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MECHANISMS OF RADIATION INDUCED AMORPHIZATION

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ABSTRACT

A brief review is presented of the mechanisms of energy storage leading to irradiation induced amorphization, with special attention to the comparison between chemical disordering and point defects. It is shown that in addition to chemical disordering, there is considerable experimental evidence for the point defect mechanism. A summary is presented of experimental results of amorphization induced by neutron, electron and ion irradiation of Zr(Cr,Fe)₂ precipitates in Zircaloy, and of their theoretical interpretation. In that system, there is evidence for forms of energy storage other than chemical disordering, notably amorphization by departure from stoichiometry under neutron irradiation.

INTRODUCTION

The crystalline-to-amorphous transformation (amorphization) of intermetallic

compounds under irradiation has received considerable attention lately. It was first observed under neutron irradiation in U₆Fe by Bloch [1], and more recently during charged particle irradiation (electron and ion) [2-5].

It was noticed from the start that some compounds underwent amorphization while others remained crystalline under similar irradiation conditions. The explanation for this difference in amorphization susceptibility was investigated by several workers, who developed various empirical criteria to predict which compounds would amorphize under irradiation. Those criteria included: ionicity of the bonds and melting temperature [6], width of phase field [5], position of the compound in the phase diagram [7], or a combination of separation in the periodic table, complexity of structure and stoichiometry > 0.33 [8]. Although useful, the empirical approach fails to explicitly take into account the interplay between the nature of the damage and the annealing mechanisms. For example, a material that does not become amorphous under electron irradiation at a given temperature might do so under cascade-producing irradiation or at a lower temperature.

Another approach, emphasized in other works [9-14] as well as in the present one, is to recognize that a certain amount of energy must be stored in the material during irradiation in order for amorphization to occur. By inferring what form of energy is stored, and studying the kinetics of that energy accumulation, a deeper insight into the amorphization process can be obtained.

In the first part of this work we discuss the two main models of energy storage that have been proposed in the literature, namely chemical disordering and increase in point defect concentration. It is our intent to show that forms of energy storage other than chemical disordering also contribute to irradiation induced amorphization of intermetallics.

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system Zr(Cr,Fe)₂ precipitates in Zircaloy are then presented. These intermetallic precipitates have been made amorphous by the three different types of irradiation (neutron, ion and electron), at various temperatures. These results support the thesis above that several different mechanisms of energy storage contribute to the occurrence of irradiation induced amorphization.

Secondarily, our aim is to show that by studying amorphization in a single system, and cross checking the information from different types of irradiation in a range of temperatures, a view of ensemble can be gleaned that gives insight into the mechanisms of irradiation induced amorphization.

ENERGY STORAGE DURING IRRADIATION

Since the amorphous state is metastable with respect to the unirradiated crystalline state, a rationale must be found for the occurrence of the crystalline to amorphous transformation under irradiation. A necessary condition for amorphization is [15]:

$$G_{irr} > G_{ac}$$
 (1)

where G_{ac} is the difference in free energy between the unirradiated crystalline and amorphous phases, and G_{irr} is the increase in free energy brought about by irradiation. Some of the energy input from irradiation must therefore be stored permanently (or for a time comparable to the amorphization time) in the material. Since most of the irradiation energy dissipates as heat, the question is then posed: what mechanisms can

accumulate enough energy in the lattice during irradiation to satisfy the criterion above and permit amorphization to occur?

The two most commonly proposed mechanisms are an increase in the concentration of point defects (topological disorder) or of anti-site defects (chemical disorder). There has been a great deal of controversy as to whether point defects or anti-site defects are responsible for amorphization under irradiation. We detail some of this discussion below.

Chemical Disordering

As has been pointed out in the literature [16-20], there is strong evidence linking the occurrence of chemical disorder and amorphization. The main experimental evidence for the chemical disordering model comes from the following facts:

- 1) No pure metals (with the exception of Ga), and no solid solutions have been amorphized under irradiation [19].
- 2) Luzzi et al [20] found that the critical temperatures for electron irradiation induced chemical disordering and electron irradiation induced amorphization in intermetallic compounds of the Cu-Ti, system were identical.

