

The role of diffusion in amorphous-phase formation and crystallization of amorphous Ni-Zr

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The Ni-Zr system is examined as a representative system for the formation of an amorphous phase by diffusion and for the crystallization of an amorphous phase by diffusion. High-resolution electron microscopy (HREM) is used to show that the amorphous phase grows by bulk diffusion through the amorphous material rather than by short-circuit diffusion. Also, the HREM shows that the amorphous phase formed by diffusion appears to be the same as the vapor-deposited amorphous phase. A correlation between crystallization temperatures (T_x) and the enthalpy of large-atom hole formation is given. This correlation predicts values of T_x that are lower than those predicted from the small-atom hole-formation model. The difference in hole-formation enthalpies for the large and small atoms is given as a criterion for amorphous-phase formation via diffusion.

I. INTRODUCTION

The Ni-Zr system has been investigated by several authors in order to examine the crystallization^{1,2} of the amorphous phase as well as the ability to form the amorphous phase by a solid-state reaction.³ Interdiffusion in the Ni-Zr system has been shown to yield an amorphous phase in which Ni is the dominant diffusing species⁴ with an activation energy^{5,6} for interdiffusion of 1.3–1.4 eV. Also, the amorphous Ni-Zr phase has been shown⁷ to be relatively stable when in contact with Zr, but compositionally unstable when in contact with Ni. A question arises as to whether the amorphous phase remains the same after the diffusion of Ni into it, or whether the resulting phase after diffusion could be better described as composed of microcrystallites yielding many short-circuit diffusion paths.

The two processes, formation of crystalline compounds and the formation of the amorphous alloys, are both reported to be dependent on long-range bulk diffusion in the amorphous phase,^{1,8} while the end phases formed in either process are thermodynamically competing phases. Buschow¹ supposes that the crystallization of the amorphous phase is characterized by the mobility of the smaller Ni atoms that is dependent on the formation of a hole the size of the smaller atom. The relationship between the crystallization temperature (T_x) and the small-hole enthalpy of formation (H_{Sv}) is given as $T_x = 7.5H_{Sv}$, where T_x is in Kelvin and H_{Sv} is in kilojoules per mole. In contrast, the model of Schwarz and Johnson⁸ proposes that the formation of the amorphous phase is characterized by the fast mobility of the smaller constituent atom. A brief review of the conflict in these two approaches was given in Ref. 9 in which the diffusion process for amorphous-phase formation was proposed to be via short-circuit diffusion through the

amorphous layer rather than by bulk diffusion. This paper will examine the suggestion of short-circuit diffusion through the amorphous Ni-Zr phase and further examine the structure of the amorphous phase formed by a solid-state reaction. The results of this investigation on Ni-Zr will then be extended to further evaluate the Buschow model for predicting crystallization temperatures in other amorphous transition-metal alloys.

II. EXPERIMENTAL

Samples were made as shown schematically in the inset to Fig. 1. (This configuration is similar to that used by Barbour *et al.*⁹) The samples were prepared by electron-beam evaporation of the constituents onto an oxidized (111) Si wafer on which first the polycrystalline Ni layer was deposited to a thickness of 400 Å, and then Ni and Zr were codeposited to form an amorphous layer 250 Å thick. Last, the polycrystalline Zr layer was deposited to a thickness of 400 Å. The layers were deposited in succession in a background pressure of 8×10^{-8} Torr, and the base pressure in the system was 5×10^{-9} Torr. Details of the deposition system are given in Ref. 9. The Zr was deposited at a rate of 4.6 Å/s while the Ni was deposited at a rate of 2 Å/s. The composition of the amorphous layer in the as-deposited sample was Ni₄₈Zr₅₂, which was confirmed with Rutherford backscattering spectrometry (RBS). The initial thickness of the amorphous layer was only 250 Å (as opposed to 500 Å used in Ref. 9) in order to have a small diffusion path and thereby allow a larger amount of the amorphous phase to be grown by diffusion before consuming all of the pure constituents.

