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AMORPHIZATION KINETICS OF Zr $(Cr,Fe)_2$ UNDER ION IRRADIATION*

A. T. Motta[1], L. M. Howe[2] and P. R. Okamoto[3]

[1]Department of Nuclear Engineering, The Pennsylvania State University
University Park, PA 16802

[2]AECL Research, Reactor Materials Research Branch
Chalk River Lab., Chalk River, Ontario, Canada K0J 1J0

[3]Materials Science Division, Argonne National Laboratory
Argonne, IL 60439

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A.T. MOTTA[1], L.M. HOWE[2] AND P.R. OKAMOTO[3]
[1]Department of Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802, USA
[2]AECL Research, Reactor Materials Research Branch, Chalk River Lab., Chalk River, Ontario, Canada K0J 1J0
[3]Materials Science Division, Argonne National Lab., Argonne, IL 60439, USA

ABSTRACT

Thin foils of Zircaloy-4 were irradiated with 350 KeV ^{40}Ar ions in the dual ion beam/HVEM facility at Argonne National Laboratory at 300 - 650 K. The irradiation-induced amorphization of the intermetallic precipitates Zr $(Cr, Fe)_2$ and Zr_2 (Ni, Fe) was studied in-situ. For Zr $(Cr,Fe)_2$ precipitates the dose-to-amorphization was found to increase exponentially with temperature, with a critical temperature of about 650 K. The amorphization morphology was shown to be homogeneous, with no preferential site for nucleation, in contrast to neutron-irradiation amorphization which started at the precipitate-matrix interface. For Zr_2 (Ni,Fe) precipitates it was found that amorphization occurred at 550 K and 600 K, whereas in neutron irradiation no amorphization has been observed at those temperatures. The results are discussed in the context of the previous experimental results of neutron and electron irradiation and likely amorphization mechanisms are proposed.

INTRODUCTION

Most of the studies on the irradiation-induced crystalline-to-amorphous transformation have been performed using charged-particle irradiations, see ref. [1-4], for example. In that respect, the system consisting of Zr $(Cr,Fe)_2$ and Zr_2 (Ni,Fe) precipitates in Zircaloy is interesting in that there is abundant neutron irradiation information from power reactor Zircaloy cladding. Amorphization induced by neutron, ion and electron irradiation has been observed in these precipitates [5]. Under electron irradiation amorphization occurs only below 300 K, and proceeds homogeneously throughout the material, with no associated change in chemical composition [6]. Under neutron irradiation at 350 K (calandria tube operation temperature in CANDU reactors), both Zr $(Cr,Fe)_2$ and Zr_2 (Ni,Fe) precipitates in Zircaloy-2 are found amorphous at the lowest fluences examined (equivalent to about 1 dpa) [7]. At 520-580 K, whereas Zr_2 (Ni,Fe) precipitates are crystalline, an amorphization front starts at the Zr $(Cr,Fe)_2$ precipitate-matrix interface that gradually moves into the crystalline core, the amorphous thickness increasing linearly with neutron fluence [8,9]. There is an associated release of iron from the amorphous layer into the matrix. Above 600 K, the Zr $(Cr,Fe)_2$ precipitates do not go amorphous, even at very high doses (up to 64 dpa at 640 K). The electron and neutron irradiation results have been explained by different amorphization mechanisms, peculiar to each irradiation [10,11].

Although Zr $(Cr,Fe)_2$ and Zr_2 (Ni,Fe) precipitates have been found amorphous after ion irradiation, [12] there is much less data available than for neutron and electron irradiation. Considerations of the kinetic aspects of the irradiation-induced crystalline-to-amorphous transformation should lead to a more complete understanding of the mechanisms involved. Consequently, in this investigation in-situ ion-irradiation experiments were performed, using the dual ion beam/HVEM facility at Argonne National Laboratory (ANL), to determine the dose-to-amorphization versus temperature curve and to observe the amorphization morphology under ion irradiation.

EXPERIMENTAL DETAILS

The annealed Zircaloy-4 material used in this investigation was supplied by Centre d'Etudes Nucleaires de Grenoble (CENG). Previous irradiations had been performed at CENG using this same material [5]. Electron transparent foils were prepared from 0.30 cm diameter discs by conventional electropolishing techniques, using a solution of 10% perchloric acid in methanol, kept at 233 K.

