

De-enhancement of gold diffusion in lead by impurities in the lead

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Measurements of the effects of alloying lead with silver and palladium on the diffusivity of gold in lead are reported. It is observed that both Pd and Ag strongly de-enhance Au diffusion in lead; in fact, the Pd de-enhances Au diffusivity in Pb more pronouncedly than alloying lead with gold. It was found that the binding energy between a Au tracer in an interstitial site and Pd, Au, or Ag atoms in substitutional sites to form substitutional dimers was the same in all three cases.

INTRODUCTION

Measurement of the diffusion of gold into lead has led to many surprises since the first measurements by Roberts-Austen.¹ The diffusion rate was found to be some five orders of magnitude faster than that of self-diffusion in lead² and was shown not to be a result of grain boundary or dislocation diffusion.³ The activation volume for diffusion was observed to be intermediate to those expected for interstitial or substitutional diffusion.⁴ Miller⁵ observed the enhancement of Pb self-diffusion by gold to be too small for substitutional diffusion but too large for interstitial diffusion, and most recently Warburton⁶ has observed a strong de-enhancement of gold diffusion in lead by gold impurities in the lead. A linear de-enhancement coefficient is defined by expanding the diffusivity as a power series in the concentration x of the impurity

$$D(x) = D(0)(1 + b_{21}x + b_{22}x^2 + \dots) \quad (1)$$

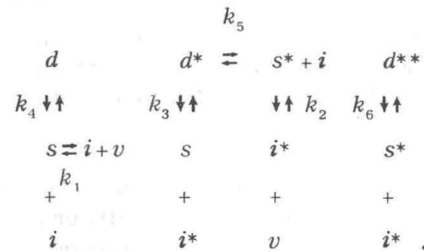
The experimental value of b_{21} for Warburton's measurements was as large as -3000 at 140°C . This means that as little as a 30-ppm gold concentration would reduce the diffusion rate of gold in lead by nearly 10%. To explain this result Warburton proposed that gold forms substitutional dimers or higher-order clusters in lead that are stable at lower temperatures. A substitutional dimer, as we define it here, is a defect in which two gold atoms exist together at a single substitutional site in the lead. One might extend this definition to include the possibility of two bound gold atoms that move together but do not need to occupy a given atomic site. This extension is not appealing because the screening in lead is so effective that electrostatic forces are basically screened even at nearest-neighbor separation.⁷ We note that the gold ion is sufficiently small⁸ to allow two of them to fit comfortably in a single atomic volume in lead. Warburton felt that his de-enhancement measurements were not adequately represented by a simple substitutional dimer mod-

el so he suggested the existence of higher-order clusters also.

Many other impurities, such as Cu, Ag, Zn, Pd, Ni, and Pt, have been observed to diffuse very rapidly in lead.⁹⁻¹⁴ The obvious next step was to look for the possible formation of substitutional dimers by these other defects in lead. Cohen and Warburton¹⁵ did this for Ag in Pb and found very little to zero de-enhancement indicating little probability of Ag-Ag substitutional dimers forming in lead even though the Ag ions are about the same size as the Au ions. One might look for de-enhancement in others of these impurity-lead diffusion couples,¹⁶ but because of the ease of measuring gold diffusion in Pb with the availability of extremely high specific-activity Au isotopes we decided first to look for de-enhancement of gold diffusivity in lead by the presence of others of these impurity atoms which diffuse rapidly in lead.

THEORETICAL ANALYSIS

In this section we will derive an expression for the de-enhancement of tracer diffusion by another impurity atom in the host. Let x be the concentration of the impurity and x^* that of the tracer. Let c_i , c_s , and c_d stand for the concentrations of impurity atoms in interstitial, substitutional, and substitutional dimer states, respectively, and let c_i^* , c_s^* , and c_d^* represent the same for the tracer. The concentration of vacancies is given by c_v and the concentration of tracer-impurity substitutional dimer is c_d^* . The following reactions may then take place:



The k 's in these reactions represent equilibrium constants. These reactions lead to the following

equations:

$$\frac{c_s c_i}{c_d} = k_4, \quad \frac{c_s c_i^*}{c_d^*} = k_3, \quad \frac{c_s^* c_i}{c_d^*} = k_5, \quad (1)$$

$$\frac{c_i c_v}{c_s} = k_1, \quad \frac{c_i^* c_v}{c_s^*} = k_2, \quad \frac{c_s^* c_i^*}{c_d^{**}} = k_6. \quad (2)$$

In addition we must consider the two equations which describe the conservation of particles:

$$c_s^* + c_i^* + 2c_d^{**} + c_d^* = x^* \quad (3)$$

and

$$c_s + c_i + 2c_d + c_d^* = x.$$

It is readily recognized from Eq. (2) that the k 's are not all independent, in fact, $k_5 = k_3 k_1 / k_2$.

