

Diffusion of Iron Group Elements in Silver

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The diffusion coefficients of nickel and cobalt into silver has been measured as a function of temperature by the tracer and lathe sectioning techniques. The results obtained were expressed as follows:

$$D = (21.9) \cdot \exp\left(-\frac{54,800}{RT}\right) \text{ cm}^2/\text{sec for nickel}$$

$$D = (104) \cdot \exp\left(-\frac{59,900}{RT}\right) \text{ cm}^2/\text{sec for cobalt.}$$

Taking into consideration the result by Mullen for the diffusion of iron into silver, the activation energy of diffusion of the first transition elements increases slowly from Cu to Ni and after showing a sharp maximum at cobalt, decreases suddenly at iron. Such behavior is different in the case of copper, in which a flat maximum is found at nickel. Also the frequency factor shown in the above expression is fairly large when compared with copper. It is pointed out here that the solid solubility limits of the first transition metals in silver are extremely small when compared with copper, which has some influence on the result of measurement of the activation energy as well as the frequency factor in the case of silver.

1. Introduction

Since Lazarus¹⁾ put forward the theory screening effect on the diffusion of impurity atoms in monovalent metals, a number of experimental studies have been made. Of them, the diffusion of transition elements is

especially interesting because it is associated with the problem of what the electronic configuration of these solutes is in such solvents. The present authors have observed the diffusion of cobalt²⁾ and nickel³⁾ in silver. Results obtained are as shown in Fig. 1, where the activation energy for diffusion is plotted as a function of the atomic number together with the data of other elements. Also those for diffusion in copper are given for comparison. From these results the following features are seen:

(1) For the diffusion of nickel that has a valence one less than that of the solvent atom, both in copper and in silver the activation energy is larger than those of the self-diffusion of solvent metals as predicted by Lazarus.

(2) In copper the activation energy decreases in the order of nickel, cobalt and iron; on the other hand, in silver reaches its maximum at cobalt.

(3) Furthermore, as is shown in the following Table I, the frequency factor D_0 is anomalously large for nickel and cobalt in silver (several tens of the value given by Zener's relation⁴⁾).

Differences (2) and (3) between in copper and in silver, may be due to the inherent

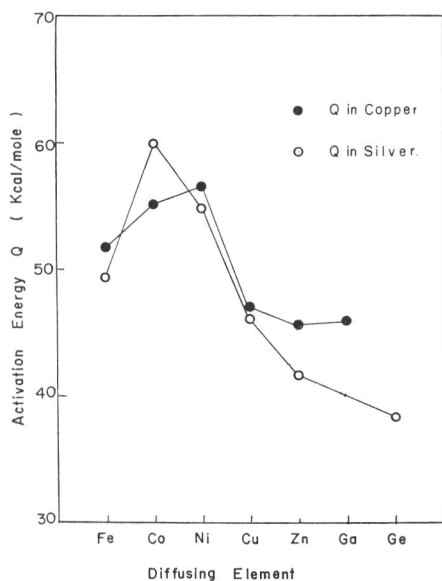


Fig. 1. Activation energy for diffusion in copper and silver plotted as a function of atomic number.

Table I. Observed values of D_0

Diffusant Solvent	Fe	Co	Ni
Ag	2.42 ⁽⁴⁾	104 ⁽²⁾	21.9 ⁽³⁾
Cu	1.4 ⁽⁵⁾ (1.01) ⁽⁶⁾	1.93 ⁽⁵⁾	2.7 ⁽⁵⁾

natures of solvents, but a problem arises from the low solubility of the solute. The solid solubility limit is considerably small for the first transition metals in silver, while in copper it is not so small as in silver, as shown in Table II. If a solute metal with

Table II. Solid solubility limit of Fe, Co and Ni in copper and silver.

Element	Solid Solubility (at.%)	
	in Cu	in Ag
Fe	0.35–2.95 (700–1000°C)	–0.007 (–m.p.)
Co	1.0–4.9 (700–1070°C)	–0.001 (–m.p.)
Ni	Soluble in all Proportions	0.08–0.18 (700–920°C)

low solubility limit is electroplated on the specimen surface and diffusion annealing is performed, then at concentrations beyond the solubility limit atomic diffusion will not normally take place. In the next section a possible analysis will be given for this phenomenon.