The samples were vacuum annealed at 250 °C for times varying from 1 h to 48 h, in a pressure of 2×10^{-8} Torr. The progress of the interdiffusion was then moni-

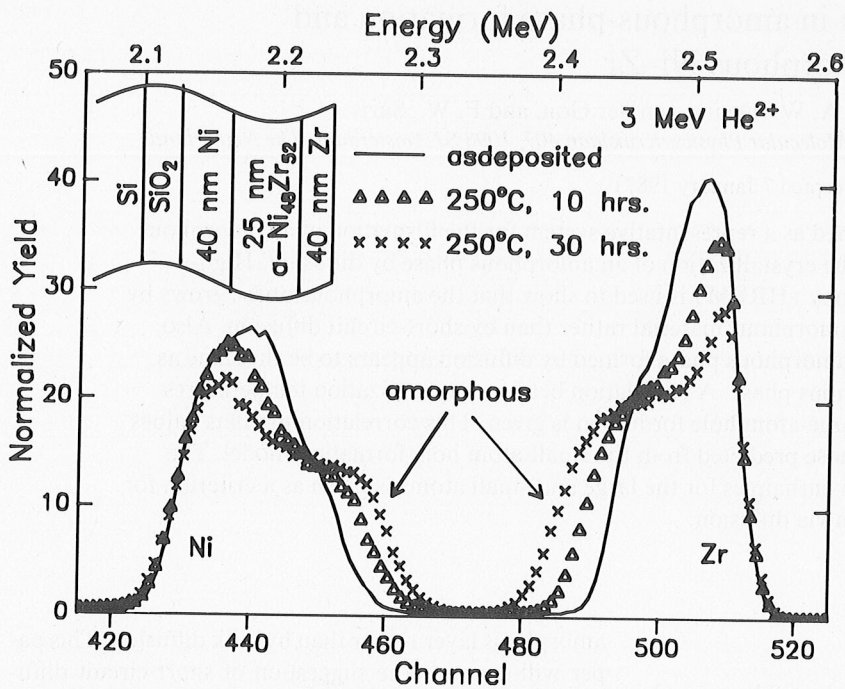


FIG. 1. The inset schematically shows the as-deposited sample configuration. Rutherford backscattering spectrometry (RBS) spectra show the extent of intermixing in the Ni-Amorphous-Zr diffusion couple after 10 and 30 h of annealing at 250 °C.

tored with RBS, and cross-sectional transmission electron microscopy (TEM) was used to examine the microstructure of the samples. Beyond 30 h of annealing, the formation of voids in the diffusion couple became so extensive that the cross-sectional samples lost all mechanical stability. The existence of void formation during the growth of the amorphous phase has previously been reported by Schroder *et al.*¹⁰ and Newcomb and Tu.¹¹ The RBS spectra were acquired with 3 MeV He⁺⁺ and a scattering angle of 171 deg. Also, the samples were tilted 60 deg to increase the depth resolution for monitoring the reaction.

III. RESULTS

The RBS spectra in Fig. 1 show the extent of the reaction after 10 and 30 h of annealing. Approximately 100 Å of the Ni layer has been consumed in the reaction after 10 h and about half of the Ni layer has been consumed after 30 h. The 647 Å thick middle layer formed in the reaction after 30 h contains a linear composition profile as reported by Barbour¹² with an average composition of Ni₅₇Zr₄₃.

Figure 2 shows an electron micrograph of this same sample that was annealed for 30 h. The sample was ori-

