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Diffusivities of Ni, Zr, Au, and Cu in amorphous Ni-Zr alloys

H. Hahn, R. S. Averback, and S. J. Rothman

Argonne National Laboratory, Argonne, Illinois 60439

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The chemical interdiffusion coefficient was measured in an amorphous $Ni_{33}Zr_{67}$-$Ni_{61}Zr_{39}$ bilayer sample. With the use of an "inert" marker layer of Au at the interface, and the regular solution approximation, tracer diffusivities for the constituent elements of the alloy were determined. In addition, tracer diffusivities of Au in this alloy, and of Au and Cu in homogeneous $Ni_{50}Zr_{50}$ amorphous alloys, were measured. The tracer diffusivities of Cu and Ni were much greater than those of Zr and Au suggesting that atomic radii strongly influence diffusion in this alloy. A preliminary value of ≈ 105 kJ/mol for the activation enthalpy of Ni diffusion was deduced. Similarities between diffusion in *a*-NiZr alloy and α-Zr are discussed.

Diffusion mechanisms in amorphous metallic alloys are not well understood. This is partly due to the difficulty in measuring the very small diffusion coefficients which are typical of metallic glasses below their crystallization temperatures. The motivation for understanding diffusion in metallic glasses, however, has recently been spurred by the demonstration that these glasses can be formed by solid-state reactions. Practical limits to the quantities and types of material that can be amorphized by this method are set by diffusion. Schwarz and Johnson[1] and Johnson, Dolgin, and Van Rossum[2] have suggested that systems which exhibit anomalously fast diffusion in the crystalline phase may also have fast diffusion in the amorphous phase. It is not obvious at this time, however, why diffusivities in crystalline materials should have significance for diffusion in metallic glasses. Preliminary measurements of diffusion in amorphous NiZr alloys indicate that diffusion is several orders of magnitude slower than Ni diffusion in α-Zr at comparable temperatures.[3,4] In this Rapid Communication we address this question by reporting measurements of the tracer diffusivities of two elements which diffuse anomalously fast in α-Zr, Ni, and Cu, and two elements which show normal diffusion in α-Zr, Zr, and Au. These elements include the constituents of the alloy, two elements which are chemically similar to each other, Au and Cu, and two sets of atoms having either large, Au and Zr, or small Ni and Cu atomic radii. Atomic size is of paramount importance for tracer impurity diffusion in α-Zr and α-Ti.[5] The study also provides a preliminary estimate for the activation enthalpy of Ni diffusion in *a*-NiZr.

In order to measure the tracer diffusion coefficients of Ni and Zr in *a*-NiZr, the Kirkendall geometry with an "inert" market, Au, was employed. This geometry is somewhat different from that used by Cheng, Johnson, and Nicolet,[6] in that our bilayer specimen was comprised of *a*-$Ni_{33}Zr_{67}$–*a*-$Ni_{61}Zr_{39}$ and contained a thin Au (≈ 0.4-nm) marker. This geometry has the advantages that there are no amorphous-crystalline interfaces present, the solution to the diffusion equation is straightforward, both chemical and tracer diffusion coefficients can, in principle, be obtained for the host elements, an upper limit for the diffusion of the inert marker element can be estimated, and, finally, backscattering analysis (BS) can be employed. The diffusivities of Au and Cu tracer impurities in homogeneous *a*-$Ni_{50}Zr_{50}$ alloys were determined by measuring the spreading of thin impurity layers by either BS (Au), or by secondary-ion mass spectroscopy (SIMS) (Cu).

