Diffusion in the Amorphous Phase of Pd–19-at.%-Si Metallic Alloy

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Diffusion of Ag^{110m} radioactive tracer has been measured in amorphous Pd–19-at.%-Si specimens characterized by a Seeman-Bohlin x-ray diffractometer. The diffusion parameters in this metallic amorphous phase have been found to have a regime distinctly different from liquid and crystalline phases.

In the recent years amorphous metallic alloys have received much attention as many of their properties have unexpected features.[1,2] Although an understanding of self- and impurity diffusion would be of great help in understanding the thermal stability and atomic structure of these phases, no measurements have been reported. This is because of the extremely shallow tracer penetration distances attainable at temperatures below the liquid-to-glass transition. By combining the radioactive tracers with a novel method of tracer microprofiling (in ~30-Å or more steps) by rf backsputtering in an Ar gas discharge[3,4] we have been able to overcome this limitation and carry out measurements of diffusion coefficients as small as 10^{-20} cm^2/sec. We believe these are the smallest impurity diffusion coefficients ever measured directly.

In this Letter, we report the diffusion measurement of Ag^{110m} radioactive tracer in a Pd–19-at.%-Si splat-quenched amorphous alloy[5] in the 186–279°C temperature range employing the microprofiling technique. The choice of Ag^{110m} radioactive tracer was made on the basis of its convenience and also because of its close similarity to Pd in Pd–19-at.%-Si amorphous phase. A Seeman-Bohlin x-ray diffractometer[6] with monochromated Cu $K\alpha$ radiation was used to assure the amorphous state of the specimens before and after the diffusion anneals. The diffractometer is capable of analyzing the structure of a thin film of 200 Å in thickness. The specimens (1.5 cm diam × 50 μm) were polished to mirror finish, analyzed by the x-ray diffractometer, and mounted in the rf sputtering apparatus for the purpose of cleaning, removing surface oxides, and the incorporating of the Ag^{110m} tracer in a single step without opening to the surroundings—the procedures have been described elsewhere.[4] The diffusion annealings were carried out in quartz ampules evacuated to 10^{-6} Torr pressure.

The x-ray diffraction spectra of the amorphous Pd–19-at.%-Si specimens before and after diffusion annealing are shown in Fig. 1. It is seen that following diffusion for the various times and temperatures listed in Table I, the specimens retained their amorphous nature fully at least up to 240°C. However, the specimen which was annealed at 279°C for 1.63×10^6 sec showed crystallization as evidenced by sharp peaks from which presence of a mixture of Pd and $\mathrm{Pd_3Si}$ crystalline phases was deduced.

The Ag^{110m} radioactive tracer penetration profiles—*plots of logarithm of specific activity versus logarithm of penetration distance*—for all the measurements are shown in Fig. 2. The maxima

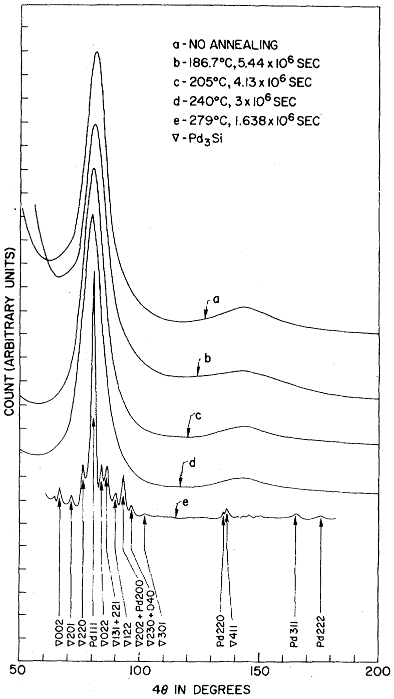

FIG. 1. The x-ray diffraction patterns of Pd–19-at.%-Si amorphous specimens before and after diffusing Ag^{110m} radioactive tracer. Monochromatic Cu $K\alpha$ radiation was used. Note the emergence of Pd and $\mathrm{Pd_3Si}$ intermetallic phase in the 279°C diffusion.

