

ANL/MSD/CP-- 88674  
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CONF-951155--72  
FEB 08 1996  
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**Influence of Stacking Faults and Alloy Composition on Irradiation Induced Amorphization of ZrCr<sub>2</sub>, ZrFe<sub>2</sub> and Zr<sub>3</sub>(Fe<sub>1-x</sub>Ni<sub>x</sub>)\***

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December 1995

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Paper presented at the 1995 Fall Meeting of the Materials Research Society, Boston, MA, November 27-December 1, 1995.

This research project was funded mainly through a CANDU Owners Group (COG) contract.

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## INFLUENCE OF STACKING FAULTS AND ALLOY COMPOSITION ON IRRADIATION INDUCED AMORPHIZATION OF $ZrCr_2$ , $ZrFe_2$ AND $Zr_3(Fe_{1-x},Ni_x)$

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### ABSTRACT

The Zr-based intermetallic compounds  $ZrCr_2$ ,  $ZrFe_2$  and  $Zr_3(Fe_{1-x},Ni_x)$  were irradiated with high energy electrons at the HVEM/Tandem facility at Argonne National Laboratory to study their amorphization behavior. Although  $ZrCr_2$  and  $ZrFe_2$  have the same Laves phase C15 fcc crystal structure, their critical temperatures for amorphization under electron irradiation were 180 K and 80 K, showing that the substitution of Cr for Fe in the sublattice had a marked effect on the annealing characteristics of the material. The low temperature dose to amorphization was higher in  $ZrFe_2$  than in  $ZrCr_2$  by a factor of two. The presence of a high density of stacking faults had a strong effect on amorphization in both compounds causing the critical temperature to be increased by 10-15 K. By contrast, the addition of Ni to  $Zr_3(Fe_{1-x},Ni_x)$  had no effect on amorphization behavior for  $x=0.1$  and  $0.5$ . These results are discussed in terms of current models of amorphization based on defect accumulation and the attainment of a critical damage level, such as given by the Lindemann criterion.

### INTRODUCTION

Amorphization of intermetallic compounds under irradiation is still a topic of great interest. It consists of the loss of long range topological order, as measured by the disappearance of the spot diffraction pattern and the appearance of a ring pattern characteristic of the amorphous phase [1]. The conditions under which this transformation occurs under electron, ion and neutron irradiation have been extensively studied [2,3]. It has been shown that a minimum dose which increases exponentially with temperature is required before amorphization can occur. Amorphization has also been shown to occur preferentially at lattice defects such as dislocations [4], anti-phase boundaries [5] and free surfaces [6].

In this paper we report on experiments that were conducted with the aim of increasing this base of knowledge. We first studied the amorphization behavior of  $ZrFe_2$  and  $ZrCr_2$  under electron irradiation. These compounds are of interest to the nuclear industry [3] and have also been proposed as possible hydrogen storage compounds [7]. We determined the amorphization kinetics

and the dose to amorphization versus temperature. We also assessed the influence of a high density of stacking faults on the amorphization process.

We also report on our study of the influence of internal stoichiometry  $x$  on amorphization behavior of  $Zr_3(Fe_{1-x},Ni_x)$  under electron irradiation.

These results are discussed in terms of current amorphization models.

## EXPERIMENTAL METHODS

Thin foil samples containing  $Zr_3(Fe_{1-x},Ni_x)$  with  $x = 1, 0.9$  and  $0.5$ ,  $ZrCr_2$  and  $ZrFe_2$  were prepared by arc melting from the pure metals. The materials utilized had the following purity: Zr 99.8%, Ni 99.98%, Cr 99.99%, Fe 99.98%. After arc melting the samples were then annealed to produce the desired phases [10]. The samples were then mechanically polished and TEM-size disks for electropolishing were prepared by spark-cutting or punching. Electron transparent thin foils were then prepared by electropolishing with a 10% perchloric acid solution in methanol kept at  $-30$  C.

