

Interaction of Vacancies with Tin Atoms in Aluminum

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The increase in resistivity due to quenched-in vacancies were measured in dilute alloys of tin in aluminum. From the observed apparent formation energy, the binding energy of a vacancy with a tin atom was calculated to be 0.4 eV. It was also shown that association of a vacancy with a tin atom decreases their resistivity compared with the sum of resistivities of a free vacancy and a free tin atom.

1. Introduction

Properties of vacancies in alloys have not been studied so extensively as in pure metals. In a dilute alloy, the binding energy between a vacancy and a solute atom is of fundamental importance as well as the energies for formation and for migration of a vacancy. It plays important roles especially in determining the concentration of vacancies and the rate of solute atom migration.

The authors have determined the binding energy of a vacancy with a copper atom, 0.2 eV¹⁾, and with a tin atom, 0.4 eV²⁾, in aluminum in connection with the rate of G-P zone formation. The latter value, however, was determined rather indirectly: namely, the rate of G-P zone formation in an Al-Cu-Sn alloy was investigated and the binding energy of a vacancy with a tin atom found to be 0.2 eV larger than that of a vacancy-copper pair, which was found to be 0.2 eV in another research. Therefore, it is necessary to determine directly the binding energy of a vacancy-tin pair with an Al-Sn binary alloy, in order to confirm the results from the vacancy mechanism of G-P zone formation in Al-Cu and in Al-Cu-Sn alloys.

Association of vacancies with solute atoms is expected to change the physical properties of vacancies and of solute atoms from those of free vacancies and solute atoms. For example, it was pointed out that the electrical resistivity of a vacancy-copper pair may be smaller than the sum of resistivities of a free vacancy and of a free copper atom¹⁾. Such effects should be taken into consideration, when changes in physical properties of alloys due to lattice defects are discussed. It is also one of the purposes of this research to examine the effect of vacancy-tin atom association on their electrical resistivity.

There are two ways to determine the binding energy in a dilute alloy. The concentration of vacancies C_v , in a dilute alloy is given by³⁾

$$C_v = A \exp\left(-\frac{E_f}{kT}\right) \left\{1 - 12c + 12c \exp\left(\frac{B}{kT}\right)\right\}, \quad (1)$$

where A is a constant related to the formation entropy of a vacancy, E_f the formation energy of a vacancy in the pure solvent metal, c the atomic fraction of solute atoms, B the binding energy of a vacancy-solute atom pair, kT the usual Boltzmann factor. B can be determined, if C_v or some other properties of which change is proportional to the concentration of vacancies is measured as a function of T , and E_f is known.

Another method is to investigate the decay of quenched-in vacancies. Because of the binding energy, the decay of excess vacancies is retarded from that in the pure solvent metal. To determine the binding energy, however, careful analysis must be made on the kinetics data^{4), 5)}.

Analysis of the kinetics data necessarily contains many simplified assumptions, for example, neglecting the effect of vacancy solute association on their physical properties measured and neglecting the possibility of clustering of solute atoms. Therefore, an accurate determination of the binding energy is more difficult in the second method than in the first, and the first method, measuring the change in electrical resistivity due to quenched-in vacancies as a function of the quenching temperature, is employed in the present research. However, care must be taken to separate the effect of quenched-in vacancies from that of tin atoms, and the detail will be described later.

2. Experimental Method

Specimens were made from 99.999 wt.% or 99.99 wt.% aluminum and 99.999 wt.% tin melted in air and drawn to wire of 0.4 mm in diameter. The concentrations of tin are 0.011 wt.% in five-nine Al and 0.025 wt.% (alloy A) and 0.015 wt.% (alloy B) in four-nine Al, respectively*.

Quenching was performed by quickly extracting the specimen out of a horizontal furnace and immersing it into calcium chloride solution at about -10°C . The electrical resistivity change, which is a measure of the amount of quenched-in vacancies, was measured at liquid nitrogen temperature with a dummy specimen to compensate the effect of fluctuation of nitrogen-bath temperature.