In addition, calculations show that the amount of chemical disordering attainable under most irradiation conditions, can store enough energy in the lattice to drive the crystalline-amorphous transformation [16,17].

Furthermore, most of the empirical criteria cited in the introduction can be related to either the ease of occurrence or the consequences of chemical disordering. For example, random atom exchanges, of the type brought about by irradiation, have a larger probability of producing anti-site defects in complex structures than in high symmetry structures, so the complex structure criterion could be related to the ease of occurrence of chemical

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disordering. The same argument is valid for A_xB_{1-x} compounds where x is either very small or close to 1 (the stoichiometry criterion). In that case a random atom exchange has a higher probability of occurring within the majority sublattice, causing no disorder, compared to the case when x=0.5. The ionicity, solubility and periodic table separation criteria can all be related to the strength of the chemical bond, and are therefore related to the consequences of creating anti-site defects.

From the above, it appears that the role of chemical disordering in the amorphization of intermetallic compounds has been established. It can thus be said to be a necessary condition for the amorphization of intermetallic compounds [17,21].

Point Defect Accumulation

Given the role of chemical disordering in the amorphization process explained above, it remains to be determined whether point defects contribute to irradiation induced amorphization as well. In contrast to chemical disordering, the role of point defects is less clearly established [17-19,21]. We will employ a two-step approach to this discussion: first we will discuss the kinetic feasibility of obtaining high point defect concentrations and then discuss the experimental evidence supporting it.

The Stability Limit of Point Defect Accumulation: It was recognized early on that defect concentrations of the order of 0.01 to 0.02 would be necessary to bring about amorphization [5,15]. If both vacancies and interstitials accumulate in the solid, with a spatially even concentration distribution, then the concentrations above are very close to the athermal recombination limit, where each newly created defect would instantaneously

recombine with an existing point defect. This limit is roughly equal to the inverse of the number of atoms in the athermal recombination volume, so a number of atoms equal to 50 would give a maximum concentration of 0.02.

This stability limit has been invoked by several authors [17,19,20] as an argument against the point defect model. Indeed, the burden of proof is on the proponents of point defects as a driving force for amorphization to come up with a mechanism for obtaining high point defect concentrations.

There are, in fact, several good answers to that limitation. Pedraza et al.[11,12] propose that the recombination limit can be circumvented if a locally favorable chemical environment stabilizes Frenkel pairs (called defect complexes) against recombination. High enough concentrations of point defects to cause amorphization can be achieved via that mechanism for a complex binding energy of 0.7 eV. The author also notes that this model can explain the inhibition of amorphization observed in simultaneous electron and ion irradiation of Zr₃Al, compared to pure ion irradiation [22].

Equally, if only one type of point defect accumulates in the lattice, the recombination limit does not apply. This can happen whenever there is preferential elimination of one type of point defect at sinks, either because of a bias or because only one point defect is mobile. Simonen [9] calculated the accumulation rate of vacancies when mobile interstitials annihilate at dislocations, and found that a vacancy concentration of 0.01 could be reached in the observed amorphization time for an interstitial migration energy of 1.0 eV. For lower values of the interstitial migration energy, (or for higher temperatures) the vacancy concentration is smaller than the critical value. The proposed model for electron irradiation induced amorphization of Zr(Cr,Fe)2 precipitates in Zircaloy mentioned later also falls into the category of models in which the concentration of one defect increases due to preferential absorption of the other defect at sinks, in that case the free surface.

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Therefore, there are instances when point defect buildup to the level required for amorphization is kinetically feasible.

The discussion above applies mostly to electron irradiation. In the case of cascade producing irradiation, the recombination limit does not apply because the assumption of an evenly distributed production of point defects is not valid. Very high defect concentrations can be achieved locally, in the core of a collapsed cascade or after cascade superposition [9].