The amorphous bilayer samples were prepared in a ultrahigh-vacuum evaporation system equipped with two rate-controlled *e*-guns and a resistance-heated tungsten boat. The *e*-guns were loaded with either pure Ni or Zr and the W boat with either Au or Cu. The compositions of the layers were controlled by separately monitoring the evaporation rates from each gun. For the Kirkendall geometry, the sequence of the deposition was a thin (≈ 0.4-nm) Au marker layer on the SiO_2 substrate, an ≈ 36-nm *a*-$Ni_{33}Zr_{67}$ layer, the second Au marker layer, and the top ≈ 48-nm *a*-$Ni_{61}Zr_{39}$ layer. The depositions were halted momentarily (≈ 1 min) after the Au marker layer was deposited to reset the rate-control parameters. In one case, the Au layer was deposited simultaneously with the first 2 nm of the top alloy layer in order to eliminate a sharp marker-alloy interface. No difference in the diffusion results was observed between the coevaporated and discrete marker deposition procedures. For the Cu and Au markers in the homogeneous *a*-$Ni_{50}Zr_{50}$ specimen, the alloy was deposited without interruption; the thin Cu or Au layer ($\approx 2\times10^{15}$ atoms/cm^2) was coevaporated in the center 2-nm portion of the specimen which had a total thickness of 160 nm. The background pressure during depositions was $< 3\times10^{-8}$ torr.

The samples were all annealed under vacuum, $< 4\times10^{-8}$ torr, by attaching them to a thick copper plate which in turn was affixed to a light-bulb heating stage. The specimen temperature was controlled to an accuracy of ± 3 K using a Chromel-Alumel thermocouple attached to the copper plate. After annealing, the specimens were checked using a Read camera to verify that they had remained amorphous during annealing. The changes in the concentration profiles in the bilayer samples were measured using BS. As the maximum He ion energy available was 1.8 MeV, rather thin samples and a low-resolution geometry were necessarily employed to resolve the separate Ni and Zr signals. The concentration profiles were deduced using a simulation program for backscattering. The chemical diffusion coefficients of the alloys were obtained by comparing the BS results with the solution of the diffusion equation for a thin film with impermeable boundaries and an initial step-function concentration profile.[7] The solution to the diffusion equation for these conditions is

$$C(x,t)=c_0+(c_1-c_0)\left[h/l+(2/\pi)\sum\left(\frac{1}{n}\right)\sin(n\pi h/l)\cos(n\pi x/l)\exp(-n^2\pi^2\tilde{D}t/l^2)\right] , \tag{1}$$

where c_1 and c_0 are the Ni concentrations in the Ni-rich and Ni-poor layers, respectively, l is the thickness of the specimen, h is the position of the interface, and t is the annealing time. This solution is based on the assumption of a concentration-independent diffusion coefficient. Otherwise, the chemical diffusion coefficient, $\tilde{D}$, in Eq. (1) is an average over the composition of the specimen. Because of the low resolution of our BS geometry, the best results could be obtained by matching the Zr and Ni concentrations at the surfaces of the film to $C(x=0,t)$ and $C(x=l,t)$ in Eq. (1). The diffusion coefficients for Cu and Au were obtained more accurately using the geometry of a thin tracer impurity layer in an infinite homogeneous medium.

Figure 1 illustrates typical backscattering spectra (Zr yield only) for the same sample annealed for different times at 528 and 573 K. It can be seen that the original concentration gradient initially decreases (at 528 K) and becomes nearly homogeneous (at 573 K). In Fig. 2, the shift in the Au marker position is shown for a similar sample annealed at 528 K. The marker shift is to higher energy in the spectrum, indicating it has moved closer to the surface. As there were no crystalline-amorphous interfaces, and in one case not even a discrete marker layer, the possibility of dragging of the marker by a moving interface can be excluded. Moreover, the width of the Au marker distribution did not change, indicating that Au behaves like an inert marker. Quantitative determinations of the variances and center points of the marker distributions were obtained by fitting the backscattering signals to a Gaussian distribution. The broadening of the Au marker signal was less than our BS detection limit, ≈ 2 nm. This is consistent with the very small diffusivities of Au measured in an a-$Ni_{64}Zr_{36}$ alloy,[8] and in our homogeneous a-$Ni_{50}Zr_{50}$ thin film (Table I).

