PHYSICAL REVIEW B VOLUME 26, NUMBER 6 15 SEPTEMBER 1982

Diffusion and electromigration of silver and nickel in lead-tin alloys

C.-K. Hu and H. B. Huntington
Department of Physics, Rensselaer Polytechnic Institute, Troy, New York 12181

(Received 22 March 1982)

Measurements of diffusion and electromigration have been carried out for ^{110m}Ag and ^{63}Ni in lead-tin solders in the α-solubility range which runs from 0 to 12 at. % tin, $150\,^{\circ}\mathrm{C} < T < 300\,^{\circ}\mathrm{C}$. For silver the diffusivity is somewhat enhanced by the addition of the tin, the effect being more marked at the lower temperatures. The increase amounts to a factor of 2.25 for a 12 at. % tin alloy at $T = 150\,^{\circ}\mathrm{C}$. The electromigration Z^* decreases in magnitude with the addition of the tin and actually changes sign from plus to minus around 11 at. % tin. On the other hand, the behavior of the nickel is marked by very strong trapping, as the addition of only 500 ppm of tin can greatly decrease the nickel mobility. The application of the standard trapping analysis leads to a binding energy of the order of 1 eV and a surprisingly large negative entropy. Insofar as it has been possible to observe, the presence of the tin does not seem to alter the electromigration Z^* for the nickel.

I. INTRODUCTION

The behavior of the so-called "fast diffuser" system has been a topic of continuing interest[1] in the field of condensed-matter physics. Many of these systems involve a multivalent solvent, such as Pb, Sn, In, or Tl, with monovalent, divalent, or transition-metal impurities of low solubility.

The high mobility of these solutes strongly argues against a vacancy mechanism for diffusion such as almost certainly operates for the much slower solvent self-diffusion. In some cases there is good quantitative evidence against the vacancy mechanism based on the small impurity enhancements that have been observed.[2–4] Yet the rapid diffusion does not proceed by the simple interstitial mechanism, apparently, judging from the isotope-effect numbers that have been found[5–7] for those systems that have been investigated. If not a simple interstitial mechanism, then there is the possibility for an interstitialcy-type mechanism. For impurity diffusion this would involve "mixed dumbbell" motion, a typical "two-step mechanism,"[8] for which one step would be the usual translation rotation motion of the inhomogeneous dipole and the second step might be a pure dumbell rotation which computer simulation indicated would be quite energy demanding.[9] A more likely candidate for the second step is the so-called "looping" mechanism first proposed by Johnson and Lam,[10] wherein the mixed dumbbell partially dissociates into an impurity and a regular dumbbell which then circulates around in the lattice to rejoin the impurity in the reverse orientation. For such a mechanism the isotopic mass of the moving impurity could only play a role (at that, a reduced one) in step one and hence the low isotope effect number appears reasonable.

Another interesting effect in these systems is the frequently observed strong, usually negative, enhancement effects resulting from high impurity concentrations[11] or the presence of another impurity.[12] For this reason it seemed inviting to study the motion of various impurities in a well-defined series of alloys. The lead-tin solders in the α-solubility range were particularly attractive because of their technological interest,[13] especially in the field of integrated circuitry.

In the field of integrated circuitry there has always been concern about the effect of electromigration, that is, mass flow of the more mobile constituents under the influence of high current densities. In the past there have been several studies of electromigration in fast diffuser systems[14–18] so it seemed natural to embark on a program of diffusion and electromigration of fast diffusing elements in the lead-tin solders. In this paper we report on investigations of silver and nickel in these systems.

The only prior work in this area, that we are aware of, is that of Godkhindi *et al.*[19] They report that the addition of 1.34 at. % Sn reduced the diffusivity of silver in lead by a factor of 45. As will be seen in what follows, results run quite counter to this study. In fact we find that the addition of tin *enhances* the diffusion of silver. We surmise that the difficulty can be attributed to too shallow sectioning confined to the surface regions where considerable "hold-up" may occur.