<u>Experimental Evidence</u>: There is also experimental evidence that chemical disordering is not always enough to cause amorphization:

- a) Koike et al [23] have found different critical temperatures for amorphization of CuTi when induced by Kr ion, Ne ion and electron irradiation. This mirrors the observation presented below of different critical temperatures for amorphization of Zr(Cr,Fe)2 precipitates when induced by neutron, electron and ion irradiation. Such a diversity of critical temperatures is more easily explained by a model that considers other contributions to the free energy in addition to chemical disordering, than by a pure chemical disordering model.
- b) The correspondence between the critical temperatures for disordering and amorphization observed by Luzzi [20], is not always present:

Howe and Rainville [4] observed complete disordering of Zr₃Al when subjected to Ar ion irradiation, up to a temperature of 693 K, but only saw complete amorphization below 300 K. Between those two temperatures a mixture of disordered crystalline and amorphous phases was observed, showing that the disordered crystalline phase is stable against amorphization. Also, Koike et al.[24] suggest that the abnormally high dose-to-amorphization observed during electron irradiation of Zr₃Al is due to accumulation of point

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defects, in addition to chemical disordering.

During proton irradiation of NiTi, Cheng et al [25,26], reported the occurrence of amorphization without any significant chemical disordering, as measured by the intensity of the superlattice reflections. They conclude that chemical disordering is not enough and that an increase in the concentration of point defects must be the main energy source for amorphization.

Nastasi [27] observed the appearance of a completely chemically disordered structure in Ni₂Al₃, when irradiated with Kr ions to a fluence of 7.5 x 10¹³ ion.cm⁻², whereas only partial amorphization was seen at 1.5 x 10¹⁴ ion.cm⁻² and complete amorphization appeared at 3 x 10¹⁴ ion.cm⁻². The author concludes that the free energy of the completely disordered state is lower than that of the amorphous state, and that additional forms of damage besides chemical disordering are required for amorphization. This behavior has a parallel in one of Luzzi's experiments (fig. 7 in ref. [20]), where during electron irradiation of Cu₄Ti₃ at 265 K, the degree of long range order S decreases from 1 to 0.3 at a dose of 2 dpa, then remains constant. Amorphization occurs only at 3.3 dpa, at the same level of chemical disorder. This could mean that another type of damage goes on accumulating in the lattice and finally reaches a critical level to cause the transformation [21].

Molecular dynamics simulations provide yet another window with which to study amorphization. In addition to an early attempt by Limoge et al on a pure metal [28], two molecular dynamics simulations of amorphization have been done so far to investigate the role of point defects and chemical disordering in amorphization, now in intermetallics. Massobrio et al [29] found that Zr₂Ni amorphized upon chemical disordering, after a reduction in S from 1 to 0.6. This shows that, for their potential, which correctly predicts several macroscopic properties of Zr₂Ni, chemical disordering can store

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enough energy for amorphization. No similar attempt was made with point defects. The opposite conclusion was arrived at in Sabochik and Lam's study of amorphization in CuTi [30], where amorphization was not achieved even for S=0. Only when point defects were introduced did the lattice amorphize.

Summary

From the foregoing, it should be clear that chemical disordering plays a very important role in irradiation induced amorphization, but that there is evidence for contributions of other forms of energy storage leading to amorphization, notably point defects.

In fact, although this discussion centered on the role of defects on amorphization, there is extensive evidence of preferential amorphization at lattice imperfections such as grain boundaries [20], dislocations [31], free surfaces [32] and anti-phase boundaries [33]. This is reasonable to expect since these are high energy regions, where the local distortion of the lattice or the high chemical energy gives an additional contribution to the free energy rise due to irradiation. Yet another form of stored energy, present in two-phase systems, a departure from stoichiometry, is presented in this paper.

It still must be assumed that chemical disordering is essential to amorphization, since no combination of the other forms of energy storage under irradiation has been shown to cause amorphization in pure metals. What is the specific role of chemical disordering in cases where amorphization occurs without any chemical disordering [26] is not clear. It is possible that the existence of chemical order either enhances the accumulation kinetics [11] or increases the formation energy of the other forms of defects (point defects, line defects, grain boundaries).

The question of which mechanisms are important for amorphization

under irradiation is, therefore, not completely resolved. A three fold approach, combining several types of irradiations that have different replacement to displacement ratios, with modeling of the irradiation induced microstructural evolution with chemical rate equations, and with the investigation of the point defect structure with molecular dynamics [34,35], should prove the most fruitful.

