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VACANCY-COPPER INTERACTION IN DILUTE Ag-0.3 wt % Cu ALLOY

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Isothermal annealing studies on quenched Ag-0.3 wt % Cu alloy show that the entities responsible for the recovery of excess quenched in resistivity are Cu-vacant pairs rather than single vacancies. The apparent activation energy of the formation of a vacancy in the alloy was found to be 0.69 eV from which the binding energy of the vacancy-copper pair was calculated as 0.21 eV. The low value of 0.33 eV obtained for the energy activating the migration process may be attributed to such a high binding energy.

1. Introduction

The differences in the recovery behaviour of quenched- in vacancies in pure metals compared to alloys at low annealing temperatures are largely due to the fact that vacancies and solute atoms form pairs bound together with specific binding energies. As a result, the equilibrium vacancy concentration can be greatly increased, since the effective formation energy of vacancies is decreased by their binding energy to the impurity atoms. This effect has a considerable technological importance, because it greatly influences the formation of small clusters[1-4] which play an important role in experiments such as quenching, annealing, aging, radiation damage and mechanical deformation.

The present work is an attempt aiming at a precise determination of the binding energy between a Cu atom and a vacancy in an alloy of Ag containing 0.3 wt % Cu by resistivity measurements. It is also undertaken to shed more light on the clustering of point defects under the testing conditions of this alloy.

2. Experimental

Analytical examination of the specimens showed that the alloy contained 99.68 wt % pure Ag and 0.3 wt % Cu with traces of Ni, Fe, Mg and Mn ($\approx$0.02 wt %). The alloy had been homogenized at 900 °C in vacuum for 4 days, swaged and cold drawn into wires 0.5 mm diameter for resistivity measurements.

Specimens 200 mm long were solution treated at 550 °C in vacuum for 4h to remove the effect of swaging, and then slowly cooled to room temperature to bring the test samples to an identical initial state. The slowly cooled specimens were then heated to temperatures T_Q of 800, 700, 600, 500 and 400 °C for 1h and quenched in water at 20 °C. After quenching, the wire was immediately clamped into a U-shape in a silica tube containing the potential and current leads as well as calibrated thermocouple. The time that elapsed after quench to band the wire into a U-shape was too short ($\approx$ 1min) to prevent any effective vacancy loss. Isothermal annealing of the specimen was carried in a tubular air furnace where the temperature inside the tube could be maintained constant for several hours within $\pm$2 °C. Temperature uniformity through the part occupied by the specimen was better than $\pm$1 °C. The time needed to achieve the annealing temperature (max. of 2 minutes) was not included in the effective time t.

The well-known 4-probe method for measuring resistivity was used in order to minimize any errors due to point contact. Voltage measurements were taken from a »Level« D. C. microvoltmeter type TM 98P of sensitivity $\pm$0.1 μV to determine the potential drop across the working length of the specimen (100 mm long). By this arrangement it was possible to detect changes in resistivity of 10^{-8} Ωcm. During measurement of ϱ the specimen surrounded by the silica tube was kept inside a double-walled container used as a water bath at 20 °C. Fairly good thermal insulation of this container ensured the temperature to maintain at 20 °C $\pm$ $\pm$ 1 °C.

3. Results and observations

A typical set of isothermal annealing curves is shown in Fig. 1 representing plots of $\Delta\varrho/\varrho_0 = (\varrho_t - \varrho_0)/\varrho_0$ against annealing time (t) for samples quenched from 400, 600 and 800 °C. Isothermal annealing temperatures were 100, 150, 175 and 200 °C. Here ϱ_0 is taken as the reference resistivity of the quenched specimens measured in air at room temperature directly after quench, and $(\varrho_t - \varrho_0)$ denoted as $\Delta\varrho$ is the change in resistivity due to thermal treatment, where ϱ_t is the resistivity of the specimen after time t of annealing measured at room temperature. From Fig. 1 it was possible to deduce that:

— on annealing, the resistivity ϱ_t measured after a time t was found to decrease as compared with its value at room temperature, ϱ_0. Thus, $\Delta\varrho$ is negative and so the relative change in resistivity, $\Delta\varrho/\varrho_0$, represents a decrease in resistivity. With increasing annealing time such a negative change in resistivity decreases and for annealing times longer than $\approx$120 min, a plateau in the value of $\Delta\varrho/\varrho_0$ was observed indicating a nearly constant value of ϱ_t with time.