II. EXPERIMENTAL PROCEDURE

A. Diffusion

The samples used in this work were composed of Cominco 99.999% pure Pb and Sn. The samples were prepared in Pyrex tubes under $\frac{1}{3}$ atm of He. The proper weight of Pb and Sn were melted in a rocking furnace and solidified by quenching in air for a few seconds and then in an ice-water bath. The solidified rods had a grain size about 0.2 mm and a large shrinkage cavity about 1 cm in length in the top part of the casting so that the top portion of the rods was not used for samples. Sometimes very small pores were found inside the samples. However, the experimental results showed that the diffusion of these fast diffusers was not detectably influenced by the pores and also was about the same in as-quenched and well-annealed samples.

Above procedure resulted in a uniform distribution of tin in lead as shown by incorporating a trace of radioactive ^{113}Sn in the melt. The resulting specific activity of the tin was uniformly distributed as a function of position—constant within 3% along the length and diameter of the rods. The tin concentrations for some specimens were also confirmed by Arnold Greene Testing Laboratories, Inc.

Prior to plating, samples were polished by using an etch-polishing procedure. The radioactive ^{110m}Ag source was either electroplated from a cyanide solution or chemideposited from a nitrate solution on to a just etched fresh face of specimen. The radioactive ^{63}Ni was plated from a plating solution which was prepared by a radioactive nickel-chloride in 10 ml of distilled water and 150 mg of boric acid.[20] The source strength deposited on the samples was about $1-10$ μCi.

After plating, the samples were reduced in diameter on a lathe by about 0.01 cm to eliminate any possibility of contamination on the lateral surface. The samples were then sealed in the Pyrex tubes at $\frac{1}{3}$ atm of He and transferred to a preheated furnace. The furnace temperature was stabilized to $\pm 0.2\,^{\circ}\mathrm{C}$. At the end of the anneals, the samples were quenched in ice water and were again reduced in diameter on the lathe by ~ 0.9 mm. The sections were obtained by using a Bausch and Lomb microtome. The typical weight of a section was about 50 mg and the uncertainty of these measurements was less than 0.04 mg.

Prior to counting ^{110}Ag, all the sections were dissolved in 1 ml of 65 vol % acetic acid and 35 vol % hydrogen peroxide. Although tin could not be dissolved by this solution, the variation of counting rate of the ^{110m}Ag's 0.66-MeV γ rays was negligible. In the case of ^{63}Ni in Pb(Sn) specimens, a 150-μl mixture of three parts glacial acetic acid, four parts nitric acid, and four parts of water was used to dissolve the samples in each vial. This change in dissolving solution was forced by the need to dissolve the tin which absorbed the β rays from the nickel strongly. It was also important to avoid the hydrogen peroxide decreasing the counting efficiency of Aquasol-2, of which 10 ml were added in the final step.

A NaI(Tl) well type scintillation counter was used to measure the activity of ^{110m}Ag, while a liquid scintillation spectrometer (Beckman LS150) determined the amount of ^{63}Ni in each section. Specific activities of each section were calculated from the measured total activity, the background, and the weight of each section.

The thickness of each section was determined from its weight, its area, and its density. The densities of Pb(Sn) alloys measured by Goebel[21] were rather dependent on the pretreatment. The values of his measurement obtained from quench cast alloys were used.

B. Electromigration

Radioactive ^{110m}Ag was electroplated on cleaned rods of Pb(Sn) solders to give a solute concentration of Ag about $4-10$ ppm; this concentration is far below the lowest limit, namely 1.5 at. % Ag, to give precipitation of $\mathrm{Ag_3Sn}$.[22] The radioactive ^{63}Ni was electroplated to give concentrations of Ni at about 0.01 at. ppm. The samples were melted in the upper part of a Pyrex tube under a vacuum of 10^{-3} Torr. This part of the tube was separated by a fritted quartz filter from a lower part with a 0.7 cm diameter. The liquid alloys were cast into the lower part of the tube through the filter by applying pressure from a 95 wt. % Ar$-$5 wt. % $\mathrm{H_2}$ gas mixture. Then the solidified rod was sealed off under $\frac{1}{3}$ atm of He in a Pyrex tube about 0.8 cm in diameter. The samples were then melted again in a rocking furnace and solidified by quenching in

