TRACER DIFFUSION OF ^{60}Co AND ^{63}Ni IN AMORPHOUS NiZr ALLOY*

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DISCLAIMER

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Tracer diffusion of ^{60}Co and ^{63}Ni in equiatomic amorphous NiZr alloy in the temperature range between 486 and 641 K can be described by:

$$D^*_{Co} = 3.7 \times 10^{-7} \exp[-(135 \pm 14) \text{ kJ mole}^{-1}/RT] \text{ m}^2/\text{sec}$$

and

$$D^*_{Ni} = 1.7 \times 10^{-7} \exp[-(140 \pm 9) \text{ kJ mole}^{-1}/RT) \text{ m}^2/\text{sec}.$$

The values of D^*_{Ni} are in reasonable agreement with those measured by the Rutherford backscattering technique. The measured diffusivities were independent of time, indicating that no relaxation took place during diffusion.

1. INTRODUCTION

A knowledge of atomic transport in amorphous metallic alloys is indispensable not only for the understanding of basic phenomena such as the tendency to glass formation and the stability and structural relaxation of the glass, but also because amorphous materials are formed by solid state reactions using diffusion couples [1-3]. However, only few measurements of diffusivity in amorphous alloys have been carried out so far because of the experimental difficulties of measuring the very small diffusion coefficients, usually less than 10^{-17} m^2/sec [4] which are typical of metallic glasses below their crystallization temperatures. Such small diffusivities are often measured by the Rutherford backscattering technique (RBS) or secondary ion

mass spectrometry (SIMS) [5-8]. Only a few direct measurements using radioactive tracers and the ion beam sputter-sectioning technique have been carried out on amorphous alloys [9-13].

In this paper, we report measurements of the impurity diffusion of ^{60}Co and the self-diffusion of ^{63}Ni in an amorphous NiZr alloy near the equiatomic composition and of the activation enthalpy and the pre-exponential factor for these. The data were obtained by the ion beam sputter-sectioning technique.

2. EXPERIMENTAL PROCEDURE

Amorphous thin layer samples were prepared by the codeposition of Ni and Zr from two rate-controlled electron guns onto a SiO_2 substrate in an ultrahigh-vacuum system as described previously [5]. The thickness of the amorphous layers was typically 450 nm. The samples were cut into ~6x6 mm squares. The isotopes ^{60}Co and ^{63}Ni were obtained from Oak Ridge National Laboratory in the form of 0.5 M HCl solutions. The pH of the tracer solution was adjusted to ~7 by the addition of NH_4OH, and the isotope was electroplated on the sample surface. The specific activity of the radioactive tracers was high enough so that the tracer deposit was a "thin layer." The samples were diffusion annealed sealed in quartz tubes evacuated to 10^{-3} Pa. The furnace temperature was controlled to ±2 K. The temperature of the anneals was monitored with a Pt-Pt 10% Rh thermocouple. The annealing time was corrected for diffusion during the heating of the samples for annealing times shorter than 1.4×10^4 sec. After the diffusion anneal, the edges of the samples were carefully ground to eliminate the possibility of additional activity diffusing from the sides of the samples.

The concentration profile of the radioactive tracer was determined using the ion beam sputter-sectioning technique [14]. The diffused specimen was fixed on a graphite cap using silver paint, and sputtered by high purity (99.999%) 500 eV argon ions. The graphite cap was attached to a copper rod which was rotated during sputtering for uniformity of irradiation. The penetration distance was evaluated from the total weight loss during sputtering, the specimen area, and the density of the materials, estimated as 7.47 g/cm^3 from the density of the equiatomic intermetallic compound NiZr. Typical mass losses during sputtering of about 80 μg were determined within ±1 μg; this corresponded to a sputtering rate of about 20 nm/min. The material removed by sputtering was collected on a Mylar foil, which was advanced 90 mm for each section and subsequently cut up into pieces corresponding to the sections. The activity of each section was counted in a well-type NaI(Tl)-crystal scintillation counter (^{60}Co diffusion: γ-rays 1.17 and 1.33 MeV) or a liquid scintillation counter (^{63}Ni diffusion: β-ray 0.067 keV max.). In order to control that the samples remained amorphous during diffusion annealing, reference samples were checked by X-ray Read camera analysis.

The distribution of specific activity, C, of a radioactive tracer for these experimental conditions can be expressed in the usual Gaussian form:

$$C = [M(\pi D^* t)^{-1/2}] \exp(-X^2/4D^* t), \tag{1}$$

where X is the penetration distance, D^* is the tracer diffusion coefficient, M is the activity per unit area deposited on the plane X = 0 at t = 0 and t is the diffusion time.

3. RESULTS AND DISCUSSION

The typical penetration plots of log C vs X^2 for the diffusion of ^{60}Co or ^{63}Ni in the amorphous $Ni_{50}Zr_{50}$ alloy (figure 1) are straight lines over 1 or 2 orders of magnitude in specific activity, except for the first several sections. The deviations from Gaussian behavior near the surface, especially apparent for the diffusion of Co, were probably caused by surface hold-up. Hold-up of electroplated isotopes on a Zr-base alloy is not unexpected; it may be due to oxidation of the near surface layers, which then act as a barrier against diffusion, or to difficulty in dissolving Co. A similar surface hold-up was also reported for diffusion in amorphous $Fe_{40}Ni_{40}B_{20}$ alloys [10]. The values of D are listed in tables 1 and 2.

