Diffusion of zinc in lead[*]

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The diffusion of Zn in Pb has been studied using radioactive-tracer techniques for the temperature range 182–299 °C. The experimental concentration profiles had the form of complementary-error-function curves due to the short time allowed for the anneal before oxidation of the Zn on the surface took place. The diffusion coefficients at various temperatures were fitted to an Arrhenius equation with the activation energy, $\Delta H = 11.3 \pm 0.2$ kcal/mole and $D_0 = 0.016 \pm 0.004$ cm^2/sec. The diffusion rate is comparable to that of the noble metals, along with Ni and Pd in Pb, suggesting a similar diffusion mechanism.

I. INTRODUCTION

The noble metals and the metals grouped around these in the periodic table are sometimes called "anomalous" diffusers in lead because their diffusivities have been found to be from two to five orders of magnitude greater than for lead self-diffusion. Many researchers have studied the diffusion of noble metals in lead[1-7] but recently work has been reported on diffusion of group-IIB elements in lead. Miller[8] has studied diffusion of Cd in Pb, and Warburton[9] measured diffusion of Hg in Pb. Their results seem to indicate that these elements diffuse more rapidly than lead self-diffusion but much slower than noble-metal diffusion in lead.

Warburton[9] points out that it would be advantageous to study the diffusion of Zn in Pb but that Zn forms such a stable oxide that serious surface-holdup problems result. This problem has been solved and the diffusion of Zn in Pb has been measured for the temperature range 182–299 °C using the radioactive-tracer technique.

II. EXPERIMENTAL PROCEDURE AND DISCUSSION

Single crystals, 5 mm in diameter, were grown from 99.9999% pure lead according to the technique described by Weyland.[3] The crystals were sectioned into right circular cylinders 4 mm in length.

Prior to electroplating, an oxide-free lead surface was obtained by slicing the crystal perpendicular to the cylindrical axis using a microtome. The clean surface was then polished with cotton to retard oxidation following Miller[8] and then plated.

The following procedure was used to prepare the electroplating solution. ^{65}Zn was obtained as zinc chloride in hydrochloric acid solution. The hydrochloric acid was boiled off leaving only a residue of zinc chloride. Concentrated ammonium hydroxide was added and the ammonia allowed to evaporate until a pH between 10.5 and 11.5 was reached.

The lead crystals were plated for 8–10 min at a current of 4.5 mA. They were removed, rinsed, and wiped dry except for the plated surface. The cylindrical surfaces were then machined to a diameter of 4.6 mm to remove any zinc from these surfaces. The samples were rapidly immersed in a silicone oil bath which had been preheated to the proper temperature. Anneal times varied from 3 min at 299 °C to 15 min at 182 °C. The crystals were removed, quenched in water, and machined to a diameter of 4.1 mm. The crystals were sectioned into 10-μm slices and counted, four at a time, in a Tracer Lab well scintillation counter.

Two serious problems were encountered in the experimental procedure. The first, finding the proper plating solution to ensure intimate contact between zinc and lead, was solved by varying the pH and composition of the plating solution. The other problem was rapid oxidation of the zinc during the diffusion anneal.

When anneal times longer than those given above were used, concentration profiles resulted which dropped rapidly just inside the plated surface, rose to a maximum further into the crystal, then decreased gradually.

Several experiments were performed in an effort to understand these results. It seemed evident that the "dip" near the plated surface, followed by a "hump" in the concentration profile, must be caused by "back diffusion" resulting from a compound which formed on the plated surface during the anneal. It seemed likely that this compound was the result of oxidation of the zinc on the surface. To check this, anneal times were shortened, and plating times lengthened to obtain thicker layers of zinc. When anneal times dropped sufficiently and plated layers were thick enough, the "hump" in the concentration profile was eliminated and counting rates just inside the plated surface were typically much higher than before.

Samples were also annealed in an argon atmosphere in which similar results were obtained. The

oxidation process appeared to be slower in the argon and longer anneal times were possible. Silicone oil was used, however, because better temperature control was attained, and it could be used as a high-pressure transmitting fluid for future experiments.

Apparently there was enough oxygen dissolved in the silicone oil and mixed with the argon to slowly oxidize the zinc. This process was enhanced at higher temperatures. As the crystal is heated, the zinc in contact with the lead diffuses while the zinc on the outer surface oxidizes. When the oxide layer reaches the lead surface, the concentration of free zinc atoms available for diffusion drops to zero, so the concentration gradients are reversed near the surface and back diffusion commences, the zinc at the surface being continuously removed by oxidation. Normal forward diffusion occurs only for anneal times shorter than the time required to oxidize the zinc layer on the surface.