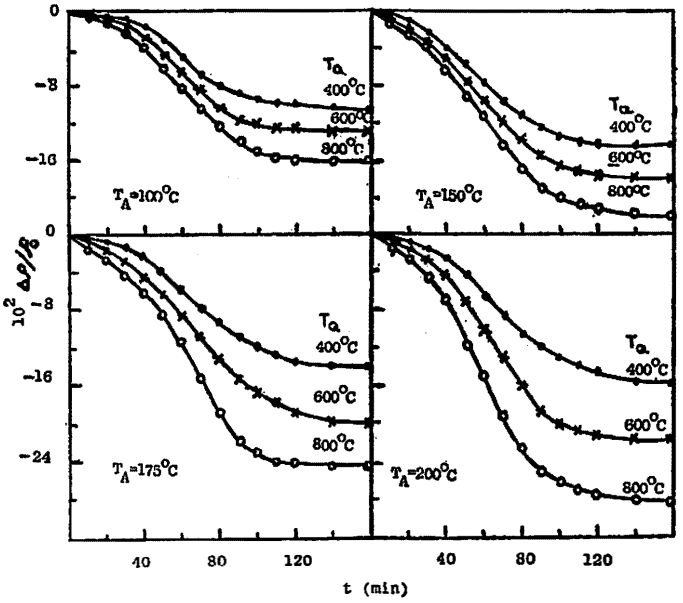

Fig. 1. Variation of the relative change in resistivity $\Delta\varrho/\varrho_0$ at different annealing temperatures T_A with annealing time (t) for specimens quenched from different temperatures T_Q.

— the rate of decrease in $\Delta\varrho/\varrho_0$ is low during the first 30 minutes of annealing, then follows an almost constant high rate of recovery for the next 90 minutes. It should be noticed, however, that the rate of recovery depends largely on T_Q; it increases with increasing the quenching temperature.

— for specimens quenched from the same temperature, the decrease in $\Delta\varrho/\varrho_0$ is larger for higher annealing temperatures.

4. *Discussion*

It is generally accepted that any form of disorder in a metallic structure, e. g. impurities, dislocations or point defects, will make a large contribution to the electrical resistance. Accordingly, the increase in the concentration of vacancies with increasing quenching temperature T_Q is assumed to be responsible for the observed increase in resistivity ($\Delta\varrho_{T_Q}$) following quenching. The effect of quenching temperature on the magnitude of $\Delta\varrho_{T_Q}$ may be described by the relation:

$$\Delta\varrho_{T_Q} = A \exp(-E_f/KT_Q),$$

where A is constant, E_f the formation energy of a vacancy and K is Boltzmann constant.

The quenching temperature dependence of the excess resistivity due to vacancies is shown in Fig. 2 by plotting $\log(\Delta\varrho_{T_Q}/\varrho_i)$ against $1000/T_Q$. Here $\Delta\varrho_{T_Q} = \varrho_0 - \varrho_i$, where ϱ_i is the resistivity of the slowly-cooled specimens measured at room temperature. From the slope of the resulting straight line, the apparent activation energy of vacancy formation E_f^* was calculated as 0.69 eV. Sakakura et al.[5] reported an activation energy of 0.84 eV for vacancy formation in pure silver. Confirmative recovery experiments were performed on the pure silver used in the preparation of the dilute Ag-Cu alloy of this study. An activation energy of 0.8 eV for vacancy formation was obtained in good agreement with that found by

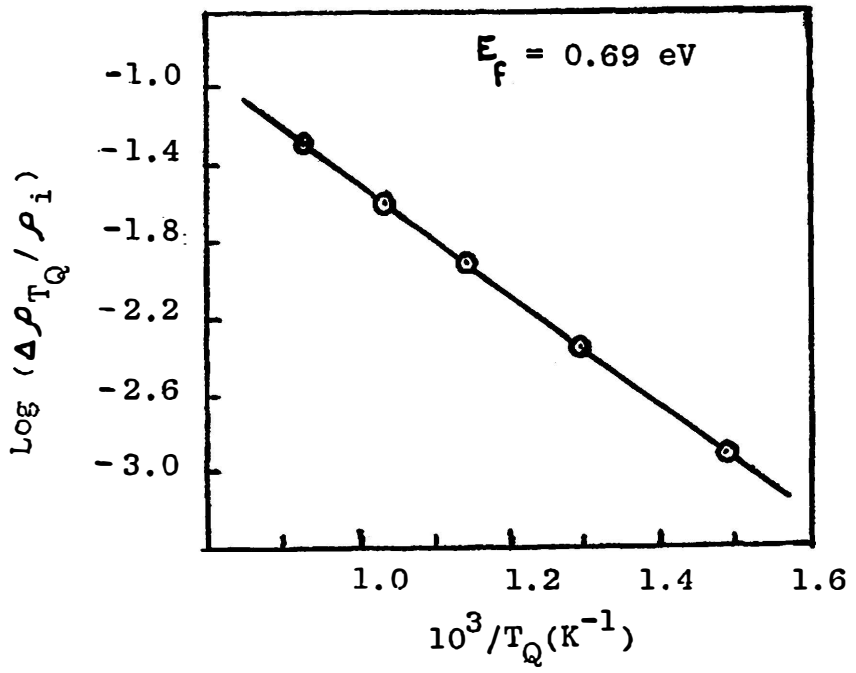

Fig. 2. Variation of $\log\left(\frac{\Delta T_Q}{\varrho_i}\right)$ with $1/T_Q$ for determination of E_f^*.