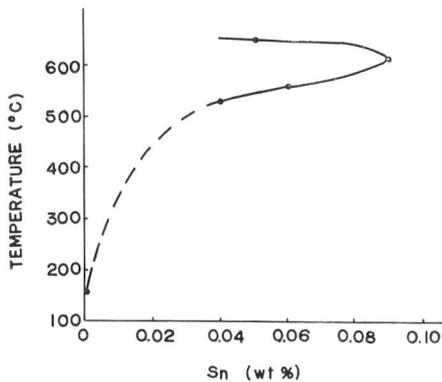


Fig. 1. Solid solubility of tin in aluminum.

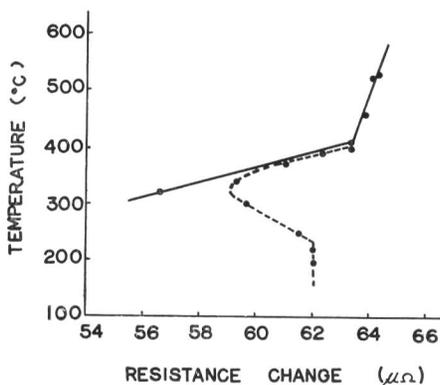


Fig. 2. Resistance change due to various heat treatment, showing the solubility of tin and the rapid precipitation range. (Resistance change is shown with an arbitrary origin.)

* The concentrations of tin were chemically analyzed in the cases of high purity alloy (using five-nine Al) and of alloy A, but not in the case of alloy B (*i.e.* intended concentration).

The solubility of tin in aluminum is very limited (Fig. 1)⁶⁾, and the precipitation of tin during heating and quenching must be avoided. Practically no precipitation occurs by quenching from the solid solution region. For quenching from a temperature in the two phase region, the precipitation may be avoided if a specimen, after solution treatment, is heated very short time at a quenching temperature. There is a temperature region where tin precipitates very rapidly, but quenching from such a temperature region is not employed. The solid solution region and the rapid precipitation region were determined experimentally. In Fig. 2, the full line shows the resistance of the high purity alloy (using five-nine Al) aged sufficiently for precipitation of tin and air cooled to avoid retaining excess vacancies and to avoid precipitation of tin. The full curve below 410°C may be considered as the solubility limit of tin and the sharp break at 410°C means that the amount of solute tin is constant above 410°C . The slight dependence of resistance on the heating temperature above 410°C may be considered to be the effect of defects due to condensation of vacancies during cooling. The solid solution region, therefore, is considered to be above 410°C for the high purity alloy. The dotted line shows the resistance of the alloy, after solution treatment, heated for 1 min at each temperature and slowly cooled (30 sec to room temperature). Rapid precipitation of tin occurs at temperatures between 400°C and 220°C . Thus, the quenching should be made from temperature above 400°C or below 220°C , but as the quenching from below 220°C cannot retain enough vacancies to measure, all the quenching was made from above 400°C after heating solution treated specimen for 1 min, which was found to be long enough to establish the thermal equilibrium concentration of vacancies. Situations are similar in other alloys made from less pure aluminum, but the temperature range of rapid precipitation is narrower than for the purer alloy. It is, for example, from 300°C to 400°C in the case of alloy A, and the quenching from below 300°C can be employed in this case.

Some vacancies become bound to solute atoms during quenching and the amount of

the vacancies bound during quenching varies from quench to quench even for a constant quenching temperature. Since the resistivity of a vacancy may be changed by the association with a solute atom, it is necessary to establish an equilibrium between free and bound vacancies at a temperature, say 0°C, before the quenched-in resistivity is measured. This is done by ageing the quenched specimen at 0°C for 5 min. The detail of the ageing at 0°C will be described in the next section.

3. Experimental Results

(1) Annealing stages and migration of free vacancies

Four annealing stages of quenched-in resistivity were found with less pure alloy (using four-nine Al): stage 1 from 0°C to 20°C, stage 2 from 40°C to 160°C (most of the quenched-in resistivity anneals out), stage 3 from 180°C to 220°C and stage 4 above 240°C. Comparing with the annealing stage for pure aluminum, the following assignment is proposed; stage 1—free vacancies disappear at nearby dislocations or meet solute atoms to establish an equilibrium between free and bound vacancies, stage 2—vacancies anneal out, keeping the equilibrium between free and bound vacancies, stage 3—secondary defects formed during stage 2 disappear and stage 4—tin atoms precipitate.

