. There is a partial loss of bend contour contrast at 5 min (0.17 dpa), suggesting the $\text{Zr}_2(\text{Ni},\text{Fe})$ precipitate is partially amorphous (Figs. 7b and 7c). At 10 min (0.35 dpa) the $\text{Zr}_2(\text{Ni},\text{Fe})$ precipitate is completely amorphous as verified by examination of the diffraction pattern (not shown) and as evidenced by the loss of bend contour contrast (Fig. 7d). Irradiation proceeded to a total dose of 0.7 dpa ($t = 20$ min). The $\text{Zr}(\text{Cr},\text{Fe})_2$ precipitate still did not amorphize completely, although it is progressively less bright in Figs. 7e and 7f.

Here are the differences in the responses of the two types of precipitates to electron irradiation [27]:

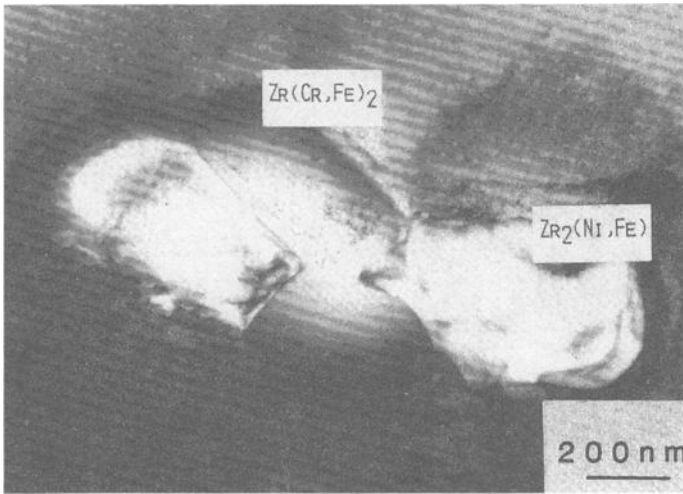


FIG. 4—Cluster composed of a $Zr(Cr,Fe)_2$ precipitate surrounded by two $Zr_2(Ni,Fe)$ precipitates irradiated at 553 K to a fluence of 5 dpa [26]. The $Zr(Cr,Fe)_2$ precipitate is amorphous, while the $Zr_2(Ni,Fe)$ precipitates are crystalline, illustrating the greater susceptibility of $Zr(Cr,Fe)_2$ precipitates to amorphization under neutron irradiation.

- (a) For the same temperature, $Zr_2(Ni,Fe)$ precipitates amorphize at a lower dose than $Zr(Cr,Fe)_2$ precipitates.
- (b) The critical temperature T_c for $Zr(Cr,Fe)_2$ precipitates is slightly smaller than for $Zr_2(Ni,Fe)$ precipitates.
- (c) The standard deviation of the measured dose to amorphization as a function of temperature for $Zr(Cr,Fe)_2$ precipitates was larger than that measured for $Zr_2(Ni,Fe)$ precipitates.

Ion Irradiation

The known examples of ion irradiation-induced crystalline to amorphous transformation of $Zr(Cr,Fe)_2$ and $Zr_2(Ni,Fe)$ precipitates are shown in Fig. 8 [6,14–18]. The data for $Zr_2(Ni,Fe)$ is not shown because it is scarcer and follows the $Zr(Cr,Fe)_2$ data. Compared to neutron and electron irradiation, there are much fewer data for ion irradiation-induced amorphization. Consequently, all the data from different types of ions were put together in a single graph, although different displacement rates are known to influence the dose to amorphization [30]. Ion irradiation also has the peculiarity of having a depth-dependent displacement rate. Figure 9 shows an example of a displacement calculation using TRIM for 127 MeV Ar ions in Zr, with a displacement energy of 25 eV. It is readily observed that errors on the order of a couple of microns in the localization of the damaged zone can have a large impact on the calculated dose. This error can be reduced if transverse thin foil specimens are utilized in TEM examination. A typical Ar ion flux in those experiments was 2×10^{11} ion $cm^{-2} s^{-1}$.

Again both types of precipitate amorphize if the temperature is low enough. The dose to amorphization rises with temperature for both types of precipitates, analogous to electron and neutron irradiation. The limited data available are not inconsistent with the same type of temperature dependence observed under electron irradiation. The observation of partial amorphization at 350 K under Ar ion irradiation suggests that T_c is on the order of 400 K.