Table I lists the results for the present interdiffusion experiments. At both temperatures, the chemical diffusion coefficient is independent of diffusion time indicating that relaxation effects in our vapor-deposited amorphous alloy are not significant. The value of $\tilde{D}$ at 528 K, 1.5×10^{-16} cm^2/s, is in good agreement with that reported by Barbour, Saris, Natasi, and Mayer.[3] To extract the intrinsic and tracer diffusivities from the chemical diffusion coefficients, it is necessary to determine the thermodynamic factor, and to measure the interface velocity, v. The relevant equations are[9]

$$\tilde{D}=(X_A D_B+X_B D_A) , \tag{2a}$$

$$v=(D_A-D_B)\partial X_A/\partial x , \tag{2b}$$

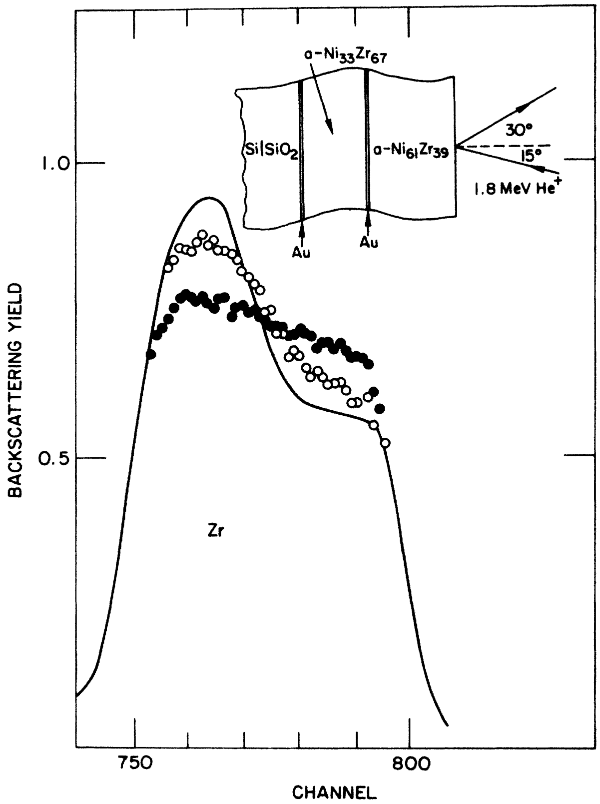

FIG. 1. Backscattering spectra (Zr yield only) showing the interdiffusion of an a-NiZr bilayer sample before annealing (——), after annealing at 528 K (○), and after additional annealing at 573 K (●). The specimen is nearly homogeneous after the anneal at 573 K.

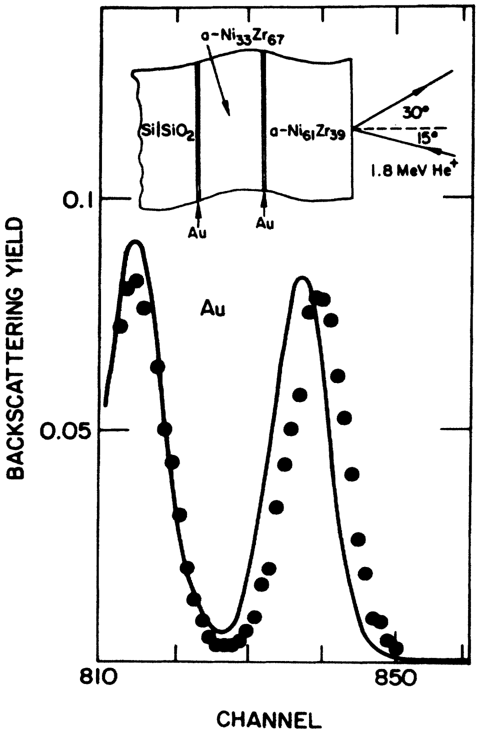

FIG. 2. Shifting of the inert Au marker toward the front surface after annealing treatment; (——) before annealing; (●) after annealing at 528 K.

TABLE I. Summary of diffusion data in *a*-NiZr.