Sakakura et al. The difference between the activation energy obtained in the present work and that of pure silver may be attributed to the binding energy between a vacancy and a copper atom B_{V-Cu}. The binding energy is quite sensitive to the difference between the formation energy of a vacancy and the apparent formation energy of a vacancy[6]. An expression similar to that used by Singh et al.[3] to find the vacancy-manganese binding energy in an Al-0.35 wt % Mn alloy is adopted here to calculate the vacancy-Cu binding energy. This is acceptable in regard of the similar crystal structure for both aluminium and silver. In addition, both aluminium and silver have nearly equal atomic radii for the coordination number $Z = 12$[1].

The difference in the values of E_f and E_f^* is related to the vacancy-Cu binding energy by[3],

$$E_f - E_f^* = \frac{12IB_{V-Cu}\exp\frac{B_{V-Cu}}{KT_Q}}{1 - 13I + 12I\exp\frac{B_{V-Cu}}{KT_Q}}$$

where I is the fractional solute concentration.

Taking I to be 5.11×10^{-3} atom fraction, a value of 0.21 eV for B_{V-Cu} was found for the mean quench temperature of 873 K. This value is relatively large than those quoted in literature namely, 0.04—0.12 eV by M. Doyama[6], and 0.027—0.045 eV by O. Takai et al.[7]. As a result, the equilibrium vacancy concentrations are expected to be greatly increased since the effective energy of vacancy formation E_f^* is decreased by the binding energy of vacancies to the solute atoms.

When the slopes of the linear portions of the curves of Fig. 1, $\frac{\partial(\Delta\varrho/\varrho_0)}{\partial t} = \Theta$, were plotted against T_Q for different annealing temperatures T_A, straight lines were obtained as shown in Fig. 3. Assuming the recovery process of the quenched-in

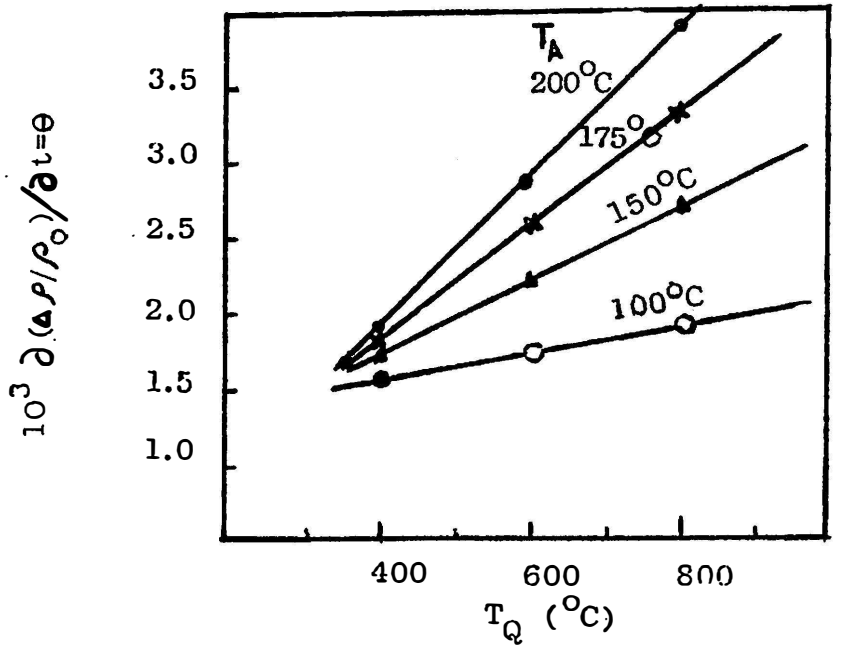

Fig. 3. Dependence of $\Theta = \frac{\partial(\Delta\varrho/\varrho_0)}{\partial t}$ on the quenching temperature T_Q for specimens annealed at different annealing temperatures T_A.

resistivity to be controlled by a reaction rate equtaion: $t \exp(-E_m/KT_A) = \text{const}$, the activation energy of migration E_m was calculated by plotting log $(\partial\Theta/\partial T_Q)$ versus $1000/T_A$ as shown in Fig. 4. From the slope of the straight line an activation energy of 0.33 eV for the recovery of resistivity was found. This value is lower than that given by Kamel and Attia[8] where a value of 0.7 eV was needed to activate the migration of a single vacancy in pure silver. The small migration energy obtained in the present work is quite reasonable in view of the large binding energy found between the Cu atom and a vacancy. Accordingly, the movement of Cu atoms with vacancies in the form of pairs is much easier.