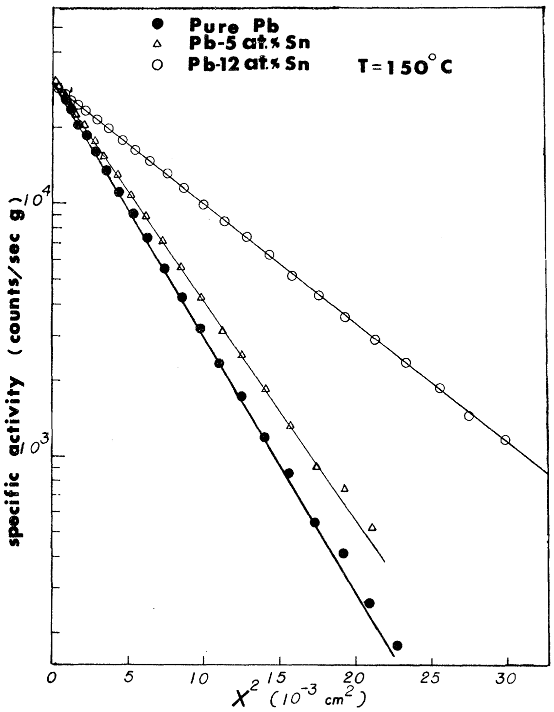

FIG. 1. Diffusion runs in silver in Pb(Sn) solders.

TABLE I. Measured diffusivities of silver in lead and lead-tin alloys at various annealing temperatures. The uncertainties of these measurements are about 3% of their quantities.

T (°C)	Alloys (at. % Sn)	D (10^{-8} cm^2/sec)
150		
	0.0	0.150
	0.0	0.161
	0.0	0.171
	1.0	0.152
	5.0	0.173
	8.4	0.265
	12.0	0.361
230	0.0	2.30
	1.0	2.72
	5.0	2.86
	5.0	2.66
	8.4	3.04
	12.0	4.53
251	0.0	4.87
	1.0	5.18
	1.8	4.77
	5.0	5.09
	8.4	5.71
	12.0	7.15
277	0.5	7.79
	1.0	8.22
	5.0	8.40
	5.0	9.40
300	0.0	15.3
	0.0	15.4
	0.5	14.2
	5.0	15.6
	5.0	15.1
	8.4	17.5

ice water. The rods were reduced in diameter from 0.8 to 0.7 cm and cut into disks of about 1–2 mm in thickness. The samples were prepared from these disks by use of a microtome. Aquadag was painted on the side of the specimens to provide a well-known and reproducible emissivity for a temperature reading by the optical pyrometer (IRCON 300 CH). The temperature calibration was obtained by melting a specimen of pure lead. The sample was surrounded by a precision bored quartz ring to prevent plastic deformation and was placed between two stainless-steel electrodes. All the measurements were made in a vacuum $\sim 10^{-5}$ Torr. The detailed description of electromigration apparatus has been given in Ref. 18.

During the first day or two of a run the current was gradually increased. The sample temperature T and the contact resistance between electrodes and sample were monitored carefully. The contact resistance usually decreased by 2 orders of magnitude from the beginning of the run to stabilization at a value $\leq 10^{-4}\ \Omega$. Once the stable condition was reached, the sample temperature was maintained constant within 3 °C for the time $t \geq t_{ss} = 4.6 l^2/\pi^2 D$ which was the time sufficient to reach the steady-state condition. Here l is the length of the sample and D is the diffusivity of the "fast-diffusers." The sample temperature, contact resistance, and current were recorded on a chart recorder. The current density was of the order of 800 A/cm^2.

After electromigration, the specimens which were run at $T < 260$ °C usually could be separated easily from the electrodes. The sample and a piece of pure Pb were stuck together with a commerical glue where this pure Pb was first mounted on the microtome and was cut to a smooth, flat surface. For $T > 260$ °C the sample was usually sintered quite tightly to the anode electrode and no gluing was necessary. Then the sample was cut into 3-μm thick slices which were collected in groups of 15 for weighing and counting. The counting procedure was essentially as described for the diffusion measurements.

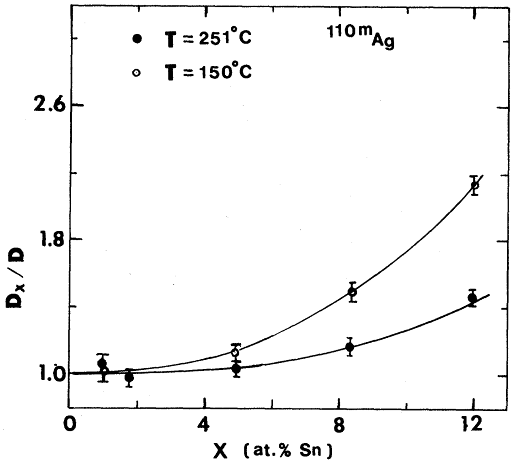

FIG. 2. Diffusion enhancement for silver as a function of solder composition at two different temperatures.

