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Crystalline–amorphous transition of $NiZr_2$, NiZr and Ni_3Zr by electron irradiation*

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Abstract

Three intermetallic compounds in the Ni–Zr system were irradiated with 1 MeV electrons in a high-voltage electron microscope over the temperature range 10–200 K. All three compounds were amorphized by the electron irradiation with varying degrees of amorphization tendency and different critical temperatures. The critical dose at 10 K and the critical temperature for amorphization were 0.22 displacements per atom (d.p.a.) and 200 K, 0.37 d.p.a and 100 K and 3.18 d.p.a. and 50 K for $NiZr_2$, NiZr and Ni_3Zr respectively. The critical dose increases from $NiZr_2$ to Ni_3Zr at all the irradiation temperatures investigated. The difference in enthalpy between the amorphous and crystalline states of these compounds, which was estimated from the Debye temperature ratio between the amorphous and crystalline states of each compound, also increases from $NiZr_2$ to Ni_3Zr. The large difference in the critical temperature of the three compounds is noteworthy, suggesting that the mobility of the point defects which are responsible for restoring the chemical order is substantially different for these compounds.

1. Introduction

The crystalline to amorphous (c–a) transition occurs in many metallic materials by a variety of solid state amorphization reactions (SSAR), such as irradiation by high-energy particles [1–3], hydrogenation [4] and mechanical alloying and annealing of multilayer thin films [5–7]. High-energy electron irradiation has been used extensively to study amorphization of intermetallic compounds by many researchers [3, 9–19]. When irradiation is carried out in a high-voltage electron microscope (HVEM), the structural change preceding the amorphization can be monitored conveniently by electron microscopy and diffraction. The structural change due to electron irradiation is well understood and is also readily examined by numerical calculations with good reliability. Therefore the electron-irradiation-induced c–a transition is well suited to study the mechanisms involved in solid state amorphization in a quantitative manner.

Efforts have been made to determine the criteria responsible for the c–a transition of intermetallic compounds irradiated by high-energy particles [8, 11–14]. The c–a transition of intermetallic compounds on irradiation has been examined by investigating many properties of the compounds, such as the solubility range, ordering energy, the composition ratio of its constituent elements, crystal structure, the relative position of constituent elements in the periodic table, etc. These factors are related to the increase in enthalpy due to irradiation effects in the crystalline state. Although a general trend exists between these properties and the amorphization tendency, further refinement is clearly needed. In addition, some incorrect conclusions have been obtained because the experiments have often been confined to higher temperature ranges. This is especially true for electron irradiation, in which nearly all point defects produced are isolated and are therefore more likely to be mobile at the irradiation temperatures, in comparison with point defect clusters produced by heavy ion irradiation. Compounds irradiated above the critical temperature for amorphization have been mislabeled as "not amorphizing". As will be shown in the present study, the presence of the critical temperature for amorphization below the temperature range obtainable by a liquid-nitrogen-cooling stage indicates that a careful re-evaluation is necessary to determine which

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intermetallic compounds can be amorphized by electron irradiation.

In addition to the enthalpy increase due to irradiation, the enthalpy difference between the amorphous and crystalline states must also be included in a consideration of the amorphization tendency. As the enthalpy increase due to irradiation must exceed the enthalpy difference, the smaller the difference, the easier the amorphization of a compound becomes. As the value of the enthalpy difference between the two states is not widely available in the literature, it was suggested that the enthalpy difference can be estimated from the Debye temperatures of a compound at two states [3]. The relationship between the Debye temperature θ_D and the enthalpy difference ΔH_c is given as

$$\Delta H_c = L_c[1-(\theta_D^a/\theta_D^c)^2] \tag{1}$$

where L_c denotes the heat of fusion and the superscripts "a" and "c" indicate the amorphous and crystalline states respectively. The heat of fusion L_c can be related to the Debye temperature and mass M according to the equation proposed by Lindemann[20]

$$L_c = kM(\theta_D^c)^2 \tag{2}$$

where k is simply a proportionality constant. Since Debye temperatures have been determined for the two states at various compositions of the Ni–Zr binary system [21–25], we have chosen three compounds of this system ($NiZr_2$, NiZr and Ni_3Zr) to examine the relation between the amorphization tendency and the Debye temperatures. The results indicate good correlation, *i.e.* the amorphization tendency increases in the order $Ni_3Zr < NiZr < NiZr_2$, and the ratio of the Debye temperatures between the amorphous and crystalline states increases in the same order.

