

Radiation-enhanced diffusion in amorphous Ni-Zr alloys

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Radiation-enhanced diffusion of Cu and Au tracer impurity atoms during Kr^+ irradiation has been measured in amorphous $Ni_{50}Zr_{50}$ and $Ni_{35}Zr_{65}$ alloys in the range 80–573 K. At low temperatures, the spreading of the thin impurity layers was due to ion beam mixing and was independent of temperature. Above ≈ 400 K, the diffusion coefficient of Cu in $Ni_{50}Zr_{50}$ shows Arrhenius behavior with an apparent activation enthalpy of ≈ 0.55 eV, and it depends on the square root of dose rate. The radiation-enhanced diffusion coefficient is greater for Cu than Au and is also larger in the Zr-rich alloy.

The relationship between point defects and diffusion in crystalline materials has been realized for many years, and in many metals consistency between measured point-defect properties and diffusion kinetics is obtained. In amorphous alloys, the level of understanding of diffusion processes is far less, and basic questions regarding the nature of point defects and their relevance to diffusion processes are controversial.¹⁻³ One of the difficulties in elucidating the basic diffusion mechanisms in amorphous alloys has been that the modern methods of probing point defects in crystalline materials, such as diffuse x-ray scattering, positron annihilation, and other nuclear methods are not well suited for amorphous alloys; moreover, the basic instability of amorphous alloys greatly restricts the temperature range of diffusion measurements. We have approached this problem of investigating the possible role of point defects in diffusion in amorphous alloys by using ion irradiation. Ion irradiation produces point defects in solids; therefore, if diffusion in amorphous materials is mediated through point-defect-like entities, as in crystalline materials, then ion irradiation should lead to radiation-enhanced diffusion (RED).

A simple model of RED can be employed to illustrate how the kinetics of diffusion depend upon point-defect parameters. In this model, the RED coefficient is expressed as⁴

$$D_{RED} = f_i D_i C_i + f_v D_v C_v, \quad (1)$$

where D_j is the diffusivity of either vacancies (v) or interstitial atoms (i) and is given by

$$D_j = D_{0j} \exp(-\Delta H_j^m / k_B T), \quad (2)$$

where ΔH_j^m is the migration enthalpy of the vacancy or interstitial atom, and $k_B T$ is the product of Boltzmann's constant and temperature. The f_j are correlation factors, and C_j are the instantaneous supersaturation concentrations of vacancies and interstitial atoms produced by irradiation and C_{j0} are the concentrations in thermal equilibrium. During irradiation, these concentrations are given by the coupled equations

$$dC_i/dt = \sigma\phi - K_{iv} C_i (C_v + C_{v0}) - K_{is} C_i C_s, \quad (3a)$$

$$dC_v/dt = \sigma\phi - K_{iv} C_v (C_i + C_{i0}) - K_{vs} C_v C_s, \quad (3b)$$

where σ is the cross section for Frenkel pair production, ϕ is the ion flux, C_s is the concentration of point-defect sinks, and the rate constants are given by

$$K_{iv} = (4\pi r_{iv}/\Omega)(D_i + D_v); \quad K_{is} = (4\pi r_{is}/\Omega)D_i;$$

and

$$K_{vs} = (4\pi r_{vs}/\Omega)D_v,$$

and r_{mn} and Ω are the relevant reaction radii and atomic volume, respectively. Equations (3a) and (3b) neglect interactions between like defects (such as vacancy-vacancy clustering reactions, etc.) and "correlated" recombination⁴ and other details of the defect production process. Three steady-state (or quasisteady state) regimes are of interest here: (i) When point defects recombine via correlated (or spontaneous) recombination, or when they annihilate predominantly at fixed sinks, the RED coefficient is independent of temperature, and it depends linearly on ion flux. (ii) When point defects annihilate by recombination, the RED coefficient has the form

$$D_{RED} = A \exp(-\Delta H_j^m / 2k_B T) \phi^{1/2} \quad (4)$$

depending exponentially on temperature and on the square root of ion flux. Here j normally refers to the slower-moving defect.⁴ (iii) When the equilibrium concentration of point defects dominates the total defect concentration, i.e., at high temperatures, the RED coefficient merges with the diffusion coefficient in absence of irradiation. In an amorphous material, the excess free volume is typically greater than that due to vacancies in crystalline materials near their melting temperatures. On this basis, it might appear that irradiation would have little influence on diffusion in metallic glasses since the production of additional vacancies would be a small perturbation on the free volume, and interstitials produced would be immediately absorbed in this free volume.² Thus, whether or not RED occurs in metallic glasses, and what the kinetics might be, are difficult to predict.