III. EXPERIMENTAL RESULTS

A. Diffusion (Ag)

The tracer concentration profiles were found to be Gaussian distributions except for a few points near the surface and so the tracer concentration $C(x,t)$ of ^{110m}Ag could be expressed as a function of penetration x and annealing time t by the standard thin-film solution

$$C(x,t)=(S_0/\sqrt{\pi Dt}\,)\exp(-x^2/4Dt)\;, \qquad (1)$$

where S_0 is the total silver deposited per unit area and D is the diffusion coefficient. Sample runs are shown in Fig. 1. These show increased diffusivities of Ag in these alloys with added tin.

The marked drop in the diffusion of Ag in Pb—1.34 at.% Sn reported by Godkhindi *et al.*[19] is not observed, as mentioned in the Introduction. The diffusion coefficients, as a function of tin concentration at various temperatures, are shown in Table I. Figure 2 shows the ratio D_x/D as a function of tin composition for two different temperatures, where D_x and D are the diffusivity of Ag in x at.% Sn and pure Pb, respectively. As can be seen in Fig. 2, the addition of the tin enhanced the diffusion moderately. The enhancement effect increased rapidly with Sn concentration larger than 5 at.% and was greater at low temperature. The Arrhenius plot of diffusion coefficients versus $1/T$ is shown in Fig. 3. The activation energies Q and pre-exponential factors D_0 are given in Table II. The values of Q and D_0 in pure Pb are in a good agreement with those by Dyson *et al.*[23] The activation energies in Pb(Sn) alloy slightly decrease with the tin concentration from a value of 0.63 eV in pure Pb to 0.57 eV in Pb—12 at.% Sn. As can be seen in Fig. 3, the D values for Pb—12 at.% Sn are higher than for Pb—8 at.% Sn, even though the diffusion parameters Q and D_0 show overlapping probable error spreads. This is not an uncommon situation since the uncertainties in slope and intercept of a least-square linear fit are correlated and reflect only indirectly the precision of the data points.

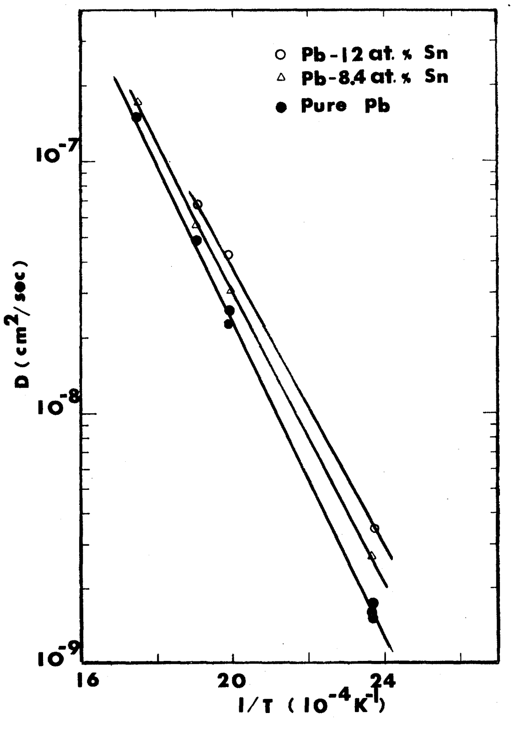

FIG. 3. Arrhenius plots of D at three compositions.

B. Electromigration (Ag)

It is customary to express the strength of the electromigration driving force as $F_e = |e|Z^*E$, where $|e|$ is the absolute value of the electron charge, E stands for the electric field, and Z^* is the effective charge number, a quantity which

TABLE II. Activation energies Q and pre-exponential factors D_0 for pure Pb and Pb(Sn) alloys.

