

Quenching Studies of a Gold-Silver Alloy*

R. KLOSKE AND J. W. KAUFFMAN

The Technological Institute, Northwestern University, Evanston, Illinois

(Received November 8, 1961)

The electrical resistance of gold—1.2 atomic percent silver samples was measured after quenching in the range 500° to 950°C. The resulting increase in resistivity immediately after the quench, $\Delta\rho_Q$, is described by the relation $\Delta\rho_Q = A \exp(-E_f^a/kT_Q)$, where A is $(7.6 \pm 1.3) \times 10^{-4}$ ohm-cm; E_f^a , the apparent formation energy equals (1.01 ± 0.03) ev. From the experimental limits of error for the formation energy in pure gold, an upper limit of 0.1 ev was established for the binding energy between lattice vacancies and the solute atoms. The recovery of quenched-in resistivity was determined in the course of annealing between 50° and 84°C following a quench from 700°C. The slope intersection method gave an activation energy of 0.85 ± 0.05 ev for the recovery of the quenched-in resistivity. The extra resistivity increased upon annealing by 8% and then annealed at a rate 30% to 40% less than that which has been observed for pure gold. The recovery behavior was interpreted in terms of vacancy-impurity complexes. A corresponding binding energy of 0.05 ev was obtained.

VACANCY formation and migration energy studies carried out in this laboratory on a gold—1.2 atomic percent silver alloy have yielded results which differ from those reported by Cattaneo and Germagnoli for more dilute alloys in this system.¹ These authors report an effective activation energy for the recovery of quenched-in resistivity of greater than 1 ev and deduce a vacancy-impurity interaction energy of the order of 0.3 ev.

In our experiments the electrical resistance of 0.016-in.-diam wire prepared from the vacuum-melted alloy was measured in liquid helium following quenching into ice water from temperatures in the range from 500° to 950°C. The resulting increase in residual resistivity, $\Delta\rho_Q$, was found to be described by the Arrhenius-type relation

$$\Delta\rho_Q = A \exp(-E_f^a/kT_Q), \quad (1)$$

where A is a constant equal to $(7.6 \pm 1.3) \times 10^{-4}$ ohm-cm, k is Boltzmann's constant, and T_Q is the temperature from which the quench is initiated. The activation energy for the resistivity increase, E_f^a , is interpreted to be the apparent energy of formation for lattice vacancies in the alloy and is found to be 1.01 ev with 90% confidence limits of ± 0.03 ev (Fig. 1). This value, which lies within the limits of error of the formation energy value of 0.98 ± 0.03 ev reported by Bauerle and Koehler for 99.999% pure gold,² indicates that any energy of interaction, B , between the lattice vacancies and the silver ions in solution must be small.

An upper limit for this binding energy was determined by considering the contributions of B to the (apparent) formation energy which would be measured experimentally. Using the relationship presented by Lomer³

$$C_v^{\text{alloy}} = A' \exp(-E_f^p/kT) \times [1 - 12C_s + 12C_s \exp(B/kT)] \quad (2)$$

(where E_f^p is the vacancy formation energy in pure gold

and C_s is the atomic fraction of solute) the equilibrium vacancy concentration in the alloy, C_v^{alloy} , was calculated at two temperatures for various values of the binding energy B . From these concentrations the apparent formation energy, E_f^a , which would be realized in a hypothetical formation energy investigation, was calculated using the usual Arrhenius-type relation

$$C_v^{\text{alloy}} = A'' \exp(-E_f^a/kT_Q). \quad (3)$$

The apparent value of the binding energy, B^a , which would be realized in this hypothetical experiment, corresponding to any given value of B was obtained from the difference

$$B^a = E_f^p - E_f^a. \quad (4)$$

Taking E_f^p to be 0.98 ev, an actual binding energy of 0.10 ev in the 1.2 at.% alloy would give rise to an apparent formation energy value of 0.95 ev and, hence, an apparent binding energy value of only 0.03 ev. Thus, as shown in Fig. 2, an actual binding energy value of 0.10 ev or less at this solute concentration will yield an

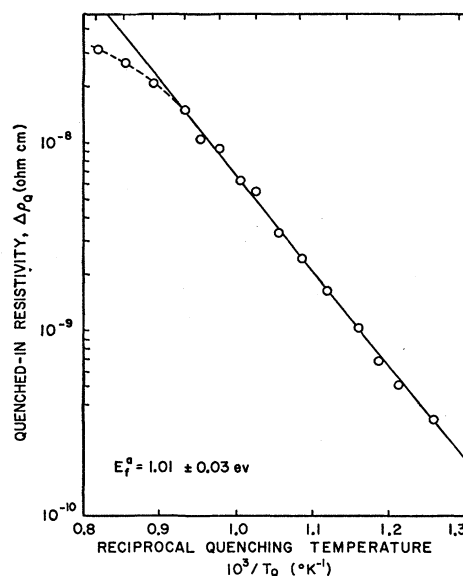


FIG. 1. Quenched-in resistivity vs reciprocal of the quenching temperature.

* Based on a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science at Northwestern University. Supported by the Office of Naval Research.

¹ F. Cattaneo and E. Germagnoli, *Phys. Rev.* **124**, 414 (1961).

² J. E. Bauerle and J. S. Koehler, *Phys. Rev.* **107**, 1493 (1957).

³ W. M. Lomer, *Vacancies and Other Point Defects in Metals and Alloys* (The Institute of Metals, London, 1958), p. 79.

