

Extreme Fast-Diffusion System: Nickel in Single-Crystal Tin

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The electromigration in the steady-state mode and anisotropic diffusion of ^{63}Ni in single-crystal β -tin have been measured by a tracer-sectioning technique. For the first time the solubility of Ni in Sn has been observed. The unusual features are extremely rapid mobility, low activation energies, and extraordinary anisotropy of diffusion ($D_{\parallel}/D_{\perp}=7\times 10^4$). The strength of the electromigration driving force in the basal plane of Sn shows a surprisingly strong temperature dependence.

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The so-called "fast diffuser" metal systems¹ exhibit a mobile impurity (noble metal, divalent metal, or transition metal ions) usually in a polyvalent metal matrix, such as lead, tin, indium, or thallium. The diffusivity of these dilute impurities runs from 10^2 to 10^5 times that of self-diffusion. The exact mechanism for such high mobility is still open for speculation, although it seems clear that some sort of interstitial action must be involved. It has been observed that there is a strong correlation between the mobility of the impurity and its lack of solubility² as illustrated in Fig. 1 where the diffusivity of several impurities in lead and tin have been plotted against their solubility. As indicated the data have been selected at homologous temperatures for the two solvents. Just why this correlation is so strongly marked has only been surmised on a qualitative basis. One would suspect that a rapidly diffusing impurity would not have formed locations in the lattice where it is strongly bound and, hence, it has only a low solubility.

On this basis the system of nickel in tin might be expected to present an extreme situation. The solubility of the nickel is so low that up to now it has not been reported in the usual references.³ However, with the use of the radioisotope ^{63}Ni we were able to assign a solubility of 0.05 wt. ppm at room temperature with a heat of solution of 5.95 kcal/mole and, furthermore, to determine the dif-

fusivity and driving force for electromigration by standard techniques.

The experimental procedure for the diffusion measurements employed here is similar to that described elsewhere.⁴ Because of the strong tetragonal nature of tin, single-crystal specimens were essential; some were sectioned by an acid saw from a commercial stock, and some were grown by the Bridgman method from 99.999% pure tin. Their orientations were determined by the Laue back-reflection method.

Prior to plating, samples were prepared by an alternate etch-polishing procedure. The radioactive ^{63}Ni was plated from a solution which was prepared with radioactive nickel-chloride in 10 ml of distilled water and 150 mg boric acid.⁵ The samples were then sealed in Pyrex tubes at $\frac{1}{3}$ atm of He and transferred to a preheated furnace where the temperature was controlled to within $\pm 0.5^\circ\text{C}$. After each run the diffusion coefficient was obtained by the standard lathe-sectioning and liquid-scintillation-counting techniques.

The tracer concentration profiles were fitted by either Gaussian or complementary error functions depending on the source strength deposited on the samples. Since $D_{\parallel} \gg D_{\perp}$ for all other fast diffusers in β -tin, we measured D_{\perp} first as it fell into a range better suited to our standard techniques. A series of measurements gave

$$D_{\perp} = (1.87 \pm 0.26) \times 10^{-2} \exp[-(12.94 \pm 0.12 \text{ kcal/mole})/RT] \text{ cm}^2/\text{sec}.$$

In measuring D_{\parallel} we faced the problem of taking into account the room-temperature diffusion that occurred between the end of the anneal and the beginning of sectioning. There was no difficulty in determining D_{\parallel} at room temperature. For temperatures above room temperature one had to apportion the integral $\int D dt$, determined from the penetration plot, to a part due to, say, 10 min at 100°C , and to a part due to 20 min at room temperature spent preparing the specimen for sectioning. The temperature dependence of the diffusivities parallel to the c axis was found to be given by

$$D_{\parallel} = (1.99 \pm 0.32) \times 10^{-2} \exp[-(4.32 \pm 0.11 \text{ kcal/mole})/RT] \text{ cm}^2/\text{sec}.$$

The Arrhenius plots of D_{\parallel} and D_{\perp} versus $1/T$ are shown in Fig. 2.

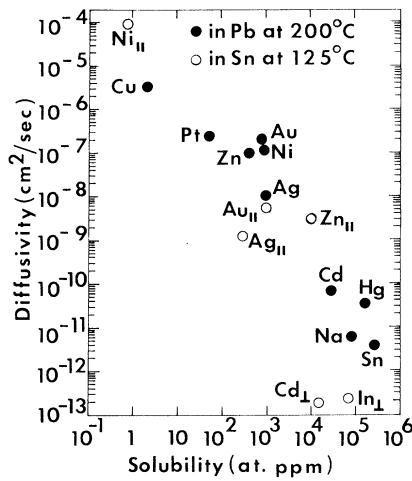


FIG. 1. Diffusivity vs solubility for Pb and Sn systems.