	Q (eV)	D_0 (cm^2/sec)
Pb	0.63 ± 0.02	$(4.6\pm2.2)\times10^{-2}$
Pb—5 at.% Sn	0.62 ± 0.02	$(4.8\pm2.2)\times10^{-2}$
Pb—8.4 at.% Sn	0.58 ± 0.02	$(2.0\pm1.1)\times10^{-2}$
Pb—12 at.% Sn	0.57 ± 0.02	$(2.2\pm1.1)\times10^{-2}$

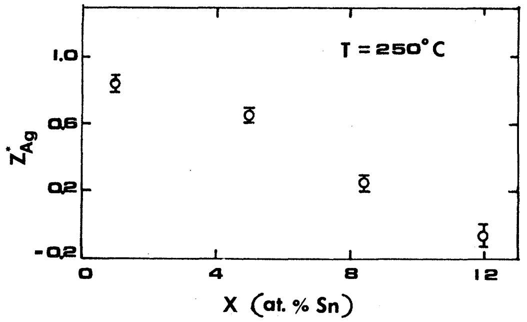

FIG. 4. Z_e^* for silver as a function of composition at $T=250\,°\mathrm{C}$.

measures the strength of electromigration driving force.

The relatively high diffusion coefficients of tracer impurities make practical measurements by the steady-state method, which yields results for the electromigration drive of higher precision and reproducibility than other methods.[24]

Before the electric field was applied across the sample, the concentration of tracer was a uniform distribution in the sample. After annealing time $t>t_{ss}$ concentration profile changes to exponential distribution due to the electric field. The apparent effective charge number $(Z_e^*)=(Z^*/f)$ is given by

$$\frac{\partial \ln C}{\partial x}=Z_e^* j\rho e/kT \ , \tag{2}$$

where f is the correlation coefficient, C is the impurity tracer concentration, x is the distance in the sample, j is current density, ρ is specific resistivity of the sample at temperature T, and k is the Boltzmann constant. The values of ρ were calculated from $\rho_0+\Delta\rho$, using for ρ_0 that obtained from pure Pb,[25] and for $\Delta\rho$ that obtained from the atomic percent of tin times 0.26 $\mu\Omega\,\mathrm{cm/at.\%}$.[26]

The electromigration studies for radio silver in the lead-tin alloy showed a marked decrease in Z_e^* with the addition of tin. As seen in Fig. 4, the Z_e^* values at 250°C start at $+0.8_3$ for 1 at.% Sn and decrease parabolically to -0.0_6 at 12 at.% Sn, changing sign at about 11 at.% Sn. It is seen from Fig. 5 that this concentration behavior is only weakly temperature dependent although the scatter in the data is more noticeable at the higher concentration.

To fit the temperature dependence of Z^* one employs a commonly used expression for Z_e^* (Ref. 24),

$$Z_e^*=Z_{el}-\kappa/\rho \ , \tag{3}$$

where Z_{el} is the effective charge number due to the electrostatic field on the moving ions and κ is a constant which depends on electron and/or hole scattering. The Z_e^* values for Ag in Pb(Sn) alloys using Eq. (3) show, within the appreciable scatter of the data, that the values of Z_{el} are about the same in all Pb(Sn) alloys. The values of κ are increased with increasing Sn concentration. This suggests that the reduction of electromigration

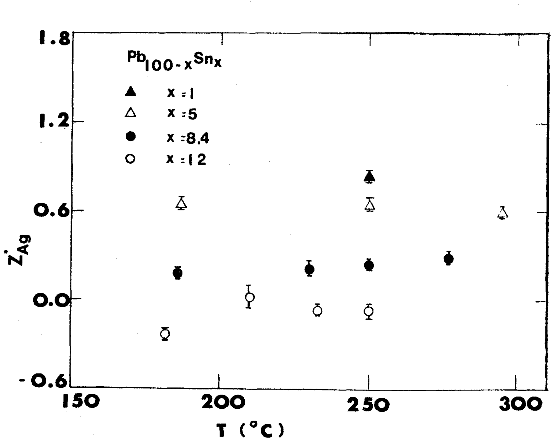

FIG. 5. Z_e^* for silver as a composition for several temperatures.