This explanation was further tested by the following experiments. A sample was annealed at 292 °C for 9 min in an argon atmosphere. Previous experiments indicated that no "hump" would be formed under these conditions. About 40 μm were removed from the crystal and counted, indicating normal diffusion. The remaining sample was then annealed for an additional 45 min, sectioned, and counted. The new surface now contained four times as much zinc as the last removed section and the diffusion profile showed the characteristic "hump." The high surface count after the second anneal definitely indicated back diffusion.

III. METHOD OF DIFFUSION ANALYSIS

Due to the low solubility of Zn in Pb and the short anneal times required to avoid oxidation, the boundary condition appropriate to this experiment is that of a constant source of impurity atoms at the surface.[6] When this condition is used in conjunction with the diffusion equation, the concentration of impurity atoms as a function of diffusion depth x and anneal time t assumes the form

$$C(x, t) = C_0 \operatorname{erfc} x/(4Dt)^{1/2} , \qquad (1)$$

where C_0 is the solubility of the impurity in the host and D is the diffusion coefficient for a given temperature. The data from each diffusion anneal were fitted by least-squares analysis to the above equation with C_0 and D as the variable parameters.

The diffusion coefficients are assumed to vary with temperature according to the Arrhenius equation

$$D = D_0 e^{-\Delta H/RT}, \qquad (2)$$

where R is the molar gas constant, T is the absolute temperature, D_0 is a preexponential constant,

and ΔH is the activation energy. The experimental values for the diffusion coefficients at various temperatures were fitted by least-squares analysis to Eq. (2).

In order to arrive at the reported values for the diffusion coefficients and the activation energy, certain corrections were made to the raw data. The count rates were corrected for background. The anneal time for each sample was corrected for heat up and cool down. This correction amounted to 7% of the total anneal time at 182 °C to 33% at 299 °C. In addition, counting rates of the plated surface and usually the next 40-μm section were not included in the analysis due to large deviations caused by surface effects. The surface count rate was typically an order of magnitude larger than the first point within the sample.

IV. RESULTS AND CONCLUSIONS

Samples were annealed at about 20 °C intervals from 182 to 299 °C. Plots of typical concentration profiles are shown in Fig. 1. The lower set of points shows a concentration profile obtained before the oxidation problem was solved. This sample was annealed at 293 °C for 25 min. The upper set of points was from a sample annealed
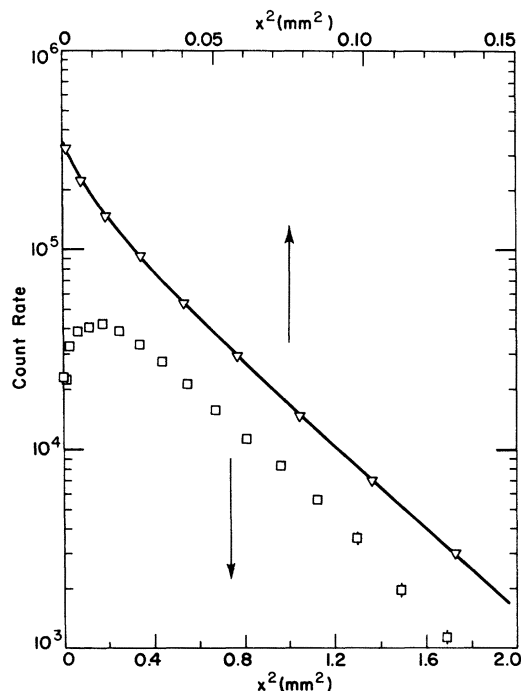

FIG. 1. Solute concentration profiles for the diffusion of Zn in Pb. Open boxes, annealed for 25 min at 293 °C; open triangles, annealed for 4.5 min at 263°C. The longer anneals show effects of back diffusion to the surface. The solid line is a least squares best fit of the triangular points to Eq. (1).
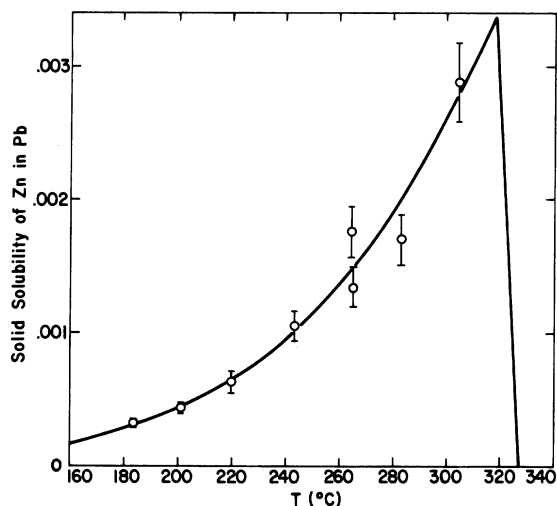
FIG. 2. Solid solubility of Zn in Pb in units of the atomic fraction of Zn. The solid line is a theoretical calculation by Lumsden (see Ref. 10). Experimental points have all been scaled to compare with the theoretical curve.

