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DIFFUSION STUDIES IN AMORPHOUS NiZr ALLOYS*

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Abstract:

Tracer impurity and self diffusion measurements have been made on amorphous (a-) NiZr alloys using radioactive tracer, Secondary Ion Mass Spectrometry and Rutherford backscattering techniques. The temperature dependence of diffusion in a-NiZr can be represented in the form $D = D_o \exp(-Q/kT)$, with no structural relaxation effects being observed. It was also found that the mobility of an atom in a-NiZr increases dramatically with decreasing atomic radius of the diffusing atom and also with decreasing Ni content for Ni concentrations below ≈ 40 at. %. These diffusion characteristics in a-NiZr are remarkably similar to those in α-Zr and α-Ti, and suggest that the diffusion mechanisms are alike. These mechanisms assume that Zr and Ti provide a close packed structure, either crystalline or amorphous, through which small atoms diffuse by an interstitial mechanism and large atoms diffuse by a vacancy mechanism.

Introduction:

Metastable materials have become of great interest in recent years due to their many desirable engineering properties. These

new materials are processed by various non-equilibrium methods: rapid quenching, ion or laser irradiation, ion implantation, solid state reactions and others. As metastable materials are not in equilibrium, they tend to transform to other lower energy phases. The stability of metastable systems and the exact path these systems follow in phase space are difficult to predict as they depend on several thermodynamic and kinetic factors. One of the important elements determining the kinetic behavior of metastable phases is the mobility of the constituent elements of the material. Diffusion in amorphous materials, however, is not well understood, with reliable data being scarce and often being plagued by structural relaxation effects. We have therefore begun a systematic study of diffusion in metallic glasses. In this paper, we report on diffusion in amorphous NiZr alloys. This investigation was of particular interest as it has been assumed for several years that diffusion in metallic glasses must be small [1]; however, the recent discovery of amorphization of metallic thin films by solid state reactions (ASSR) has proved otherwise [2]. This study is intended to elucidate the diffusion processes which occur during ASSR. In the broader sense, the study is intended to elucidate diffusion mechanisms in amorphous materials and other metastable systems.

Experimental:

The diffusion experiments were carried out by measuring the broadening of tracer impurity atoms, or markers, deposited at the center of a thin metal film, or the penetration profile of radioactive tracer atoms deposited on the surface of the film. The specimens were prepared by co-deposition of Ni and Zr from two rate-controlled electron beam guns onto oxidized Si wafers. The compositions of the evaporated thin films (typical thicknesses ≈200 - 400 nm) were checked by Rutherford backscattering analysis (RBS) using He-ions; they were found to be homogeneous over the thickness of the specimen to within ≈ 2% of their average composition. The

marker layers, which had thicknesses of ≈ 4 x 10^{15} atoms cm^{-2}, were deposited near the midplanes of the specimens from a resistance heated W boat by briefly opening a shutter during the growth of the film. In this way the marker atoms were dispersed over a 1.5 nm thickness of the alloy and thereby avoided discrete interfaces and the possibility of interfacial contamination. The specimens were diffusion annealed under UHV conditions. The temperature during the anneal was controlled to ≈ 2 °C. The specimens were checked by x-ray diffraction using a Read camera after annealing at the highest temperature to ensure that they had not crystallized.

The concentration-depth profiles of the markers were determined either by Secondary Ion Mass Spectrometry (SIMS) [3] for light markers (Cu, Fe or Ti) or by RBS for the heavy marker (Au). The determination of tracer diffusivities from these data is described elsewhere [4]. Tracer diffusivities of Ni (i.e. self diffusion) and Co were determined by radioactive tracer methods using sputter sectioning [5].

Results and Discussion:

The plots of the log c vs. x^2 for the diffusion of ^{60}Co and ^{63}Ni in a-$Ni_{50}Zr_{50}$, shown in Fig. 1, are linear over two decades in activity, aside from some tracer hold-up at the surface, so that reliable diffusivities can be obtained.

The values of D for ^{60}Co, ^{63}Ni, Cu and Au, shown in Fig. 2, follow an Arrhenius dependence

$$D = D_o \exp\{-Q/kT\} \qquad (1)$$

over 2 to 5 orders of magnitude; this indicates that a single diffusion mechanism is rate determining. Values of the pre-exponential factor D_0 and the activation enthalpy Q are listed in Table 1.

