

## ELECTRON ENERGY DEPENDENCE OF AMORPHIZATION IN $Zr_3Fe$

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### ABSTRACT

This paper reports the results from a study conducted to determine the effect of electron energy on the dose-to-amorphization of  $Zr_3Fe$  at 23-30 K.  $Zr_3Fe$  samples were irradiated in the HVEM at Argonne National Laboratory, at energies ranging from 200 to 900 keV. Amorphization occurred at electron energies from 900 keV down to 250 keV. Three distinct regions were observed: between 900 and 700 keV amorphization occurred at a constant low dose of  $\sim 4 \times 10^{21}$  e  $cm^{-2}$ ; a higher plateau at  $10^{22}$  was observed between 600 and 400 keV, and finally there was a sharp increase in the dose-to-amorphization below 400 keV, so that at 250 keV the necessary dose was an order of magnitude higher than that at 900 keV. In the region below 400 keV there was evidence of a dependence of the dose-to-amorphization on the orientation of the sample with respect to the electron beam. The results can be analyzed in terms of a composite displacement cross section dominated at high energies by displacements of Zr and Fe atoms, by displacements of Fe atoms at intermediate energies and of secondary displacements of lattice atoms by recoil impurities at low energies.

### INTRODUCTION

Intermetallic compounds undergo a crystalline-to-amorphous transformation (amorphization) under electron irradiation [1,2]. A great deal of research has been performed to find out which compounds amorphize [3], to derive empirical criteria aimed at predicting amorphization [4], and to develop universal criteria that can discern the controlling parameter for the transformation [5,6]. The question of the actual kinetic modelling of damage evolution in ordered intermetallic compounds leading to amorphization, although emphasized in several studies [7-11], has received comparatively less attention in the literature. The primary reason for this is that damage evolution in those compounds is quite complex since in addition to point defects, there are anti-site defects in two sublattices. It is possible that defect complexes exist as well, as proposed by Pedraza [8], although it is difficult to obtain direct experimental evidence for them and thereby validate the kinetic calculations based on their existence.

In addition, it is expected that the displacement energy is different in the two sublattices as is the case for ceramic materials [12]. In pure metals and solid solutions the displacement energies are determined in situ in the High Voltage Electron Microscope (HVEM) by measuring the threshold electron energy for the formation of visible damage such as dislocation loops [13]. The displacement energy is then the maximum transferrable fraction of the threshold electron energy. Using this method the orientation dependence of the damage can be explored as well [14]. Since the intermetallic compounds susceptible to irradiation-induced amorphization do not form secondary defects under irradiation [8], this method is not applicable, but amorphization can be used instead to obtain information on the displacement energies and defect properties in these compounds.

In this study  $Zr_3Fe$  was irradiated with high energy electrons, from 200 to 900 keV, at very low temperatures. This compound was selected because its amorphization behaviour has been

extensively studied under electron [11] and ion irradiation [15]. The results are analyzed in terms of the change in the displacement cross section with electron energy.

## EXPERIMENTAL METHODS

An alloy of composition  $Zr_{0.8}Fe_{0.2}$  containing the orthorhombic  $Zr_3Fe$  phase [16] was prepared by arc melting and prolonged heat treatment, using Zr and Fe of 99.95% and 99.9985% purity, respectively. A combination of cutting, mechanical polishing and electropolishing produced the electron-thin foils, as detailed in [11,15].

The sample was irradiated with high energy electrons, ranging from 200 to 900 keV in the Kratos HVEM at Argonne National Laboratory, at temperatures of 23-30 K. All irradiations were performed in the same grain (with one exception detailed below), at the same orientation. The dose rates did not vary by more than a factor of 2 from one electron energy to the other, and as shown in [11], the dose rate effect on the dose-to-amorphization at those low temperatures is relatively small. Bright-field electron micrographs and diffraction patterns from the region of interest were recorded at regular intervals during irradiation. The beam heating was estimated to be  $< 10$  K. Vacuum during the experiments was better than  $6 \times 10^{-7}$  torr.