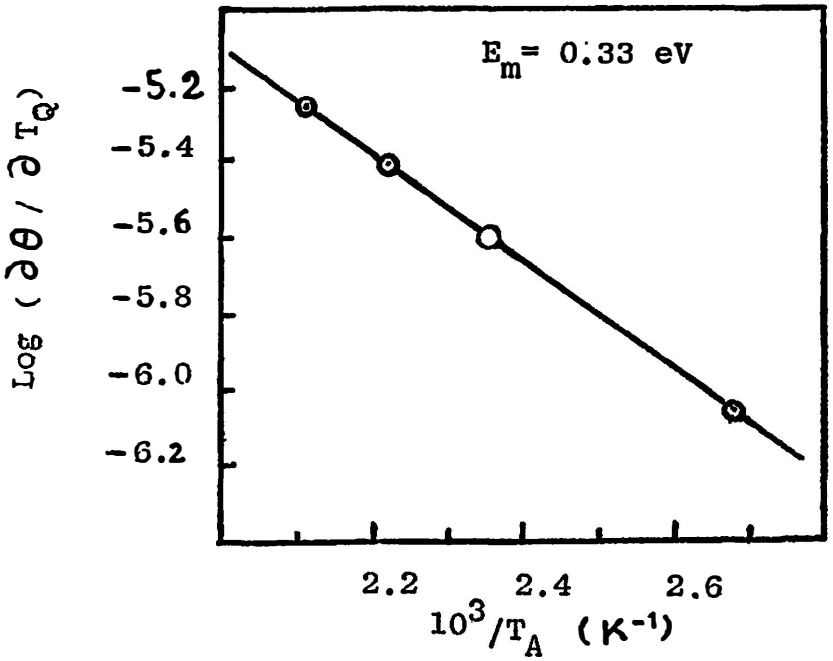

Fig. 4. Variation of $\log(\partial\Theta/\partial T_Q)$ with $1/T_A$ for determination of E_m.

In addition, the thermal equilibrium fractional concentration of vacancy-Cu pairs C_{V-Cu}, in the dilute Ag-Cu alloy used was calculated using the formula[6],

$$C_{V-Cu} = A_{V-Cu}\, Z\, I \exp\left(-\frac{E_f - B_{V-Cu}}{KT_A}\right),$$

where Z is the coordination number and A_{V-Cu} is the entropy factor.

Taking A_{V-Cu} the entropy term as unity, the concentration of vacancy- Cu pairs obtained for the annealing temperatures of 373, 423, 448 and 473 K are $6.65 \times \times 10^{-10}$, 5.81×10^{-9}, 1.43×10^{-8} and 3.21×10^{-8}, respectively. This observed increase in the concentration of vacancy- Cu pairs, as the annealing tempe-

rature is increased, may give the most satisfactory explanation of the low activation energy obtained for vacancy migration. It would suggest that the vacancy-Cu pairs formed are more energetically favourable mode of migration than the migration of single vacancies.

From another point of view, there may exist a possibility that the small vacancy-Cu clusters formed acquire other solute atoms as they move within the structure leading to their gradual growth up to the critical value needed for effective electron scattering. However, since no resistivity rise has been observed, it is expected that the number of clusters formed is so small as to cause any interference with electron flow. This is conceivable in view of the low concentration of copper in the alloy.

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MEĐUDJELOVANJE IZMEĐU VAKANCIJA I BAKRA U RAZRIJEĐENOJ Ag-0.3 tež. % Cu SLITINI

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Istraživanje promjene električne otpornosti tokom izotermnog napuštanja kaljenih uzoraka Ag-0.3 tež. % Cu slitine pokazuje da su za proces otpuštanja ukaljene otpornosti odgovorni parovi Cu-vakancija a ne pojedine vakancije. Iz mjerene aktivacione energije za nastajanje vakancije u slitini ($E_f^* = 0.69$ eV) izračunata je energija vezanja para vakancija — Cu od 0.21 eV. Razmjerno niska vrijednost energije aktivacije procesa migracije defekata u toj slitini ($E_m = 0.33$ eV) pripisana je visokoj energiji vezanja vakancija sa Cu atomima.