One notes that the diffusivity is tremendously fast along the tetragonal axis, being 1.3×10^{-5} cm²/sec at room temperature. The diffusivities of various metals in liquid Sn are presented along with the results of this work for comparison in Fig. 3. It is remarkable that the mobility of Ni along the tetragonal axis of Sn is in the same range as that of various metals in liquid Sn. Actually, if one extrapolates the diffusion date for $D_{\parallel}^{\text{Ni}}$ to the melting point, the corresponding values exceed those for impurities in the liquid state by a factor of 2 or 3.

Another striking feature is that the diffusivity of Ni in Sn is highly anisotropic, with D_{\parallel} along the tetragonal axis at $T=120^{\circ}\text{C}$ about 7×10^4 times that at right angles. This is perhaps the largest ratio ever observed for the anisotropy of diffusion in a simple metal.

A question arose as to why the points on the Arrhenius plot for the diffusion along the a axis showed such small scatter since the angular accuracy of specimen orientation by the Laue back-reflection method could hardly be better than $\pm 1^{\circ}$. With the large anisotropy of D the standard expression for diffusion at an angle θ to the preferred axis,

$$D(\theta) = D_{\parallel} \cos^2\theta + D_{\perp} \sin^2\theta,$$

would predict a marked scatter in D_{\perp} ($D_{\parallel}/D_{\perp} = 7 \times 10^4$) from the uncertainty in orientation. Actually, an interesting effect was working in our favor, namely that, for a specimen slightly off alignment, the surfaces of constant composition tended rather quickly to come into coincidence with the basal crystal planes in the initial stages of diffusion so that only D_{\perp} influenced the subsequent mass motion. We predict that such an effect will be im-

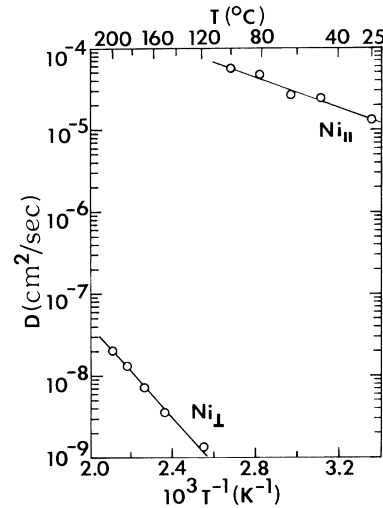


FIG. 2. Temperature dependence of diffusivity for Ni along a and c axes of Sn.

portant for misalignment angles less than the ratio of the diffusion distance to the specimen diameter. With the intention of verifying this intuitive prediction, it was decided to make computer simulations of the atomic diffusion process with $80^{\circ} < \theta < 90^{\circ}$, and also to make an experimental crosscheck at these angles.

If the specimen axes y and z are misoriented by a small angle ϕ with respect to the crystal axes, the diffusion equation becomes

$$\frac{\partial C}{\partial t} = A' \frac{\partial^2 C}{\partial y^2} + 2B' \frac{\partial^2 C}{\partial y \partial z} + C' \frac{\partial^2 C}{\partial z^2},$$

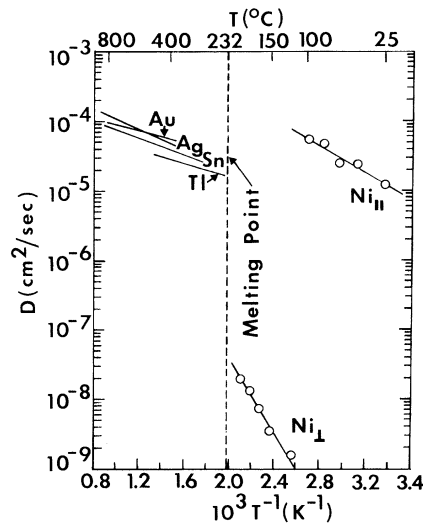


FIG. 3. Temperature dependence of diffusivity of various elements in liquid Sn and Ni in β -Sn [Au, Ag, Sn (Ref. 6), Tl (Ref. 7)].

where

$$A' = D_{\parallel} \sin^2 \phi + D_{\perp} \cos^2 \phi,$$

$$B' = [(D_{\parallel} - D_{\perp}) \sin^2 \phi] / 2,$$

$$C' = D_{\parallel} \cos^2 \phi + D_{\perp} \sin^2 \phi.$$

The numerical solution of the above parabolic equation in two-dimensional space for mixed derivatives can be obtained by finite-difference approximations with the alternating direction implicit (ADI) method. The scheme, developed by McKee and Mitchell⁸ for obtaining practical convergence for such cases, splits the diffusion equation into two tri-diagonal sets of difference equations. It was employed here to give numerical solutions to the above equation and the corresponding values for the diffusivity. The values of diffusivity obtained from numerical solution and those calculated from the standard expression $D(\theta) = D_{\parallel} \cos^2 \theta + D_{\perp} \sin^2 \theta$ for $80^\circ < \theta < 90^\circ$ at $T = 120^\circ\text{C}$ are compared in Fig. 4. Four experimental results with different orientations at 120°C are also included in Fig. 4. Fair agreement between the experimental results and numerically computed values is consistent with the uncertainty of the angular determination and supports the intuitive prediction that a small degree of misalignment will be automatically corrected for in the initial stages of diffusion. During this time the component of the concentration

