

Diffusivity of Ni in an Amorphous Ni-Zr Alloy

J. C. Barbour

Department of Materials Science, Cornell University, Ithaca, New York 14853

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The Ni diffusivity and composition profile were measured in an amorphous Ni-Zr alloy formed in a Ni/*a*-NiZr/Zr binary diffusion couple. The Ni diffusion coefficient at 250 °C was found to be 1×10^{-16} cm²/sec. The concentration profile within this amorphous phase is linear and the compositions at the interfaces between the amorphous alloy and the pure Ni and pure Zr tend to the constant values of 68% Ni and 47% Ni, respectively.

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Thin-film alloy formation from a solid-state reaction is often considered to be governed by the same thermodynamic functions and criteria as bulk alloy formation. However, this assumption is rarely verifiable. This Letter addresses the basic assumptions common to the models¹⁻³ of diffusional growth in thin films, and it relates the Gibbs free energy of an amorphous Ni-Zr alloy to the formation of the amorphous phase made by the method of a solid-state reaction.⁴ The Gosele-Tu³ model and the Sekerka-Jeanfils-Heckel² model are used to calculate the diffusivity of Ni in an amorphous Ni-Zr alloy.

The models to describe the diffusion-controlled growth of a thin film¹⁻³ are based upon the assumption that the interface compositions are constant and, therefore, the concentration difference remains fixed. Further, the composition gradient, at a given time, is often approximated^{2,3} as a constant throughout the growing layer in order to make the mathematics of modeling more tractable. The concentration gradient is the driving force for solid-state diffusion in the alloy. A measure of both the composition profile, as a function of time, and the interface concentrations is essential to confirm the validity of the use of these models. Many compounds exist only over a narrow composition range; and as a result of the difficulties involved in measuring small concentration differences, the growth models for binary diffusion couples are often difficult to apply quantitatively. However, the formation of amorphous materials made by the method of a solid-state reaction⁴ is a good test for these models because the growth of the amorphous phase is diffusion controlled and because the amorphous phase exists over a wide range of compositions.

Samples were made, as shown in the inset to Fig. 1, to model a binary diffusion couple between crystalline Ni and crystalline Zr. The samples were prepared by electron-beam evaporation of the constituents onto an oxidized Si wafer. Barbour *et al.*⁵ have shown that the interdiffusion coefficient in amorphous Ni₅₀Zr₅₀ is at least a factor of 10⁴ smaller than the diffusivity of Ni in crystalline Zr. Therefore, the samples were made with an interposing amorphous layer, in the as-

deposited state, in order to eliminate the effects resulting from anomalously fast diffusion⁶ of Ni in Zr. The Ni layer was deposited to a thickness of 50 nm, and then Ni and Zr were deposited simultaneously to form an amorphous layer. The amorphous layer was 44 nm thick and had a uniform composition of Ni₅₅Zr₄₅ before annealing. Last, a Zr layer was deposited to a thickness of 45 nm. 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. 5. The Zr was deposited at a rate of 3.5 Å/sec while the Ni was deposited at a rate of 2 Å/sec. Formation of the amorphous layer was checked by cross-sectional transmission electron microscopy.

The samples were vacuum annealed at 250 °C from 1.2 to 67.9 h in a pressure of 2×10^{-8} Torr. The annealing temperature was chosen such that it was below