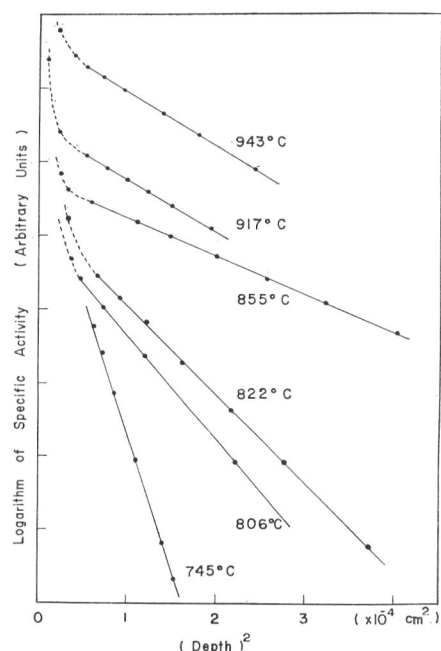
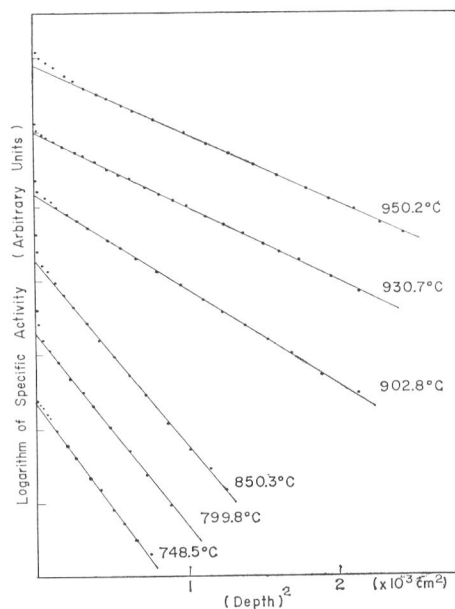
2. Method of Analysis

In the initial period of diffusion annealing the concentration at and near the surface of the specimen will still be beyond the solubility limit, then the penetration curve will show anomaly. It may be said, for instance, that the surface effect as seen in the diffusion of cobalt (Fig. 2) and nickel (Fig. 3) in silver is its evidence. In this situation the penetration curve should not be considered to follow the usual equation

$$C(x, t) = \frac{C_0}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}, \quad (1)$$

even if it looks as if it were expressed by (1) below the solubility limit.

The surface effect should be smaller as the amount of electroplated diffusing atoms

Fig. 2. Penetration curves for diffusion of Co in Ag.²⁾Fig. 3. Penetration curves for diffusion of Ni in Ag.³⁾

decreases. In the present experiments, the layer of Fe⁵⁹ deposited on the specimen surface of the silver single crystal was less than 1 Å in thickness. In order to avoid the evaporation of iron atoms during annealing, a silver layer 0.6 to 1 mm thick was electroplated

furthermore on the iron coated surface. Diffusion annealing was carried out at 895°C for various annealing periods. The resulting penetration curves are shown in Figs. 4 and

5. Since the concentration of iron was estimated less than 0.0001 at. % in each case, it may be considered to lie below the solubility limit at any penetration depth.