The possibility of structural relaxation processes occurring during the diffusion anneals was checked by measuring the diffusion coefficient of Co tracers in a sample which was pre-annealed at the same temperature as, and for a time a factor of ten longer than the diffusion anneal, and in a sample given no pre-anneal. The diffusion coefficients for the two treatments were the same within the experimental uncertainty. Moreover, for the Cu, Fe, and Au markers, the diffusion coefficient was independent of time, again indicating that no significant structural relaxation occurred during the diffusion anneal. Apparently, the constituent atoms in the amorphous alloy can arrange themselves into a structurally relaxed state during the growth of the sample. Given the bulk diffusion parameters shown in Table 1, significant surface diffusion and relaxation during the growth of the specimen at room temperature (or perhaps somewhat above due to radiation heating of the substrate during film growth) is not surprising.

Table 1 reveals that diffusion in a-$Ni_{50}Zr_{50}$ decreases with increasing atomic radius of the tracer atom. This trend was noted previously [6]; the details will be discussed elsewhere [7]. Comparison of the present diffusion data in a-NiZr with that in α- or β- Zr and Ti suggests that similar mechanisms of diffusion may be at play. Tracer diffusivities in these crystalline materials show the same dependence on atomic radius as that observed for a-NiZr [8,9]. Moreover, the activation enthalpy for fast diffusers in these crystalline materials is rather low, $\approx$ 1 eV, which is similar to that in a-NiZr. Although the mechanisms of diffusion in Zr and Ti have not yet been firmly established, it is currently believed that tracer impurities with small atomic radii, like Ni and Co, diffuse predominantly by an interstitial mechanism and those with large radii, like Zr or Ti, diffuse via a vacancy mechanism. More direct evidence for this model has been obtained through quasi-elastic neutron scattering measurements on a β-Zr-2 at.% Co-alloy [10]. It has been suggested from these measurements

that Co atoms are located in substitutional sites but that they are easily excited to interstitial sites where they undergo rapid interstitial migration, with most of the long range diffusion occurring via the interstitial mechanism. We believe that a similar process takes place in a-NiZr, i.e., that diffusion of atoms with small radii takes place by an interstitial-like process. In an amorphous structure, the definition of an interstitial is not precise, although the Bernal holes in a random close-packed structure are not unlike interstitial sites. Whereas the jump process from interstice to interstice has a unique activation enthalpy in crystalline materials the jumping from hole to hole in a-NiZr may not due to the size distribution of holes in an amorphous structure. However, the measured activation enthalpy for long range diffusion depends only on the rate limiting jump. This diffusion mechanism can also explain how long range diffusion takes place without concomitant crystallization, as the Zr atoms are too large to rearrange themselves. Additional evidence for a point defect like model of diffusion in a-NiZr derives from radiation-enhanced diffusion measurements [11]. These measurements show that the kinetics of RED are entirely similar to those in crystalline metals, with point defect-like entities, assumed to be the interstitial-like, making hundreds of jumps before finding recombination partners (vacancies).

Finally, we have measured the dependence of the tracer diffusion coefficient on the composition of the amorphous alloy at 573 K. These data are listed in Table 2. The diffusion coefficent is rather constant at high Ni compositions but it begins to increase rapidly with decreasing Ni composition at $\approx$ 40 at.% Ni. We can not be certain whether this critical composition, X_c, is a consequence of (1) a transition in the amorphous structure or (2) a critical filling of interstices in the random close packed structure of Zr- atoms by Ni atoms, i.e., a percolation effect. In regards to (1), the data can not be explained by scaling the diffusion data to homologous temperatures, i.e., T/T_g. We also

note that if the diffusion data for α-Zr (0.0 at. % Ni) is extrapolated downward to 573 K, the diffusion coefficients are two orders of magnitude higher than in a-$Ni_{50}Zr_{50}$, which is in the direction of the trend shown in Table 2.