of these profiles have been brought to the same specific activity level on an arbitrary scale. It is seen in profile (1) in Fig. 2 that the as-incorporated Ag^{110m} tracer ions showed a depth distribution of ~200 Å in the specimen even without diffusion annealing. The observation is not surprising as the tracer incorporation method used is akin to ion implantation with an energy of ~500 eV which would correspond to Ag ion ranges of several tens of angstroms in crystalline Pd. The large Ag ion ranges in the present case appear to be related to the amorphous nature of the specimens and somewhat less dense atomic packing therein. The procedure, however, did eliminate the intervening oxide film which would have been inevitable otherwise. Subsequently, the profiles (2 through 6) showed systematic broadening and shifts to greater depths as the diffusion times and temperatures increased (Table I).

Since the Ag^{110m} profiles could not be satisfactorily plotted as either Gaussian or complementary error functions, a less precise analytical procedure was used to extract diffusion coefficients. The profile widths were noted at half-heights and the half-profile broadening was related to the diffusion coefficient by

$$\tfrac{1}{2}(\mu - \mu_0) \simeq 2(D_a t)^{1/2}, \qquad (1)$$

where μ is the profile width at half-height after annealing for time t, μ_0 referring to the as-incorporated Ag^{110m} distribution, and D_a is the diffusion coefficient. The Arrhenius parameters, the pre-exponential factor D_a^0 and the activation energy Q_a, were then determined from the temperature-dependent diffusivities; the subscript a refers to the amorphous phase. The various measured and derived quantities are listed in Table I and the diffusivities displayed in Fig. 3 which show a confidence of ± 50%. The parameters for Ag^{110m} diffusion in the amorphous Pd-19-at.%-Si alloys are determined as $D_a^0 = 2\times10^{-6}$ cm^2/sec and $Q_a = 1.3(\pm0.1)$ eV and differ little from their preliminary estimates reported recently.[7] We note in Fig. 3 that the diffusivity extracted from the partially crystallized specimen annealed at 279°C also matched the other data points. Apparently, partial crystallization at this level does not have any significant effect on the diffusion measurement. It seems that diffusion of Ag^{110m} in the emergent crystalline Pd and Pd_3Si phases is orders of magnitude smaller in comparison to that in the amorphous phase; e.g., self-diffusion in Pd at 279°C is $\sim10^{-26}$ cm^2/sec[8], and the contribution of diffusion along the submicroscopic interfaces is negligibly small. No phase separation or crystalline grains could, however, be detected in the electron micrograph of the surface replica of the specimen even at 70 000×. The implication is that for a grain size of the order of a few hundred angstroms, the

TABLE I. Ag^{110m} diffusion in amorphous Pd-19-at.%-Si alloy.

	Temp. (°C)	t_A (10^6 sec)	½ broadening[a] (Å)	D_a[b] (cm^2/sec)
1.	186.7	5.44	ND[c]	ND[c]
2.	205.0	4.13	60	2×10^{-20}
3.	219.0	3.37	70	3.6×10^{-20}
4.	240.0	2.94	160	2.2×10^{-19}
5.	279.0[d]	1.638	300	1.4×10^{-18}

[a] All ± 20 Å.

[b] Arrhenius parameters are $D_a^0 = 2\times10^{-6}$ cm^2/sec and $Q_a = 1.3$ (± 0.1) eV.

[c] None detected within the experimental precision of the tracer profiling.

[d] Partially crystallized.