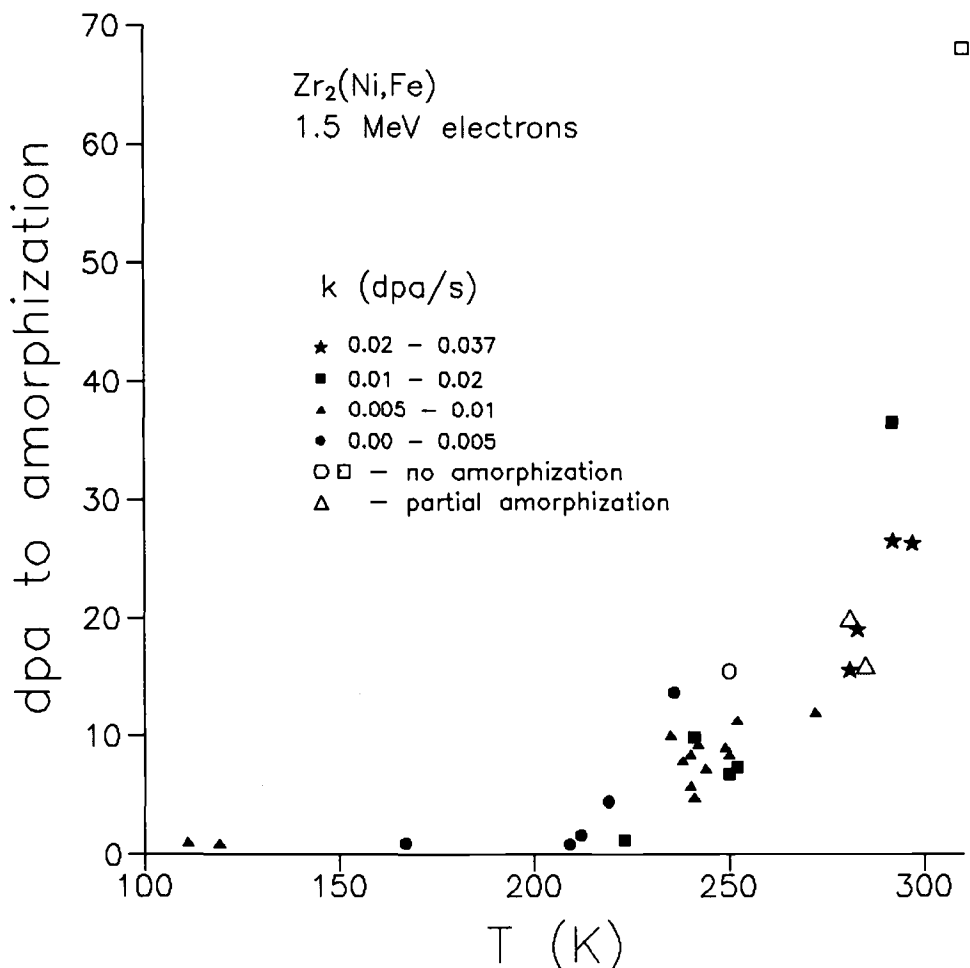


FIG. 5—Dose to amorphization under electron irradiation versus temperature for $Zr_2(Ni,Fe)$ precipitates in Zircaloy [27]. The different dose rates are indicated.

However, the observed amorphization of precipitates under Kr irradiation to a dose of 25 dpa at 873 K is not consistent with that assignment, unless the critical temperature for amorphization under Kr ions is different than that for amorphization under Ar ions as observed in Ref 30. It should be mentioned that there is a large error bar associated with the experiment in which the temperature of 873 K was obtained, since the temperature measurement in that case was done by visual estimation of the sample color during irradiation. Also, as mentioned above, it is worth noting that ion induced-amorphization occurs without the preferential depletion of Fe observed under neutron irradiation [15]. That is, the Cr/Fe ratio does not vary as the material amorphizes (Fig. 10).

Even though the doses to amorphization are comparable for the two types of precipitates (Fig. 8), there is some evidence of different irradiation responses. Crystalline $Zr_2(Ni,Fe)$ and amorphous $Zr(Cr,Fe)_2$ precipitates have been found next to each other after Ar ion irradiation at 353 K to 3 dpa [17]. This means that even though they were at the same depth within the irradiated material, and therefore received the same dose, the $Zr(Cr,Fe)_2$ pre-

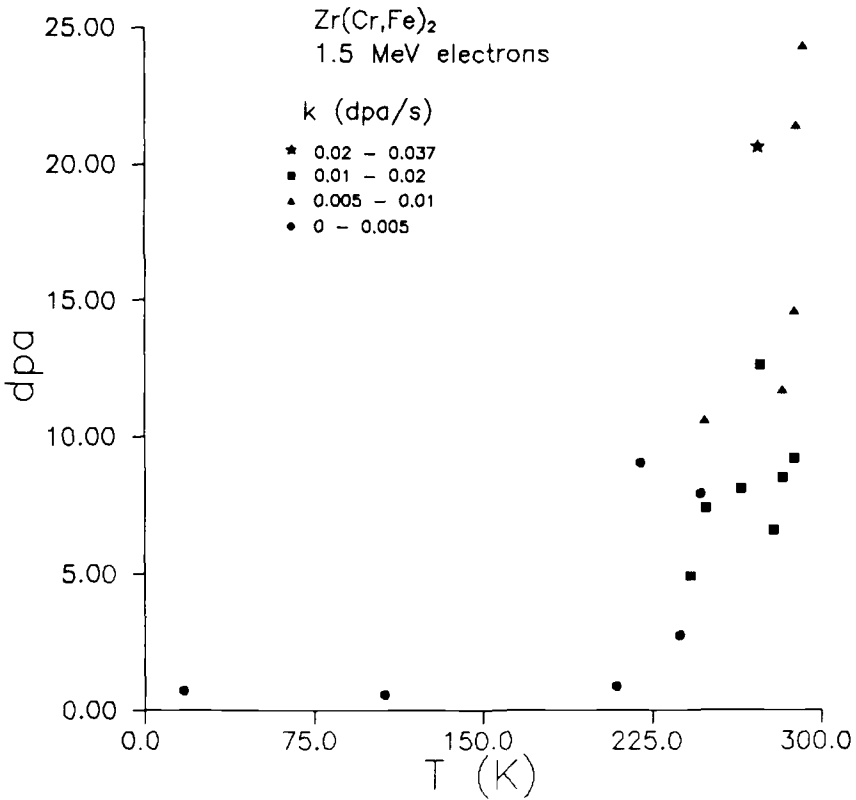


FIG. 6—Dose to amorphization under electron irradiation versus temperature for $Zr(Cr,Fe)_2$ precipitates in Zircaloy. Dose rate symbols are the same as for Fig. 5.

precipitate was amorphous while the $Zr_2(Ni,Fe)$ precipitate was not. At very low temperatures there is some indication that the situation may be reversed, as amorphous $Zr_2(Ni,Fe)$ precipitates have been found after 0.2 dpa He ion irradiation at 121 K, when $Zr(Cr,Fe)_2$ precipitates were still crystalline [17].

No conclusive observations have been reported of precipitates made partially amorphous by ion irradiation. Precipitates were either completely amorphous or completely crystalline, which gives no information on the amorphization mechanism under ion irradiation. Research is ongoing to obtain information on the mechanism.