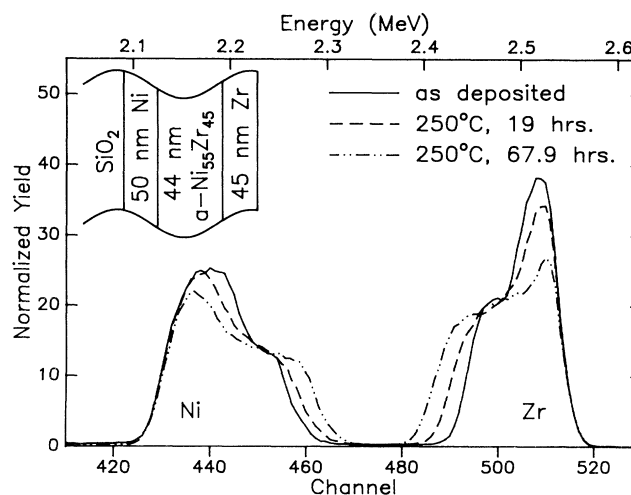


FIG. 1. The backscattering (RBS) spectra of 3-MeV He⁺⁺ ions from a Ni-Zr binary diffusion couple annealed at 250 °C for up to 67.9 h. The inset shows the sample configuration before annealing. The steps (from the interposing amorphous layer) in both the Zr and Ni signals indicate the presence of a concentration gradient. (Sample tilt is 47.5° to the incident beam.)

the reported⁷ crystallization temperature for an amorphous $\text{Ni}_{55}\text{Zr}_{45}$ alloy (410°C). Rutherford backscattering spectrometry (RBS), with 3-MeV He^{++} ions, was used to measure the amount of reaction.

Figure 1 shows three RBS spectra indicating the progression of the amorphous-phase growth as a function of time. The signal from the Zr atoms is to the right in the figure and the signal from the Ni atoms is to the left. The spectrum from the sample in the as-deposited state (solid line) is representative of a sample with a mixed layer of Ni and Zr (constant concentration) between the pure Ni and Zr layers. The signal from the amorphous region appears as a step in the back edge of the Zr signal and the front edge of the Ni signal. The dashed line indicates the amount of amorphous-phase growth after annealing for 19 h. Slopes in both the Zr step and the Ni step reveal that a concentration gradient exists within the amorphous layer. The concentration gradient in the sample annealed for 67.9 h (dash-dotted line) is less pronounced than the gradient in the sample annealed for 19 h because the concentration difference across the middle layer remains fixed, whereas the width of this layer increases. The compositions at the end points of the gradient are determined from the relative Ni to Zr backscattering yields at that point in the spectrum corresponding to the front and back interfaces.

Figure 2 shows the RBS spectrum from the sample which was annealed for 48.2 h. The triangles are experimental data and the dashed line is a simulated

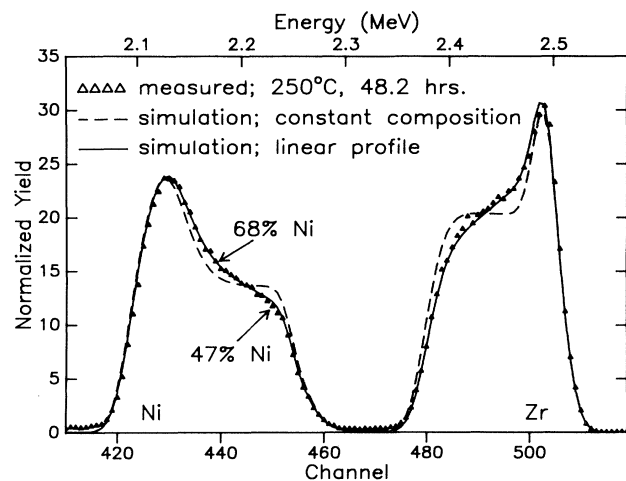


FIG. 2. The RBS spectrum (triangles) from the sample after being annealed for 48.2 h. The simulated spectra (dashed and solid lines) show that the data can be best fitted by use of a linear concentration profile with compositions of 68% Ni and 47% Ni at the end points. Both simulations were calculated with a detector resolution of 20 keV (four channels) and with the energy straggling from the Bohr theory (Ref. 8).

spectrum representing a sample with a middle layer containing a uniform composition ($\text{Ni}_{57.5}\text{Zr}_{42.5}$). A spectrum based upon a linear concentration profile is simulated by the solid line. In the case of the linear profile, the composition of the amorphous phase varies between 68% Ni (at the Ni-amorphous interface) and 47% Ni (at the Zr-amorphous interface). The simulated spectra were calculated by use of the program RUMP⁸ in which the concentrations at the end points are fixed from the data, as described above. Each specimen, for the different annealing times, was analyzed to determine the composition at the end points of the gradient and then a simulated spectrum was fitted to the data to determine the width of the amorphous phase. The widths calculated from the simulations are based upon the assumption that the density of the amorphous layer is the weighted sum of the densities of Ni and Zr. This assumption was determined to be accurate, to about 15%, by comparison of the areal density of the as-deposited amorphous sample with the thickness measured in cross-sectional transmission electron microscopy. Finally, these simulated spectra show that the data are well modeled by a linear composition profile.