Activation energy of the stage 1 is determined with a less pure alloy. Fig. 3 shows the two step annealing of the stage 1, and the activation energy was determined to be about 0.6 eV from the slopes of both curves at the intersection. This value agrees fairly

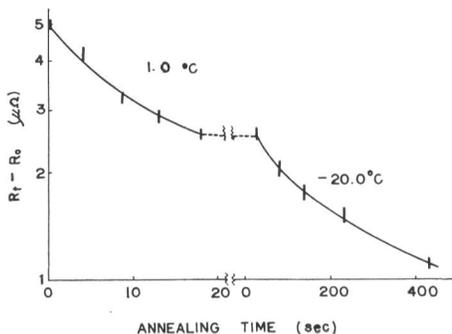


Fig. 3. Two step annealing of stage 1.

R_t : Resistance at time t .

R_0 : Resistance at the end of stage 1.

well with the activation energy for migration of vacancies in pure aluminum, 0.64 eV. Number of jumps, n , an average vacancy makes during the stage 1 is calculated to be 2×10^5 from the equation, $n = \beta z \nu t \exp\left(-\frac{E_M}{kT}\right)$,

where β is a constant, about 10, z the coordination number, 12, ν atomic vibrational frequency, 10^{13} , t time, about 10^2 sec, and E_M the activation energy for migration, 0.64 eV. The concentration of the trapping centers for vacancies is the reciprocal of the number of jumps, *i.e.* 5×10^{-6} , which is in fairly good agreement with the concentration of tin. From the activation energy and the number of jumps, stage 1 is considered to be the process of free vacancy annealing. Moreover, the existence of stage 1 means that the association of vacancies with tin atoms decreases the resistivity of vacancies and of tin atoms.

(2) Determination of the binding energy

After quenching, the specimen was aged at 0°C for 5 min. It was found experimentally that during this annealing the stage 1 was completed and the stage 2 did not begin. This means that practically all the vacancies are considered to get bound with solute tin atoms during this annealing. Quenching experiments were performed using specimens air-cooled from 200°C after 1 min heating, which are considered to contain no second-

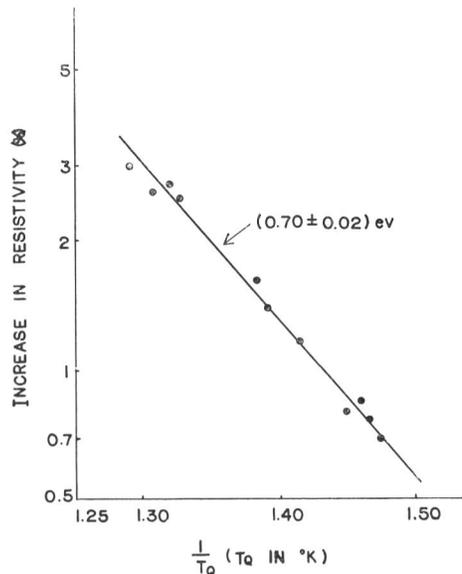


Fig. 4. Apparent formation energy of a vacancy in Al-Sn alloy.

ary defects due to condensation of vacancies and no precipitate of tin atoms (Fig. 2).

Fig. 4 shows the increase in resistivity, %, vs the reciprocals of quenching temperature in Kelvin. The apparent formation energy of a vacancy is calculated to be (0.70 ± 0.02) eV. Formation energy of a vacancy in pure aluminum was also determined in the same technique and found to be 0.76 eV.

Concentration of vacancies, C_v , is calculated from Eq. (1) with assumed values of B , and the apparent formation energy of a vacancy is determined as a function of the assumed value of B , as shown in Fig. 5.

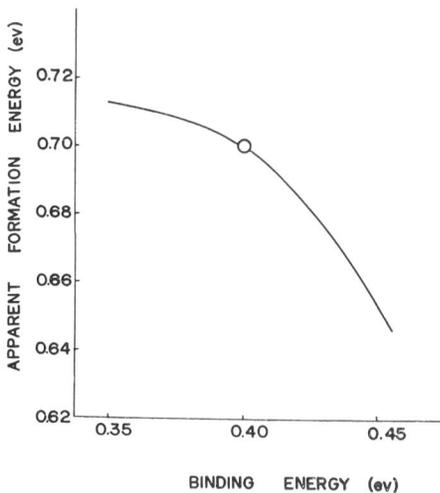


Fig. 5. Binding energy and apparent formation energy calculated.