A case in point is CuTi, where the observation of a greater amorphization susceptibility of Cu_{0.485}Ti_{0.515} compared to Cu_{0.525}Ti_{0.475} [36], was explained by Shoemaker et al [34], by the greater ability of the Cu vacancy to cross Ti planes when some Cu atoms are present in those planes.

It must be noted, finally, that this whole discussion is simplified, in that the very notion of a localized point defect may not be applicable to intermetallics, where the equlibrium defect configuration can be quite complex and delocalized [34], as is the case in concentrated solid solutions [37].

AMORPHIZATION OF Zr(Cr,Fe)2 PRECIPITATES IN ZIRCALOY

We now show some results of irradiation induced amorphization of intermetallic precipitates in Zircaloy. This is an interesting system to study because there is a large amount of neutron irradiation data from power reactors, at 350 K (Candu reactors) and 550 to 650 K (Light Water Reactors). In addition to neutron irradiation, those precipitates have been extensively irradiated with 127 MeV Ar ions from 260 to 600 K [38] and with 1.5 MeV electrons from 7 to 320 K [39]. Moreover, the peculiarity of studying the amorphization of precipitates in a matrix can induce interesting interface effects, as shown below.

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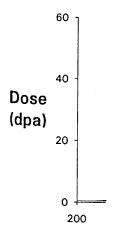


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Laves phase Zr(Cr,Fe)₂ precipitates are present in as-fabricated Zircaloy. Their structure and composition has been extensively described elsewhere [40,41]. Those precipitates have been made amorphous by neutron [42,43], ion [38], and electron [13] irradiation.

The experimental results are as follows:

- a) Amorphization occurs under the three types of irradiation, when the irradiation temperature is below a critical temperature T_c . At that temperature the dose-to-amorphization increases exponentially, and above T_c it is not possible to amorphize the material.
- b) The critical temperature T_C is specific to each type of irradiation. The lowest critical temperature occurs under electron irradiation (300 K), the next higher occurs under ion irradiation (400 K) and the highest occurs under neutron irradiation (580 K), as can be seen in figure 1.

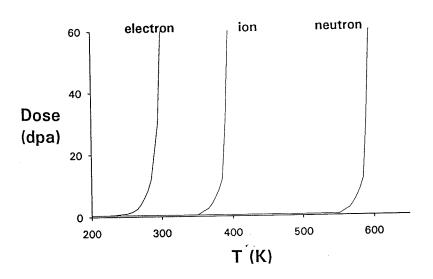


Figure 1. Dose to amorphization of Zr (Cr,Fe)2 precipitates versus irradiation temperature for electron, ion and neutron irradiation.

- c) Under neutron irradiation, the transformation starts at the precipitate/Zr matrix interface, and gradually moves into the precipitate until it is completely amorphous. There is a depletion of Fe from 40 at.% to 10 at.% in the amorphous layer. The increase in the thickness of the amorphous layer is linear with irradiation dose.
- d) Under <u>electron irradiation</u> amorphization occurs homogeneously and abruptly, towards the end of the irradiation time. There is no variation in composition either during or after amorphization.
- e) Under <u>ion irradiation</u> the transformation morphology could not be determined, since partially amorphous precipitates were not found in the samples examined. It could be ascertained, however, that there is no variation in composition associated with amorphization.

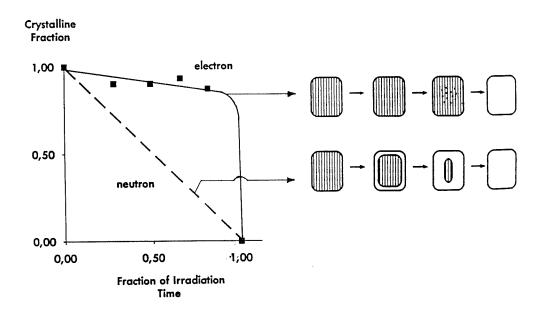


Figure 2. Measured crystalline fraction as a function of fraction of total irradiation time under electron and neutron irradiation of Zr (Cr,Fe)₂ precipitates in Zircaloy.