The Ni concentrations at the respective interfaces are shown as functions of time in Table I. ($a\text{Ni}$ in the superscript stands for the amorphous-Ni interface.) The composition difference across the amorphous layer changes until the constant concentrations of approximately 47% Ni, at the Zr-amorphous interface, and 68% Ni, at the Ni-amorphous interface, are reached. Initially, the samples did not have a composition gradient within the middle layer and therefore at least 5.5 h of annealing time were needed for the composition difference to begin to approach the steady-state value. After this time, the simulations show that the assumption of fixed interface compositions in the binary diffusion couple is consistent with the data. Thus, the approximations of a linear concentration profile and constant interface compositions are valid.

The interdiffusivity can be calculated from the treat-

TABLE I. The interface compositions as a function of time.

Time (h)	Mole fraction of Ni	
	$X_{\text{Ni}}^{a\text{Ni}}$	$X_{\text{Ni}}^{a\text{Zr}}$
0.0	0.55	0.55
1.2	0.572	0.568
5.5	0.61	0.54
19.0	0.67	0.48
30.0	0.68	0.46
48.2	0.68	0.47
67.9	0.66	0.49

ment of Sekerka, Jeanfils, and Heckel² in which the concentrations at the interfaces are assumed to be constant and governed by the equilibrium phase diagram. Also, the component atoms are allowed to have varying atomic volumes in the couple. The Ni-to-Zr volume ratio in the amorphous phase can be estimated as 0.53. If the constant compositions measured in this experiment are assumed to be those concentrations obtained from a phase diagram containing Ni, Zr, and an amorphous Ni-Zr alloy, then the average value for the interdiffusion coefficient, D , is 1×10^{-16} cm²/sec. In comparison, Barbour *et al.*⁵ initially estimated D as 1×10^{-17} cm²/sec. The original report of the interdiffusion coefficient was based on the relationship $\Delta W = (Dt)^{1/2}$, where ΔW is the amount of layer growth. This Letter bases the analysis of D on more rigorous diffusion models, and the measurements of ΔW obtained with the aid of the simulations in this experiment are more accurate than the original estimate.

The large difference in atomic volumes between Ni and Zr suggests that the Ni atoms can diffuse via voids independent of the Zr flux. In fact, Ni has been shown^{9,10} to be the dominant moving species in amorphous Ni-Zr alloys. If the Ni and Zr fluxes are decoupled and the Ni is the dominant diffusing atom, then the measured interdiffusion coefficient closely approximates the diffusivity of Ni in the amorphous alloy.

A basic assumption used in the Sekerka-Jeanfils-Heckel model is that the interface compositions are determined by local equilibrium conditions. The interfaces in a binary diffusion couple are regions where two phases exist; and a two-phase region is at thermodynamic equilibrium when the compositions of the phases correspond to the tangency points on the common tangent between the free-energy curves for the phases. An amorphous phase is often^{4,11} approximated by a supercooled liquid in order to calculate the free energy. The Gibbs free energy, G , of a Ni-Zr supercooled liquid at 250 °C is shown in Fig. 3. This curve was calculated from the equation reported by Charles, Gachon, and Hertz¹³ to model the liquidus line of the bulk equilibrium phase diagram. The standard states were taken to be face-centered-cubic Ni at 250 °C and hexagonal Zr at 250 °C. Experimental values (triangles) for the free energy, determined from the heats of amorphous-phase formation given by Buschow,¹² are also shown. The composition at the minimum in the free energy (55% Ni) agrees to within 3 at.% with the average composition of the amorphous alloy formed by diffusion. Therefore, the growing amorphous phase corresponds to the lowest-free-energy state for an amorphous Ni-Zr alloy.