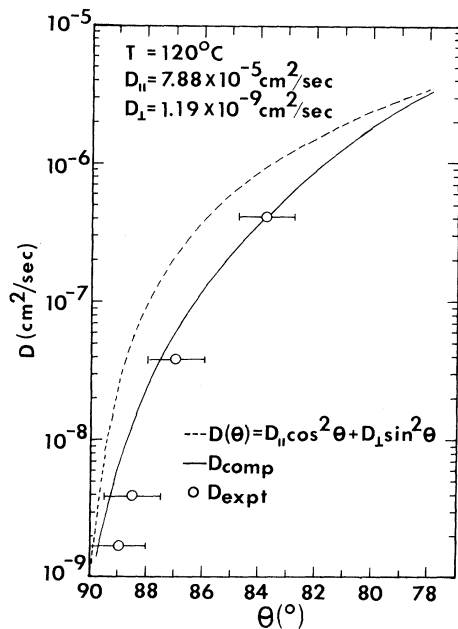


FIG. 4. Comparison of numerically computed values and experimental results for diffusion of Ni close to the basal planes of Sn.

gradient parallel to the c axis is "shorted out" by the rapid diffusion in this direction.

The very low activation energies for Ni diffusion in Sn, 4.32 kcal/mole for Q_{\parallel} and 12.94 kcal/mole for Q_{\perp} , make a striking contrast with the activation energies for self-diffusion, 26.0 kcal/mole for Q_{\parallel} and 25.9 kcal/mole for Q_{\perp} .⁹ An examination of the geometrical configuration in Sn reveals that the atoms in the β -Sn structure form a set of relatively open square channels along the c axis, while passages transverse to c axis are more restricted. An interstitial mechanism is usually invoked to explain the high mobility of the fast diffusers even though the ratios of atomic diameters do not obey Hagg's empirical rule.¹⁰ However, Dyson, Anthony, and Turnbull¹¹ have pointed out that it may be possible to account for the tendency toward interstitial formation in the fast-diffuser systems if the packing of the host metal is limited by ionic rather than by atomic size. For example, the radius of channels along the c axis of Sn bounded by the Pauling ion cores of Sn would be 2.20 Å for quadruply ionized Sn. Therefore it appears that noble-metal, Ni, and Zn atoms (atomic radii¹²: Cu, 1.278 Å; Ag, 1.445 Å; Au, 1.442 Å; Ni, 1.246 Å; Zn, 1.394 Å) could be placed in the channels along the c axis of Sn with little or no distortion. Here the Ni atomic size (1.246 Å) is smallest, compared with other elements, and the diffusivity is largest of all the impurities in tin.

In regard to electromigration the relatively high mobility of Ni along the a axis of Sn makes feasible the use of the steady-state technique to measure the effective charge number Z^* .¹³ Slices of the Sn single crystal about 2 mm thick were cut perpendicular to the a axis by an acid string saw and diffused uniformly with the radioisotope ^{63}Ni . Each slice was then cut into four approximately equal square pieces, one of which was used as a control to check the constancy of the Ni concentration. The remaining three pieces were used as specimens for electromigration measurements as described elsewhere.¹⁴ The data obtained from the study are shown in Fig. 5 as a plot of Z^* versus temperature.

The values for Z^* were large, ranging from -67 at 166°C to -36 at 203°C . They show a surprisingly strong temperature dependence. This kind of temperature dependence of Z^* can clearly not be attributed to the variation of the electron mean free path as is usually done. The origin of this behavior is still a topic of speculation.

In conclusion, the system composed of single-crystal tin with diluted nickel impurities is unusual for the following reasons: (1) The diffusivity of the

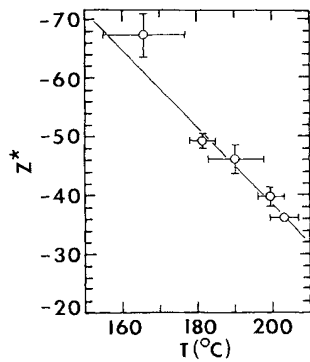


FIG. 5. Temperature dependence of effective charge number for electromigration of Ni along a axis of Sn.

nickel shows extraordinary anisotropy ($D_{\parallel}/D_{\perp} \sim 7 \times 10^4$ at 120°C), apparently the most anisotropic of any metal system known. (2) The fast diffusion coefficient, D_{\parallel} , along the tetragonal axis exceeds that of diffusion in the liquid phase if the crystalline coefficient is extrapolated to the melting point. (3) The strength of the electromigration drive in the basal plane (Z_{\perp}^*) shows an anomalously large increase as temperature decreases.

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spectrometer.

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¹³The force of electromigration may be expressed as $F_{\text{eff}} = |e|EZ^*$, which is the defining equation for the dimensionless effective charge number Z^* . Here E is the applied electric field and e is the electronic charge.

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