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Figure 2 compares the amorphization kinetics under neutron and electron irradiation, by plotting the crystalline fraction as a function of the fraction of the total irradiation time. It can be seen that under electron irradiation, the crystal retains its crystallinity until close to the end of the irradiation time and then transforms abruptly to amorphous, whereas under neutron irradiation the amount transformed is directly proportional to the dose. A qualitative scheme of the two transformations is also shown in fig.2, illustrating the two different transformation morphologies, explained in c) and d) above.

ENERGY STORAGE MODELS FOR Zr(Cr,Fe)2

Electron Irradiation

Under electron irradiation it was found that the kinetics of Zr(Cr,Fe)₂ precipitate amorphization could be accounted for by a model incorporating the contributions of both point defects and anti-site defects to the free energy rise under irradiation [21].

The chemical disordering contribution was calculated using the Bragg-Williams model to find the change in the number of unlike atom pairs when the long range order parameter S decreases due to random recombination. The increase in free energy due to disordering is then proportional to the decrease in the number of unlike atom pairs.

The mechanism of point defect accumulation was proposed to be a thin foil artefact, related to the elimination of a "fast" (interstitial) defect at the foil surface, while the "slow" defect (vacancy) accumulates in the lattice. There is

then a competition between recombination in the bulk and elimination at the surface. The results of the calculation show that at the critical temperature, there is a drastic reduction in the fraction of defects eliminated at the surface, which reduces the accumulation of point defects in the lattice and impedes amorphization. The defect energies required for this model to account for the temperature dependence of the dose-to-amorphization are a fast defect with a migration energy of 0.45 eV and a "slow" defect of the opposite polarity with a migration energy bigger than 0.95 eV.

Neutron Irradiation

In contrast, neutron irradiation induced amorphization of Zr(Cr,Fe)2 precipitates is proposed to be controlled by a departure from stoichiometry caused by cascade (or ballistic) mixing in a thin layer close to the crystalline/amorphous precipitate interface [44]. The departure from stoichiometry in line compounds causes a large increase in its free energy. This explains why there is preferential amorphization in the affected zone close to the interface. The Fe concentration in the amorphous phase of 0.33 no longer being in equibrium with that in the matrix, amorphization is followed by a discharge of iron from the amorphous precipitate into the matrix, which allows amorphization to advance into the precipitate. The fact that the amorphous layer thickness has a linear, rather than square root, dependence on the dose, indicates a ballistic rather than a thermal mixing process. The temperature of 0.3 T_m has been associated with a decrease in cascade mixing due to the onset of the thermally assisted mixing regime [6,45]. Since the critical temperature is in this case equal to 0.3 T_m , it is likely that a reduction in cascade mixing efficiency is responsible for the absence of amorphization above that temperature.

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Amorphization and Annealing Mechanisms

In table 1 a tentative assignment is made of radiation damage mechanisms that cause amorphization in Zr(Cr,Fe)₂ precipitates with their respective annealing mechanisms operative at the critical temperatures.

For each type of irradiation, the proposed damage mechanism is shown in the first line. At the critical temperature, listed in the second line, this damage mechanism is swamped by the annealing process shown. The defect that activates such process is also shown along with its activation energy. Lastly a comparison is made of the irradiation induced amorphization of $Zr(Cr,Fe)_2$ with that of $Zr_2(Ni,Fe)$.

The annealing of electron irradiation damage is controlled by the motion of the interstitial (or "fast" defect) with a migration energy of 0.4 eV, found by fitting to the critical temperature. In the case of ion irradiation, the amorphization mechanism is largely unknown, but the hypothesis of a long range reordering process taking place around 400 K is not incompatible with the requirements of a slow defect with a migration energy of 0.9 eV, originating from the electron irradiation model. Given a disordering rate dS/dt of 10⁻³ to 10⁻²s⁻¹, a calculation using any one of the standard expressions for vacancy reordering [21,46-49] yields a migration energy of 1 eV for the reordering defect, in order for the equality between disordering and reordering to happen at 400 K.