The foils were characterized using the Philips CM30 electron microscope at Chalk River Laboratories (CRL), which operated at 300 kV. The samples were irradiated with 350 keV ^{40}Ar ions at 300 - 650 K in the dual-ion-beam HVEM facility at ANL. The progress of the crystalline-to-amorphous transformation was followed in-situ, by recording the changes in both the bright and dark field images of the precipitates (disappearance of bend contours and stacking faults) and in the diffraction pattern, which changed from a spot to a ring pattern. During the recording stage, 300 keV electrons were used. The precipitates irradiated were the same precipitates that were characterized previously. On average, three or four precipitates were followed at each irradiation temperature. The ion dose was carefully recorded using a Faraday cup. Temperature control was achieved using a heating holder, that featured a thermocouple placed close to the specimen cup.

Post-irradiation examination at CRL, on the precipitates previously irradiated and characterized, focused on the search for any chemical compositional variations. This was done by checking the Fe/Cr Fe/Ni, (Fe+Cr)/Zr and (Fe+Ni)/Zr ratios in the precipitates. The degree of amorphization undergone by the precipitates in the sample was also verified.

RESULTS AND DISCUSSION

The results of pre-irradiation examination in the TEM showed that in addition to the Zr $(Cr,Fe)_2$ precipitates commonly found in Zircaloy-4, a few Zr_2 (Ni,Fe) precipitates were also present. Since Zircaloy-4 contains very little Ni, these observations are not unexpected. While the Cr/Fe atomic ratio in the Cr-rich precipitates was on the average 1.6, the Ni/Fe ratio in the Ni-rich precipitates was approximately 0.07. The $Zr(Fe,Cr)_2$ precipitates are a $MgZn_2$ structural type Laves phase with a hexagonal crystal structure, C14, with a = 0.504 nm and c = 0.816 nm. The electron diffraction patterns from the $Zr_2(Ni,Fe)$ precipitates could be indexed with the C16 body-centered-tetragonal structure, with a = 0.646 nm and c = 0.523 nm.

Examples of the irradiation-induced amorphization at 550 K of the Ni-rich and Cr-rich precipitates are shown in Figures 1 and 2. Figure 1 contains a cluster composed of a $Zr(Cr,Fe)_2$ (A) and a $Zr_2(Ni,Fe)$ (B) precipitate, whereas Figure 2 only contains the former. Initially, stacking faults are present in the $Zr(Cr,Fe)_2$ precipitates and twins exist in the $Zr_2(Ni,Fe)$ precipitates. As the irradiation proceeds, the precipitates undergo amorphization. The stacking-fault and twin contrast gradually disappears, while the diffraction patterns change from discrete spots to diffuse rings. $Zr(Cr,Fe)_2$ was completely amorphous after irradiation at 550 K with 3.4×10^{14} Ar ions cm^2, and a slightly higher ion dose of 4.3×10^{14} Ar ions cm^{-2} was required to completely amorphize $Zr_2(Ni,Fe)$.