The specimens for these experiments were produced by simultaneous vapor deposition of Ni and Zr atoms from separate electron-beam guns onto oxidized Si substrates. Either Au or Cu tracer impurity atoms $\approx 1 \times 10^{15} \text{ cm}^{-2}$, were deposited near the midplanes of the samples. The

tracer atoms were deposited during the growth of the alloy over a thickness of ≈ 2 nm to avoid discrete impurity layers. Continuous deposition also prevents contamination at the marker layer, a common problem encountered when alloy growth is momentarily interrupted for the deposition of the impurity layer. The background pressure during deposition was $\approx 5 \times 10^{-8}$ Torr. The 1-MeV Kr irradiation beam was rastered to provide a homogeneous flux. A mask over the specimens restricted the size of the beam on the specimen to spots of 2-3-mm diam; a small spot size helps to reduce beam heating. The current densities ranged between ≈ 0.1 and $2 \mu\text{A cm}^{-2}$ for different irradiations; they were kept constant, however, for each irradiation. Diffusion profiles were measured using secondary-ion mass spectroscopy (SIMS) and Rutherford backscattering spectrometry (RBS) for the Cu and Au tracer atoms, respectively. Several specimens were analyzed by x-ray diffraction (using a Read camera) to verify that the ion irradiation had not induced crystallization.

Plotted in Fig. 1 as a function of inverse temperature are the normalized diffusion parameters, $Dt/\Phi F_D$, for several specimens. Here t is the time of the irradiation, Φ is the ion fluence, and F_D is the damage energy deposition per unit length normal to the specimen surface. This parameter is useful for describing RED as it normalizes the diffusion coefficient to the rate of "damage energy" deposition, and to a first approximation, to point-defect production. Thus, $Dt/\Phi F_D$ is helpful for comparing RED in different materials and for different types of ion irradiation. The results show that $Dt/\Phi F_D$ is nearly independent of temperature at low temperatures and increases with temperature at higher temperatures. The increase in $Dt/\Phi F_D$ at higher temperatures is generally an indication of the onset of RED. The figure also shows (1) the onset of RED for Cu tracer impurities in α -Ni-Zr occurs at much lower temperatures than it does for Au tracer impurities; (2) $Dt/\Phi F_D$ is larger for Cu than Au tracer atoms; and (3) $Dt/\Phi F_D$ for Au is larger in $\text{Ni}_{35}\text{Zr}_{65}$ alloy than in the $\text{Ni}_{50}\text{Zr}_{50}$ alloy.

Further analysis of the RED behavior requires separation of the temperature-independent and temperature-dependent contributions to the diffusion coefficient. We

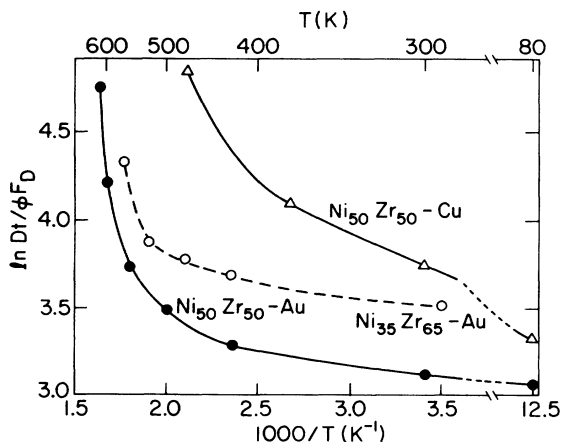


FIG. 1. The normalized diffusion coefficient, $Dt/\Phi F_D$, plotted as a function of inverse temperature.

assume that the temperature-independent part of the diffusion coefficient at low temperature is due to ion mixing, and the higher temperature part is due to RED so that

$$D_{\text{RED}}(T) = D(T) - D(78 \text{ K}),$$

where $D(T)$, $D_{\text{RED}}(T)$, and $D(78 \text{ K})$ are the measured, radiation-enhanced, and ion beam mixing diffusion coefficients, respectively. The resulting values of $D_{\text{RED}}(T)$ are illustrated in Fig. 2. These data show Arrhenius behavior with an apparent activation enthalpy of ≈ 0.55 eV. The diffusion coefficient in the same alloy during thermal annealing is also shown in this figure to illustrate the strong enhancement of diffusion due to Kr irradiation.