The electron dose measurements were described in [5,11]. In this case, since we were concerned with the dose necessary to reach an amorphous diameter of 0.3  $\mu\text{m}$ , the peak dose rate was utilized in the evaluation of the dose. It is estimated that the drop-off in the dose from the center of the beam to a radius of 0.15  $\mu\text{m}$  is less than 5%. Post-irradiation examinations were conducted at Chalk River Laboratories, in a Philips CM-30 transmission electron microscope equipped with STEM/EDX and operated at 295 keV.

## RESULTS

The results are summarized in figure 1, where the dose (in  $\text{e cm}^{-2}$ ) to reach an amorphous diameter of 0.3  $\mu\text{m}$  is plotted against electron energy. The error in the dose measurements has been estimated to be in the range 5-20%. The results presented in figure 1 show that amorphization can occur from 900 keV down to 250 keV.

As the electron energy decreases, the dose (electron fluence) to amorphization increases. There is evidence of three distinct regions in figure 1: from 900 to 700 keV, the dose-to-amorphization remains approximately constant, increasing by a factor of 2 between 700 and 600, then again remaining constant between 600 and 400 keV, and finally increasing sharply below 400 keV. The stages in the dose-to-amorphization appear to correspond with the decrease in the displacement cross sections for Zr and Fe calculated by Oen [17], if a displacement energy of 24 eV is used, as seen in figure 2. It is then possible that the three regimes are broken down as follows:

- a. above 700 keV both Zr and Fe atoms are displaced, leading to a high displacement rate and fast amorphization.
- b. between 600 and 400 keV only Fe atoms are displaced, increasing the electron dose to accumulate the necessary amount of damage.
- c. below 400 keV, the contribution of secondary displacements from impurity atoms starts to become important [18].

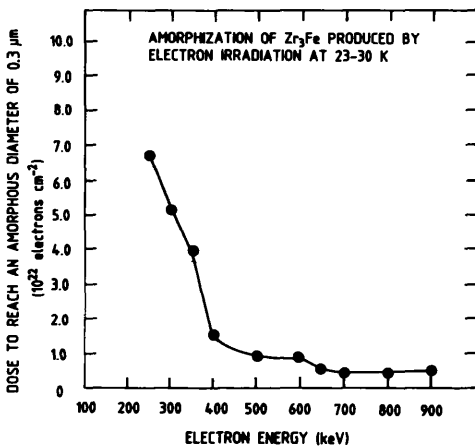


Figure 1:  
Electron dose required to produce amorphization in  $Zr_3Fe$  as a function of the energy of the incident electrons.

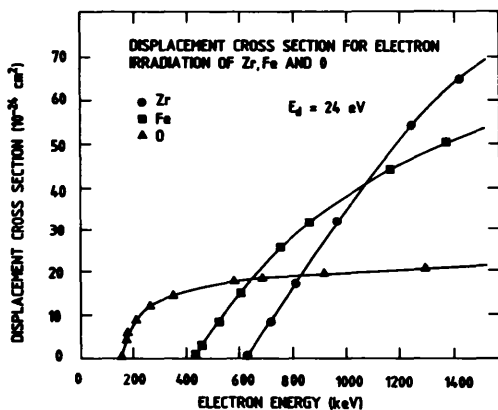


Figure 2:  
Calculated displacement cross sections from Zr, Fe and O at various incident electron energies [17]. In the calculation of the displacement cross sections a value of  $E_d = 24$  eV was used for Zr, Fe and O.

An additional feature is that we observed a dependence of the dose-to-amorphization on the orientation of the sample relative to the electron beam at low electron energies. This is apparent in figure 3a, where the beam was centered on a triple junction of three  $Zr_3Fe$  grains, and irradiated at 250 keV. This was the only irradiation series that was performed in a different grain and at a different orientation from the other ones. The three grains were identified by both compositional and diffraction analysis as being orthorhombic  $Zr_3Fe$ . One grain has turned completely amorphous while the other grains show no signs whatsoever of amorphization (as evidenced by diffraction analysis) nor of any other form of damage upon post-irradiation examination. The dependence of amorphization on sample orientation can also be seen in figure 3b from an irradiation performed at 300 keV: the amorphous spot does not exactly follow the shape of the beam, but contains "wisps" of amorphous material (arrowed) in directions that follow the bend contours of the thin foil sample. Such dependence disappears above 400 keV. An orientation dependence of the dose-to-amorphization under

electron irradiation has also been observed by Mori et al in  $Zr_3Al$  [19], but at higher electron energies. This orientation dependence can be qualitatively explained if the damage-producing process operates preferentially along particular lattice directions, that is, if the displacement energy is orientation-dependent.