		Bilayer sample: $Ni_{33}Zr_{67}$-$Ni_{61}Zr_{39}$[a]		
t (s)	T (K)	$\tilde{D}_{NiZr}$ (cm^2/s)	D^*_{Ni} (cm^2/s)	D^*_{Zr} (cm^2/s)
10 990	528	1.54×10^{-16}	9.2×10^{-18}	$< 1.0D^*_{Ni}$
33 660	528	1.57×10^{-16}	9.4×10^{-18}	$< 0.1D^*_{Ni}$
3490	573	9.3×10^{-16}	6.0×10^{-17}	$< 0.1D^*_{Ni}$
9260	573	9.1×10^{-16}	5.9×10^{-17}	$< 0.1D^*_{Ni}$
		Tracer impurity diffusion in $Ni_{50}Zr_{50}$		
	T (K)	D^*_{Au} (cm^2/s)	D^*_{Cu} (cm^2/s)	
	573	4.3×10^{-20}	2.6×10^{-17}	

[a] The activation enthalpy for Ni tracer diffusion in this sample is $Q_{Ni} = 105$ kJ/mol.

and

$$D_i = D_i^*(1 + \partial \ln\gamma_i / \partial \ln X_i) \ , \tag{2c}$$

where X refers to the mole fraction of A or B. D_A and D_B, and D_A^* and D_B^*, are the intrinsic and tracer diffusivities in an *a*-NiZr alloy, and γ is the activity coefficient. For the present work, the thermodynamic factor is approximated using the regular solution model to obtain

$$1 + \partial \ln\gamma / \partial \ln X = (1 - 2\Delta H_{\rm mix}/kT) \ , \tag{3}$$

where $\Delta H_{\rm mix}$ is the heat of mixing; its value was obtained from tables calculated by Miedema.[10] The regular solution approximation is likely to be reasonable for metallic glasses. In analyzing the results, we first note in Fig. 2 that the Au marker moves away from the back Au reference marker. This means that Ni is the predominant moving species. The limited resolution of the BS system precluded an accurate measurement of $\partial X_A / \partial x$ and hence the marker velocity. However, from measurements of the marker shift after the specimen had become nearly homogeneous it was deduced that within the uncertainties, $\approx 10\%$, only Ni atoms move. This is in agreement with Cheng *et al.*[6] who have shown that $D_{Zr} < 0.05 D_{Ni}$. Solving Eqs. (2a)–(2c) with $D_{Zr} = 0$ yields the tracer diffusivities listed in Table I. If we assume for the present that the diffusion behavior in this amorphous alloy is Arrhenius, then the values of D^*_{Ni} at 528 and 573 K yield an activation enthalpy of diffusion of ≈ 105 kJ/mol. We emphasize that until Arrhenius behavior is confirmed, this value for the activation enthalpy must be regarded as very preliminary.

Figure 3 shows the SIMS data for the spreading of a Cu tracer impurity in *a*-$Ni_{50}Zr_{50}$. Each channel represents a depth increment of 0.052 nm. The sputtering beam was 5.5 keV O_2^+. The sputtered area was $\approx 6.25\times10^{-4}$ cm^2, whereas the area sampled by the mass spectrometer was $\approx 9\times10^{-6}$ cm^2. The sputtering rate was deduced from a Tally-Surf measurement of the final crater depth. The standard deviation of the Cu profile in an unannealed sample is ≈ 3.0 nm. This depth resolution of the system was factored from the diffusion profile assuming that the profiles were Gaussian and using the expression,

$$\Omega^2_{\rm diff} = \Omega^2_{\rm measured} - \Omega^2_{\rm unannealed} \ , \tag{4}$$

where Ω^2 is the variance of the distribution, and $Dt = 1/2\Omega^2_{\rm diff}$. The measurement of the spreading of the Au marker in the homogeneous alloy was determined similarly, only using BS rather than SIMS. The results of the Cu and Au diffusion measurements are also listed in Table I.

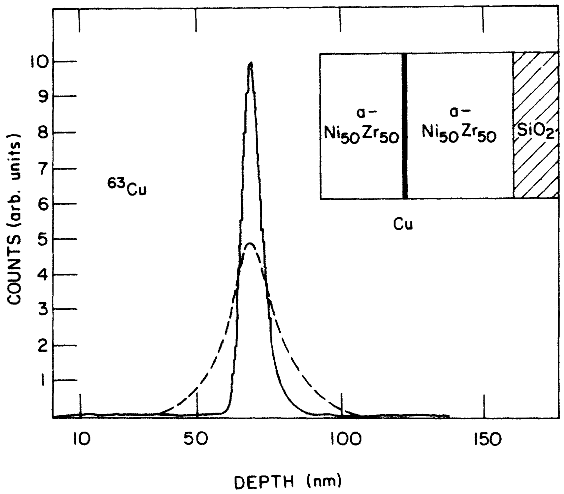

FIG. 3. Typical SIMS profile for the spreading of a Cu tracer impurity layer in *a*-$Ni_{50}Zr_{50}$ after annealing at 573 K.