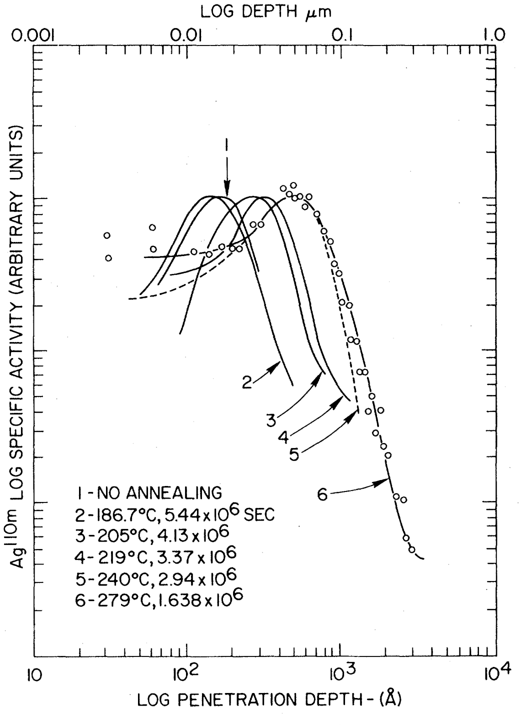

FIG. 2. Plots of logarithm of Ag^{110m} specific radioactivity versus logarithm of tracer penetration distance in the Pd-19-at.%-Si amorphous specimens at various temperatures. Typical scatter in the data is shown in profile 6. The 279°C diffusion showed evidence of partial crystallization as shown in Fig. 1.

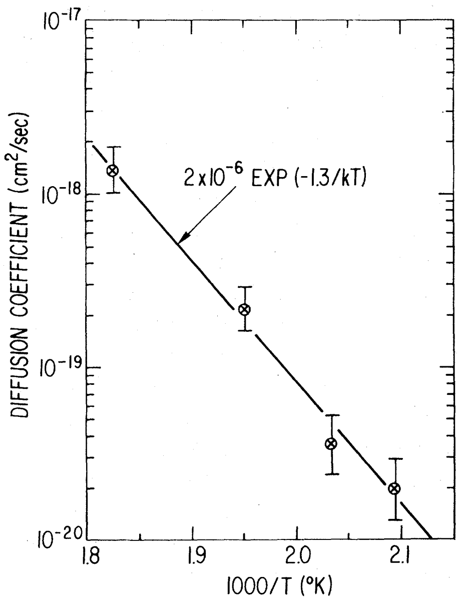

FIG. 3. Arrhenius plot of Ag^{110m} diffusion coefficients in Pd–19-at.%-Si amorphous specimens.

needed diffusion lengths and diffusivities are at least of the same order as shown in Table I.

It is obvious that the controlling factor behind the observed small diffusivities (in the 10^{-18}–10^{-20}-cm^2/sec range) is the unusually small pre-exponential factor rather than a high activation energy. To our knowledge, the present investigation is the first of its kind in a metallic amorphous phase, and consequently, no comparisons are possible. In view of the supercooled nature of the amorphous alloy specimens the parameters for diffusion may be expected to follow the pattern $Q_l < Q_a < Q_c$ and $D_a^0 \leq D_l^0 \ll D_c^0$ where the subscripts a, c, l refer to the amorphous, crystalline, and liquid phases, respectively. We note that diffusion in liquids is characterized by $D_l^0 \approx 10^{-3}$ cm^2/sec and $Q_l \sim 7T_m$[9] and diffusion in the crystalline solids is characterized well by $D_c^0 \sim 1$ cm^2/sec and $Q_c \sim 34T_m$, where T_m is the melting temperature in degrees kelvin and Q in kilocalorie per mole. Thus, the observation of the diffusion parameters $D_a^0 = 2\times10^{-6}$ cm^2/sec and $Q_a \sim 30T_m$ in the present investigation defines the regime of diffusion in the amorphous metallic alloys as different from the liquid and crystalline solid phases. Several viscosity measurements have been reported in amorphous Pd-based alloys[10] showing a viscosity of $\sim10^{16}$ P in the 500–600°K range. Maddin and Masumoto have calculated a diffusion coefficient of 2.3×10^{-22} cm^2/sec at 500°K in the Pd–20-at.%-Si amorphous alloy using the Stokes-Einstein relationship between the viscosity and the diffusion coefficients; the corresponding value in the present case is $\sim10^{-19}$ cm^2/sec. We believe that this difference is an evidence that the correlation length in the Stokes-Einstein relationship, which is usually taken of the order of the atomic dimension in liquids and crystalline solids, may be several atomic diameters in the amorphous metallic alloys.