2. Experimental details

Alloy buttons of $NiZr_2$, NiZr and Ni_3Zr were arc melted and then annealed approximately 50 K below their melting temperatures for 10 days to allow the compounds to become fully ordered in structure and homogeneous in composition. Samples for high-voltage electron microscopy were prepared by conventional jet polishing in a methanol–$HClO_4$ acid solution. The average grain size of these samples was in the range 20–100 μm depending on the compounds. Therefore a number of irradiation experiments can be performed within a single grain. The irradiation was carried out *in situ* with 1 MeV electrons in a HVEM from 10 K to the critical temperatures above which the amorphization of the corresponding compounds cannot take place. In order to keep the important experimental factors, such as thickness and orientation, constant, all irradiations for the determination of the temperature dependence of the critical dose for amorphization of the compounds were carried out using the same bend contour and at positions which were the same distance away from the edge of a hole. A fully focused electron beam, with a gaussian distribution (peak dose rate, $(1\text{–}2)\times10^{-3}$ displacements per atom (d.p.a.) s^{-1}) was used for all irradiations. In order to keep the dose rate as constant as possible, a specimen was irradiated for an appropriate time, according to the gaussian beam profile, so that the actual dose rate was nearly the same for all irradiations for the critical dose determination of an intermetallic compound. The method of determining the critical dose of each compound at a certain temperature has been described elsewhere [17]. For the calculation of the critical dose in d.p.a., the cross-sections $\sigma_{Ni}=54.88$ barns for pure Ni and $\sigma_{Zr}=31.87$ barns for pure Zr, with threshold energies of $T_d=20.7$ eV and $T_d=25$ eV respectively, were assumed according to Oen's table [26]. The total cross-sections σ_{total} $(=C_{Ni}\sigma_{Ni}+C_{Zr}\sigma_{Zr})$ for the intermetallic compounds $NiZr_2$, NiZr and Ni_3Zr were taken as the weighted average values of the cross-sections for pure Ni and Zr atoms.

3. Experimental results

The three compounds $NIZr_2$, NiZr and Ni_3Zr were irradiated by 1 MeV electrons at 10 K and were found to be amorphized with varying critical doses. The irradiation was then carried out at successfully higher temperatures to establish the temperature dependence of the critical dose and the critical temperature for amorphization for each compound.

Figures 1(A)–1(F) are typical examples of a series of micrographs and corresponding selected area diffraction (SAD) patterns, showing the progressive amorphization process of the intermetallic compound $NiZr_2$ irradiated by 1 MeV electrons at 60 K. In order to measure the long-range order parameter S and the critical dose Φ_c at a certain temperature, the specimen was tilted to a specific orientation to produce a systematic diffraction row which consists of the superlattice and fundamental spots in the SAD patterns and the corresponding single thick bend contour in the micrographs ((xxo) systematic diffraction row and (xxo) bend contour as shown in Fig. 1).

Before irradiation, there is a well-defined bend contour in the micrograph and strong (110) diffraction spot coexisting with (220) diffraction spot in the SAD pattern (Fig. 1(A)). After irradiation to a dose of 0.115 d.p.a., the bend contour becomes narrower, the ratio of the intensity of the (110) spot to that of the (220) spot decreases and a faint amorphous halo appears simultaneously (Fig. 1(B)). This indicates that chemical