We now substitute Eq. (2) into Eq. (3) and introduce $q^* = c_i^* / x^*$ and $q = c_i / x$ to arrive at

$$1 + \frac{c_v}{k_2} + \frac{2q^* x^* c_v}{k_2 k_6} + \frac{q x c_v}{k_1 k_3} = \frac{1}{q^*}, \quad (4)$$

$$1 + \frac{c_v}{k_1} + 2 \frac{q x c_v}{k_1 k_4} + \frac{q^* x^* c_v}{k_1 k_3} = \frac{1}{q}.$$

The q and q^* represent the fraction of impurities and tracers that are in interstitial sites at equilibrium.

One could also include interstitial-vacancy pairs¹⁷ in the theory. However, since these pairs are merely a step in the breakup of a substitutional state to an interstitial state and a vacancy, one arrives at the same expressions, Eq. (4), with slightly different definitions for k_1 and k_2 .

In our case, because of the high specific activity of the tracer, x^* is very small everywhere and will not affect the diffusion so we assume $x^* = 0$ in Eq. (4). This assumption is justified *a posteriori* by the Gaussian diffusion profiles.¹⁸ We now solve Eq. (4) to get

$$q^*(x) = q_0^* a / [a - 1 + (1 - 2ab_{31}x)^{1/2}], \quad (5)$$

with the following definitions:

$$q(0) = q_0 = (1 + c_v / k_1)^{-1}, \quad q^*(0) = q_0^* = (1 + c_v / k_2)^{-1}, \quad (6)$$

$$a = 4k_3 q_0 / k_4 q_0^*, \quad b_{31} = -c_v q_0 q_0^* / k_1 k_3. \quad (7)$$

If we assume that the diffusion rates of substitutional and substitutional dimer states are very slow compared to that of interstitial states, then¹⁹

$$D(x) = q^*(x) D_i, \quad (8)$$

where D_i is the pure interstitial diffusion constant for the tracer. This expression is valid under the assumption that x^* is everywhere negligible.¹⁸ Substituting Eq. (5) into Eq. (8) and expanding in a power series in x we get

$$D(x) = D_i q_0^* (1 + b_{31} x + \dots). \quad (9)$$

Thus b_{31} is the linear solute de-enhancement coefficient which we label b_{31} to distinguish it from the linear self-solute de-enhancement coefficient which is called b_{21} . In other words, b_{21} is used when the tracer diffusion is de-enhanced by the same kind of atoms that constitute the tracer and b_{31} when the de-enhancement is caused by a third party of solute atoms. In the limit as the solute approaches the tracer, $k_2 \rightarrow k_1$, $k_6 \rightarrow k_4 - 2k_3$, and $q_0 \rightarrow q_0^*$ and we find

$$b_{21} = -2c_v q_0^{*2} / k_2 k_6 \quad \text{and} \quad a = 2. \quad (10)$$

In order to compare the experiments with the theory we note that with the substitution of Eq. (5) into Eq. (8) it becomes

$$D(x) = D(0) a / [a - 1 + (1 - 2abx)^{1/2}]. \quad (11)$$

One then does a least-squares fit of the experimental data $D(x)$ at a constant temperature to this expression with the three parameters a , b , and $D(0)$. $D(0)$ is the diffusion rate of the tracer into a pure host, and b is the linear de-enhancement coefficient. We fit Warburton's de-enhancement of Au diffusing into Pb(Au) alloys to Eq. (11) with $a = 2$. This is equivalent to the expression derived by Warburton but not used by him to analyze his data.

EXPERIMENTAL PROCEDURES

Details of this procedure are given in Melville's dissertation.²⁰

Diffusion measurements: Weighed amounts of 99.9999% pure lead were mixed with 99.999% pure Ag or Pd, sealed under vacuum in a Pyrex tube, and then melted. This melt was stirred by agitation and then air cooled. The resulting ingots were remelted in a graphite mold under vacuum in a uniform-temperature furnace and then cooled to ambient temperature in about three hours. This procedure was developed to homogenize the Ag or Pd impurities in the Pb. Attempts to grow single crystals always resulted in concentration gradients along the rods. The samples were 4.8 mm in diameter and sliced into diffusion sections about 5 mm long after discarding the ends of the rod. Each diffusion measurement consisted of four samples, three of which were alloys, the fourth being a pure lead sample for reference. They were all plated from a ¹⁹⁵Au solution in HCl by dropping 25 μ l of solution on a freshly microtomed surface using a Hamilton gas-tight syringe with a plastic needle. After two minutes of plating, the remaining solution was removed with a Kimwipe dampened with NH₄OH and the surface was rubbed on paper saturated with methanol. The samples were then air dried and placed in the diffusion furnace