

Diffusion and saturation solubility of platinum in lead

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(Received 6 August 1979; revised manuscript received 17 December 1979)

The diffusivity and saturation solubility of Pt in Pb has been measured over the temperature range 217–320°C using a serial-sectioning technique. The concentration profiles were determined by observing the variation in the melting curve for each slice using differential scanning calorimetry. Thick boundary layers of Pt were deposited which yielded the complementary error function solution to the diffusion equation. The temperature dependence of the diffusivity is given by $D(T) = (0.011 \pm 0.002)$

$\times \exp[-10.1 \pm 0.02(\text{kcal/mole})/RT] \text{cm}^2/\text{sec}$. The eutectic temperature was measured as $291.8 \pm 0.3^\circ\text{C}$

and the saturation solubility below the eutectic is given by $c_0 = (21.9 \pm 2.1)$

$\times \exp[-12.2 \pm 0.1(\text{kcal/mole})/RT]$ atomic fraction.

INTRODUCTION

Over the past several years there has been a great deal of interest in the anomalous impurity diffusion in high- Z polyvalent solvents. The lead system which is typical of this class has probably received the greatest amount of attention. Numerous measurements involving the noble and near-noble metal impurity diffusion in Pb and Pb alloys have been made. These include diffusion in Pb of Cu, Ag, Au, Ni, Pd, Zn, Cd, and Hg, along with Pb self-diffusion.¹⁻⁴ The diffusion of Sn, Tl, Bi, and Na in Pb has also been measured.⁵⁻⁷ Kidson,⁸ in an earlier paper where he reported the diffusivity of Au in Pb, included a rather obscure statement suggesting that the diffusion of Pt in Pb is very slow and similar to that for Pb self-diffusion. However, no data were presented.

EXPERIMENTAL PROCEDURE

The diffusion of Pt in Pb has been measured at atmospheric pressure over a temperature range 217–320°C. Concentration profiles were measured by the serial-sectioning technique in conjunction with differential scanning calorimetry measurements.⁹ Single crystals of lead, 99.9999% pure, 6.4 mm in diameter, and 5 cm in length were grown by the Bridgman technique. Diffusion samples 3 mm in length were cut from these crystals and Pt was then chemideposited on a freshly microtomed surface from a 0.033-normal solution of $\text{K}_2\text{Pt}(\text{OH})_6$ at a temperature of 50°C. The cylindrical surfaces and the end opposite to the plates surface were first machined to remove any possible Pt contamination. The samples were then annealed with constant agitation in a 6.4-mm i.d. glass tube containing silicone oil which in turn was inserted into a controlled-temperature liquid metal bath. The samples were removed from the bath, quenched to room temperature, and the cylindrical sides were again machined off to remove surface

diffusion effects. The annealing bath and procedure is the same as described by Decker, Melville, and Vanfleet.¹⁰ The samples were then sectioned in 20- μm slices to a depth of 800–1000 μm , the sections were weighed on a microbalance, and the melting curve for each slice was accurately determined on a Perkin-Elmer DSC-2 differential scanning calorimeter for the determination of its Pt impurity concentration.

Most of the diffusion anneals were made using rather thick impurity boundary layers (several hundred atomic layers), which resulted in the complementary error function solution or the self-enhanced nonlinear solution of the diffusion equation.¹¹ Near the end of the data-taking period a few runs with thin boundary layers and hence Gaussian solutions were obtained.

RESULTS

The differential scanning calorimetry technique yields the impurity concentration from each slice directly. Typical concentration profiles for both the Gaussian and complementary error function solutions are shown in Fig. 1. The diffusivity of Pt in Pb versus the reciprocal temperature is shown in Fig. 2. The least-squares fit of the data in Fig. 2 to an Arrhenius curve yields an activation energy of 10.1 ± 0.2 kcal/mole and a pre-exponential factor of 0.011 ± 0.002 cm^2/sec . The zero-penetration intercept of the complementary error function solution to the diffusion equation yields the saturation solubility for temperatures both above and below the eutectic temperature. The result is shown in Fig. 3. The saturation solubility for temperatures below the eutectic follow the usual exponential relation $c_0 = (21.9 \pm 2.1) \times \exp[-12.2 \pm 0.1(\text{kcal/mole})/RT]$ atomic fraction. The best measurement of the eutectic temperature using differential scanning calorimetry techniques gave $T_{\text{eut}} = 291.8 \pm 0.3^\circ\text{C}$.