Summary

Tracer diffusion in a-NiZr alloys has been measured for various atomic species as a function of temperature. The principal results are: (1) The temperature dependence of the diffusion coefficients indicate a single mechanism of diffusion over the temperature range of the experiments. (2) The diffusion coefficients decrease strongly with increasing atomic radius of the tracer atoms. (3) The diffusion coefficient for a particular tracer is nearly independent of alloy composition for Ni concentrations greater than $\approx$ 40 at. % but it increases rapidly with decreasing Ni concentration below this critical value. The data can reasonably be explained on the basis that diffusion in a-NiZr takes place by point defect-like entities, vacancies and interstitials. Atoms with small atomic radii diffuse mostly by an interstitial mechanism whereas atoms with larger atomic radii diffuse mostly by a vacancy like mechanism. The exact character of point defects in a-NiZr, however, remains unspecified.

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Table 1. Tracer diffusion coefficient parameters in amorphous $Ni_{50}Zr_{50}$.

Tracer	Atomic radius (nm)	D_o ($10^{-3}cm^2/s$)	Q (eV/atom)	D(573 K) ($10^{-18}cm^2/s$)
^{60}Co	0.126	3.6	1.40	1852.0
^{63}Ni	0.125	1.7	1.45	318.0
Cu	0.128	1.8	1.57	29.8
Fe	0.128	7.5	1.64	30.2
Au	0.144	0.15	1.77	0.044
Ti	0.147	-	-	0.160

Table 2. Dependence of the Cu-diffusion coefficient on alloy composition at 573 K.

x_{Ni} [at%]	D_{573K} [10^{-17} cm^2/s]
0.0	720.00 [a]
35.0	18.10
38.3	6.58
44.4	2.70
50.0	2.57
54.9	2.87
62.9	1.05
65.0	1.46

[a] extrapolated value from high temperature data (890 - 1130 K) [11]