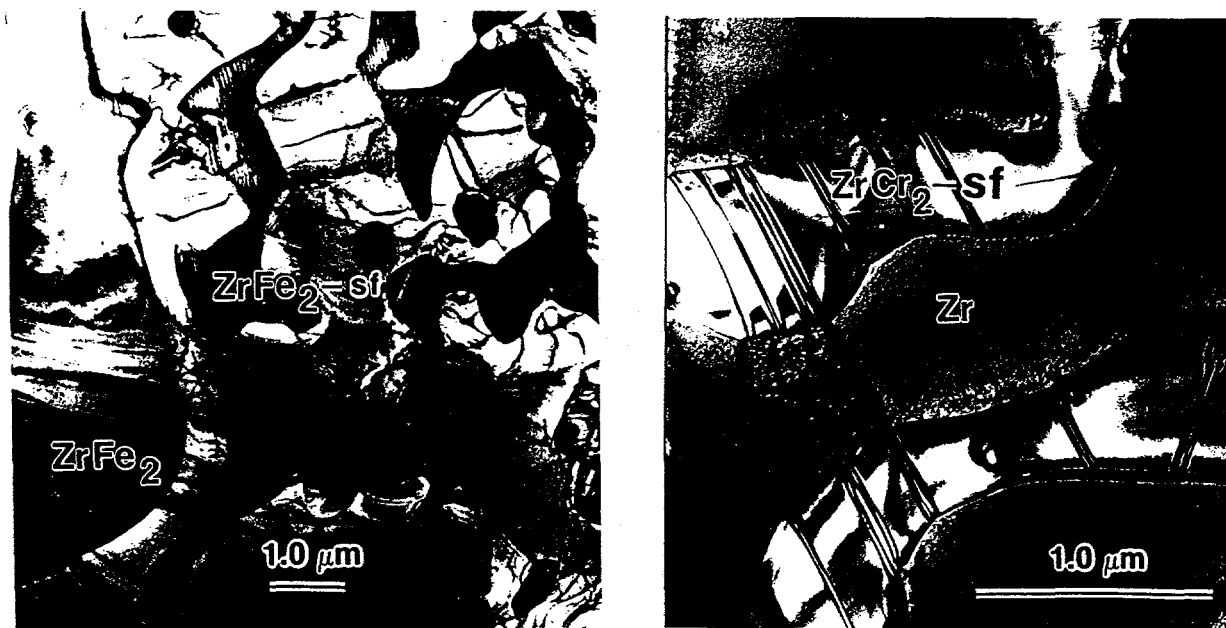


Figure 1: Bright field micrographs of (a)  $ZrFe_2$  and  $ZrFe_2$ -SF and (b)  $ZrCr_2$ -SF. The SF phases have a higher stacking fault density.

The samples were examined prior to irradiation in the Philips CM-30 microscope at Chalk River Laboratory and in the Philips 420 microscope at the Materials Characterization Laboratory at Penn State or at the Jeol 100 CX at Argonne National Laboratory. The phases present were identified by EDX and diffraction analysis. Specific areas were then identified for later irradiation. Pre irradiation examination revealed that the C15 fcc Laves phase had formed in both the  $\text{ZrCr}_2$  and the  $\text{ZrFe}_2$  samples. Both samples however exhibited two variants of the Laves phase, one with a higher stacking fault density than the other. Figure 1 (a) shows the two variants of the C15 structure for the  $\text{ZrFe}_2$  sample, denoted  $\text{ZrFe}_2\text{-SF}$  and  $\text{ZrFe}_2$ . In figure 1 (b), the high-stacking fault density phase  $\text{ZrCr}_2$ : (called here  $\text{ZrCr}_2\text{-SF}$ ) is seen. The  $\text{Zr}_3(\text{Fe}_{1-x}\text{Ni}_x)$  samples were shown to have the orthorhombic phase as  $\text{Zr}_3\text{Fe}$  [9]

Electron irradiations at 0.9 MeV were performed in the Kratos HVEM Facility in the Electron Microscopy Center at Argonne National Laboratory. The regions previously identified in each sample were irradiated at several temperatures until amorphous. For the purposes of this experiment the dose to amorphization was defined as the electron dose necessary to create an amorphous zone large enough so that using the smallest diffraction aperture ( $0.3 \mu\text{m}$ ) it was possible to obtain a spotless ring diffraction pattern. Careful beam dosimetry allowed us to also study the effect of dose rate on amorphization using the method described in [10].

## RESULTS

The electron dose to amorphization (in  $\text{electron.cm}^{-2}$ ) versus irradiation temperature for  $\text{Zr}_3(\text{Fe}_{1-x}\text{Ni}_x)$  was determined for  $x=0, 0.1$  and  $0.5$ . No difference was found between the curves for  $x=0, 0.1$  and  $0.5$ , that is, both the critical temperature and the critical dose were identical in the three cases. It was also observed that at a lower dose rate the amorphization domain of the three different compositions was diminished by approximately 10-20 K, in agreement with previous results [10].