The results of these experiments show that the tracer diffusivities of Ni and Cu are $\approx 1\times10^{-16}$ and 2×10^{-17} cm^2/s, respectively, in *a*-NiZr alloys near the equiatomic composition at 573 K. The diffusivity of Au at 573 K in this alloy is about 3 orders of magnitude smaller, and D^*_{Zr} is less than $0.1D^*_{Ni}$ (and less than $0.05D^*_{Ni}$ using the data of Cheng *et al.*[6]).

In evaluating the significance of these results, it is illuminating to compare these diffusivities to corresponding values in α-Zr. First, we note that in α-Zr the tracer diffusivities of Ni and Cu are more than 3 orders of magnitude greater than for Au or Zr (Ref. 11). The relative magnitudes of these diffusivities agree with those in our *a*-NiZr alloy. It has also been found in α-Zr and α-Ti that the activation enthalpy for fast diffusers like Ni and Cu, is ≈ 120–160 kJ/g atom,[12-14] whereas it is ≈ 285 kJ/g atom for self diffusion in α-Zr (Ref. 15). Diffusion in α-Zr and α-Ti has been explained on the basis of an interstitial diffusion mechanism, rather than a vacancy mechanism. Consistent with this interpretation is the fact that tracer diffusivities for metallic impurities scale with atomic radius. In the present study in amorphous NiZr alloys, we observe that the diffusivity also scales with atomic radius for the four tracers. In addition, we obtain an activation enthalpy for Ni diffusion of ≈ 105 kJ/mol, which is close to that observed in crystalline α-Zr. We are led to the hypothesis that the mechanism of diffusion in *a*-$Ni_{50}Zr_{50}$ alloy is perhaps similar to that in the pure crystalline α phase.

The magnitudes of the diffusivities in α-Zr and *a*-NiZr are more difficult to compare. However, if we extrapolate the measurements on α-Zr performed at 975–1075 K to ≈ 575 K, then we obtain a value of $\approx 2.8\times10^{-15}$ cm^2/s for D^*_{Cu} (Ref. 12) and somewhat larger for D^*_{Ni} (Ref. 13). These values are ≈ 3 orders of magnitude greater than the corresponding values in the amorphous alloy. Moreover, since the melting temperature of α-Zr is much higher than those for Ni-Zr compounds near equiatomic compositions, or for a hypothetical solid solution of hcp Zr-Ni alloy, the relative diffusivities in the amorphous phase are even smaller than those in the α-Zr when compared at homologous temperatures. As the activation enthalpy for diffusion in a-NiZr is similar to the crystalline phases, the preexponential factor for diffusion in the amorphous phase must be correspondingly smaller than in α-Zr. One factor that may decrease the value of the preexponential involves the variable size of the interstices in a random network. If an interstice is too small to hold a diffusing atom, that position is unreachable, and diffusion in its neighborhood is impeded. Since an activation barrier is not involved in this process,the decrease in the diffusion coefficient appears in the preexponential, specifically, in the physical correlation factor. However, this process can usually not account for a decrease of a factor of 500 in the diffusion coefficient.

In summary, we have measured the diffusion coefficients of Ni, Zr, Au, and Cu, in an a-NiZr alloy near the equiatomic composition. It was observed that Ni and Cu diffuse several orders of magnitude faster than either Au or Zr in this alloy. A preliminary activation enthalpy of 105 kJ/mol for Ni diffusion in the alloy was obtained. Comparison of the present diffusion results for activation enthalpies and influence of atomic radii with those for α-Zr and α-Ti suggests that the mechanisms of diffusion in the amorphous alloy and in the pure crystalline elements are similar.

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