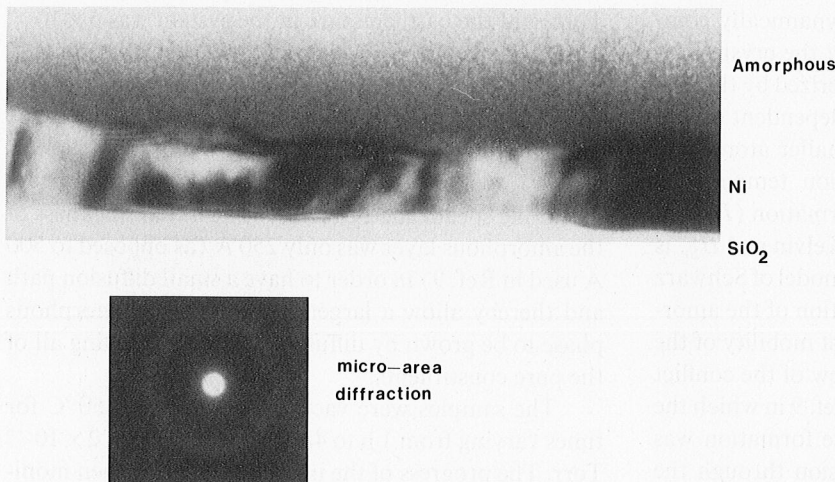


FIG. 2. A cross-sectional transmission electron microscope (TEM) image is shown for the amorphous Ni-Zr and Ni layer in the diffusion couple annealed for 30 h at 250 °C. The microarea diffraction pattern shows that the amorphous layer yields a typical amorphous diffraction pattern.

ented such that the electron beam is parallel to the Ni-SiO₂ interface by tilting the Si substrate to the (110) pole. Also shown is a microarea diffraction pattern from the middle layer in the diffusion couple. The diffraction pattern confirms that this layer appears amorphous by electron diffraction, and it confirms that the amorphous phase forms by diffusion through a predeposited amorphous layer. Further, the TEM image shows that the amorphous phase is continuous and contains no apparent short-circuit diffusion paths as suggested previously.⁹ Dark-field imaging also showed the amorphous phase to have a continuous contrast without evidence for microcrystallinity. Further, the position of the original crystalline-amorphous interface shows no contrast in the TEM image, which suggests that the microstructure of the amorphous phase formed by the solid-state reaction is similar to that of the amorphous material formed by coevaporation of the constituents.

In order to further examine the scale of structural order in the amorphous phase, the sample annealed for 30 h was examined with a 400 keV high-resolution (1.8 Å point-to-point resolution) electron microscope. The image shown in Fig. 3 is from a region of the amorphous Ni-Zr near the Ni-amorphous interface. The Ni-amorphous interface is particularly important because this interface is less stable than the Zr-amorphous interface.⁷ The amorphous material exhibits small amounts of fringes (as seen in other amorphous materials such as in the Pd-Si system¹³) that are randomly distributed across the layer in packets about 20 Å in size. An example of these fringes is encircled in Fig. 3. These packets are approximately twice the size of a unit cell of one of the Ni-Zr intermetallic compounds. Near the edge of the amorphous material the packets are larger, but the apparent increased degree of positional order may result from ion milling, or the interaction of the sample with the high-energy electron beam. However, extensive differences in contrast due to microcrystallinity on a scale greater than 20 Å are not observed in the bulk layer of the amorphous material, and therefore a description of the amorphous material in terms of microcrystallites with an extensive grain boundary (crystallite boundary) network is inapplicable. Thus, diffusion through the amorphous phase is appropriately described in terms of a bulk-diffusion process rather than a short-circuit diffusion process. Also, even though the amorphous material when in contact with Ni is unstable to diffusion, the amorphous phase formed by diffusion appears the same in the TEM as that phase formed by codeposition.

IV. DISCUSSION

Thermodynamic considerations imply that the formation of the amorphous material and crystalline compounds are competing processes, both requiring diffu-