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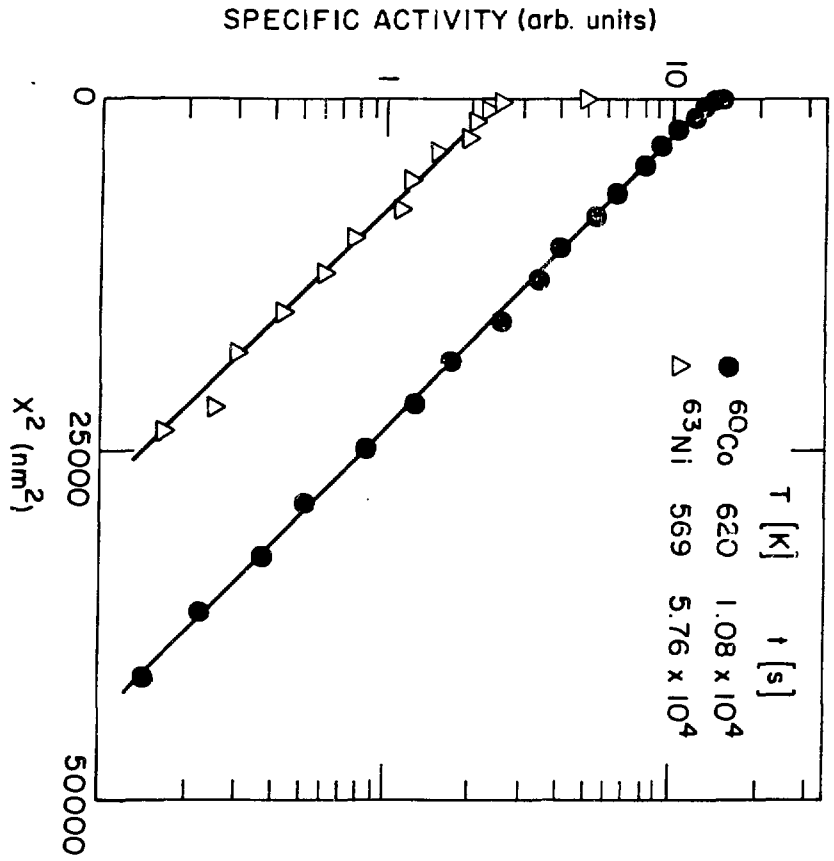
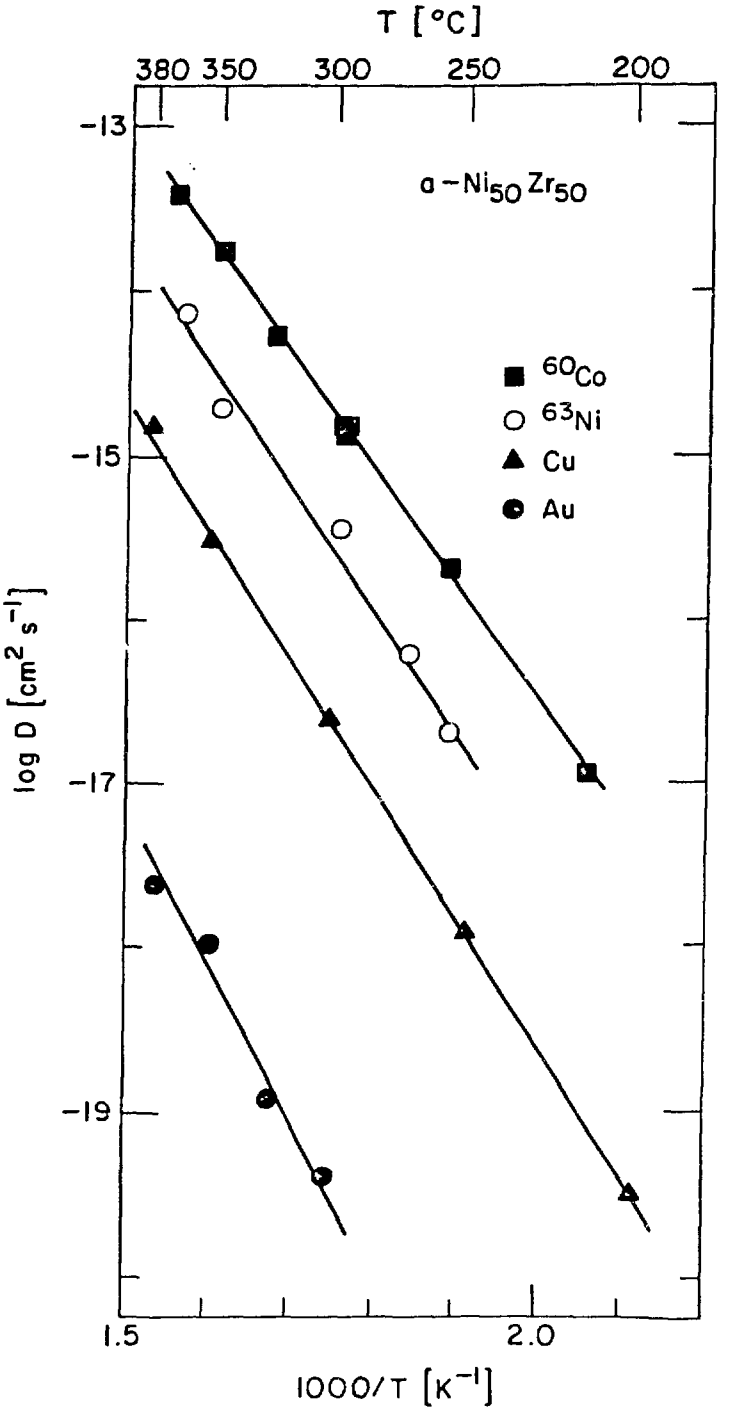
Figure Captions

Fig. 1. Typical penetration plots for ^{60}Co- and ^{63}Ni-diffusion in amorphous $Ni_{50}Zr_{50}$-alloys determined by sputter sectioning.

Fig. 2. Arrhenius-plots for the diffusion of ^{60}Co, ^{63}Ni, Cu and Au in amorphous $Ni_{50}Zr_{50}$-alloys.


SPECIFIC ACTIVITY (arb. units)
10
0
25000
50000
X² (nm²)
● ⁶⁰Co 620 1.08 x 10⁴
△ ⁶³Ni 569 5.76 x 10⁴
T [K] t [s]


T [°C]
380 350 300 250 200
-13
-15
-17
-19
a-Ni50 Zr50
60Co
63Ni
Cu
Au
log D [cm2 s-1]
1.5
2.0
1000/T [K-1]

F. 2