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Self-Diffusion in Silver-Zinc*

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The diffusivities of Ag^{110} and Zn^{65} in an alloy of 70 atomic percent Ag and 30 atomic percent Zn have been measured over the temperature range 500–700°C, by using sectioning techniques. The temperature dependence of the diffusion coefficients is given by $D_{Ag}=(0.29\pm0.07)\exp[-(35\,990\pm410)/RT]$ cm²/sec, and $D_{Zn}=(0.46\pm0.08)\exp[-(35\,200\pm290)/RT]$ cm²/sec. Consideration of the effects of small differences in chemical composition indicates that the activation energy varies linearly with composition. The activation energies for diffusion apparently differ significantly from the average value derived from internal friction measurements. This difference is shown to be compatible with the fundamental diffusion process in a binary system. Comparison of the results with measurements in AgCd alloys shows that Zn is considerably more effective than Cd in increasing the rate of diffusion relative to that in pure Ag.

INTRODUCTION

IN recent years, there has been considerable interest in the field of intermetallic diffusion, stimulated in part by the ready availability of radioisotopes of high purity and high specific activity. With such facilities, it has become possible, by use of precision sectioning techniques on carefully prepared specimens, to measure diffusion coefficients to an accuracy of a few percent.[1] To date, most of the precise measurements have been concerned with studies of self-diffusion and impurity diffusion in pure metals or dilute solid solutions.[2] For concentrated solutions, precise self-diffusion measurements have been made only for the CuZn[3,4] and AgCd[5] systems.

The AgZn system is of particular interest because of the accurate internal friction measurements made by Nowick[6] on alloys of composition between 15.8 and 30.2 atomic percent Zn. The observed relaxation effects have been interpretated as resulting from a stress-induced ordering of the atoms. With this assumption, the relaxation rate is expected to be diffusion limited, the activation energy for the process being identical with that for atomic diffusion of the slower diffusing constituent.

Except for systems exhibiting considerable changes in degree of order with temperature,[4,7] the temperature dependence of measured diffusion coefficients is found to be given to a high degree of accuracy by an Arrhenius equation of the form $D=D_0\exp(-Q/RT)$, where R is the gas constant, T the absolute temperature, and the frequency factor D_0 and activation energy Q are temperature independent. This result is consistent with first-order theories[8,9] of diffusion in pure materials. However, it is not apparent, even with a first-order theory, that D_0 and Q should be temperature-independent for self-diffusion in concentrated solid solutions.[10]

Overhauser,[11] and Hoffman, Turnbull, and Hart[12] have considered the effects of finite additions of impurities on self-diffusion of solvent atoms. These investigators found that at fixed temperature, the diffusion coefficient of the solvent increases exponentially with increasing impurity concentration, with a temperature-dependent proportionality factor. These considerations will be discussed later.

EXPERIMENTAL PROCEDURE

An ingot of silver-zinc was prepared by melting together in a purified graphite crucible under vacuum measured amounts of 99.99% pure silver and 99.999% pure zinc.[13] The molten metals were mixed thoroughly by use of a tiltable furnace. The ingot and mold, in an evacuated, sealed Vycor container, was then lowered slowly through a Bridgman furnace, at a rate of about 1 in./hr. After this procedure, the recrystallized ingot was examined and found to be composed of two or three large grains.

The ingot was then sectioned, by means of a thin water-cooled cut-off wheel, into thirteen cylindrical wafers of about 2-cm diameter and 7-mm length. The wafers were hand ground to flatness on graded emery paper and etched in dilute nitric acid to remove the worked layers. Following this procedure, the specimens were again sealed in an evacuated Vycor container and

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[1] C. Tomizuka and D. Lazarus, J. Appl. Phys. **25**, 1443 (1954).

[2] For example, see C. Tomizuka and L. Slifkin, Phys. Rev. **96**, 610 (1954).

[3] Hino, Tomizuka, and Wert, Bull. Am. Phys. Soc. Ser. II, **1**, 150 (1956).

[4] Kuper, Tomizuka, and Lazarus, Bull. Am. Phys. Soc. Ser. II, **1**, 149 (1956).

[5] A. Schoen, Bull. Am. Phys. Soc. Ser. II, **1**, 149 (1956).

[6] A. Nowick, Phys. Rev. **88**, 925 (1952).

[7] Possible exceptions have been noted for diffusion in pure metals at very low temperatures. These have generally been attributed to the presence of low-angle boundaries.