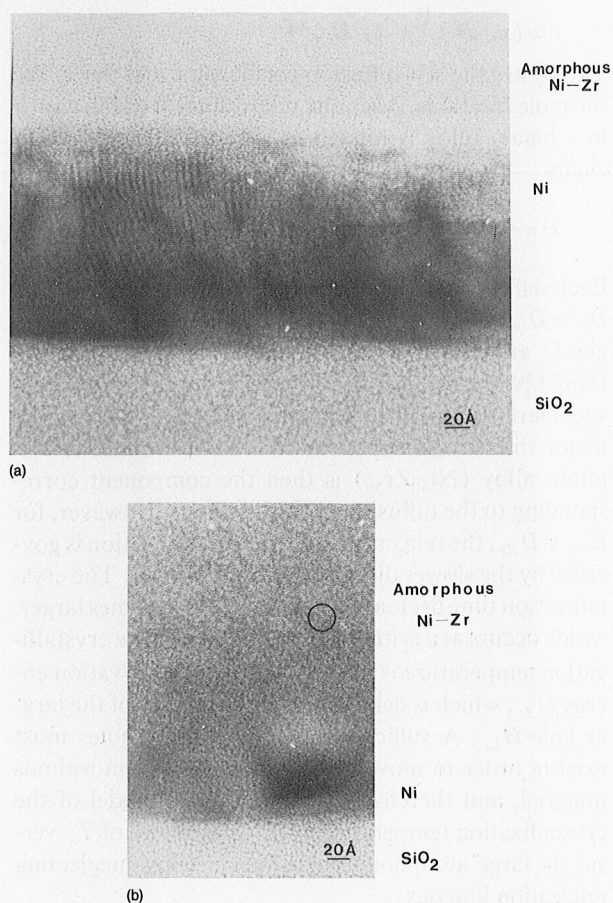


FIG. 3. High-resolution electron microscopy (HREM) images from the amorphous layer near the Ni-amorphous interface. The HREM images throughout the amorphous layer showed no change in contrast. This result confirms the absence of short-circuit diffusion paths and shows the amorphous-crystalline boundaries that were present prior to annealing are also absent after annealing. The encircled region shows that the image of the amorphous phase does contain packets of fringes that are about 20 Å in size.

sion. Further, Buschow¹ reports that if crystallization occurs by a diffusion process, then the crystallization temperature is proportional to the enthalpy of hole formation of the smaller constituent. Diffusion for the formation of amorphous Ni-Zr is dominated by the smaller and faster moving Ni atoms (as stated above) and this article presents evidence that the diffusion process can proceed via bulk diffusion through an amorphous phase without the necessity for short-circuit paths and also without crystallization. Therefore the physical basis of the crystallization temperature versus small-atom hole enthalpy plot, given in Ref. 1, is not supported for the Ni-Zr system.

If amorphous Ni-Zr crystallization occurs by diffusion, then the crystallization process can be characterized by a relaxation time τ for the diffusion process¹⁴:

$$\tau \propto (x_{\text{Ni}} D_{\text{Zr}}^{-1} + x_{\text{Zr}} D_{\text{Ni}}^{-1}).$$

The D_i are the self-diffusion coefficients, and the x_i are the mole fractions. Also, the interdiffusion coefficient D in a binary alloy is related to the self-diffusion coefficients

$$D \propto (x_{\text{Ni}} D_{\text{Zr}} + x_{\text{Zr}} D_{\text{Ni}}).$$

Each self-diffusion coefficient can be written in the form $D_i = D_{i,0} \exp(-Q_i/kT)$, where the activation energies Q_i are related to the hole-formation enthalpies H_{Sv} (small Ni atom) and H_{Lv} (large Zr atom). For a reasonable difference in hole energies (e.g., $Q_{\text{Ni}} \ll Q_{\text{Zr}}$), the major diffusion component in a concentrated amorphous alloy ($\text{Ni}_{50}\text{Zr}_{50}$) is then the component corresponding to the diffusion of the Ni atoms. However, for $D_{\text{Ni}} \gg D_{\text{Zr}}$, the relaxation time for crystallization is governed by the slower diffusing component D_{Zr} . The crystallization time decreases rapidly as D_{Zr} becomes larger, which occurs at a critical temperature T_x . The crystallization temperature is proportional to the activation energy Q_{Zr} , which is determined by the energy of the larger hole H_{Lv} . A sufficient number of large holes must exist in order to move a large atom in the amorphous material, and therefore a more physical model of the crystallization temperature is given by a plot of T_x versus the large-atom hole-formation enthalpy (neglecting nucleation kinetics).

Figure 4 shows T_x of the binary amorphous transition-metal alloys plotted versus the enthalpy of hole formation for the smaller atom (triangles) and for the larger atom (circles). The solid line through the triangles

shows the Buschow correlation ($T_x = 7.5H_{Sv}$), which could be used to predict the crystallization temperatures. In comparison, the dashed line through the circles shows the correlation between T_x and the enthalpy of formation for large holes (H_{Lv}). The slope of the dashed line yields a proportionality constant of 4.2 such that $T_x = 4.2H_{Lv}$, where T_x is in Kelvin and H_{Lv} is in kilojoules per mole. This dashed line has at least as good a correlation as the relationship given in Ref. 1. Moreover, the proportionality constant for this line is less than that given by the solid line and therefore, for nearly equal large and small hole enthalpies, this new relation yields lower estimates in predicting crystallization temperatures of binary-amorphous metal alloys than estimates predicted from the Buschow relation. Further work is being pursued to examine the applicability of such a plot to compare crystallization for different alloys with different methods of crystallization.