The tangency points (e.g., X^{aZr} shown in Fig. 3) for equilibrium between a supercooled liquid at 250 °C and either Zr or Ni are at compositions of 33% Ni at the Zr interface and 80% Ni at the Ni interface. The interface

compositions for the binary diffusion couple in this experiment were measured as 47% Ni and 68% Ni, respectively. Short-range ordering in the amorphous phase would cause the curve for the supercooled liquid to shift downward toward the free-energy values for crystalline compounds; and in fact, the experimentally derived values of G are below those values for the supercooled liquid. The interface composition between Zr and the amorphous alloy predicted from the experimentally derived data is less definite than the tangent to the curve for the supercooled liquid. The experimental data indicate that X_{Ni}^{aZr} is between 35% Ni and 42% Ni (shaded region in Fig. 3), which is close to the measured composition but differs by about 5 at.%. Therefore, the measured interface compositions approach fixed values which are shifted slightly inward toward the minimum in free energy from the predicted local equilibrium values.

Gosele and Tu³ describe the growth of a phase in a binary diffusion couple which has fixed compositions at the interfaces and a constant gradient. Their model allows the interface compositions to be less than the equilibrium concentrations as a result of interfacial reaction barriers. Also, their model assumes that the atomic volumes of the Ni and Zr atoms are constant

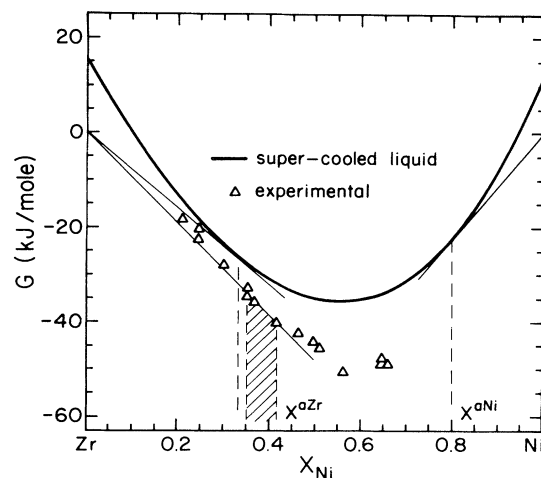


FIG. 3. The Gibbs free energy (G) of an amorphous Ni-Zr alloy obtained by approximation of the amorphous phase as a supercooled liquid. The standard states are face-centered-cubic Ni and hexagonal Zr at 250 °C. Experimental values (triangles) for the free energy were determined from the heats of amorphous-phase formation given by Buschow (Ref. 12). The common tangent rule shows that the equilibrium concentration of the supercooled liquid is 33% Ni at the Zr-amorphous interface and 80% Ni at the Ni-amorphous interface. The tangent to the experimentally derived data, at the Zr-amorphous interface, is between 35% Ni and 42% Ni (shaded region). The constant interface compositions for the binary diffusion couple in this experiment were measured as 47% Ni and 68% Ni.

and equal throughout the diffusion couple. Steady-state diffusion does not require equilibrium conditions and therefore the fluxes in this experiment may obtain a steady state which is only close to the conditions of local equilibrium at the interfaces. The interdiffusivity can be calculated by use of the Gosele-Tu model with the experimentally measured values for the fixed concentrations rather than predicted equilibrium values. The average interdiffusion coefficient based on the measured interface compositions given above is 1×10^{-16} cm²/sec, which is in agreement with the value calculated from the Sekerka, Jeanfils, and Heckel treatment.

In summary, the diffusivity of Ni in an amorphous alloy of average composition Ni_{57.5}Zr_{42.5} is determined to be 1×10^{-16} cm²/sec at 250 °C. The concentration profile within the amorphous phase, growing in a binary diffusion couple, was shown to be linear. The interface compositions between the amorphous Ni-Zr alloy and the pure Ni and pure Zr were found to be fixed at 68% Ni (at the Ni interface) and 47% Ni (at the Zr interface), which differ from the concentrations predicted for local equilibrium at the respective interfaces. Interfacial reaction barriers may cause the measured interface compositions to be slightly less than the local equilibrium values.

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