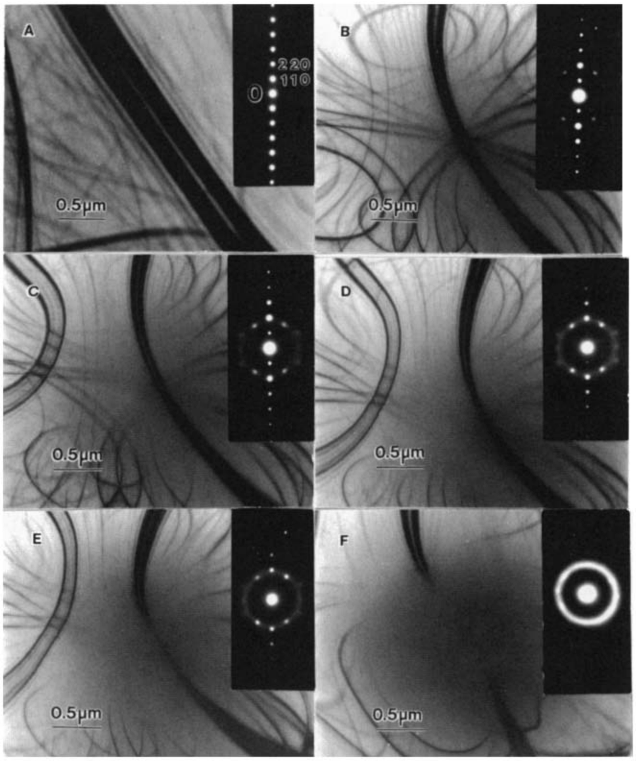

Fig. 1. Series of micrographs and corresponding selected area diffraction patterns showing the amorphization process of $NiZr_2$ irradiated by 1 MeV electrons at 60 K. The doses (determined at the center of the beam) were 0, 0.115, 0.141, 0.179, 0.217 and 0.307 d.p.a. for (A), (B), (C), (D), (E) and (F) respectively.

disordering has taken place and amorphization has started to occur. Further irradiation produces more chemical disorder, since the intensity ratio of these two spots decreases with the decrease of Bragg-Williams long range order (LRO) parameters, as confirmed by the structure factor calculation at 0.141 d.p.a. (Fig. 1(C)), almost complete chemical disorder at 0.179 d.p.a. (Fig. 1(D)) and complete chemical disorder at 0.217 d.p.a. (Fig. 1(E)), as indicated by the progressive decrease in the ratio of the intensity of the (110) spot to that of the (220) spot and the final disappearance of the (110) spot (Figs. 1(B)–1(F)). At the same time, the amorphous volume fraction increases and, finally, complete amorphization takes place, demonstrated by the progressive increase in the intensity of amorphous haloes and the final replacement of all crystal spots by fully diffuse amorphous haloes (Figs. 1(B)–1(F)). The continuous decrease in chemical ordering to zero and increase in amorphous volume fraction to unity are also implied by the fact that the bend contour becomes thinner and thinner and finally is interrupted by electron irradiation in the center region (Figs. 1(A)–1(F)). By measuring the distance between the ends of the interrupted bend contour in Fig. 1(F) and using the gaussian beam profile, it was found that the critical dose for complete amorphization of the compound $NiZr_2$ is 0.246 d.p.a. at 60 K. The other two compounds NiZr and Ni_3Zr demonstrate similar amorphization behavior on electron irradiation.

Similar experiments were carried out at various temperatures in $NiZr_2$, NiZr and Ni_3Zr and the experimental results are summarized in Fig. 2, in which the critical doses are plotted against the irradiation temperatures for all three compounds. It can be seen in Fig. 2 that the three compounds show similar temperature dependences. The critical dose is smallest at low temperature, remains constant over a certain temperature range and then increases gradually at first and finally very rapidly with temperature. The critical temperature for amorphization is defined as the temperature above which no complete amorphization can be confirmed (no interruption in a bend contour) for extended irradiation and is about 50, 100 and 200 K for Ni_3Zr, NiZr and $NiZr_2$ respectively. The critical doses for amorphization at 10 K are found to be 3.18, 0.37 and 0.22 d.p.a. respectively.

It is not apparent in Fig. 2 that there are small recovery steps between 10 K and the critical temperature. The critical dose is replotted with an enlarged vertical scale in Fig. 3 where the step between 40 and 50 K for NiZr and the step between 110 and 120 K for $NiZr_2$ are clearly seen. In addition, there may be another step (or steps) between 40 and 70 K for $NiZr_2$. The observation of a small recovery step has been reported previously in CuTi [17–19]. The experimental data are summarized together with other properties of the compounds $NiZr_2$, NiZr and Ni_3Zr in Table 1.