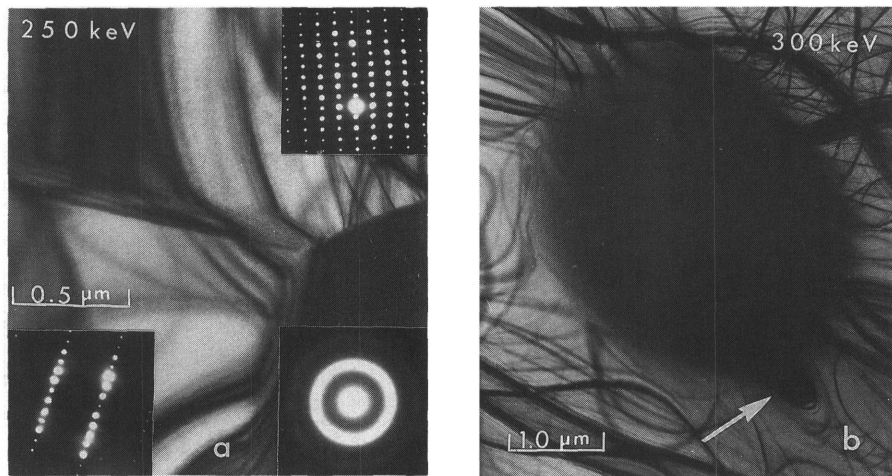


Figure 3: Bright-field electron micrographs (and associated diffraction patterns in (a)) of  $Zr_3Fe$  irradiated at 23-30 K with electrons having the following energies (a) 250 keV, (b) 300 keV.

## DISCUSSION

Amorphization of ordered intermetallic compounds under electron irradiation results from the damage to the lattice that follows the production of Frenkel pairs (vacancy + interstitial) and anti-site defects [20]. This in effect accumulates energy in the lattice in the form of an increase in the concentration of point defects and/or a higher degree of chemical disorder. The dose-to-amorphization is then determined by the damage accumulation kinetics, resulting from the balance between damage production and annealing.

Chemical disordering under irradiation can arise from the production of Frenkel pairs through a replacement collision sequence (RCS) along a mixed row of atoms or from subsequent point defect reactions such as random recombination [21] or defect conversion [22]. While it is possible (although unlikely) to create point defects without creating chemical disorder, it is not possible to create chemical disorder without displacing atoms from their sites. If we assume that amorphization is caused by a combination of chemical disordering and point defects, then the observation of amorphization means that atomic displacements are being produced.

In this experiment we observed irradiation-induced amorphization of  $Zr_3Fe$  with 250 keV electrons. There are two possibilities to explain this:

1. Amorphization occurs by a direct displacement mechanism of the Zr and/or the Fe atoms. Since the maximum energies that can be transferred from 250 keV electrons to Zr and Fe are 7 and 12 eV respectively, one of the displacement energies for either Zr or Fe in  $Zr_3Fe$  would have to be at least that low.

2. Amorphization occurs by a secondary displacement mechanism. Electrons at 250 keV can transmit a much higher energy to light element impurities such as C or O. For example, the maximum energy transferred by a 250 keV electron to an O atom is 42 eV, compared to 7 and 12 eV for Zr and Fe atoms, respectively. The impurity atom can then transfer a much larger portion of its energy to the lattice atoms.