Above the critical temperature, in the case of <u>ions</u>, although cascades are still present and still cause disorder, long range reordering by free vacancies can offset that disordering and prevent amorphization.

At the higher temperatures and longer irradiation times present under neutron irradiation, the storage mechanism based on a departure from stoichiometry becomes available, because now the product (Dt)^{1/2} is large enough for the amorphous layer to discharge its iron into the matrix, which

TABLE 1 Mechanisms of Irradiation Induced Amorphization in $\mathrm{Zr}(\mathrm{Cr,Fe})_{\underline{z}}$

	Electron	lon	Neutron
Mechanism of Free Energy Rise Under irradiation	Accumulation of vacancies in the lattice because of interstitial migration to surface, supplemented by chemical disordering	Cascade Damage Point Defects + Chemical Disorder (?)	Departure from stoichiometry caused by ballistic mixing and cascade damage
Tc [K]	300	~ 400	580
Annealing Mechanism at Tc	Sustainable vacancy supersaturation is lower near Tc because of increased recombination in the bulk	(?) Long range vacancy reordering activated at critical temperature	Increased annealing in cascades close to critical temperature 0.3 Tm .=> less mixing and disorder
Defect & Activation Energy	"Fast" defect with Em = 0.4 eV and Em fast - Em slow > 0.5 eV	Migration Energy of Reordering Defect ∼ 1 eV	N/A (Mobiliry in Cascades)
Comparison with Zr ₂ [Ni,Fe]	Zr ₂ (Ni,Fe) amorphizes easier Amorphization easier at higher dose rates	Low temperature irradiations: Zr _z [Ni,Fe] amorphizes easier High temperature irradiations: Zr{Cr,Fe} _z amorphizes easier	Zr (Cr,Fe) ₂ amorphizes easier

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allows it to advance into the precipitate. Given that the disappearance of amorphization at the critical temperature in the case of neutron irradiation is thought to be due to increased annealing in the cascades, no defect is assigned to that temperature. At the critical temperature, the cascades become ineffectual at producing mixing and disorder, so that the damage is eliminated at the source, and amorphization is again not possible.

In comparing the amorphization susceptibility of the two types of precipitates present in Zircaloy, Zr(Cr,Fe)₂ and Zr₂(Ni,Fe), it is interesting to note that for the low temperature irradiations (electron and low temperature ion), Zr₂(Ni,Fe) precipitates are less stable against amorphization than Zr(Cr,Fe)₂ precipitates are, whereas the reverse is true at higher temperature irradiations (neutron and high temperature ion) [50]. This could indicate that different amorphization mechanisms are present at low and high temperatures.

Another noteworthy observation is that Zr₂(Ni,Fe) precipitates are found completely amorphous after 1 dpa neutron irradiation at 350 K, and are completely crystalline after 10 dpa irradiation at 523 K. This is not inconsistent with a critical temperature of for neutron irradiation induced amorphization at 0.3 T_m, equal to 440 K for Zr₂(Ni,Fe). Although it would be interesting to observe the Zr₂(Ni,Fe) precipitates in Zircaloy 2 irradiated to 1-10 dpa, at 400-440 K such samples are not available since this is, unfortunately, not a common power reactor temperature.

The dose-to-amorphization under electron irradiation in Zr₂(Ni,Fe) was also found to be lower for higher dose rates, in accord with the observations of Xu et al. in CuTi [51], Basu et al. in YBaCuO [52] and Linnros et al. in Si [53].

CONCLUSIONS

A brief review was made of the models in the literature for energy storage in the lattice during irradiation-induced amorphization.

Chemical disordering is probably the main contribution to energy storage during irradiation, but several other mechanisms contribute as well. Those are point defect buildup, departure from stoichiometry, and all existing lattice imperfections (grain boundaries, dislocations, and anti phase boundaries). Although they are marginal mechanisms, they are often the controlling mechanism for amorphization, providing the extra energy needed to amorphize the material.

The system Zr(Cr,Fe)₂ precipitates in Zircaloy provides interesting examples of alternative forms of energy storage, notably in the case of neutron irradiation, where amorphization is caused by a departure from stoichiometry at the precipitate/matrix interface.

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