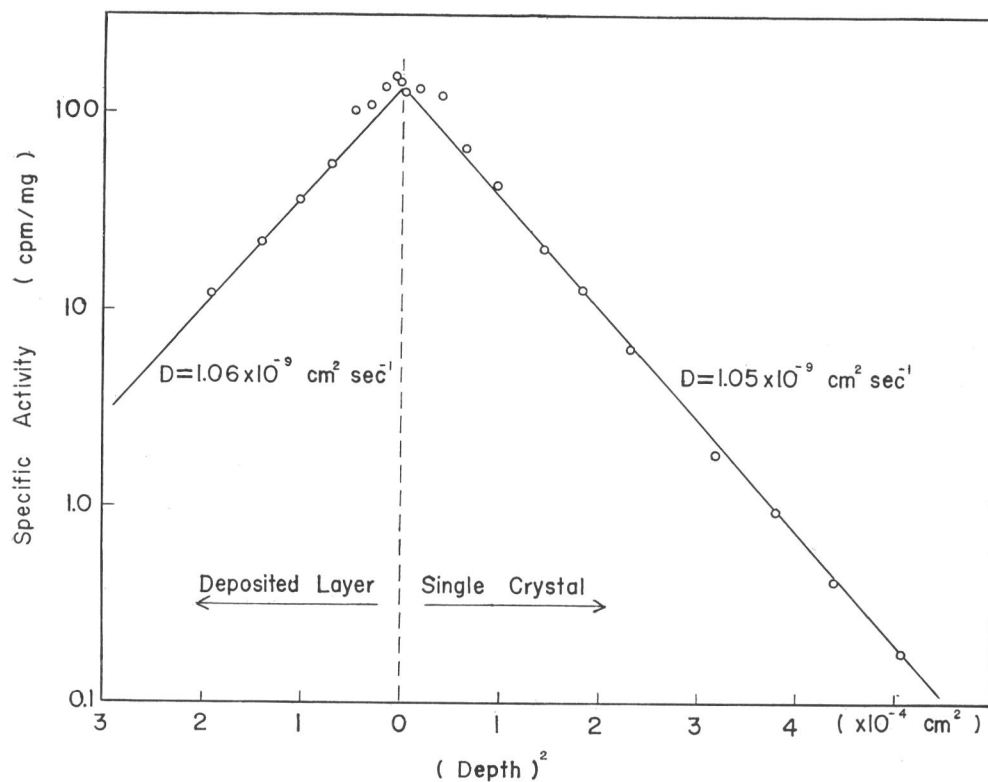


Fig. 4. Penetration curves for diffusion of Fe in an Ag-couple of a single crystal and a deposited polycrystal, at 895°C for 5 hours.

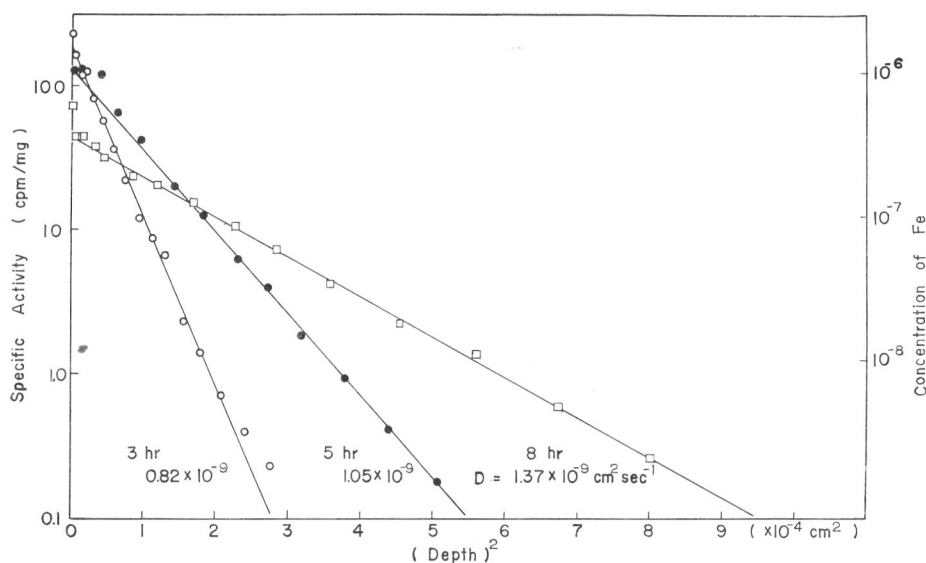


Fig. 5. Penetration curves for diffusion of Fe in Ag single crystal side at 895°C for various annealing time.

Although the penetration curves are linear except in the extreme vicinity of $x=0$, the values of D which are calculated by using Eq. (1) do not agree with one another as predicted above. Then, the diffusion coefficients thus obtained are denoted by the apparent diffusion coefficient D_{app} .

Now, let t^* be a certain time when the maximum concentration, *i.e.*, the surface concentration had been reduced below the solubility limit; also let us assume that the penetration curve at this critical time is again linear. This assumption will be reasonable from the above experimental results (Fig. 5). It is therefore possible to define D^* as satisfying the relation

$$C(x, t^*) = \frac{C_0}{2\sqrt{\pi D^* t^*}} e^{-\frac{x^2}{4D^* t^*}}. \quad (2)$$

In general D^* is not equal to D , then we put

$$D^* = D(1 + \Delta).$$

For $t > t^*$, in which the atomic diffusion with the coefficient D takes place throughout the specimen, the concentration is expressed by integrating Fick's equation as

$$C(x, t) = \frac{C_0}{2\sqrt{\pi D(t + \Delta t^*)}} e^{-\frac{x^2}{4D(t + \Delta t^*)}}. \quad (3)$$