Summary

All of these observations are summarized schematically in Fig. 11. The results for electron irradiation of $Zr(Cr,Fe)_2$ precipitates are not shown; they lie between the high and low dose rates for $Zr_2(Ni,Fe)$ precipitates. The hypothetical critical temperature for $Zr_2(Ni,Fe)$ precipitates under neutron irradiation based on Naguib and Kelly's criterion is shown as a dotted line.

The important points to note are that, for a given type of precipitate, there are different critical temperatures for the three types of irradiation. Electron irradiation has the lowest critical temperature for amorphization, showing also a dose rate effect, ions are next and

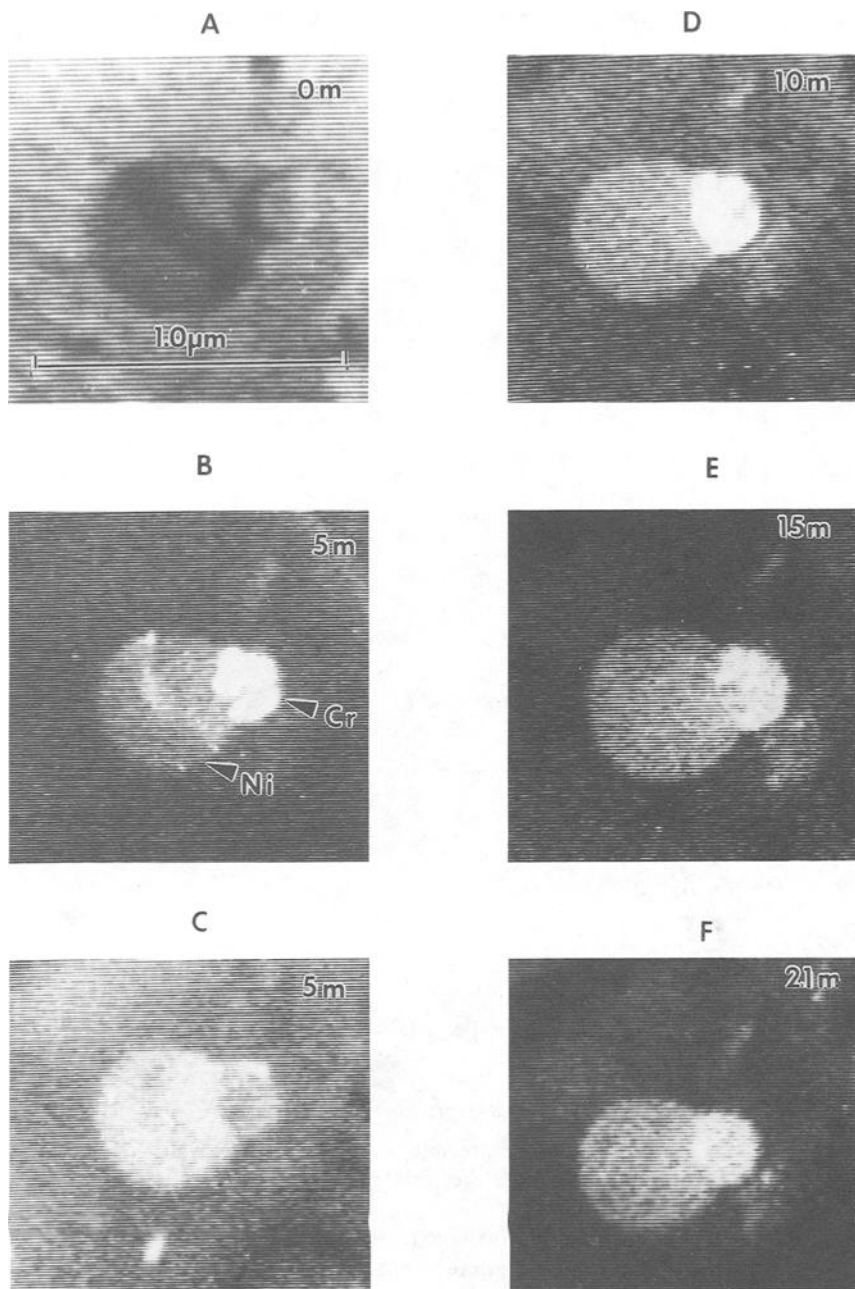


FIG. 7—Photographic series of amorphization experiment at HVEM. The temperature was 7 K, the dose rate 6×10^{-4} (dpa/s), the voltage 800 kV. In (a), a cluster composed of one $\text{Zr}(\text{Cr},\text{Fe})_2$ precipitate and one $\text{Zr}_2(\text{Ni},\text{Fe})$ precipitate is shown before the start of irradiation. A dark field using the crystalline spots from both precipitates is shown in (b), taken at $t = 5$ min. The bend contour in the $\text{Zr}_2(\text{Ni},\text{Fe})$ precipitate is less visible. Dark field (c) is taken using a portion of the amorphous ring, showing that amorphization has started on the $\text{Zr}_2(\text{Ni},\text{Fe})$ precipitate. In (d), (e) and (f), dark fields taken under the same conditions as (b), we can notice the amorphous $\text{Zr}_2(\text{Ni},\text{Fe})$ precipitate in (d), while the $\text{Zr}(\text{Cr},\text{Fe})_2$ precipitate is crystalline until (f). This shows that $\text{Zr}_2(\text{Ni},\text{Fe})$ precipitates are more susceptible to amorphization under electron irradiation.