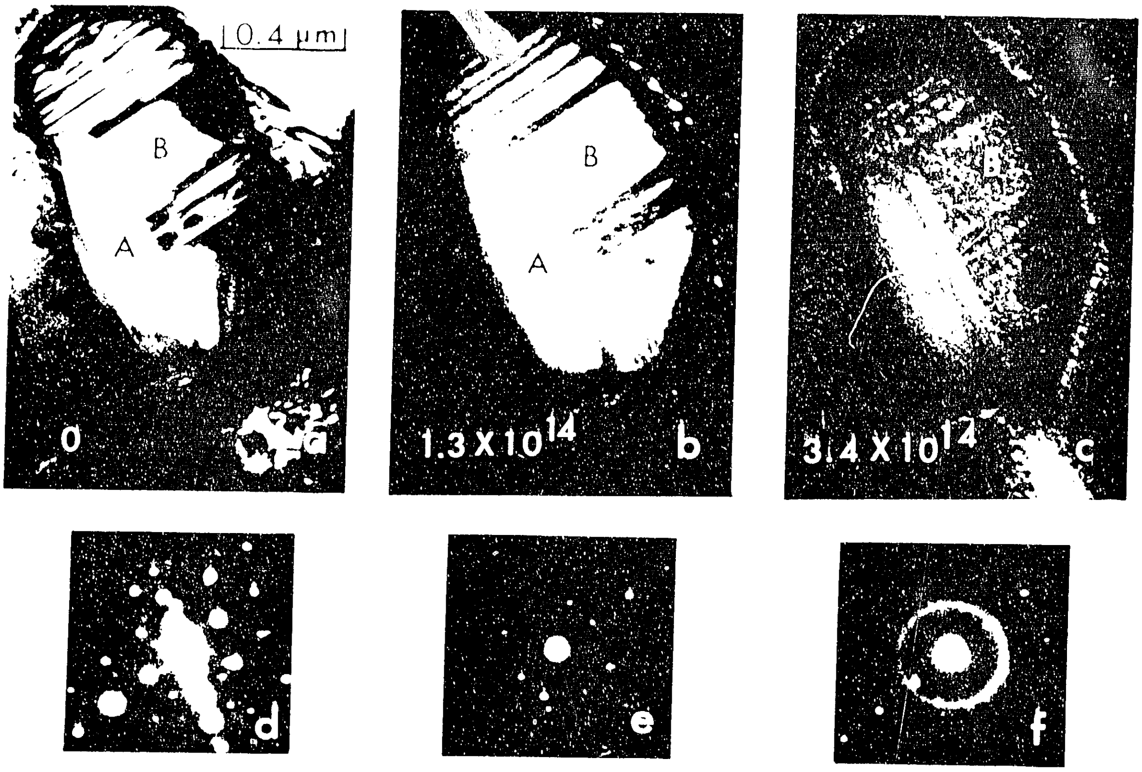

FIGURE 1: Bright-field electron micrographs (a,b,c) and corresponding diffraction patterns (d,e,f) of $Zr(Cr,Fe)_2$ (A) and $Zr_2(Ni,Fe)$ (B) precipitates in Zircaloy-4 irradiated at 500 K with 350 keV ^{40}Ar ions. Irradiation doses were 0 (a,d), 1.3×10^{14} ions cm^{-2} (b,e) and 3.4×10^{14} ions cm^{-2} (c,f).