The uncertainties in the diffusion coefficients determined from a least-squares fit of the data to equation 1 are less than 5%, the reproducibility is ±9%. The largest uncertainty in D arises from the determination of the sputtering rate, which is evaluated from the weight change, density, and area of specimen. This increases the uncertainty in the absolute value of diffusivity to about 10%.

The temperature dependence of D_{Co}^* and D_{Ni}^* in the a-NiZr alloy (figure 2) exhibits Arrhenius type behavior, indicating that the diffusion process can be
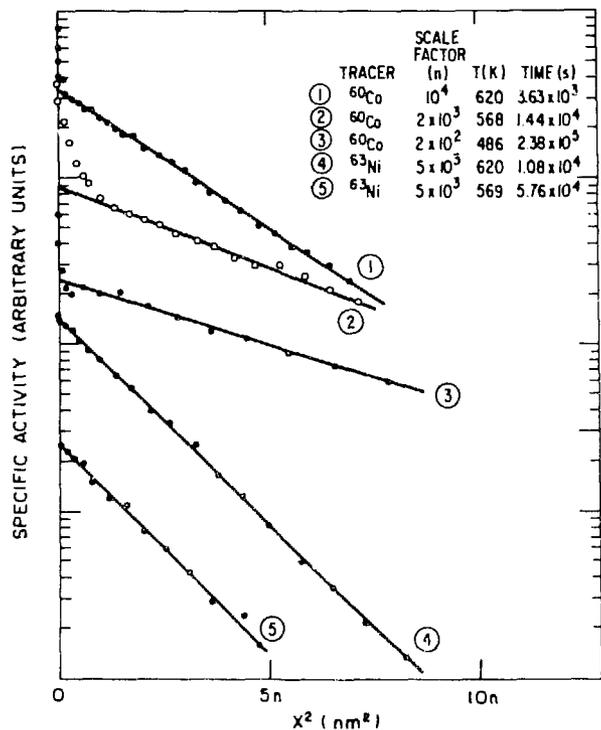

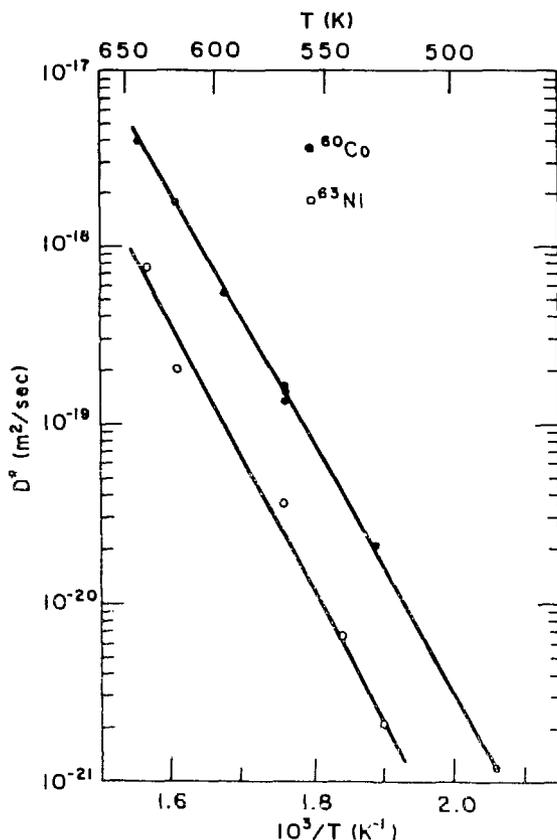Fig. 1. Typical plots of log C vs X^2 for the diffusion of Co and Ni in a-NiZr alloy.

Fig. 2. Temperature dependence of D_{Co}^* and D_{Ni}^* in a-NiZr alloy.

Table 1. Diffusion coefficients of ^{60}Co in amorphous NiZr alloy.

Diffusion Temperature (K)	Diffusion Time (sec)	D^*_{Co} (m^2/sec)
486	2.38×10^5	1.21×10^{-21}
530	8.64×10^4	2.16×10^{-20}
567	1.44×10^4	1.35×10^{-19}
568	1.44×10^4	1.54×10^{-19}*
568	5.76×10^4	1.60×10^{-19}
596	3.65×10^3	5.37×10^{-19}
620	3.63×10^3	1.80×10^{-18}
641	1.44×10^3	3.91×10^{-18}

*Annealed at 568 K for 1.73×10^5 sec, prior to deposition of tracer.

Table 2. Diffusion coefficients of ^{63}Ni in amorphous NiZr alloy.