This experiment has multiple uncertainties and unknown parameters that do not allow us to unambiguously distinguish between the two possibilities. The light element impurity level is not known precisely. Although the Zr and Fe used for making the alloys have fairly low impurity levels, the possibility that impurities (such as oxygen) have been introduced during the alloy preparation cannot be discarded. Preliminary measurements using an elastic-recoil detection technique indicate oxygen levels of 1-3 at% in the bulk of the alloy, hence a value of 1 at% was used in the present analysis. The displacement energies for Zr, Fe or O in  $Zr_3Fe$  are not known and the number of Fe/Zr secondary displacements per O displacement, is also not known. Under these circumstances, the following analysis should be viewed as preliminary, necessitating independent confirmation and further experimental observations.

Considering both primary and secondary displacement mechanisms, the total dose  $D$ , expressed as displacements per atom (dpa), in a multi-component alloy is given by:

$$D = \Phi t(E) \sum_i x_i \sigma_d^i(E_d^i, E) + \sum_j x_j \sigma_s^{j \rightarrow i}(E_d^i, E_{m i n}^{j \rightarrow i}, E) \bar{v}_{j \rightarrow i}(E) \quad (1)$$

Here  $\Phi t(E)$  is the electron fluence,  $x_i$  is the concentration of alloying element  $i$ ,  $E_d^i$  is the displacement energy for element  $i$  in the compound,  $E_{m i n}^{j \rightarrow i}$  is the minimum energy for impurity  $j$  (of concentration  $x_j$ ) to impart  $E_d^i$  to atom  $i$  and  $\bar{v}_{j \rightarrow i}(E)$  is the average number of displacements in sublattice  $i$  caused by a secondary displacement event initiated by impurity  $j$ .  $\sigma_d^i(E)$  is the displacement cross section for element  $i$  in the compound and  $\sigma_s^{j \rightarrow i}(E_d^i, E_{m i n}^{j \rightarrow i})$  is the scattering cross section for an energy transfer from electron energy  $E$  to impurity  $j$  that is greater than  $E_{m i n}^{j \rightarrow i}$ . The orientation dependence of the displacement and scattering cross sections is neglected in this first approximation.

Assuming that O is the major impurity, and neglecting secondary displacements in the Zr sublattice, eqn. 1 can be written as follows for  $Zr_3Fe$ :

$$D = \Phi t(E) \{0.75 \sigma_d^{Zr}(E_d^{Zr}, E) + 0.25 \sigma_d^{Fe}(E_d^{Fe}, E) + 0.01 \sigma_s^{O \rightarrow Fe}(E_d^{Fe}, E_{m i n}^{O \rightarrow Fe}, E)\} \quad (2)$$

The displacement cross sections are given by Owen [17]. If the displacement energies are known, then  $D$  for a given electron energy can be determined from eqn. 2. Because of the low temperature of the irradiations, it was assumed that no thermal annealing of the defects occurred. If the same amorphization mechanism is operative at all energies, the dose  $D$  calculated from eqn. 2 should be independent of the electron energy. The displacement energies of the Zr and Fe atoms were adjusted to give the smallest variation in  $D$  from 250 to 950 keV. The set that gave the best results was  $E_d^{Zr} = 24$  eV and  $E_d^{Fe} = 14$  eV. By comparison, using  $E_d^{Zr} = 24$  eV and  $E_d^{Fe} = 24$  eV yielded values for  $D$  that were reasonably constant at high electron energies but dropped off appreciably at low electron energies.

## CONCLUSIONS

1)  $Zr_3Fe$  undergoes amorphization when irradiated with high energy electrons ranging from 900 to 250 keV at 23-30 K.

2) The dose-to-amorphization (in electrons  $cm^{-2}$ ) increases as the electron energy decreases. Three distinct regions were observed, two flat plateaus from 900-700 and 600-400 keV and a sharp increase below 400 keV.

3) The dose-to-amorphization (in electrons  $\text{cm}^{-2}$ ) at low electron energies, depends strongly on the orientation of the sample relative to the electron beam.

4) The results can be analyzed in terms of a composite displacement cross section, that considers the effect of secondary displacement of lattice atoms via light element impurities.

5) The results of this work show that there is potential for using irradiation-induced amorphization as a probe to study defect properties in intermetallic compounds.

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