at 263 °C for $4\frac{1}{2}$ min, which time is short enough to avoid back diffusion because of chemical reactions of the tracer at the surface. Drops in concentration of about two orders of magnitude were typically obtained for successful anneals. The
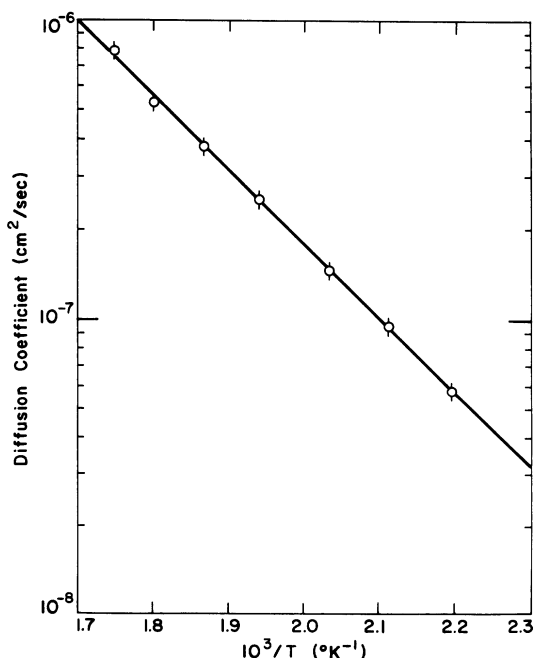
solid line in Fig. 1 is a least-squares fit of the data to Eq. (1). It is obvious from the curvature that the concentration profile is not gaussian but is excellently represented by a curve of the form of Eq. (1). If this is the case then C_0 should correspond to the saturation solubility of Zn in Pb. We do not get the solubility directly without converting from count rate to chemical concentration, which requires a calibration of the counting system. We can, however, determine the relative solubility versus temperature from the measurement at the several temperatures. This relative solubility is shown in Fig. 2. The data have been scaled to compare with the theoretical solubility of Zn in Pb.[10]

Zinc was found to diffuse relatively rapidly in Pb with diffusion coefficients varying from 5.75 $\times 10^{-8}$ cm^2/sec at 182 °C to 7.86×10^{-7} cm^2/sec at 299 °C. This is much faster than Cd and Hg diffusion in Pb and even faster than Ag, but slower than Cu, Au, and Pd.[11] The Zn diffusion rate is the same as that for Ni (Ref. 12) to within experimental error. The diffusion coefficient versus temperature is plotted in Fig. 3. The two high-temperature points are within 6% of the "best-fit line" and the other five, well within 3%. The activation energy was found to be 11.3 ±0.2 kcal/mole and D_0 was 0.016 ±0.004 cm^2/sec. Table I compares the activation energies of various tracer elements diffusing in lead. It is observed that the Zn diffusion in Pb has a much smaller activation energy than the other group-IIB elements.

TABLE I. Activation energies for impurity diffusion in lead.

Solute	ΔH (kcal/mole)	Solute	ΔH (kcal/mole)
Cu[a]	7.0±1.2	Bi[b]	18.5
Au[c]	9.5±0.3	Hg[d]	22.7±0.2
Pd[e]	8.6±0.4	Tl[f]	24.3±0.4
Ni[g]	10.6±0.4	Cd[h]	21.2±0.2
Zn[j]	11.3±0.2	Sb[i]	22.2
		Sn[b]	23.8
Ag[k]	14.6±0.4	Pb[h]	25.5±0.3

[a]An average of the measurements by Refs. 2 and 7.
[b]W. Seith and J. G. Laird, Z. Metallk. 24, 193 (1932).
[c]Reference 3.
[d]Reference 9.
[e]Reference 11.
[f]H. A. Resing and N. H. Nachtrieb, J. Phys. Chem. Solids 21, 40 (1961).
[g]Reference 12.
[h]Reference 8.
[i]S. Nishikawa and K. Tsumuraya, Philos. Mag. 26, 941 (1972).
[j]This work.
[k]From Table I in Ref. 2.

FIG. 3. Temperature dependence of the diffusion of Zn in Pb.

The diffusion rate of Zn in Pb is so much faster than that of Cd and Hg that the mechanism is not likely the correlated motion of interstitials and vacancies proposed by Miller[8] for Cd or the modified model proposed by Warburton[13] for Hg diffusion in Pb. More probably the diffusion contains a large contribution from the motion of free interstitials,[14-16] or other more complicated fast-diffusing defects.[17,18] One cannot say much more about the mechanism from the present experiment but we plan to make measurements of pressure effects on this diffusion to add more information concerning the possible nature of the defect that leads to this rapid diffusion.

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