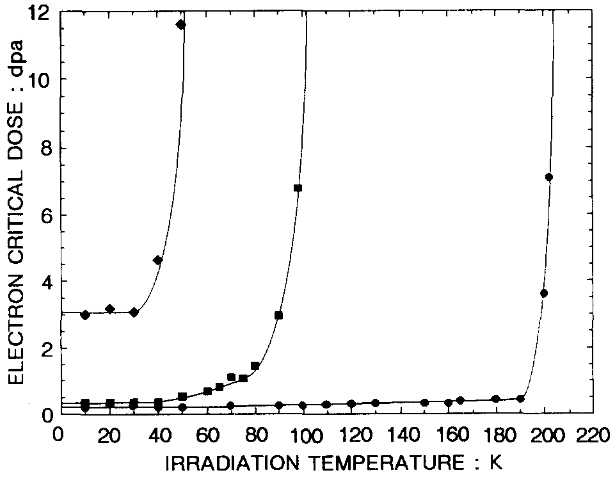

Fig. 2. Critical dose for amorphization *vs.* irradiation temperature for Ni_3Zr (◆), NiZr (■) and $NiZr_2$ (●).

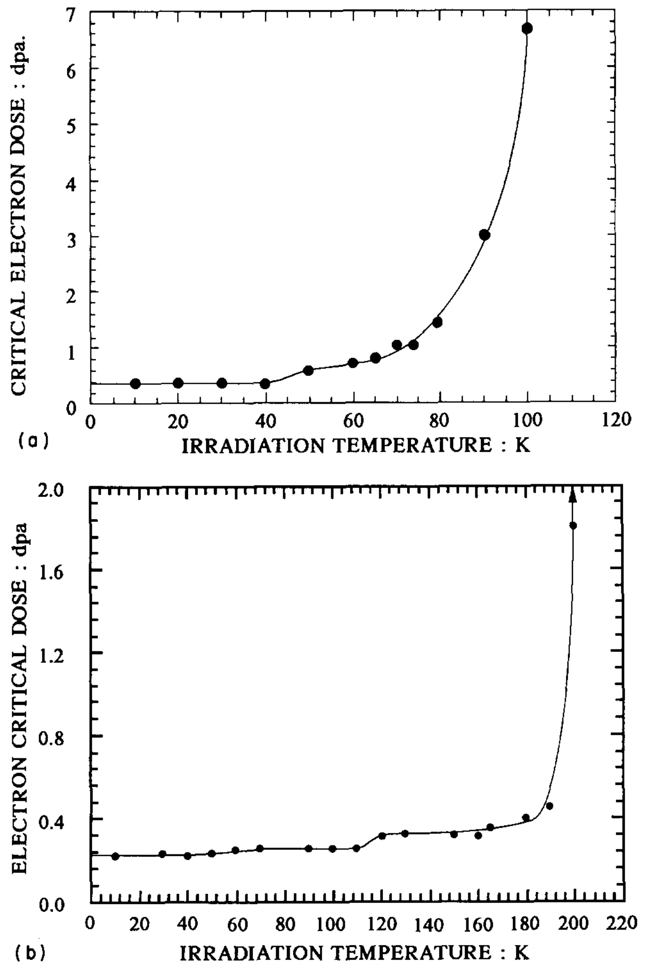

Fig. 3. Critical dose for amorphization *vs.* irradiation temperature for NiZr (a) and $NiZr_2$ (b). The scale for the critical dose is magnified so that a small recovery stage can be seen between 40 and 50 K for NiZr and between 110 and 120 K for $NiZr_2$.

4. Discussion

The critical dose for amorphization at 10 K represents the amorphization tendency of an intermetallic compound on irradiation, provided that no thermal migration of the irradiation-induced point defects takes place. Since the critical dose for amorphization remains constant at low temperatures in the three compounds examined here and in CuTi [3, 17, 19], it is reasonable to assume that no point defect migration takes place in this temperature range and that the steps found above this range represent recovery stages due to thermal migration of point defects. The results show that $NiZr_2$ is amorphized with the lowest dose of irradiation, suggesting that it has the highest tendency to become amorphous. Therefore it is expected that the enthalpy difference between the amorphous and crystalline states is smallest in $NiZr_2$. The enthalpy difference should be largest in Ni_3Zr and intermediate in NiZr. The values of the enthalpy difference can be estimated from the Debye temperatures for the amorphous and crystalline states of the intermetallic compound according to eqn. (1).