The dose to amorphization against temperature for  $\text{ZrCr}_2$  and  $\text{ZrFe}_2$  is shown in figure 2. The shape of the curve is similar to others reported in the literature. At low temperature, the dose to amorphization does not vary with temperature, and as the temperature increases there is an exponential increase of the dose to amorphization. We term the dose to amorphization at low temperature the *critical dose for amorphization* and the temperature beyond which amorphization ceases to be possible the *critical temperature for amorphization*.

The results show that there is a difference of 100 K in the critical temperature for amorphization under electron irradiation of  $\text{ZrCr}_2$  and  $\text{ZrFe}_2$ , even though they have the same crystal structure. The critical dose for amorphization of  $\text{ZrFe}_2$  is also double that of  $\text{ZrCr}_2$ . Both of these results indicate that it is more difficult to amorphize  $\text{ZrFe}_2$  than  $\text{ZrCr}_2$ .

Another interesting feature is that the critical temperatures are higher by 10 K in the phases with a high density of stacking faults. Also a higher density of stacking faults decreases the critical dose in  $\text{ZrFe}_2$  by half, but does not change the critical dose of  $\text{ZrCr}_2$ . Finally, we observe that the curve for the  $\text{ZrFe}_2\text{-SF}$  phase exhibits a "step" (two-fold increase) to a higher plateau at a temperature corresponding to the critical temperature for the low stacking fault density phase. It should be

corresponding to the critical temperature for the low stacking fault density phase. It should be noted that no preferential amorphization was detected near the stacking faults during in-situ irradiation, as seen for example by Mori and Fujita [6] on dislocations in NiTi. In our case this could be due to a lack of resolution in the HVEM.

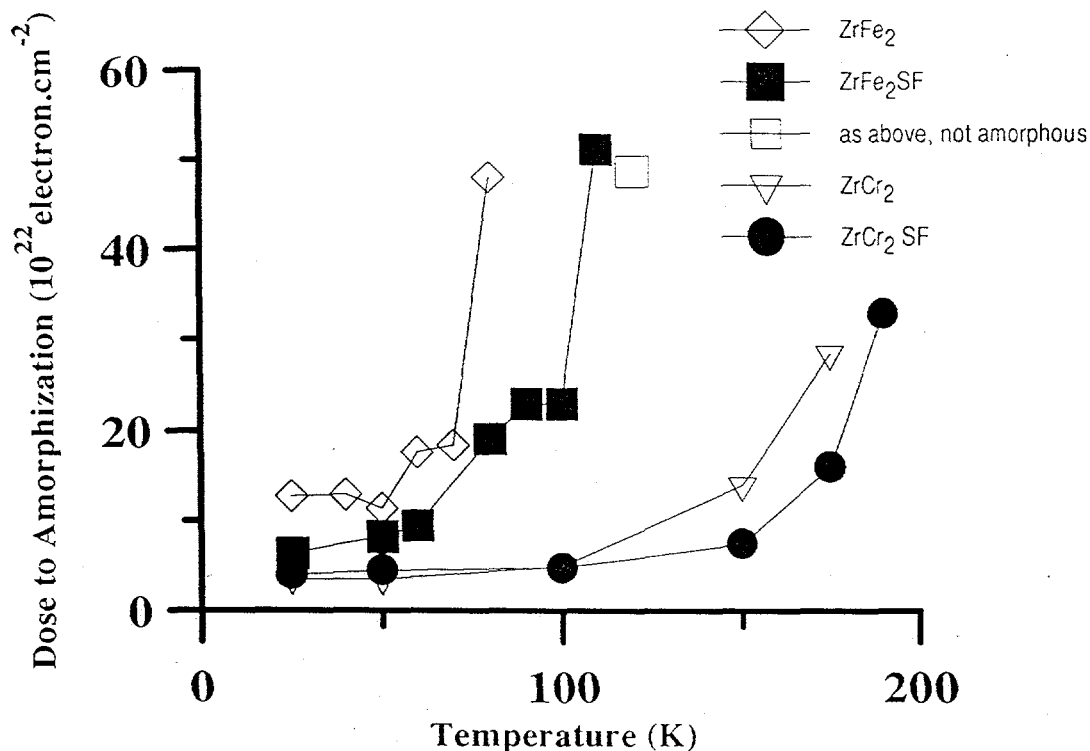


Figure 2: Dose to amorphization under electron irradiation versus temperature for ZrCr<sub>2</sub> and ZrFe<sub>2</sub> with and without a high density of stacking faults