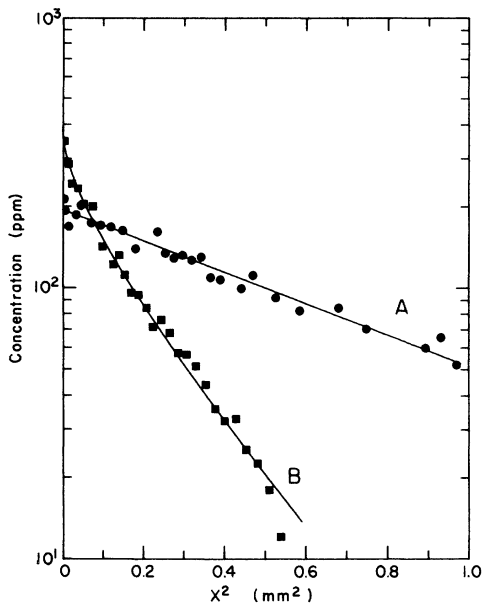


FIG. 1. Concentration profiles for the diffusion of Pt in Pb in atomic ppm versus the square of the penetration distances. Curve A (Gaussian) was annealed at 289.5°C for 153 sec and curve B (error function) was annealed at 296.5°C for 420 sec.

CONCLUSIONS

The diffusion of Pt in Pb, contrary to the results of Kidson,⁸ is very rapid and seems to be completely dominated by an interstitial mechanism.

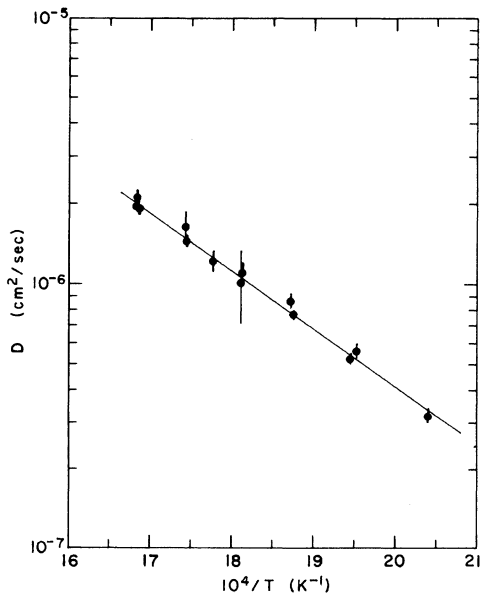


FIG. 2. The diffusivity of Pt in Pb versus the reciprocal temperature is shown. The intercept of the curve yields a pre-exponential factor of 0.011 ± 0.002 cm²/sec and the slope yields an activation energy of 10.1 ± 0.2 kcal/mole.

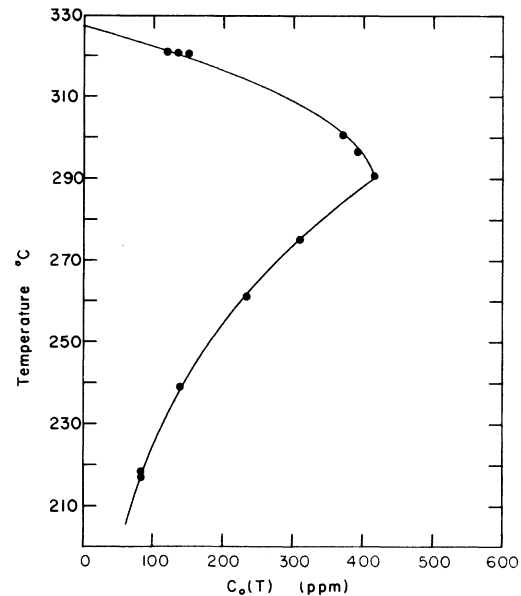


FIG. 3. The saturation solubility temperature versus atomic parts per million. The eutectic temperature is measured at 291.8 ± 0.3 °C with maximum solubility of 418 ppm.

The results for Pd and Pt diffusion in Pb at atmospheric pressure are very similar and appear to differ primarily by the inverse of the square root of the mass dependence. Normalizing these diffusivities to the mass of lead, one finds that they differ only by 2% which is well within the uncertainty of the measurements.

The fact that Pd and Pt are so similar chemically suggests that they might be considered equivalent defects with different masses. The same argument can also be made for the diffusion of Cd and Hg in Pb. The results are interesting in that they yield isotope effect parameters defined in the usual way by

$$f\Delta k = \frac{D_a/D_b - 1}{(m_b/m_a)^{1/2} - 1}$$

of 0.85 and 0.93, respectively, where f is the correlation factor and Δk is a correction factor usually assumed to be near unity. For the results to be meaningful it must also be assumed that the fractions of interstitial defects in both Pd and Pt are the same. The same condition must also hold for the Cd and the Hg. The expected values of f for the Pd and Pt diffusivity in Pb which, by their large values appear to be interstitially dominated, are 1.0 and for the Cd and Hg diffusivity in Pb which, by their small values appear to be substitutionally dominated, is 0.784. The agreement is really quite good; however, it may be fortuitous considering all of the assumptions.

ACKNOWLEDGMENTS

I would like to thank Norman Ship for his assistance in making the diffusion and solubility mea-

surements for Pt in Pb and also the National Science Foundation for their partial support of this project.

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