The determination of the Debye temperatures has been carried out extensively in both the amorphous and crystalline states at various compositions in the Ni–Zr system [21–25] as shown in Fig. 4. The Debye temperature decreases from pure Zr to $NiZr_2$ and then increases to pure Ni in the crystalline state. In the amorphous state the Debye temperature increases linearly with Ni content. Therefore the Debye temperatures for the two states are closest for $NiZr_2$ and furthest apart for Ni_3Zr. Consequently, the enthalpy difference, as shown in Table 1, is smallest for $NiZr_2$ and largest for Ni_3Zr. This is consistent with the observation that $NiZr_2$ is amorphized with the smallest critical dose and Ni_3Zr with the largest dose.

NiZr exhibits the highest probability of replacement of Ni–Zr bonds with Ni–Ni and Zr–Zr bonds by a unit replacement of atoms as it is at the equiatomic composition and Ni_3Zr exhibits the lowest probability. Therefore the enthalpy increase by disordering per unit displacement is expected to be largest for NiZr and smallest for Ni_3Zr. This drives the critical dose of NiZr to a lower value and that of Ni_3Zr to a higher value. At the same time, considering the low critical temperature for amorphization of this compound, it cannot be ruled out that a recovery mechanism operates in Ni_3Zr even at the lowest temperatures. The measurement of the long-range order parameter S showed that the final S value prior to amorphization is zero for

TABLE 1. Debye temperatures for amorphous and crystalline states (θ_D^a and θ_D^c) relative enthalpy difference (ΔH_c), critical dose for amorphization (Φ_c), temperature for recovery stage, (T_m) and critical temperature for amorphization (T_c) for $NiZr_2$, NiZr and Ni_3Zr

Compound	θ_D^a (K)	θ_D^c (K)	$(\theta_D^a/\theta_D^c)^2$	Relative ΔH_c	Φ_c at 10 K (d.p.a.)	T_m (K)	T_c (K)
$NiZr_2$	190	217	0.767	1.00	0.22	120	200
NiZr	208	269	0.598	2.47	0.37	50	100
Ni_3Zr	229	346	0.438	5.10	3.18	?	50

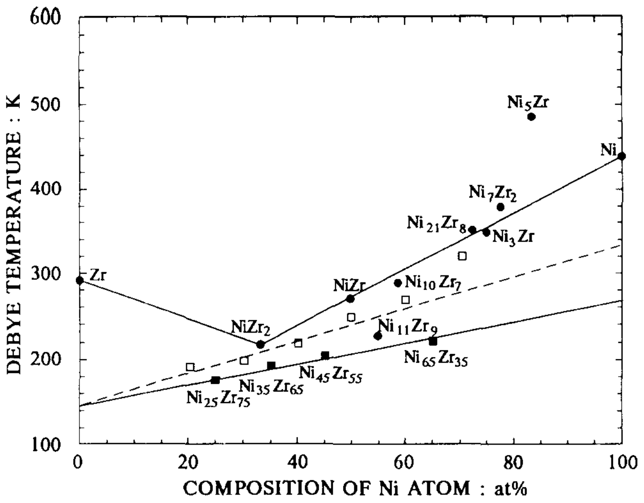

Fig. 4. Debye temperatures for amorphous and crystalline states *vs.* composition in the Ni–Zr system: ■, amorphous [23]; □, amorphous [24, 25]; ●, crystalline [22].

Ni_3Zr, and about 0.4 for $NiZr_2$ and NiZr. After complete chemical disordering, further irradiation has to be carried out for amorphizing Ni_3Zr; indicating that the accumulation of point defects is necessary to trigger amorphization in this compound. The need for extra point defects also drives the critical dose for amorphization of Ni_3Zr to a higher value. The trend indicated in Fig. 2 and Table 1 appears to be in good agreement with these assessments. A more detailed analysis will be reported in the future in conjunction with the measurement of the disorder kinetics.

It is interesting to note that the critical temperature for amorphization differs significantly between the three intermetallic compounds. This observation is contrary to the finding in the Cu–Ti system in which the critical temperature for amorphization by electron irradiation was determined for several intermetallic compounds and was found to be similar [3, 12]. If the same point defect migration mechanism controls the critical temperature, a fourfold difference in the activation energies of $NiZr_2$ and Ni_3Zr is expected. It was suggested previously [3, 16–19] that the migration of lattice vacancies efficiently reorders the atomic arrangement. Further investigation, in particular numerical calculations with molecular dynamics simulation, is desirable in this regard.

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