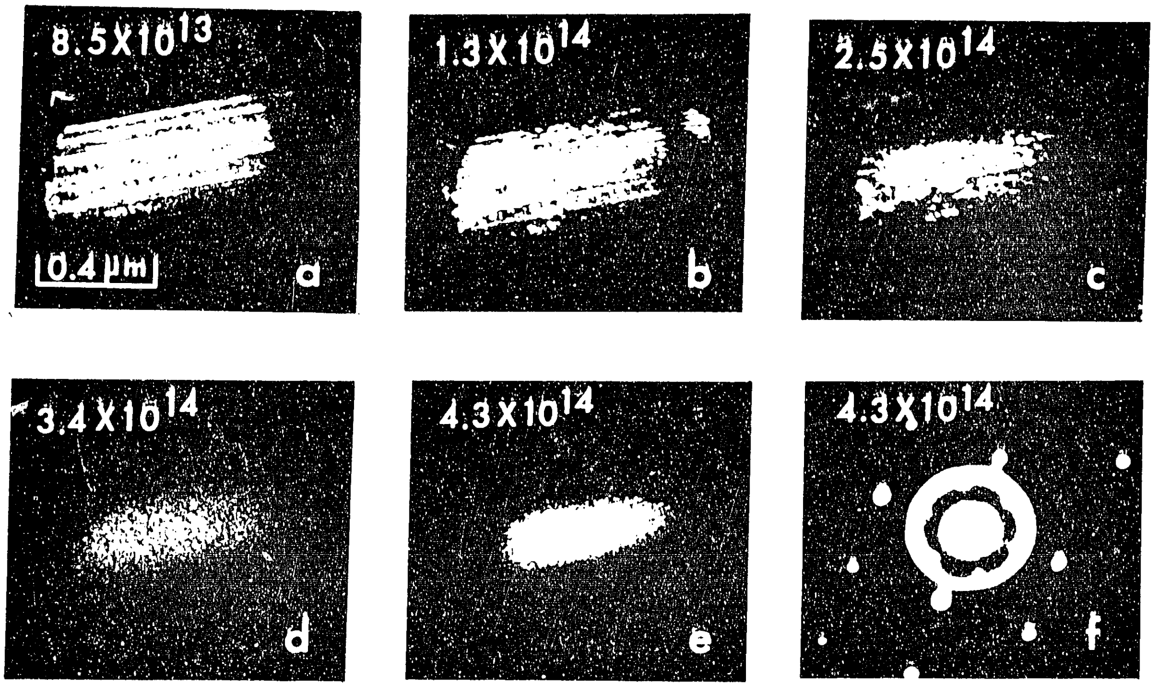

FIGURE 2: Dark-field electron micrographs (a-e) and diffraction pattern (f) of a $Zr(Cr,Fe)_2$ precipitate in Zircaloy-4 irradiated at 500 K with 350 keV ^{40}Ar ions to doses of 8.5×10^{13} (a), 1.3×10^{14} (b), 2.5×10^{14} (c), 3.4×10^{14} (d) and 4.3×10^{14} ions cm^{-2} (e,f).

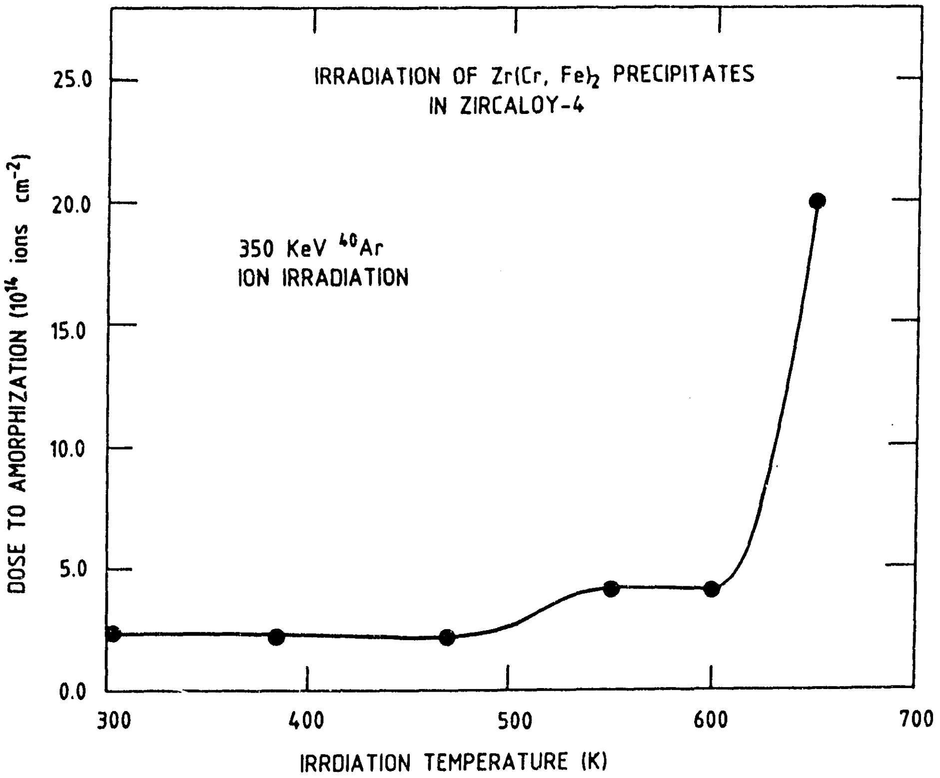

FIGURE 3: Irradiation dose required to produce amorphization versus irradiation temperature for 350 keV ^{40}Ar ion irradiation of $Zr(Cr,Fe)_2$ precipitates in Zircaloy-4.

It can be seen that amorphization does not start preferentially either at the precipitate-precipitate interfaces, nor does it start at the twins or stacking faults, but occurs in a homogeneous fashion throughout the precipitates. The word "homogeneous" here means that all parts of the precipitate amorphize in the same way, at the same dose, except for inhomogeneities in the damage deposition. The contrast features apparent in Figure 1(a-c) and Figure 2 (b,c) suggest that discrete amorphous regions are continuously developing during the irradiation. The proposed amorphization mechanism during ion irradiation is direct amorphization in the cascade core complemented by cascade superposition at the cascade periphery, eventually leading to a complete coverage of the material and total amorphization. Detailed studies on collision cascades in Zr_3Fe are in support of this model [13-15]. It should be noted that, although faint, the stacking-fault contrast is present until the end of the irradiation, suggesting that the bulk of the transformation takes place relatively quickly towards the end of the irradiation time, as also reported in a previous investigation [6].