[8] C. Zener, J. Appl. Phys. **22**, 372 (1951).

[9] D. Lazarus, Phys. Rev. **93**, 973 (1954).

[10] D. Lazarus in *Impurities and Imperfections* (American Society for Metals, Cleveland, 1955), p. 107 ff.

[11] A. Overhauser, Phys. Rev. **91**, 246 (1953).

[12] Hoffman, Turnbull, and Hart, Acta Metallurgica **3**, 417 (1955).

[13] Silver obtained from Handy and Harmon; zinc from New Jersey Zinc Company.

annealed at about 600°C for about 24 hours to promote any possible recrystallization. A light etch following this heat treatment showed that no recrystallization had occurred.

Radioisotope layers of Ag^{110} and Zn^{65} [14] of 100–1000 A thickness were deposited on the specimens by electroplating from solutions of high specific activity, using platinum anodes. The plated diffusion specimens were then sealed in individual evacuated Vycor containers. For diffusion annealing, the sealed specimens were placed inside massive Nichrome containers at the center of linear diffusion furnaces. The furnaces were regulated in temperature to about $\pm\frac{1}{2}$°C by means of resistance-bridge controllers. This equipment is described in reference 2. Temperatures were measured with calibrated chromel-alumel thermocouples placed inside the Nichrome containers immediately adjacent to the specimens. Temperature readings are presumed accurate to ± 1°C.

After diffusion, the specimens were removed from the furnaces for sectioning on a precision lathe. The detailed sectioning procedure has been described previously.[2] Ten to twenty cuts of 50–100 microns thickness were machined from each specimen. The cuts were individually weighed and the activity measured either by solution beta counting or by means of a gamma scintillation counter.

In all cases, the activity was found to decrease exponentially with the square of the penetration distance, indicating that no effects due to surface or grain-boundary diffusion were present. Values for the diffusion coefficients were determined from the slopes of the plots of log (specific activity) *versus* (penetration distance),[2] and a knowledge of the time of the diffusion anneal from the usual relation $D^{-1} = -[d\ \ln I/d(x^2)]4t$ between the specific activity I, the penetration distance x, and the diffusion time t.

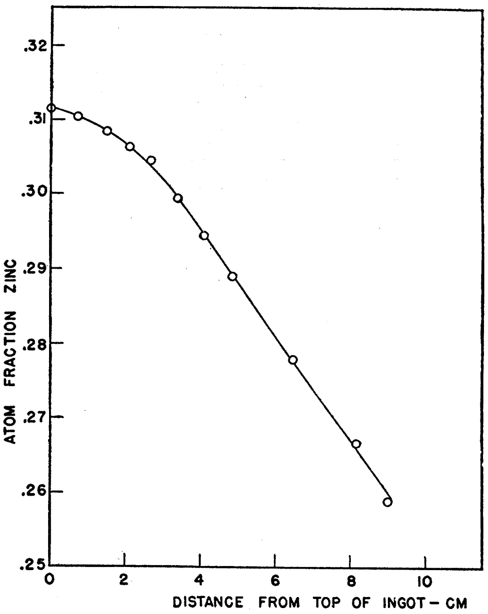

FIG. 1. Chemical composition gradient in AgZn crystal after passage through a Bridgman furnace.

TABLE I. Diffusion of Ag and Zn in AgZn.

Tracer	T °K Diff. temp.	c Measured atomic fraction Zn	$D(c)$ cm²/sec Measured diff. coeff.	D^a (0.30) cm²/sec Corrected diff. coeff.	b^b cal/mole Correction factor
Ag	971	0.3046	2.51×10^{-9}	2.35×10^{-9}	26 860
Ag	951	0.2780	1.07×10^{-9}	1.46×10^{-9}	26 290
Ag	921	0.3129	1.06×10^{-9}	8.73×10^{-10}	27 000
Ag	872	0.3085	3.20×10^{-10}	2.81×10^{-10}	26 830
Ag	830	0.2944	8.25×10^{-11}	9.02×10^{-11}	26 370
Ag	773	0.2644	1.08×10^{-11}	2.00×10^{-11}	26 490
					Mean $\bar{b}$ =26 640
Zn	969	0.2964	4.77×10^{-9}	5.02×10^{-9}	21 540
Zn	963	0.2664	3.45×10^{-9}	5.06×10^{-9}	21 650
Zn	921	0.3065	2.21×10^{-9}	2.05×10^{-9}	21 940
Zn	871	0.2889	5.87×10^{-10}	6.75×10^{-10}	21 900
Zn	830	0.3107	3.05×10^{-10}	2.65×10^{-10}	22 240
Zn	811	0.2591	8.73×10^{-11}	1.52×10^{-10}	21 970
Zn	768	0.5792	3.31×10^{-11}	4.46×10^{-11}	21 910
					Mean $\bar{b}$ =21 820