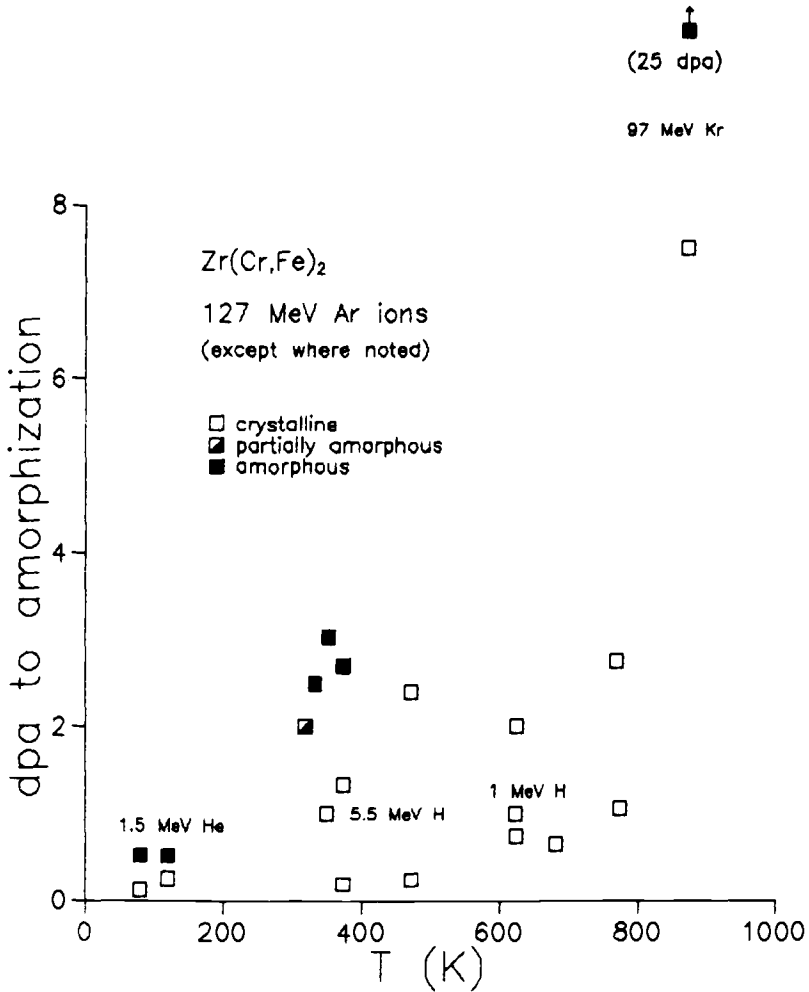


FIG. 8—Dose to amorphization under ion irradiation versus temperature for $Zr(Cr,Fe)_2$ precipitates in Zircaloy [6,14–18]. The majority of the data comes from 127 MeV Ar ion irradiation.

neutrons are highest. Also, the type of precipitate influences the critical temperature for neutron irradiation, the critical temperature for $Zr_2(Ni,Fe)$ precipitates apparently being lower than for $Zr(Cr,Fe)_2$ precipitates.

It is also worthy of note that for the two low temperature irradiations (electron and low temperature ion), the $Zr_2(Ni,Fe)$ precipitates were easier to amorphize, whereas for the high temperature irradiations (neutron and high temperature ion), the $Zr(Cr,Fe)_2$ precipitates amorphized easier.

Discussion

General Comments

The response of a material to irradiation is determined by a competition between athermal and thermal processes. Athermal, or ballistic, processes are basically the displacements,

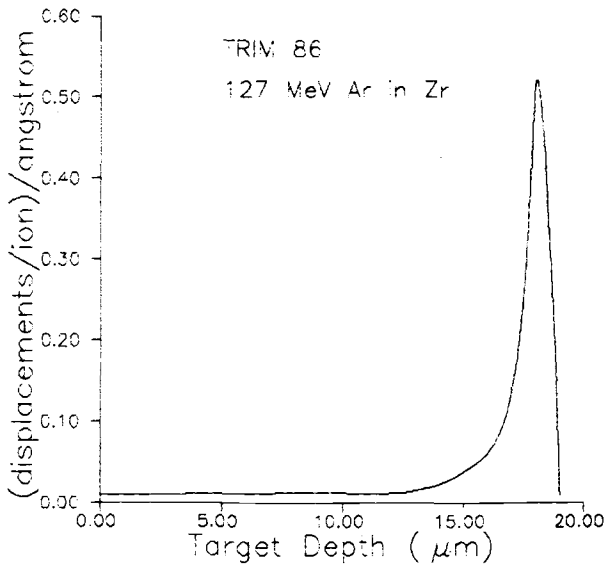


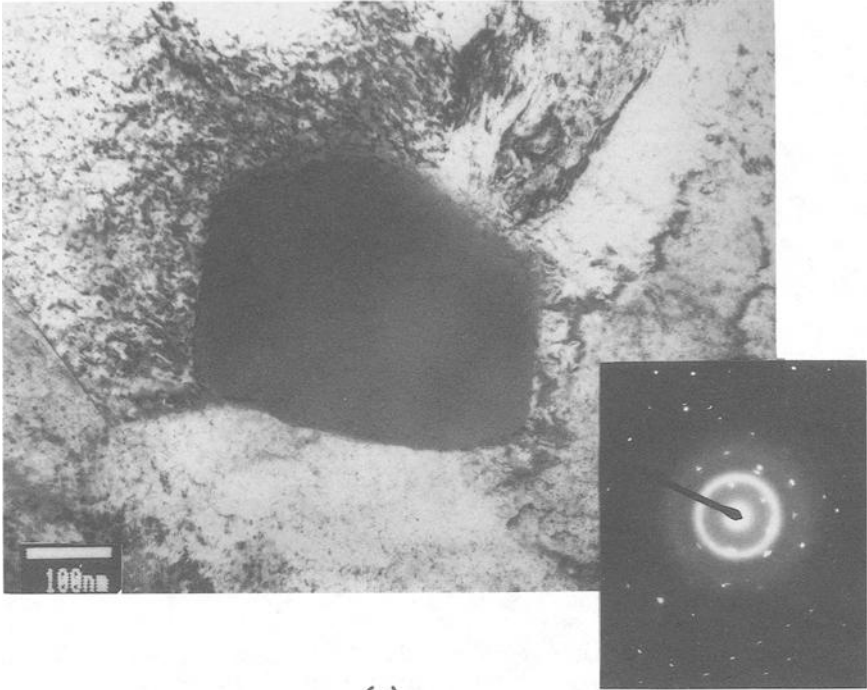
FIG. 9—Number of displacements per unit volume versus sample thickness for 127 MeV Ar ions in Zr, calculated using TRIM 86, with $E_d = 25$ eV.