Similar amorphization was observed at all the temperatures studied. The experimental results of the dose-to-amorphization against temperature are shown in Figure 3. These results are valid for $Zr\ (Cr,Fe)_2$ precipitates and only partially true for $Zr_2\ (Ni,Fe)$, since this latter precipitate was not always identified in the samples prior to the irradiation. Wherever identified as such, the $Zr_2\ (Ni,Fe)$ precipitates behaved in the same way as the $Zr\ (Cr,Fe)_2$ precipitates. The dose is given in units of ions cm^{-2} rather than dpa because of the lack of data on the threshold displacement energies (E_d) in $Zr\ (Cr,\ Fe)_2$ and $Zr_2(Ni,Fe)$. Using the TRIM-90 code and $E_d = 25$ eV, for 350 keV Ar ions implanted in $Zr\ (Cr,\ Fe)_2$ for an average flux of 5.9×10^{11} ions $cm^{-2}s^{-1}$, the average displacement rate in the first 100 nm of a thin foil is 1.3×10^{-3} $dpa.s^{-1}$.

It can be seen that the dose-to-amorphization increases abruptly with temperature between 600 and 650 K. This form of exponential dependence of the dose-to-amorphization with temperature has been observed frequently in neutron and charged particle irradiations of various intermetallic compounds [3,4,16]. The critical temperature above which amorphization does not occur for Ar ion irradiation of $Zr(Cr,Fe)_2$ is, therefore, at least 650 K, which is considerably higher than the previously reported value of 400-450 K [12]. It is interesting to note that there is a step in the dose-to-amorphization near 500 K, representing a two-fold increase in the dose-to-amorphization between 473 and 550 K. This type of step increase has been reported in other studies [13,14,17], and can be attributed to the activation of an annealing mechanism that partially offsets damage production, without completely overwhelming it. In that way damage accumulation, and thereby amorphization, can still proceed, but at a slower rate.

Post-irradiation examination revealed no change in chemical composition associated with amorphization as far as could be determined, either in the Ni-based or Cr-based precipitates. Various individual precipitates irradiated at several different temperatures were examined before and after irradiation and no change of the Fe/Cr, Fe/Ni, (Fe + Cr)/Zr or (Fe+Ni)/Zr ratios was detected. No concentration gradients within the precipitate were seen, nor any change in alloying element content detected in the Zr matrix.

The basic features of irradiation-induced amorphization of $Zr(Cr,Fe)_2$ and $Zr_2(Ni,Fe)$ precipitates in Zircaloy-4 may be summarized as follows:

a) Under electron irradiation, both types of precipitates amorphize if the irradiation temperature is lower than 300 K. Amorphization happens homogeneously and is thought to occur as a result of increased chemical disordering and a higher concentration of the less mobile point defect caused by the loss of the more mobile defect to the free surface [10].

b) Under low temperature neutron irradiation, amorphization occurs for both types of precipitates, through some combination of cascade chemical disordering and bulk point defect concentration increase. Under high temperature neutron irradiation, the Zr_2 (Ni,Fe) precipitates remain crystalline and the Zr $(Cr,Fe)_2$ precipitates amorphize, while developing a duplex structure with amorphization starting at the precipitate-matrix interface and proceeding inwards. Amorphization is thought to happen in that case by a combination of less effective cascade disordering and a departure from exact stoichiometry at the precipitate-matrix interface caused by ballistic mixing [11].

c) Under Ar ion irradiation, the Zr $(Cr,Fe)_2$ precipitates amorphize at temperatures up to 650 K while the Zr_2 (Ni,Fe) precipitates do so at least up to 600 K. Amorphization is homogeneous, and without associated changes in chemical composition. The amorphization mechanism is thought to be chemical disordering and possibly defect clustering induced by collision cascades. There is no need for a supplement from other mechanisms such as a departure from stoichiometry because due to its higher damage rate, the damage produced by ion irradiation is more effective than that produced by neutron irradiation in causing amorphization. The step in the dose-to-amorphization for $Zr(Cr,Fe)_2$ shown in Figure 3 is attributed to an annealing mechanism that reduces the rate of damage production without completely offsetting it. The critical temperature (650 K) for amorphization of $Zr(Cr,Fe)_2$ under Ar ion irradiation is close to the critical temperature (600 K) for neutron irradiation. $Zr_2(Ni,Fe)$ precipitates were found to amorphize at 550 K, and possibly at 600 K during Ar ion irradiation, whereas amorphization in this temperature range has not been observed under neutron irradiation.

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