## DISCUSSION

The results presented here can be explained in the context of an amorphization model based on the slow accumulation of defects in the crystalline structure until the damage accumulated is so great that the irradiated crystalline structure is unstable with respect to the amorphous phase. As mentioned before [11], this is equivalent to the exchange of long range topological order in order that short range chemical order can be maintained. The damage level at which such transformation becomes favorable depends on the difference in free energy between the crystalline and amorphous phases. It has been shown before that because the transformation occurs quickly compared to the irradiation time, once conditions are ripe, the amorphization process is controlled by the kinetics of defect accumulation in the lattice.

The determination of the critical level of damage for amorphization can be done for example using the Lindemann criterion for amorphization proposed by Okamoto and Lam [12]. This criterion states that when the mean square static displacement due to the sum of all defects present in the

lattice (caused by irradiation or not) reaches a critical value, the material becomes amorphous. This approach has the advantage of unifying, from the point of view of the critical damage level, all the different contributions to lattice strain, such as point defects, anti-site defects, dislocations, and other defects.

The Lindemann criterion cannot however predict or explain kinetic curves such as those shown in figure 3. In order to rationalize the features in the dose-to amorphization curve versus temperature, such as the critical dose, the critical temperature and the steps observed close to  $T_c$ , it is necessary to model the kinetics of defect production and accumulation. It is also not possible to unify all the different defects since the critical temperatures and the steps will be associated with the motion of different point defects at different temperatures.

If the critical level of damage is  $L_{crit}$ , then:

$$L_{crit} = (G - A)t_{irr}^{am} \quad (1)$$

where  $G$  is the damage rate,  $A$  is the annealing rate and  $t_{irr}^{am}$ . From equation 1 we define the critical temperature as the temperature at which  $G = A$ . It is then clear that a higher dose rate will imply a higher critical temperature. The steps observed in the dose to amorphization can be explained by observing that for any ordered intermetallic compound there are at least six different defects: vacancies on either sublattice, interstitials on either sublattice, and anti site defects on either sublattice. The defects that are not mobile at the irradiation temperature will then accumulate in the lattice. If for example at 25 K, there are two types of defects accumulating in the lattice, amorphization can be achieved at the critical dose for the compound. As the temperature is increased, a point is reached where one of the defects becomes mobile and cannot contribute anymore to the accumulation of damage. A step is then observed, because although amorphization is still possible to achieve using the other (immobile) defect, the damage rate is lower. It is then comprehensible that the dose to amorphization increases by a factor of two at that point.

As far as the difference between the stacking fault and non-stacking fault material, the difference in amorphization behavior can be explained by assuming that the stacking faulted material had a lower  $L_{crit}$ . This is because according to the Lindemann criterion a stacking fault would also represent static displacement in the lattice. In other words, the presence of the stacking faults facilitated amorphization because less energy had to be accumulated in the lattice because it already had some damage before irradiation started.

## CONCLUSIONS

1. The amorphization behavior of the compounds  $ZrCr_2$  and  $ZrFe_2$  was studied. It was found that the critical temperature for amorphization of  $ZrFe_2$  is 80 K while that of  $ZrCr_2$  is 180 K. The critical amorphization dose for  $ZrFe_2$  is twice as much that of  $ZrCr_2$ .

2. The presence of a high density of stacking faults increased the critical temperature by 10-15 K in both  $ZrFe_2$  and  $ZrCr_2$ . The critical dose was the same for  $ZrCr_2$  and  $ZrCr_2$ -SF but that of  $ZrFe_2$ -SF was half that of  $ZrFe_2$ .

3. The addition of Ni in  $Zr_3(Fe_{1-x},Ni_x)$  had no effect on either the critical temperature or critical dose for  $x=0, 0.1$  and  $0.5$ .

## ACKNOWLEDGMENTS

The authors would like to thank D.Philips and H.H.Plattner of Chalk River Laboratories for their expert technical assistance, as well as E.Ryan and S.Ockers of Argonne National Laboratories, for their excellent technical support during the experiments. J.A.Faldowski is grateful for the support from the Division of Educational Programs for his thesis work. This research program was funded through a Candu Owners Group (COG) contract. We wish to thank the members of Working Party 32 Committee for their financial support and interest in the program.

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