replacements, replacement chains, cascades, and all the direct results of the atomic collisions between the incident particle and the atoms in the material. The energy imparted to the affected atoms is typically much greater than thermal energies [31]. That energy input, brought into the material by atomic collisions between the incident particles and the target atoms, can either accelerate the approach to equilibrium, in which case there is an irradiation *enhanced* process, or cause a departure from equilibrium, in which case there is an irradiation *induced* process [31]. Irradiation induced processes compete against thermal recovery processes, which tend to establish thermodynamic equilibrium.

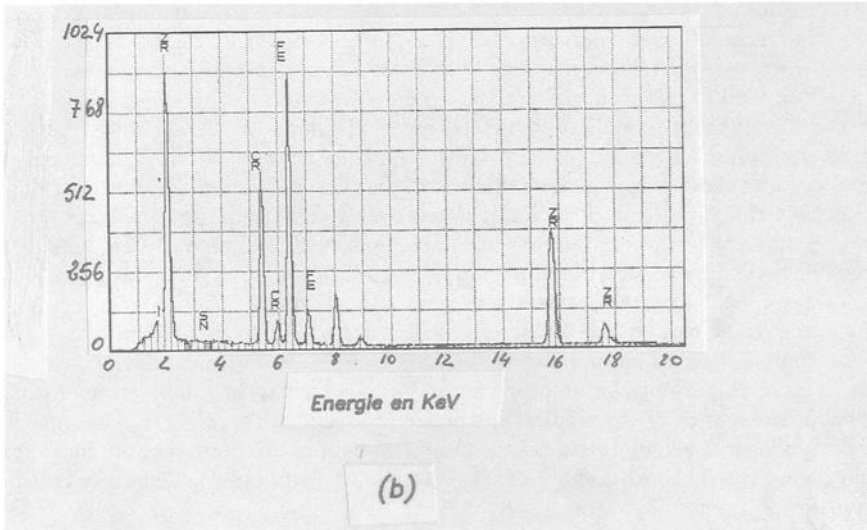
In the specific case of radiation-induced amorphization, irradiation shifts the material from its equilibrium crystalline phase to a metastable amorphous phase. This can only occur at temperatures that are low enough that the rate of thermal recovery is much smaller than the rate of irradiation damage buildup. If the dose to amorphization increases with temperature, it means that there is either less damage or increased recovery at higher temperatures. Since damage processes are for the most part athermal, it is expected that recovery stages are responsible for the observed temperature dependence. Thermal recovery is usually associated with the motion of point defects, so it is reasonable to try to identify the observed critical temperatures for amorphization with the migration energies of defects.

The critical temperature for amorphization is interpreted as the temperature at which the thermal processes neutralize irradiation damage production. Therefore it is not unexpected to see different critical temperatures for different types of irradiation, since the characteristics of the damage vary, most notably the dose rate, the distribution of damage, and the replacement-to-displacement ratio.

This Discussion section analyzes the experimental results in order to determine which mechanisms could be operative in producing both the damage and the thermal recovery processes that give rise to the temperature dependence of the dose to amorphization. The proposed mechanisms must provide an explanation for the existence of a dose-to-amorphization, its temperature and dose rate dependence, its variation with precipitate type, and



(a)



(b)

FIG. 10—Amorphous $Zr(Cr,Fe)_2$ precipitate in Zircaloy-4 (a) after irradiation to 25 dpa with 97 MeV Kr ions at 873 K [14]. The insert diffraction pattern shows a ring characteristic of the amorphous phase. Chemical analysis (b) shows no Fe depletion.