Diffusion Temp. (K)	Diffusion time (sec)	D^*_{Ni} (m^2/sec)
527	3.46×10^5	2.12×10^{-21}
543	3.46×10^5	6.61×10^{-21}
569	5.76×10^4	3.63×10^{-20}
620	1.08×10^4	2.05×10^{-19}
638	3.70×10^3	7.65×10^{-19}

expressed by a single activation barrier over the temperature range investigated. The least-squares fit of the diffusion data yields:

$$D^*_{Co} = 3.7 \times 10^{-7} \exp\left(-\frac{135 \pm 14 \text{ kJ/mole}}{RT}\right) \text{ m}^2 \text{ s}^{-1} \qquad (2)$$

and

$$D^*_{Ni} = 1.7 \times 10^{-7} \exp\left[-\frac{140 \pm 9 \text{ kJ/mole}}{RT}\right] \text{ m}^2 \text{ s}^{-1} \tag{3}$$

The present data for D^*_{Ni} are in reasonable agreement with the published data measured by RBS; $D^*_{Ni} = 10^{-19} \sim 10^{-20}$ m^2 s^{-1} at 523 K [7,8] and 10^{-20} m^2 s^{-1} at 573 K [5]. The RBS values of ref. 5 are an average over a wider concentration range, which may account for part of the difference, as the diffusion is considerably composition dependent [15]. These diffusion coefficients are much larger than the diffusion coefficient of Zr in this material, as already observed by Hahn et al., who have pointed out [5,16] the similarity of the size effect for diffusion in amorphous NiZr and α-Zr [17].

A comparison of the diffusion parameters of Co and Ni in a-NiZr with their diffusion parameters in α-Zr is difficult because the data for the diffusion of Ni [18-20] and Co [21] in Zr are rather scattered owing to anisotropy of diffusion in the HCP α-Zr lattice and to complications brought on by very low solubilities. The activation energy for the diffusion of Co in α-Zr, $\perp$ to c and for T > 650°C, $\approx$ 147 kJ/mol, is probably representative of the easy interstitial jump of Co in α-Zr, and it is nearly the same as the activation energy for the diffusion of Co in the amorphous material. On the other hand, the size effect correlations [17,19,23] predict a much smaller activation energy for the diffusion of Ni and Co in α-Zr.

The values of D_0 in α-Zr are considerably higher than in amorphous NiZr. The comparison with values for the diffusion of Co [22] and Ni [18] in α-Ti is similar. The much smaller value of the pre-exponential factor for diffusion in amorphous materials may be related to a small physical correlation factor [5]. It seems likely that amorphous structures have variably sized 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 the unreachability of this site is independent of temperature, the decrease of the diffusion coefficient due to this effect appears in the pre-exponential factor. That Co and Ni diffuse through interstices in the amorphous NiZr network has been suggested by Hahn et al. [5], on the basis of the similarity of the size effect for diffusion in amorphous NiZr and α-Zr mentioned above. Atoms with a small metallic radius, such as Ni and Co, are considered to diffuse by a dissociated interstitial mechanism in α-Zr because they diffuse some eight orders of magnitude more rapidly than self-diffusion [20,24], and the same size dependence is observed for amorphous NiZr.

In order to investigate the time dependence of diffusivity and the effect of structural relaxation on diffusivity, three diffusion runs for Co tracer were carried out at 568 K. As listed in table I, the diffusion coefficients in the specimens diffused for 4 and 16 h are identical; thus a time-independent diffusivity was confirmed. Also, the absence of a structural relaxation effect on diffusivity was confirmed because the same values of the diffusivity were observed for both specimens not annealed before diffusion and annealed 48 h before diffusion. Although the effect of relaxation processes on diffusivity has been observed often in the amorphous materials produced by rapid quenching techniques [10], the specimens in the present study, which were produced by the evaporation technique, are free from structural relaxation as expected from previous RBS and SIMS measurements [16].

The results of Horváth et al. [12,25] are also valid for fully relaxed amorphous metals, so it seems desirable to compare their results and ours. Only their value of D_0 for the diffusion of ^{59}Fe in 91Fe-9Zr alloy is near our D_0's; the other range from 4.6×10^{-5} to 7×10^6 $m^2 s^{-1}$. This vast range of D_0 may indicate different structures and different diffusion mechanisms; at first glance, however, it bears a disturbing resemblance to the chaotic situation that existed for diffusion in crystalline metals in the early 1950s [26].

Impurity diffusion in α-Zr [23], as in many metals, follows the relation suggested by Zener [27] that $ln(D_0)$ varies linearly with Q; these plots usually have a positive slope. When the (rather sparse) data for a-NiZr are plotted in the same way, the slope is negative, for unknown reasons. Plotting all the data of Horváth et al. as well as ours in the same coordinates leads to an overall positive slope.

In summary, the diffusion coefficients of ^{60}Co and ^{63}Ni have been determined in an amorphous NiZr alloy near the equiatomic composition. The diffusion coefficients are time-independent. From comparison of the present activation enthalpies and atomic size effect with those for crystalline α-Zr, it is suggested that Co and Ni diffuse via interstices in the a-NiZr alloy.

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