The magnitude of the diffusion is also of interest. If we assume that

$$Dt = \frac{1}{6} n \lambda^2 \tag{5a}$$

and use Kinchin-Pease expression for defect production,

$$N = 0.8 E_D / 2 E_d, \tag{5b}$$

where n is the jumps per atom in a time t , λ is the jump distance, N is the number of Frenkel pairs created during the irradiation, E_D is the deposited damage energy, and

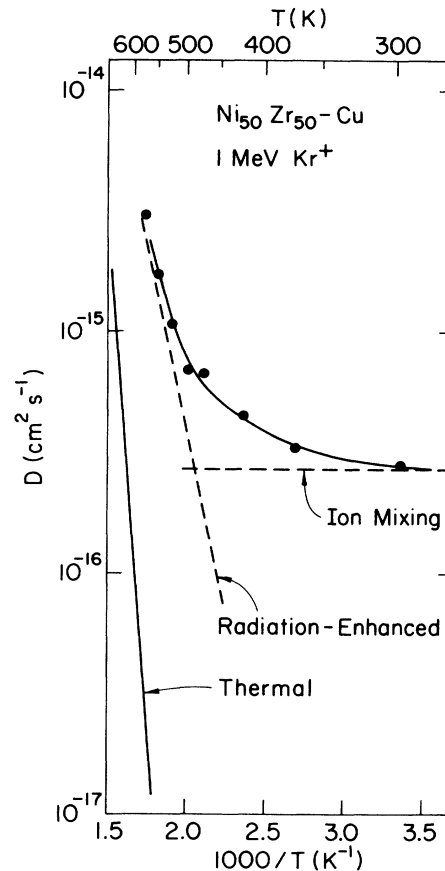


FIG. 2. The contributions of RED, ion beam mixing, and thermal annealing to the diffusion coefficient of Cu in $\text{Ni}_{50}\text{Zr}_{50}$ as a function of inverse temperature. ● indicate measured diffusivities during irradiation.

E_d is the displacement energy for Frenkel pairs, we find that the number of jumps per Frenkel pair is given by

$$\alpha = Dt/\Phi F_D (n_0 E_d / 0.067 \lambda^2) . \quad (5c)$$

At low temperatures, where $Dt/\Phi F_D$ is $\approx 25 \text{ \AA}^5/\text{eV}$, $\alpha \approx 100$. At high temperatures, this value increases to over 2000. Moreover, as it is generally found that the Kinchin-Pease expression overestimates defect production by a factor of 3 (Ref. 5) and that the fraction of these point defects that escape correlated recombination in a cascade is lower,^{6,7} we estimate that the number of jumps per Frenkel pair is greater than 5000. Thus, if point defects are responsible for the diffusion, they must undergo a long-range diffusion process.

Measurements of the dose-rate dependence of $D_{\text{RED}}t/\Phi F_D$ have also been performed; these results are plotted in Fig. 3 as $D_{\text{RED}}t/\Phi F_D$ vs $\dot{\phi}^{-1/2}$ [see Eq. (4)]. Within the uncertainties, the data are linear, although the line fails to pass through the origin at infinite flux as predicted by Eq. (4). There are many possible reasons why the line does not pass through the origin: (i) the point defects are not produced randomly, as assumed in Eq. (3a), but rather in cascades so that some interstitial atoms return to their nascent cascade and recombine. This mechanism, correlated recombination, reduces $D_{\text{RED}}t/\Phi F_D$ least at high dose rates (small $\dot{\phi}^{-1/2}$) where the migration distance of an interstitial, for example, to a foreign vacancy is similar to that to a vacancy in its nascent cascade. (2) Other approximations in the RED model leading to Eqs. (3a) and (3b) for example, a constant sink structure, do not adequately describe RED behavior in heavy-ion-irradiated amorphous materials. (3) Some beam heating of the specimens irradiated at the higher dose rates increases their temperatures, thus increasing their diffusion rates.

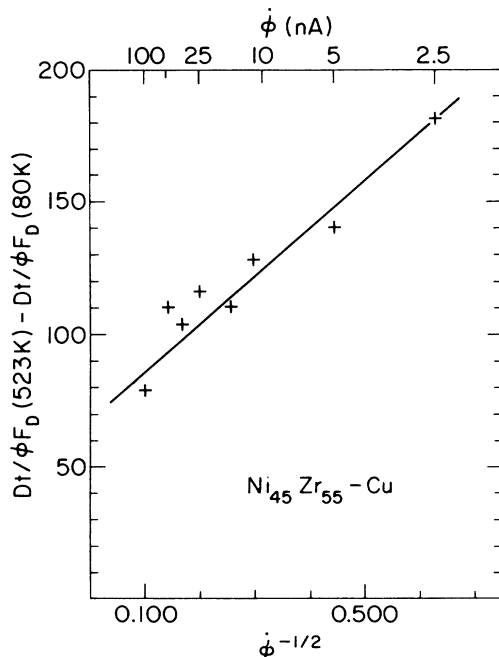


FIG. 3. The normalized diffusion coefficient, $Dt/\Phi F_D$, plotted as a function of the inverse square root of ion flux.