The model to determine the mobility of a species in the amorphous phase as related to its hole-formation energy also yields another important consequence obtained when classifying the possible type of binary systems that can form an amorphous phase by diffusion. Namely, the difference in hole formation enthalpies for the larger and smaller atoms ($H_{Lv} - H_{Sv}$) should be examined, and the larger is the difference between H_{Lv} and H_{Sv} then the greater is the ability to form the amorphous phase by diffusion.

V. CONCLUSION

In summary, an amorphous Ni-Zr phase is formed by a bulk-diffusion process through an as-deposited

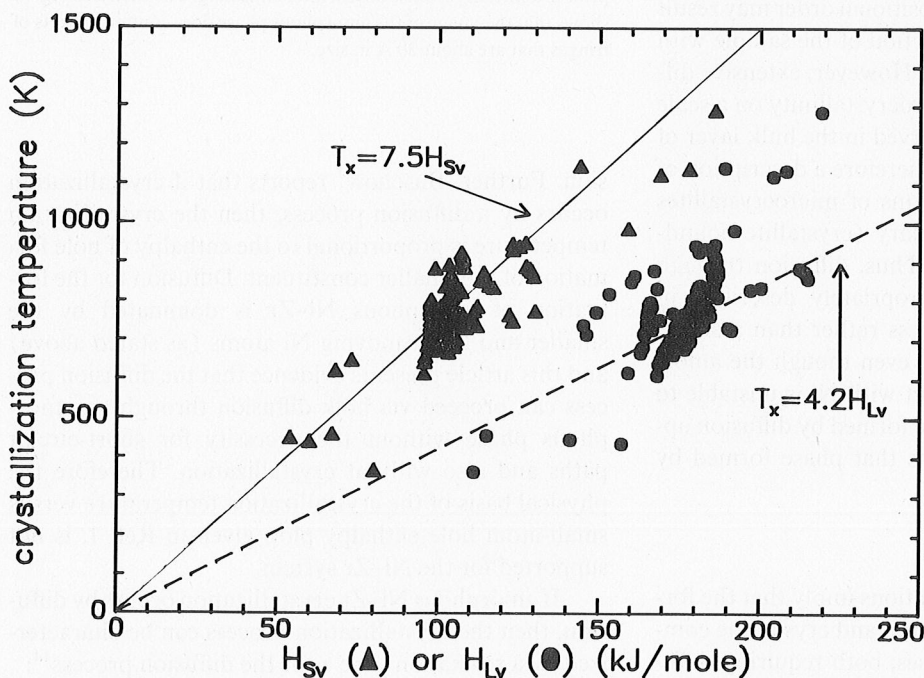


FIG. 4. Crystallization temperatures (T_x) for the amorphous transition-metal alloys are plotted as a function of either the large-atom hole-formation enthalpy (H_{Lv}) or the small-atom hole-formation enthalpy (H_{Sv}). The values for T_x were taken from Ref. 15.

amorphous film. The amorphous phase formed by diffusion appears, in the electron microscope, to be the same as the vapor-deposited amorphous film, and a description of this amorphous phase in terms of microcrystallites is inappropriate. The results of this article suggest that predictions for the crystallization temperature (T_x) of a binary-amorphous metal alloy are physically described better by the relationship between T_x and the large-atom hole-formation enthalpy ($T_x = 4.2H_{Lv}$) than by the relationship between T_x and the small-atom hole-formation enthalpy ($T_x = 7.5H_{Sv}$). The large-atom relation predicts lower crystallization temperatures than those temperatures predicted from the Buschow relation. Finally, the difference in hole-formation enthalpies for the constituent atoms is proposed as the appropriate criterion to predetermine the ability for easy amorphous phase formation by solid-state diffusion.

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