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Effect of Pressure on the Intermetallic Diffusion of Silver in Lead*

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The diffusion of silver-110 into lead has been investigated using radioactive-tracer techniques in a temperature range within 200°C of the melting point of lead for six pressures between 0 and 40 kbar. The activation energy was found to increase from 15.2 to 21.9±0.3 kcal/mole as the pressure increased from atmospheric to 39.2 kbar. The activation volume for pressures below 11.9 kbar ranged from 0.54±0.06 to 0.48±0.05 atomic volumes as the temperature decreased from 769 to 556°K. Above 11.9 kbar the activation volume was nearly constant at 0.38±0.03 atomic volumes over the same temperature interval. As a result of the large decrease in the activation volume that occurs between 0 and 11.9 kbar it is suggested that the diffusion process for silver into lead changes from a composite of interstitial plus vacancy to an interstitial mechanism. Therefore the activation volume of 0.38±0.03 atomic volumes as measured for pressures above 11.9 kbar represents the activation volume of motion ΔV_m characterizing the interstitial mechanism. Within the accuracy of the experimental data for $\ln D$ versus T_m/T the results suggest that $\Delta H(P)/T_m(P)$ is independent of pressure to 40 kbar.

I. INTRODUCTION

THE diffusion of silver-110 in lead has been investigated using radioactive-tracer techniques in a temperature range within 200°C of the melting point of lead for six pressures between 0 and 40 kbars. The pressure effect on diffusion has generally been interpreted in terms of the "activated-state theory" of absolute reaction rates using equilibrium thermodynamics. The theory¹ leads to an expression for the diffusion coefficient of the form

$$D = \alpha a^2 \nu w e^{-\Delta G_m/RT}, \quad (1)$$

where ΔG_m is the increase in free energy necessary to move one mole of diffusing atoms from their equilibrium positions to the so-called "activated positions," a is the lattice constant, ν is the mean vibrational frequency of the diffusing atoms, α is a geometrical constant, and w is the probability of finding a vacant site adjacent to the diffusing atom into which it can jump. For interstitial diffusion, in the limit of low concentrations, w is approximately unity. For vacancy diffusion w is the mole fraction of vacant lattice sites, i.e.,

$$w = e^{-\Delta G_f/RT}, \quad (2)$$

where ΔG_f is the free energy necessary to form one mole of vacancies. One can show that Eqs. (1) and (2) are equivalent to the usual Arrhenius equation

$$D = D_0 e^{-\Delta H/RT},$$

where

$$D_0 = \alpha a^2 \nu e^{\Delta S/R}. \quad (3)$$

Differentiation of Eqs. (1) and (3) with respect to pressure and inverse temperature gives the equations for the activation volume and activation energy.

$$\Delta V = (\partial \Delta G / \partial P)_T = -RT(\partial \ln D / \partial P)_T + (\gamma - \frac{2}{3})K_T RT, \quad (4)$$

$$\Delta H = \Delta G + T\Delta S = -R(\partial \ln D / \partial (1/T))_P + (\gamma - \frac{2}{3})R\beta T^2. \quad (5)$$

The activation volume ΔV , as defined by Eq. (4), is the sum of the volume of formation ΔV_f and the volume of motion ΔV_m for the vacancy mechanism and equal to ΔV_m only for interstitial diffusion. Physically the volumes ΔV_m and ΔV_f represent the volume increase of the system which would result from the addition of one mole of activated complexes and one mole of vacancies, respectively. The activation energy or enthalpy ΔH from Eq. (5) can be separated in a manner similar to that for ΔV . The quantities γ , β , K_T are the Grüneisen constant, coefficient of thermal expansion, and the isothermal compressibility.

In recent years chemical diffusion in metals has been studied at high pressures by a number of investigators. The results of these investigations have yielded the activation volume of self diffusion for a number of metals. The activation volume of sodium,² alpha-white phosphorus,³ and lead⁴ have been determined by Nachtrieb and co-workers in a high-pressure bomb utilizing pressures up to 8 kbar. Hudson and Hoffman⁵ using a "belt"⁶ apparatus measured the activation volume of lead at pressures up to 40 kbar. Tomizuka and co-workers have measured activation volumes of

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³ N. H. Nachtrieb and A. W. Lawson, J. Chem. Phys. 23, 1193 (1955).

⁴ N. H. Nachtrieb, H. A. Rising, and S. A. Rice, J. Chem. Phys. 31, 135 (1959).