It is also instructive to examine the measured diffusion parameters in the light of the state of the atomic packing in the metallic amorphous phases. A dense random packing (DRP) model is now generally acceptable for amorphous metallic alloys[11-13] as distinct from a tetrahedrally bonded random network for amorphous semiconductors.[14-17] The structure of an amorphous alloy is visualized as random packing of the metal atoms analogous to the hard-sphere packing of Bernal[11] with the metalloid species filling in the larger voids. The space filling may be described by a high density of tetrahedrons and a lower concentration of larger voids. Typically, the amorphous metallic structures are a few percent less dense than the same alloy after it has been crystallized.[12]

Diffusion of Ag tracer in the Pd–19-at.%-Si amorphous alloy according to the above model may be conceived to occur in more than one manner: (1) interstitially if the larger voids are interconnected to some degree, and (2) through a cooperative process involving an unspecified number of atoms utilizing the larger fraction of tetrahedral voids available in the DRP. The interstitial process is most likely untenable as the larger voids occur only in a small concentration as evidenced by only a small density difference between the two states, and are consequently not likely to be interconnected. In addition, we note that the measured $D_a^0 = 2\times10^{-6}$ cm^2/sec is a few orders of magnitude smaller than that generally expected for interstitial motion. In the second process, an atomic volume equivalent to a vacancy in the crystalline structure may be conceived to be distributed among a group or cluster of unspecified number of atoms retaining some sort of short-range order. It may be hypothesized that thermal vibrations below the glass transition temperature result in continual redistribution of the free space in DRP thereby occasionally permitting atomic diffusion to occur whenever an atom finds itself adjacent to an "embryonic vacancy" which, of course, would be transient: The probability of its occurrence is rather small and the attempted atomic interchanges may be largely unsuccessful. In other words, diffusion would be highly correlated as envisioned in the free-volume model by Turnbull and Cohen[13] with an effective frequency much smaller than the normal Debye atomic frequency thus lowering D_a^0 by orders of magnitude. The precise value of D_a^0 would depend on the number of atoms involved in the cluster, the thermal vibrations, and the availability of the free space; it is not yet possible to quantify them at this stage. Energetically, the diffusion process would be easier in view of the looser atomic packing in the amorphous phase and a relaxed state at the saddle point through which atomic jumps are made.

Finally, as seen in Fig. 2, the Ag^{110m} profiles show spatial shifts which were quite unexpected. Electron microprobe and Auger spectroscopic studies indicated a presence of ~1 at.% dissolved oxygen in the as-splat-quenched specimens. During diffusional annealing the oxygen diffused out as evidenced by formation of progressively thicker silicon oxide layers on the specimen surface and oxygen depletion in the interior. While a precise explanation of the observed shifts must await detailed studies, it may be remarked that the presence of the dissolved oxygen in the splat-quenched amorphous Pd–19-at.%-Si alloy has been characterized for the first time.

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New Method for Investigating Magnetic Tricritical Points*

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A new method, based on the observation of hysteresis effects at the first-order phase transition, has been used to study the behavior of dysprosium aluminum garnet near one of its tricritical points. The magnetization-temperature phase diagram and the exponents β_u, δ_+, δ_-, and γ_u have been determined and found to be in good agreement with the present theory.

Recent theoretical studies[1] have given clear predictions for the asymptotic behavior near tricritical points (TCP's). The exponents turn out to be the same as those given by classical Landau theory, in sharp contrast to the situation at ordinary critical points, and it is clearly of interest to test this prediction. TCP's have been identified experimentally in a wide variety of physical sys-