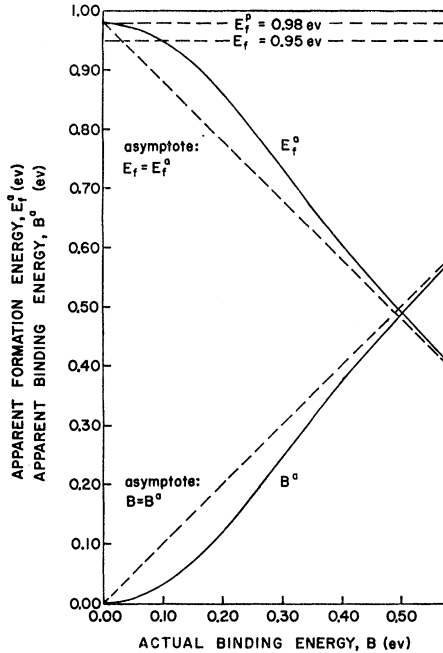


FIG. 2. Variation of the apparent formation and binding energies in a 1.2 at.% alloy.

apparent formation energy value within the limit of error of that for pure gold and, hence, escape detection in a real formation energy investigation. Therefore, although this analysis does not guarantee the existence of a binding energy, we submit that any binding energy between lattice vacancies and silver atoms at this alloy composition can be no greater than 0.1 ev.

However, since the vacancy concentration about a solute atom may be increased over that in the pure solvent metal by the factor $\exp(B/kT)$, the effects of a small binding energy should be more readily detected in an investigation of the low-temperature annealing characteristics of the vacancies. In an annealing study following a quench from 700°C, the extra resistivity was found to increase rapidly by 8% (after 1200 sec at 50°C) and then recover between 50° and 84°C with an activation energy of only 0.85 ± 0.05 ev (Fig. 3). On the basis of the physical model proposed by Damask and Dienes,⁴ one can deduce the following expression relating the apparent activation energy for recovery in the alloy, E_m^a , to the migration energy for vacancies in pure gold, E_m^p , and the binding energy B .

$$\exp(E_m^a/kT) = \exp(E_m^p/kT) \times [1 - C_s + C_s \exp(B/kT)]. \quad (5)$$

A binding energy value of 0.05 ev was calculated from the resulting expression

$$B = \frac{kT_1T_2}{T_2 - T_1} \ln \left\{ \frac{\exp[(E_m^a - E_m^p)/kT_1] - (1 - C_s)}{\exp[(E_m^a - E_m^p)/kT_2] - (1 - C_s)} \right\} \quad (5a)$$

for the activation energy value, $E_m^a = 0.85$ ev, the value

⁴ A. C. Damask and G. J. Dienes, Phys. Rev. **120**, 99 (1960).

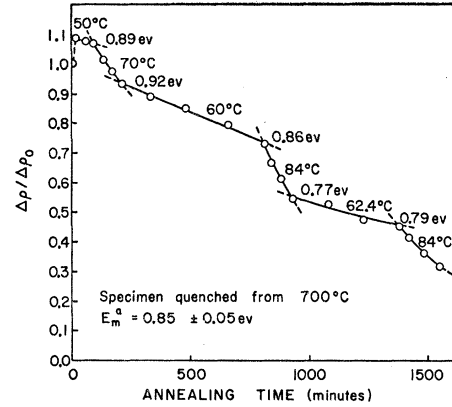


FIG. 3. Slope intersection determination of the apparent migration energy following a quench from 700°C.

of Bauerle and Koehler for pure gold,² $E_m^p = 0.82$ ev, and the annealing temperatures, 50° and 84°C. This value, having the range of limits, $+0.08$ ev and -0.05 ev, is consistent with the upper limit of 0.1 ev imposed by the formation energy study.

Offering additional support to this value is the relationship deduced by Pearson and Bradshaw,⁵ based on a similar physical model,

$$E_m^a - E_m^p = B \{ 1 - [1 + 12C_s \exp(B/kT)]^{-1} \}, \quad (6)$$

which may be used to predict the difference in activation energies, $E_m^a - E_m^p$. For the binding energy value of 0.05 ev and the given annealing temperatures, one obtains the result, $E_m^a - E_m^p \approx 0.02$ ev, which is in agreement with the experimentally measured difference of 0.03 ev.

It is of interest to compare the rates of recovery in pure gold with that of the alloy. At an annealing temperature of 60°C, the difference in activation energies of 0.03 ev predicts a ratio of the alloy annealing rate to the pure gold annealing rate of 0.35. Comparing this with results of Bauerle and Koehler,² for example, it is found that the rate ratio at 60°C and a fractional concentration of 0.85 is about 0.7 to 0.8. In experiments with pure gold having a ratio of resistance at room temperature to that at 4.2°K of 3500 (compared to a ratio of 1400 reported by Bauerle and Koehler for 99.999% pure gold), Mori, Meshii, and Kauffman⁶ observe a still more rapid rate of decay of the quenched-in resistivity and an activation energy for recovery of only 0.73 ev; the corresponding rate ratio is about 0.2. These results further illustrate the tendency toward a reduction in annealing rates with increasing impurity content.

ACKNOWLEDGMENTS

We thank Professor L. Slifkin for helpful comments and criticism of the manuscript and Dr. G. J. Dienes and Dr. A. C. Damask for stimulating discussion.

⁵ S. Pearson and F. J. Bradshaw, Phil. Mag. **2**, 1387 (1957).

⁶ T. Mori, M. Meshii, and J. W. Kauffman (private communication).