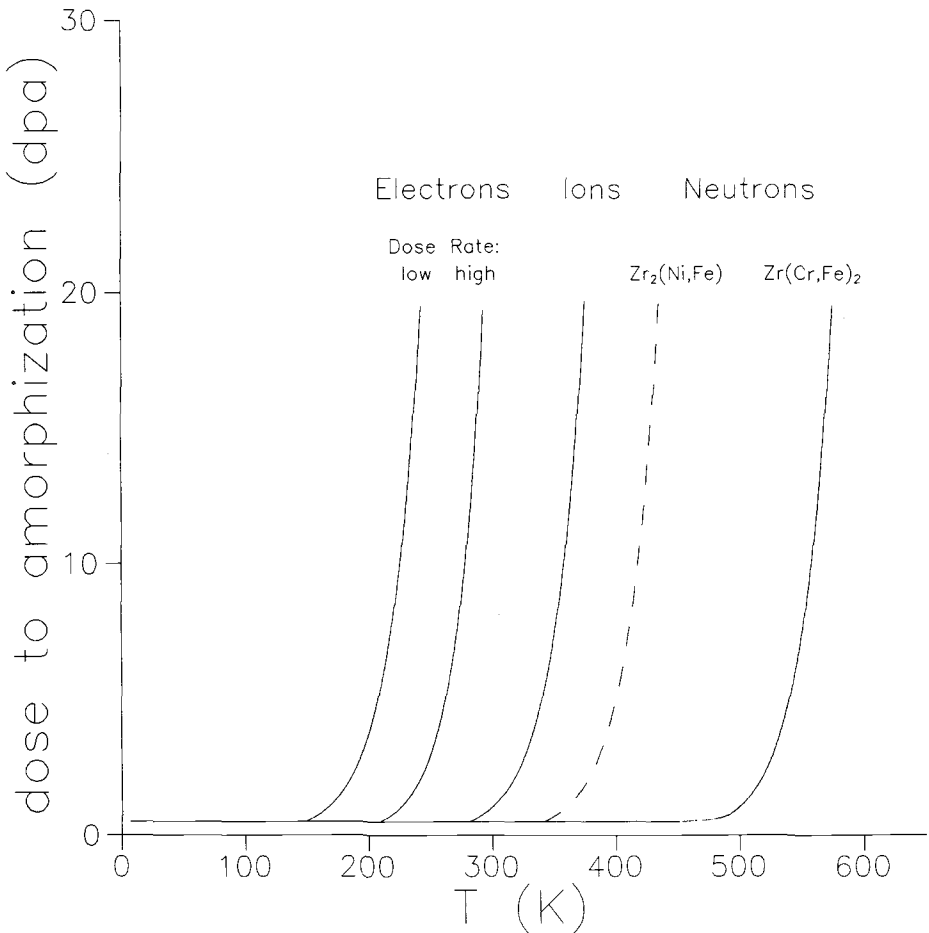


FIG. 11—Schematic plot of the dose to amorphization versus temperature for the three types of irradiation. The critical temperatures are shown for each. The dotted line indicates that the critical temperature for neutron irradiation induced amorphization of $Zr_2(Ni,Fe)$ precipitates is unknown.

the qualitative aspects of the transformation. Those factors will be dealt with in the following subsections.

Free Energy Storage under Irradiation

In order to shift the equilibrium between phases, irradiation must store enough energy in the lattice to make up for the difference in free energy between the amorphous and crystalline phases. That argument leads to the amorphization condition [5]:

$$G_c^{irr} \geq G_a \quad (2)$$

where G_c^{irr} is the increase in free energy of the irradiated crystalline phase relative to the unirradiated material, and G_a is the energy difference between the amorphous and crystalline phases. The energy difference G_a is on the order of 0.02 eV/atom [32,33].

The irradiation-induced increase in free energy that, according to Eq 2, leads to amorphization has been postulated to be due to the increase in point defect concentrations (topological disordering) [9,34,35], creation of anti-site defects (chemical disordering) [36,37], or both [5,27].

For either of the two basic damage accumulation mechanisms above to influence the amorphization process, it must be shown that they can lead to an accumulation of a sizable fraction of the energy difference mentioned above (say, about 0.005 eV/atom) for the irradiation conditions used during the experimentally observed amorphization time.

Electron Irradiation

A mechanism for attaining high levels of free energy storage in the lattice through the increase in point defect concentration has been proposed in Ref 5. According to that model, the fast-moving defects (usually interstitials) migrate to the free surface, leaving the slow-moving defects (vacancies) to accumulate in the lattice. The model is valid when the difference between the migration energies of the fast and slow moving defects is at least 0.3 eV and the foil is thin enough that the free surfaces are important sinks. Both conditions are usually fulfilled under electron irradiation.

The experiments of Luzzi et al. in the Cu-Ti system [36] have shown convincing evidence of a link between amorphization and chemical disordering. They monitored the maximum attainable irradiation-induced decrease on the order parameter S as a function of temperature, finding that at the critical temperature it was no longer possible to disorder the material. In other words, the critical temperatures for amorphization and for significant chemical disordering were the same.

For the precipitates in Zircaloy, such experiments are more difficult to perform since $Zr(Cr,Fe)_2$ and $Zr_2(Ni,Fe)$ belong to a class of ordered compounds that do not change their symmetry upon disordering. This means that there are no superstructure spot extinctions as S goes to 0 [23]. Variations in S cannot be monitored directly and must be inferred from calculations. Those calculations indicate that disordering does occur for the irradiation conditions used. A calculation of the kinetics of disordering was included in the model presented in Ref 27. For that case, it was found that both disordering and point defect increase were necessary to rationalize amorphization kinetics.

The critical temperature for amorphization under electron irradiation is ≈ 300 K (Fig. 11). Such temperature dependence can be explained in terms of either a decrease in attainable point defect supersaturation or an increase in reordering rates:

(a) *Decrease in Attainable Supersaturation*—In this case the temperature dependence comes from the higher vacancy supersaturation sustainable at low temperatures. The attainable supersaturation decreases at the critical temperature because at that temperature defect recombination in the bulk increases relative to interstitial annihilation at the surface sink. The controlling defect is the interstitial whose apparent migration energy in the intermetallic is found to be 0.4 to 0.45 eV [5].

(b) *Reordering*—The temperature dependence would come from increased reordering by one of the two defects, vacancy or interstitial, which would be activated at the critical temperature. If a vacancy mechanism is assumed [36], in order for the vacancy to be activated at ≈ 300 K, its migration energy must be <0.7 eV. This not only is lower than most vacancy migration energies, but also precludes the association of any higher critical temperature with the motion of the vacancy. It is unlikely that interstitials [38] could produce significant reordering, because the large size difference between Zr and [Fe,Cr,Ni] atoms makes it difficult for lattice interchange and hence reordering, to occur during interstitial migration [26].

Another point to be addressed is that $Zr_2(Ni,Fe)$ precipitates amorphize more easily for higher dose rates (Fig. 5). That effect can be explained by the defect accumulation model as well, as explained in Ref 5. The vacancy concentration (C_v) is given in that case by:

$$C_v = \text{const} \cdot (k/K_{iv})^{1/4} \cdot (kt)^{1/2} \quad (3)$$

where k is the dose rate (dpa s^{-1}), K_{iv} is the recombination coefficient, and t is the irradiation time. Equation 3 is valid for the approach to steady-state in a thin foil when there is a large difference in mobility between the slow defect and the fast defect. Thus for the same dose the concentration of vacancies is higher for higher dose rates and the critical values for amorphization are achieved more quickly.