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self diffusion for silver⁷ and gold⁸ and activation volumes for silver and gold⁹ tracers in a gold 34 at. % silver alloy using a gas-pressure system to 9 kbar.

The values for the activation volume as measured by self diffusion at high pressure have generally been in good agreement with corresponding data obtained from quenching experiments.⁸ This substantiates other evidence that self diffusion takes place primarily by the vacancy mechanism. Activation volumes measured for systems characterized by interstitial diffusion should be considerably different (smaller) than for self diffusion.

On a hard-sphere model one would expect ΔV_f to be of the order of one atomic volume for close packed structures and as small as 0.386 atomic volumes for relaxed bcc structures. Theoretical calculations by Johnson and Brown,¹⁰ Tewordt,¹¹ and Bennerman¹² for lattice relaxation about a vacancy in copper (fcc) however yields values for ΔV_f ranging from 0.47 to 0.60 atomic volumes. These values correlate well with the experimental value of 0.53 ± 0.04 atomic volumes obtained by Huebener and Homan¹³ from high-pressure quenching experiments on gold. The contribution ΔV_m might be expected to be small in comparison to ΔV_f inasmuch as it represents the momentary volume increase of the system as the diffusing atom passes from one equilibrium position to another. From an investigation of the pressure effects on the annealing rate of vacancies quenched into gold Emrick¹⁴ found $\Delta V_m = 0.15 \pm 0.014$ atomic volumes.

It is evident that there exists a possibility of determining the mechanism of diffusion by comparing measured activation volumes with those of known processes. As a result of the abnormally large relative value of D for the diffusion of gold^{15,16} and silver¹⁵ into lead it is suggested that the diffusion may occur by the interstitial mechanism, and hence one would expect a relatively small activation volume. The purpose of this investigation is to measure the activation volume for the diffusion of silver into lead and to correlate the measured value with a mechanism of diffusion.

⁷ C. T. Tomizuka, in *Progress in Very High Pressure Research*, edited by F. Bundy *et al.* (John Wiley & Sons, Inc., New York, 1961), p. 266.

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II. EXPERIMENTAL PROCEDURE

1. Sample Preparation

Lead, 99.999% pure, supplied by A. D. Mackay, Inc., New York, was placed in a graphite mold and single crystals $1\frac{1}{2}$ in. long and $\frac{1}{8}$ in. in diameter were grown 10 at a time by the Bridgman method. The mold was then sawed off perpendicular to the axes of the lead cylinders and the surface ground on successively finer grades of silicon carbide paper. The final grinding was on No. 600 grit paper using methyl alcohol as a lubricant to minimize the depth of the amorphous layer which results from the grinding.¹⁷ The freshly-ground surface was then rinsed in alcohol and the mold containing the exposed lead cylinders was placed in a drying oven at 110°C for at least 6 h. This treatment served to remove the alcohol and water which might have been absorbed by the mold and to recrystallize and strain anneal the damaged lead surfaces.

In order to remove any surface contamination from the lead that may enhance or impede diffusion the lead surfaces were bombarded with argon ions prior to vacuum deposition of Ag¹¹⁰. Using a movable vacuum probe it was possible to ion bombard and then vacuum deposit the Ag without opening the vacuum system. Approximately 1 μ Ci of Ag¹¹⁰ was plated on the face of each lead cylinder.

It is to be noted that during the entire operation, the lead crystals were contained in the same mold in which they were grown. The reason for this is threefold. First, the fact that carbon has a lower conductivity than lead causes the surfaces of the lead crystals to be at a slightly higher (negative) potential than the surrounding material, thus giving more effective ion cleaning. Second, by leaving the crystals in the original casting mold it was possible to plate the entire surface with no fear of silver plating the cylindrical sides of the crystals. Third, this procedure protected the crystals from deformation and general contamination due to handling.

One-tenth of an inch was then sawed off the silver-plated end of the mold containing the crystals. The crystals were removed from the mold by cooling to liquid-nitrogen temperature. The difference in coefficients of thermal expansion between graphite and lead allowed the plated samples to drop from the mold without damage.

2. Diffusion Anneal

The lead samples were diffusion-annealed in General Electric Viscasil 100 000-centistoke silicone fluid contained inside a specially designed tetrahedral high-pressure sample holder as shown in Fig. 1. It is to be noted that this design puts the thermocouple in intimate contact with the lead. This was necessary because of

¹⁷ B. W. E. Aivert and H. Wilman, *Brit. J. Appl. Phys.* **13**, 521 (1962).