[a] Corrected values obtained by taking

$$D(0.30) = D(c)\exp[\bar{b}(0.30-c)/RT].$$

[b] b is defined by $b=(RT/c)\{\ln[D(c)/D(0)]+\ln[D_0(0)/D_0(c)]\}$, where $D(0)$Zn $=0.54\exp(-41\ 700/RT)$ [A. Sawatzky, Bull. Am. Phys. Soc. Ser. II, 1, 149 (1956)], $D(0)$Ag $=0.40\exp(-44\ 090/RT)$ [C. T. Tomizuka and E. Sonder, Phys. Rev. **103**, 1170 (1956), this issue].

A quantity of material was removed from each specimen for chemical analysis, from a region immediately adjacent to the diffusion zone. The specimens were analyzed by the Volhard method to a precision of 0.01%. The analyses were kindly performed by Mr. E. Tanda of the University of Illinois Chemistry Department.

Least squares solutions for the activation energies and frequency factors were performed by using the University of Illinois electronic digital computer (Illiac).

RESULTS

Chemical Analysis

The chemical analyses showed that a considerable amount of gravity segregation was present in the specimen, as shown in Fig. 1. The segregation presumably occurred during passage of the ingot through the Bridgman furnace.

To normalize the measured diffusion coefficients to the nominal composition of 30 atomic percent zinc, an exponential correction factor was used. Following the experience of Hoffman, Turnbull, and Hart,[12] the assumption was made that the change in diffusion constant with impurity concentration can be described by a simple exponential relationship. If the change in activation energy between diffusion in a pure solvent and in an alloy of impurity concentration c is considered to be directly proportional to c, then the diffusion coefficient in the alloy, $D(c)$, is given in terms of that

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[14] Isotopes obtained from Isotopes Division, Oak Ridge National Laboratory.

in the pure matrix, $D(0)$, by

$$D(c)=D(0)\frac{D_0(c)}{D_0(0)}\exp(bc/RT), \qquad (1)$$

where b is a constant. Values of b were determined for each specimen of measured composition, relative to the known values for diffusion of Ag[15] and Zn[16] in pure Ag, by using a self-consistent method to determine $D_0(c)/D_0(0)$. The mean value of b, for each tracer, was then used to correct the observed diffusion coefficients to their values at exactly 30 atomic percent zinc composition. As shown in Table I, this procedure leads to self-consistent results with very little scatter. The mean values for b were determined as 26 640±110 cal/mole for Ag, and 21 820±70 cal/mole for Zn.

Diffusion Coefficients

Typical penetration plots showing the logarithm of the specific activity *versus* the square of the penetration distance are given in Fig. 2. Values for all the measured and corrected diffusion coefficients are presented in Table I, together with measured compositions and the correction factors described above. The measured and corrected diffusion coefficients are plotted on a logarithmic scale as a function of reciprocal absolute temperature in Fig. 3, together with the results for diffusion of Ag and Zn in pure Ag.

The temperature dependence of the diffusion coefficients in the 30% zinc alloy is found to be

$$D_{\mathrm{Ag}}=(0.29\pm0.07)\exp[-(35\,990\pm410)/RT]\ \mathrm{cm^2/sec},$$

$$D_{\mathrm{Zn}}=(0.46\pm0.08)\exp[-(35\,200\pm290)/RT]\ \mathrm{cm^2/sec},$$

where the limits of error are given by the standard deviation in a least-squares analysis. The individual diffusion coefficients are expected to be accurate to about ±3% on the basis of previous experience, the errors arising primarily from inaccuracies in determination of the penetration depth.