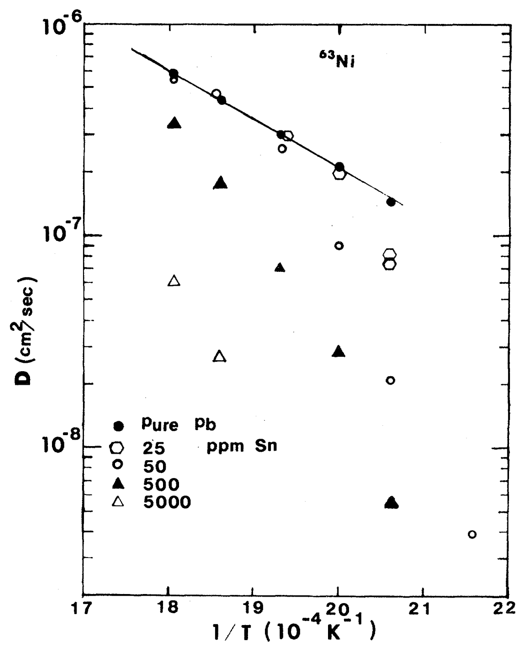

FIG. 6. Deenhancement of the diffusivity of nickel in lead-tin alloys. The solid line is a fit of data D in pure Pb to $D_0\exp(-Q_0/kT)$; $Q_0=0.47\pm0.02$ eV and $D_0=(1.1\pm0.05)\times10^{-2}$ cm²/sec in good agreement with Ref. 20.

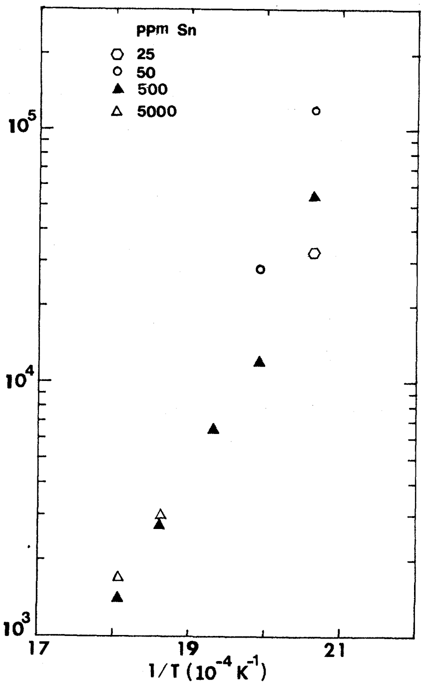

FIG. 7. Plot of $(D/D_x-1)/x$ vs $1/T$.

driving force of Ag in Pb(Sn) is primarily from the electron wind drive rather than from the electrostatic force.

C. Diffusion (Ni)

The addition of only 0.05 at. % Sn has a drastic effect on the diffusivity of nickel in the alloy, reducing it by nearly a factor of 100 around 212 °C. A complete picture of the deenhancement is shown in Fig. 6 as a function of composition and temperature. One can only conclude that the tin acts as very active trapping centers for the nickel and that their effectiveness increases with lower temperatures. The situation can be simply modeled.

Let N be the concentration of the tracer impurity and x that of tin. If N_f and N_t are, respectively, the concentration of free and trapped tracer, the total concentration of tracer is

$$N=N_f+N_t\ . \tag{4}$$

For the postulated reaction: free tracer + tin $\rightleftarrows$ trapped tracer, the application of mass action leads to

$$N_t=N_f x z e^{-g/kT} \tag{5}$$

(assume $x \gg N$). Here g is the free energy of trapping and the z is the number of equivalent trapping sites for tin ions (presumably 6). The k and T have their usual meanings of Boltzmann's constant and absolute temperature. The effective tracer diffusivity D_x can then be written

$$D_x=(N_f D+N_t D_t)/N\ , \tag{6}$$

where D and D_t are, respectively, the diffusivity of the free and trapped tracer atoms. Let us assume that the mobility of trapped atoms is negligible ($D_t \simeq 0$). From Eqs. (4)–(6) one then derives

$$(D/D_x-1)/x=ze^{-g/kT}\ . \tag{7}$$

The plot of $\ln(D/D_x-1)/x$ is shown in Fig. 7 vs $1/T$. It appears that within the rather large scatter of the data a linear fit can be applied in support of the trapping model.