The important feature, however, is that $Dt/\Phi F_D$ decreases with increasing dose rate, thus revealing kinetics greater than first order.

These experiments show that RED occurs in NiZr amorphous alloys with kinetics remarkably similar to those expected for crystalline materials.⁴ Since particle irradiation produces point defects, it is natural to attribute the RED behavior to a point-defect-like mechanism. We exclude the possibility that the observed temperature dependence of RED is a consequence of a temperature dependence in ion beam mixing since the inverse square-root dependence of $Dt/\Phi F_D$ on $\dot{\phi}$ is inconsistent with this mechanism.

Although the observed kinetics of diffusion at elevated temperatures indicate that the dominant mechanism of defect loss is through recombination, i.e., regime (ii) above, the nature of these defects is unclear. Our recent measurements of diffusion in α -Ni-Zr during thermal annealing provides helpful clues. These studies have revealed the following. (i) The tracer diffusion coefficient of an atomic species is predominantly determined by its atomic radius, varying over four orders of magnitude between small atoms (e.g., Ni or Co) and large atoms (e.g., Ti, Bi).⁸ (ii) The temperature dependence of diffusion has Arrhenius behavior with an activation enthalpy of diffusion of 1.6 and 1.8 eV for Cu and Au tracer diffusion, respectively.⁹ (iii) The tracer diffusion coefficients increase rapidly with decreasing Ni content in alloys containing less than ≈ 45 at. % Ni.⁹ Results (i) and (ii) are remarkably similar to diffusion behavior in α -Ti (Ref. 10) and α -Zr (Ref. 11) and suggest a common diffusion mechanism. It has been proposed that diffusion of small atom impurities in these hcp metals occurs by the activation of the impurity from substitutional sites to interstitial sites followed by rapid interstitial diffusion.^{10,11} We propose that a similar mechanism takes place in α -Ni-Zr. The diffusion of small impurity atoms and host Ni atoms occurs by their activation from "substitutional" or relaxed positions to interstitial sites followed by migration via interstitial sites. The possibility of an interstitial mechanism of diffusion in metallic glasses has been suggested previously.³ A vacancy in this model of diffusion for amorphous Ni-Zr is defined by the site vacated by the small atom impurity, or host Ni atom. Consequently, this site can accommodate a small atom but not a large one.

With these identifications of vacancies and interstitials, the observed RED behavior acquires a rather straightforward interpretation. Irradiation of the amorphous material displaces atoms from their relaxed, "substitutional" sites. If a Zr atom is displaced, it leaves a large hole which is rapidly reduced in size by a combination of relaxation and filling by small Ni atoms. When the size of the hole obtains a small critical size, its collapse stops as even small Ni atoms cannot relax into it. Vacancy motion can then proceed by its exchange with small atoms, Ni or impurity; large atoms cannot fit within the small vacancy. It is expected also that the interstitial atoms will be predominantly small atoms as the strain energy for small interstitials in a close-packed structure should be smaller than that of large atoms. This is the case in crystalline materials.¹² Thus, the observed kinetics of RED in amorphous

Ni-Zr alloys can be explained similarly to that in crystalline materials, i.e., through recombination of vacancies and interstitials. Since the interstitial atoms are small atoms and vacancies exchange only with small atoms, the observation that Cu is far more mobile than Au under irradiation is reasonable. Using a Kirkendall geometry with a Ni-Zr diffusion couple, we have also determined that Ni is far more mobile than Zr in irradiated amorphous Ni-Zr.¹³ The apparent activation enthalpy of diffusion in this RED model corresponds to half the migration enthalpy of the slower moving defect, vacancy or interstitial, i.e., $\Delta H_f^m \approx 1.1$ eV [Eq. (4)]. Although this simple diffusion model is capable of explaining the RED behavior in a straightforward manner, we do not suggest that this explanation is unique. For example, we can imagine rapid relaxation or delocalization of the interstitial atom and migration of only the small vacancy. Recombination in this model would correspond to vacancy-

vacancy clustering and annihilation by relaxation of the larger hole. Thus, the details of the point-defect processes are not elucidated by this RED experiment. Nevertheless, the experiment does provide evidence that RED does take place in metallic glasses with kinetics similar to those in crystalline materials. The simplest explanation for these results is that diffusion in α -Ni-Zr is mediated through point-defectlike entities and that these defects can undergo "recombination" reactions.

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