DISCUSSION

It is apparent from the results of the present experiment, that the presence of a high concentration of zinc in the silver lattice produces an enormous increase in the rates of diffusion of both Ag and Zn. This increase is 140-fold for Ag and 58-fold for Zn at 500°C. The accompanying changes in activation energy are 8.1

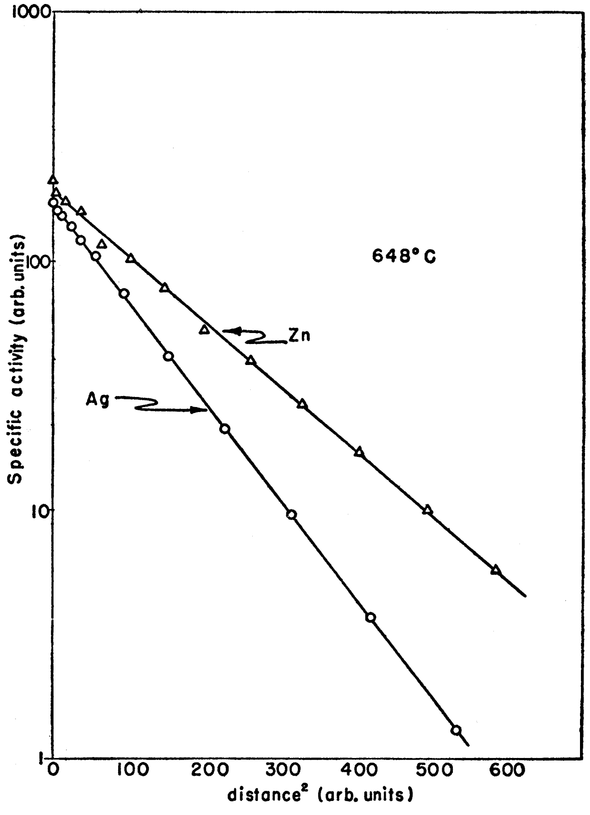

FIG. 2. Penetration curves for diffusion of Ag and Zn in an AgZn alloy of 30 atomic percent Zn composition.

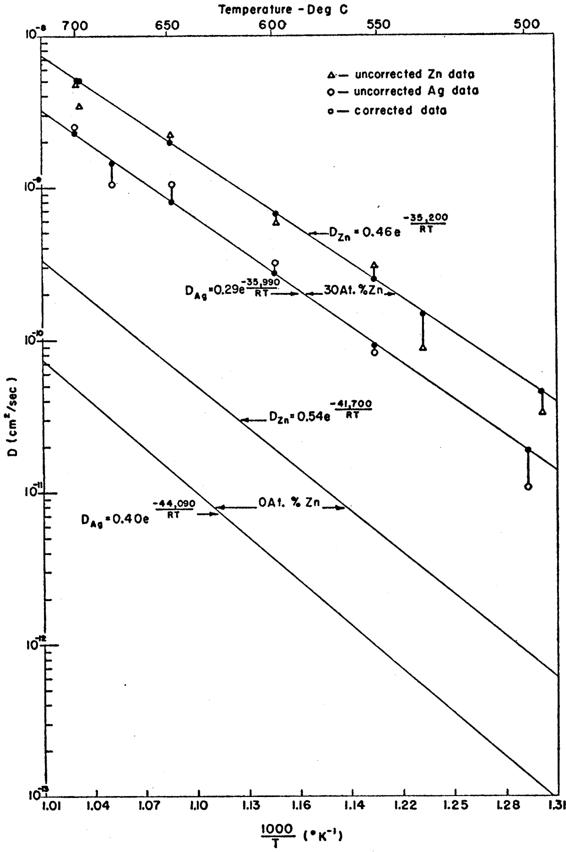

FIG. 3. Temperature variation of the diffusion coefficients for Ag and Zn for pure Ag and for an AgZn alloy of 30 atomic percent Zn composition.

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[15] C. Tomizuka and E. Sonder, Phys. Rev. **103**, 1170 (1956), this issue.

[16] A. Sawatzky, Bull. Am. Phys. Soc. Ser. II, **1**, 149 (1956).

kcal/mole for Ag and 6.5 kcal/mole for Zn, presumably arising from changes in the energies required for formation and motion of the lattice imperfections responsible for diffusion.