D. Electromigration (Ni)

The study of electromigration of nickel in the lead-tin alloys has been complicated by certain artifacts which have made difficult the determination of Z_e^* for high tin concentrations and low temperature. The situation is illustrated in Fig. 8, which shows the results of three recent attempts to use the steady-state method. For specimens containing

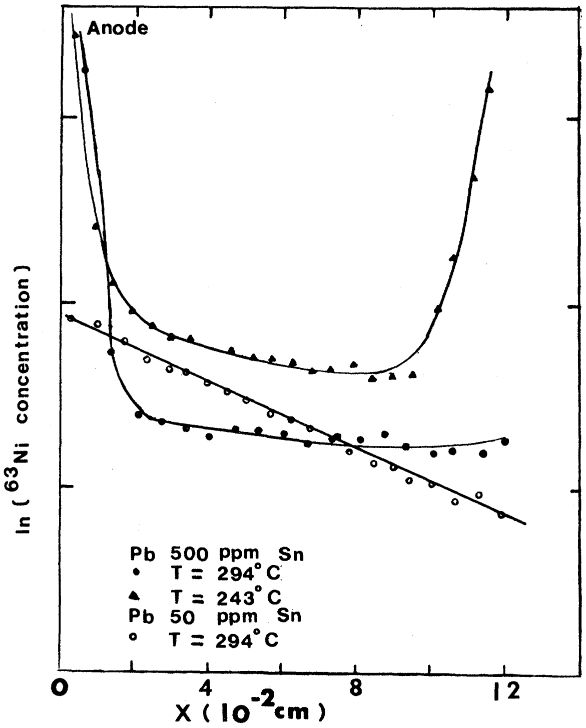

FIG. 8. Attempted steady-state electromigration runs for Ni in lead-tin solders.

500-ppm tin, very large concentrations of nickel isotope appear at the surfaces, at 294 °C only on the anode side and at 243 °C at both surfaces. On the other hand, for only 50-ppm tin a quite satisfactory linear profile was obtained which yielded a Z_e^* value of -4.8 ± 0.2 in good agreement with values obtained earlier[17] for Ni in pure lead. Future plans call for a return to this investigation, exploring intermediate compositions such as 100, 200 ppm, etc. It appears that the high surface concentration may perhaps be reduced by shortening the run time of the electromigration anneal.

IV. DISCUSSION

These initial investigations of atom movements of the fast diffusers in the lead-tin solders have shown, interestingly enough, two quite different behaviors for the silver and nickel as dilute impurities. In the case of the silver, the addition of the tin increases the diffusivity moderately, but causes the electromigration to decrease and eventually change direction. On the other hand, the diffusivity of the nickel is very drastically decreased by the presence of only a small amount of tin, but the electromigration, insofar as it has been observed, appears to be unaffected by the trapping with the tin atoms. This suggests that the presence of the tin enhances the diffusion of the silver and at the same time changes the electron distribution which influences the wind force of electromigration for these more mobile silver atoms. With the nickel, however, the trapping is so strong that the trapped atoms make no contribution to the electromigration current which is sustained solely by the untrapped atoms. In order that no decrease in electromigration be observed (which may be the case) the trapping-untrapping reaction must be fast enough to maintain local equilibrium and the number of trapping atoms must greatly exceed the number of tracer atoms.

It is not clear how the tin atom increases the mobility of the silver. Heuristically, one might point to the lowered melting point of the alloys as compared to the pure lead. Somewhat more satisfactory is the suggestion by Turnbull[27] that the smaller size of the tin ion enhances the jumping probability for interstitial silver atoms in its neighborhood. If one explores this possibility in somewhat more detail, it would appear clear that the change in the activation free energy for jumping includes a considerable negative entropy, since the Arrhenius lines in Fig. 3, when extrapolated back, appear to cross well before reaching the $1/T=0$ axis. An alternate point of view is that the lines are actually curves and coalesce on extrapolation with the pure lead curve at higher temperatures (unfortunately above the melting point).

The matter of curvature also enters into the interpretation of Fig. 7 where one can deduce rather different parameters for $g=h-Ts$, the free energy of the trapping process, according to whether one attempts to fit a straight line through all the data or only for the lower two thirds, as there appears to be a significant curvature to the plot. For a line through all the data h turned out to be approximately 1.25 eV and s about $-21k$. Fitting only the lower points yields h more nearly 1 eV and s about $-16k$. These entropy values are indeed so large as to throw the trapping concept, as here applied, into question.