We suggest that amorphization under electron irradiation is caused by the increase in free energy due to *both* point defect increase and chemical disordering. The point defect increase contribution to the free energy increase accounts for the temperature and dose rate dependencies of the dose to amorphization as shown in Eq 3. A model that included only chemical disordering would need to assume a low vacancy migration energy to rationalize the temperature dependence of the dose to amorphization.

Neutron Irradiation

Due to the low point defect concentrations that are obtained under neutron irradiation [39], and to the fact that a steady-state is very quickly reached, it is hard to conceive how the increase in the concentration of point defects can provide the basic mechanism for free energy increase that leads to neutron irradiation-induced amorphization. Chemical disordering is much more likely than point defect accumulation, since the effective dose rate for disordering is much higher than that for point defect creation due to the fact that the replacement-to-displacement ratio under neutron irradiation is between 30 and 100 [40]. Also, the low point defect concentrations do not favor reordering. Chemical disordering is therefore more likely to be responsible for the buildup of free energy with dose under neutron irradiation.

The fact that the critical temperature for neutron-irradiation-induced amorphization of $Zr(Cr,Fe)_2$ correlates well with Naguib and Kelly's criterion [23], as mentioned in the Experimental Data section, suggests that the amorphization mechanism could be linked to cascade production. Cascade overlap has been suggested as an amorphization mechanism in ion irradiated NiTi [34]. With such a mechanism, however, amorphization would be as likely in the center of the precipitate as in the periphery. It is thus probable that cascade overlap is not the amorphization mechanism in this case.

It is suggested, therefore, that the buildup of free energy with dose under neutron irradiation is caused by cascade-induced chemical disordering in the precipitate. If the correspondence with Naguib and Kelly's criterion is meaningful, then the temperature dependence comes from increased cascade crystallization above $0.3 T_m$.

There is also the question of why precipitates amorphize preferentially at the interface with the matrix. One possible explanation, proposed by Griffiths [41], involves the preferential diffusion of Fe into the matrix, the resulting change in stoichiometry then driving up the free energy of the line compound. One problem with this explanation is that it is then difficult to account for the linear dependence of the thickness of the amorphous layer with fluence [2].

An alternative explanation is that mixing due to solute sputtering and recoil introduction can cause a departure from stoichiometry near the interface. Once the Fe atoms are sputtered into the matrix, since Fe diffuses very quickly in Zr, they could leave the vicinity of the precipitate in a short time and therefore not be reabsorbed back into the precipitate.

Since this mixing is induced by a ballistic process, this pre-amorphization departure from stoichiometry would be proportional to the fluence, as observed experimentally, and would involve Fe *and* Cr. The observed Fe depletion would therefore not be a cause of the amorphization, but a result of it. This happens because the Fe in the amorphous precipitate would not be in equilibrium with the matrix [15]. Neutron-irradiation-induced amorphization would then follow the path:

1. Irradiation causes cascade disordering in the bulk and mixing at interface.
2. The free energy in the bulk augments because of disordering. At the precipitate periphery the increase is bigger because of the added contribution of variation in stoichiometry to the free energy rise.
3. Amorphization occurs when Eq 2 is satisfied. This occurs first at the precipitate periphery.
4. After amorphization, there is Fe depletion and expansion of an Fe depletion ring.

Ion Irradiation

As mentioned in the Ion Irradiation part of the Experimental Results section, fewer data are available for ion irradiation than for the other two types of irradiations. Specifically, there are fewer data on partially amorphized precipitates. Therefore the transformation process is not so well understood as in the two previous cases. It is critical, therefore, to examine precipitates that were partially amorphized under ion irradiation in order to have an idea of how the transformation proceeds.

Under ion irradiation, since no free surfaces are available for interstitial annihilation, no mechanism for increase in point defect concentration is evident, and we must rely on chemical disordering to produce the bulk of the free energy change.

After a critical amount of chemical disorder accumulates, additional cascade impacts could provide enough local fluctuations in the free energy level to nucleate the transformation locally. This would imply an essentially homogeneous transformation on the precipitate size scale. Amorphization would then follow the same path described for neutron irradiation, except that there would be no preferential amorphization at the precipitate-matrix interface.

Alternatively, the transformation could be nucleated at the precipitate/matrix interface as in the case of neutrons. It could conceivably happen preferentially in the direction that faces the ion beam, if mixing was biased enough in that direction. No clear experimental evidence of such an effect has been found, however.

The critical temperature, although not well determined (Fig. 11), is higher than for electrons and lower than for neutrons. Since the critical temperature does not correspond to a cascade mechanism, it is tempting to attribute the temperature dependence of the dose-to-amorphization to reordering caused by migration of the vacancy. Although this explanation would seemingly be at odds with the occurrence of chemical disordering at higher temperatures under neutron irradiation, it is possible that, due to the large gradients in the damage deposition rate, the vacancy flux, and hence the magnitude of vacancy reordering, is larger under ion than neutron irradiation. Owing to a lack of experimental data, however, this must for the moment remain speculation.

Conclusions

We have reviewed the experimental results and theoretical models of amorphization of precipitates in Zircaloy under neutron, ion, and electron irradiation. It is concluded that different mechanisms are operational in each case, because of the observed differences in critical temperatures and modes of amorphization.