In previous work,[9] it has been shown that the energy of motion of an imperfection, E_m, can be estimated by consideration of the lowest energy shear deformation of the unit cell, by

$$E_m \approx \tfrac{1}{2}Ca^3/n, \tag{2}$$

where C is the smallest shear modulus, a the lattice parameter, and n the number of atoms in the unit cell. Substituting appropriate values for Ag $[C=\frac{1}{2}(C_{11}-C_{12})=1.528\times10^{-11}$ ergs/cm^3; $a=4.078\times10^{-8}$ cm; $n=4]$, the motion energy is estimated at 0.812 ev or about 18.7 kcal/mole, in fair agreement with theory,[17] and in excellent agreement with recent results on the quenching of vacancies in gold.[18] The effect of impurity addition on the elastic constants of silver has recently been determined by Bacon.[19] He found, for 2.4 and 3.5 atomic percent Zn alloys, a mean decrease in $\frac{1}{2}(C_{11}-C_{12})$ of 1.22% per atomic percent zinc. Extrapolating these results to 30% zinc, one would estimate a change in E_m of 7.3 kcal/mole. This value is seen to be comparable to the total measured change in energy for diffusion in the alloy. This result indicates that the ratio of energy of motion to energy of formation of the defects responsible for atomic diffusion in the present system is about 1/2, in contradiction to the value of 2/1 determined by Nowick.[20] Further, the present estimate indicates that the entire change in ratios of diffusion between the pure metal and the alloy may be due only to the decrease in (110) shear modulus in the alloy.

The ratios of activation energies for diffusion in the pure metal and alloy are 1.22 for both Ag and Zn. This number is almost exactly equal to the ratio of the melting temperatures of the pure metal and alloy, consistent with the observations of Zener[8] and Dienes.[21]

The observed activation energies for tracer diffusion (35.99 kcal/mole for Ag, 35.20 kcal/mole for Zn) are considerably greater than that observed by Nowick (32.5 kcal/mole) for anelastic relaxation in alloys of the same composition. This discrepancy is far outside the probable error of either set of measurements. Hino, Tomizuka, and Wert[3] have recently found similar disparities in studies of diffusion and relaxation in the CuZn (30 atomic percent zinc) system. Since the relaxation experiments show a very sharp peak with variation of temperature or frequency, it is improbable that the discrepancy is due to the presence of chemical composition gradients.

The difference between the activation energies observed for the two processes can be interpreted by consideration of the fundamental interactions between constituents which must occur for diffusion in a binary substitutional system. As shown previously,[10] the diffusion coefficient in a binary solid can only be rigorously expressed as a sum of terms, and not by an Arrhenius equation. Over any small range in temperature, the resulting equation may be very closely approximated by an Arrhenius equation, within reasonable experimental error. Over an extended temperature range, the Arrhenius "activation energy" must be expected to decrease with decreasing temperature. Thus, the discrepancy between diffusion and relaxation measurements is almost certainly due to the difference in range of temperatures involved in each experiment (500–700°C for diffusion, 120–360°C for relaxation). Indeed, Nowick, whose range of absolute temperatures was extremely large, observed a departure from the Arrhenius equation. It is apparent, therefore, that for a reasonable comparison between the two types of experiment, one must compare the activation energy determined only by the lowest temperature diffusion data with that determined only by the highest temperature relaxation data. For the present system, the energies obtained in this manner are 35 kcal/mole for both experiments. It is thus apparent that the anelastic measurements are completely consistent with a simple diffusion process.

It is also of interest to compare the results of the present investigation with those obtained by Schoen[5] on diffusion of Ag in AgCd alloys. Schoen found that in a 30 atomic percent Cd solution, the temperature variation of the diffusion coefficient for Ag was characterized by an activation energy of 38.5 kcal/mole, a change of 5.6 kcal/mole from the energy for diffusion in the pure solvent. Applying Bacon's data for the change in shear modulus with composition for this system, by use of Eq. (2), one may estimate a change in E_m of about 3 kcal/mole for a 30% Cd alloy. Thus for a Cd impurity, the change in shear modulus is not sufficient to explain the change in diffusivity. A fundamental difference between Zn and Cd as impurities in Ag, due to their different closed-shell configurations, is evidenced by the fact that Zn contracts the Ag lattice while Cd expands it. The interaction proposed by Overhauser[11] should then be much more effective in decreasing E_m for a Cd-rich than for a Zn-rich alloy. This expectation is at least qualitatively verified by comparison of the diffusion data.

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[17] H. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

[18] Bauerle, Klabunde, and Koehler, Phys. Rev. **102**, 1182 (1956).

[19] R. Bacon, thesis, Case Institute of Technology, 1955 (unpublished).

[20] A. Nowick, Bull. Am. Phys. Soc. Ser. II, **1**, 45 (1956).

[21] G. J. Dienes, Phys. Rev. **89**, 185 (1953).