The segregation of the diffusing isotope to the end surfaces is an annoying, but not completely new phenomenon. Its explanation presents a challenge in its own right. From prior work we know that it does not appear for Ni in pure lead[17] and is greatly reduced for alloy specimens annealed in vacuum or an inactive atmosphere.[28] It would seem that oxygen at the surface can penetrate the metal when tin is present and that this oxygen has a strong affinity for the Ni drawing it out of the bulk to the end surfaces. Somewhat similar behavior is also shown by Cu and Au in the solders,[29] but there are important differences that remain to be explored.

ACKNOWLEDGMENTS

We are happy to acknowledge the support of the IBM research and development facility at East Fishkill, New York. We are also indebted to the chemistry department of Rensselaer Polytechnic Institute for the use of their Beckman LS150 liquid scintillation spectrometer. We express our gratitude to D. Turnbull for many helpful discussions of this work.

---

[1] W. K. Warburton and D. Turnbull, in *Diffusion in Solids: Recent Developments,* edited by A. S. Nowick and J. J. Burton (Academic, New York, 1974), Chap. 4.

[2] J. W. Miller, Phys. Rev. B 2, 1624 (1970).

[3] W. K. Warburton, Scr. Metall. 7, 105 (1973).

[4] B. M. Cohen and W. K. Warburton, Phys. Rev. B 12, 5682 (1973).

[5] J. W. Miller, J. N. Mundy, L. C. Robinson, and R. E. Loess, Phys. Rev. B 8, 2411 (1973).

[6] J. W. Miller and W. A. Edelstein, Phys. Rev. 188, 1081 (1969).

[7] J. N. Mundy, J. W. Miller, and S. J. Rothman, Phys. Rev. B 10, 2275 (1974).

[8] M. Y. Hsieh, H. B. Huntington, and R. N. Jeffery, Cryst. Lattice Defects 7, 9 (1977), Sec. 4.

[9] P. H. Dederichs, C. Lehmann, H. R. Schober, A. Scholz, and R. Zeller, J. Nucl. Mater. 69&70, 176 (1978).

[10] R. A. Johnson and N. Q. Lam, Phys. Rev. B 13, 4364 (1976).

[11] W. K. Warburton, Phys. Rev. B 11, 4945 (1975).

[12] D. L. Decker, J. G. Melville, and H. B. Vanfleet, Phys. Rev. B 20, 3036 (1979).

[13] P. A. Totta and R. P. Sopher, IBM J. Res. Develop. 13, 226 (1969).

[14] C. Herzig and E. Stracke, Phys. Status Solidi A 27, 75 (1975).

[15] M. Y. Hsieh, H. B. Huntington, and R. N. Jeffery, Cryst. Lattice Defects 7, 9 (1977).

[16] E. Stracke and C. Herzig, Phys. Status Solidi A 47, 513 (1978).

[17] D. A. Golopentia and H. B. Huntington, J. Phys. Chem. Solids 39, 975 (1978).

[18] H. Nakajima and H. B. Huntington, J. Phys. Chem. Solids 42, 171 (1981).

[19] M. M. Godkhindi, K. K. Ray, and V. Balasubramanian, Scr. Metall. 6, 489 (1972).

[20] C. T. Candland and H. B. Vanfleet, Phys. Rev. B 7, 575 (1973).

[21] J. Goebel, Z. Mettalkd. 14, 357 (1922).

[22] W. Hofmann, *Lead and Lead Alloys* (Springer, Berlin, 1970), p. 116.

[23] B. F. Dyson, T. Anthony, and D. Turnbull, J. Appl. Phys. 37, 2370 (1966).

[24] H. B. Huntington, in *Diffusion in Solids: Recent Developments,* Ref. 1, Chap. 6.

[25] A. J. Leadbetter, D. M. T. Newsham, and N. M. Picton, Philos. Mag. 13, 371 (1966).

[26] B. M. Cohen, D. Turnbull, and W. K. Warburton, Phys. Rev. B 16, 2491 (1977).

[27] D. Turnbull, private communication.

[28] Private communiation from Dr. D. Pierce who studied thermomigration of nickel in lead.

[29] C.-K. Hu and H. B. Huntington (unpublished).