The summary of our suggestions for the theoretical models are presented in Table 1. For each type of irradiation the suggested mechanism of free energy rise is shown as well as the

TABLE 1—*Theoretical models.*

	Mechanism for Free Energy Rise Under Irradiation	Temperature Dependence of Dose to Amorphization	Qualitative Aspects of Amorphization
Electron	Accumulation of vacancies in the lattice because of interstitial migration to surface. This is supplemented by chemical disordering	Sustainable vacancy supersaturation is lower near critical temperature because of increased recombination in the bulk	High dose rates facilitate amorphization because the vacancy concentration is higher for a given dose
Neutron	Chemical disordering caused by cascades supplemented at the precipitate/matrix interface by a departure from stoichiometry caused by ballistic mixing	Increased annealing in cascades close to respective critical temperatures	Preferential depletion of Fe from precipitates observed after amorphization
Ion	Chemical disordering caused by cascades	Long range vacancy reordering activated at critical temperature (?)	Inversion of relative precipitate stabilities from high to low temperature could indicate different amorphization mechanisms.

suggested annealing mechanism that is activated at the critical temperature. Some distinguishing qualitative features of the amorphization process are also shown. It should be noted that the suggestions for the case of ion irradiation are for the moment little more than speculation.

More research is needed to determine the amorphization mode under ion irradiation, the critical temperature, as well as possible dose rate effects analogous to those exposed in Ref 30. It would also be of great interest to examine a sample of Zircaloy-2 irradiated with neutrons at ≈ 420 K to determine the morphology of the partially amorphized $Zr_2(Ni,Fe)$ precipitates.

On the theoretical side, calculations must be made to verify that the models proposed can, in fact, explain the results, as is the case for electron irradiation.

The ensemble of the experimental results and their interpretation show that, while charged-particle irradiation is a useful means of obtaining information about radiation-induced processes, comparisons with neutron irradiation should be done with care, since different radiation damage and annealing processes might be prevalent in each case.

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DISCUSSION

*R. B. Adamson*¹ (written discussion)—(1) We have observed complete dissolution of small precipitates, particularly those with an Fe/Cr ratio, by neutron irradiation. Have you observed such a phenomena in your experiments with ions or electrons?

(2) Have you observed, as reported by Dr. H. Chung in this meeting, amorphization of Zr₂(Fe,Ni) precipitates at temperatures near 300°C?

A. T. Motta et al. (authors' closure)—(1) Under electron irradiation and low temperature ion irradiation, no changes in precipitate composition were observed upon amorphization. Under high temperature ion irradiation, no morphological changes were observed, but we did see a depletion in Fe and Cr from the precipitates (Ref 6 in text).

(2) The results we have reported for amorphization of Zr₂(Ni,Fe) are from Ref 2 in the text. We have only examined neutron irradiated Zircaloy-4 to a fluence of about 9 dpa at

¹GE Nuclear Energy, Pleasanton, Calif.

a temperature of 300 to 330°C. In those, we saw only the $\text{Zr}(\text{Cr},\text{Fe})_2$ precipitates, which were partially amorphous, with the same duplex structure as reported in Ref 2.

B. Cox² (written discussion)—Have you looked at the “metallic glass” literature with respect to amorphization under irradiation? There are some interesting correlations with effects of composition in the $\text{Zr}(\text{Fe},\text{Cr})$ system on both the ability to quench in amorphous structures and recrystallization temperatures.

A. T. Motta et al. (authors' closure)—Thank you for the indications. It is always an interesting question whether thermodynamic or kinetic considerations control the amorphization process. The quantities you refer to are related to the amorphization susceptibility as a function of composition and should therefore be considered to be thermodynamical in nature. Given that $\text{Zr}(\text{Cr},\text{Fe})_2$ is a stoichiometric compound, and that the Fe/Cr ratio varies only between about 0.8 and 1.2, it seems to us that the difference in free energy between the crystalline and amorphous phases (or the amorphization susceptibility) should not vary much from precipitate to precipitate.

S. Ishino³ (written discussion)—(1) Your ion irradiation experiment is interesting. Is your conclusion drawn from observations near the range of the incident ion? If you apply the cross-sectional method, point defect contribution predominates the cascade effect at the shallower region. Thus one can obtain the whole range of phenomena from those like electron irradiation to those of high energy cascade.

(2) In your mechanism diagram for ion irradiation, you do not include the effect of high local energy deposition, which sometimes reaches several tens of eV per atom. This might create local very high temperature regions which may lead to amorphization.

A. T. Motta et al. (authors' closure)—(1) It is true that the displacement rate under ion irradiation varies significantly as the ion penetrates the target, progressively losing energy, and that by using cross-sectional samples more exact and plentiful information can be extracted from one sample. The nature of the damage, however, does not change much from the shallower region to the end of the ion range. Except for the possibility of cascade overlap in the region close to the displacement peak, the only difference is that cascades become more frequent towards the end of the ion range. Therefore, even for equivalent dose rates, ion and electron irradiation are still fundamentally different because of the absence of cascades in the latter.

(2) We do include the effect of high local energy deposition by considering that, for irradiations at the same temperature to comparable doses and dose rates, the presence of cascades facilitates amorphization under ion and neutron irradiation, as compared to electron irradiation.

J.-J. Kai⁴ (written discussion)—In our previous work in proton-irradiated Zircalloys, we have seen the Fe/Cr ratio decreases with increasing dose level in $\text{Zr}(\text{Fe},\text{Cr})_2$ intermetallic precipitates. Have you seen that in your ion irradiation studies? If not, could it be possible that, because the irradiation temperature in your study is low, the point defect migration ability is reduced?

²University of Toronto, Toronto, Ontario, Canada.

³University of Tokyo, Department of Nuclear Engineering.

⁴National Tsing Hua University, 101, Section 2, Kuang-Fu Road, Hsinchu, Taiwan 30043, Republic of China.

A. T. Motta et al. (authors' closure)—As stated above, no change in Fe or Cr concentration was observed in low temperature ion irradiation. A depletion of Fe *and* Cr was observed in 97 MeV Kr ion irradiation at 600 to 700°C (Ref 6 in text). No variation in Fe/Cr ratio was detected in the latter case, however. The lack of compositional variation could just mean that, in our experiments, the temperature was either so low that neither Fe nor Cr could diffuse out or so high that both species were mobile.