Therefore comparing (1) and (3) we have

$$D_{app} = D(1 + \Delta t^*/t). \quad (4)$$

D_{app} is linear with respect to $1/t$ and D_{app}

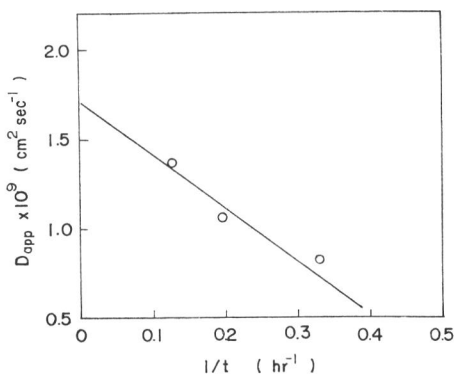


Fig. 6. Time dependence of the apparent diffusion coefficient for diffusion of Fe in Ag at 895°C.

approaches the true value D as t tends to infinity. In Fig. 6 the dependence of D_{app} on time is shown, where the relation (4) is found to hold and the curve gives $D = 1.7 \times 10^{-9} \text{ cm}^2 \text{ sec}^{-1}$.

3. Discussion

Considering the low diffusivity at a concentration above the solubility limit, D^* should be smaller than D , and hence Δ is negative. Thus D_{app} is always smaller than D . For this reason it may be said that the observed values of D were under-estimated. This tendency will be more dominant at lower temperatures since the solubility limit is generally smaller the lower the temperature. Therefore the activation energy may be overestimated in such cases as cobalt and iron, since they have an extremely low solubility limit in silver. The frequency factor D_0 will also be subjected to such influence. The observed value D_{app} coincides with the true value D at a temperature T' at which the solid solubility limit reaches 100%. If $T' = \infty$, D_0 does not change in spite of the above tendency of D_{app} . If T' is a finite temperature, the correct value of D_0 is lower than observed. Experimentally, however, it appears that $D_{app} = D$ is established at fairly low solubility, say, at a few atomic percent, for instance, as in the diffusion of cobalt in copper⁵⁾. Taking into consideration of this fact, T' will be practically a comparatively low temperature. In such a case it may be pointed out that D_0 will be considerably lowered by correction.

References

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- 2 T. Hirone and H. Yamamoto: J. Phys. Soc. Japan **16** (1961) 455.
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- 4 C. Zener: *Imperfection in Nearly Perfect Crystals*, John Wiley and Sons, Inc., New York (1952) p. 299.
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DISCUSSION

Williams, G. P.: Anomalous behavior similar to this has been reported by Williams and Slifkin for the diffusion of the rare earths in single crystals of silver, where the tracer solubility is vanishingly small.

However, in these rare earth systems the steep initial slope was attributed to volume diffusion, whereas the deeper penetration was demonstrated to be due to diffusion along dislocation pipes.

Hirone, T.: In the present experiments the flattening of the slope was sometimes found at far deeper penetration beyond those indicated in the figure, which was accompanied by a fairly large scattering of observed points. This portion of penetration curve will be due to the diffusion through dislocation pipes.

Tomizuka, C. T.: We observed the surface hold-up effect in the first 1μ (micron) layer in case of the diffusion of zinc in copper where the solubility limit is large. The six points obtained within the first micron of the penetration profile clearly indicate a volume diffusion. This result was obtained a week before I left for this conference and I do not intend to offer any explanation for it. The deeper portion of the penetration plot agrees with the published value of volume diffusion by Hino.

Blandin, A. P.: A calculation of the interaction energy between impurities and vacancies may be made along similar lines than in the paper that I am giving in this conference (IB-6)*.

Transitional impurities cannot be treated by perturbation theory, as they are strong perturbation. But, the model of "virtual bound states" as suggested by Friedel and and Pargdy developed now may be used. It predicts for the whole transitional series two peaks of the binding energy. A rapid and rough calculation seems to agree with the observed experiments reported in the paper of T. Hirone *et al.* Such a model would give an attraction for transitional impurities in aluminium, the binding energy showing only one peak in the series. But, I do not know if there are any measurements in aluminium alloys.

* *Proc. Int. Conf. Cryst. Latt. Def.* (1962): J. Phys. Soc. Japan **18** Suppl. II (1963) 85.

Tomono, Y.: I and Ikushima observed a penetration profile as a function of the magnitude of deposited radioactive tracer for the diffusion of iron into copper.

We could also observe a surface effect but the concentration corresponding to the knick point is not a unique function of temperature but much depends upon the magnitude of deposited tracer. So that we think that the surface effect can not be interpreted only by solubility.

Hirone, T.: When the concentration of diffusion just below the surface lies above the solubility limit, the solution of Fick's equation does not take the usual form even in the region where the concentration is less than the solubility limit, and we are now thinking that the penetration curve does not always bend at the solubility limit. We would like to confirm this point experimentally.