Comparing the experimental apparent formation energy with Fig. 5, the binding energy between a vacancy and a solute tin atom is determined to be 0.40 ± 0.05 eV.

The apparent formation energy in alloy A was found to be 0.60 eV, and the binding energy was determined to be 0.42 ± 0.02 eV, which agrees quite well with that obtained in the purer alloy.

4. Discussion

The binding energy, 0.4 eV, was obtained with alloys of different compositions, and it agrees with the value obtained indirectly from the retardation of G-P zone formation in Al-Cu-Sn alloy.

The origin of this rather large value, 0.4 eV, of binding energy is not known yet.

The very limited solid solubility of tin in aluminum means that the nature of tin atom, *e.g.* the size and the electronic structure, is very much different from that of aluminum atom. On the other hand, atoms of which binding energy with a vacancy is about 0.2 eV show fairly extended solid solubility at high temperatures. Copper atoms and magnesium atoms in aluminum are good examples. The solid solubility at a high temperature may have some relation with the binding energy.

It is already shown that association of a vacancy with a tin atom decreases their resistivity. This is also shown by comparison of quenched-in resistivity and amount of quenched-in vacancies in pure aluminum and in alloys. Resistivity of the pure alloy was found to be $0.232 \mu\Omega$ cm and that of pure aluminum $0.221 \mu\Omega$ cm at liquid nitrogen temperature, and quenched-in resistivity for quenching from 500°C is $7.30 \times 10^{-9} \Omega$ cm for the purer alloy and $9.30 \times 10^{-9} \Omega$ cm for pure aluminum. The atomic fraction of vacancies quenched-in from 500°C is calculated to be $1.31 \times 10^{-5} A$ for the purer alloy with $E_f = 0.76$ eV and $B = 0.40$ eV, and $1.20 \times 10^{-5} A$ for the aluminum with $E_f = 0.76$ eV. The resistivity per 1 at.% vacancies is $(5.58/A) \mu\Omega$ cm for the purer alloy and $(7.75/A) \mu\Omega$ cm. Here the vacancies in the alloy are considered to be bound to the solute atoms. The resistivity per 1 at.% vacancies in pure aluminum was determined by Simmons and Balluffi⁷⁾ to be $3 \mu\Omega$ cm. Using this value and assuming that the entropy factor A is the same in alloys and in aluminum, the decrease in resistivity due to association of a vacancy with a solute atom is found to be $0.85 \mu\Omega$ cm per 1 at.% of pair, which is (the sum of resistivity of 1 at.% vacancies and of 1 at.% tin atoms)—(the resistivity of 1 at.% pairs of a vacancy and a tin atom).

Although it is almost certain that the association decreases the resistivity, the above derived value, $0.85 \mu\Omega$ cm per 1 at.% pairs, is not accurate because the entropy factor A in Eq. (1) was assumed to be the same in alloys and in pure aluminum. The same effect was observed with the less pure alloys.

5. Conclusion

Changes in resistivity due to quenched-in

vacancies and due to precipitation of tin atoms were separated and the increase in resistivity due to quenched-in vacancies were measured for various quenching temperatures with dilute alloys of tin in aluminum. From the observed apparent formation energy, the binding energy of a vacancy with a tin atom was calculated to be 0.4 eV. It was also shown that association of a vacancy with a tin atom decreases their resistivity about $0.8 \mu\Omega$ cm per 1 at.% of pairs.

Acknowledgement

The purer alloy and 99.999% pure aluminum specimens were offered by the Central Research Laboratory of Furukawa Electric Co. The chemical analysis of all the alloys were also made by them. The authors express their deep thanks to the Furukawa

Electric Co. The authors also thank to Professor J. Takamura for his continued discussion and to Mrs. A. Kimura for her effort in performing the experiment in the early stage of this research.

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DISCUSSION

Lazarus, D.: Dr. M. de Jong, in our laboratory, has attempted similar measurements in very dilute gold-tin alloys, but found large effects due to oxidation of the tin at vacua of the order of 10^{-6} mm Hg or worse. This work will be continued at ultra high vacua of the order of 10^{-6} mm Hg. Do you have any knowledge of the possible effects of oxidation in your experiment?

Hasiguti, R. R.: We did not consider about it. Thank you very much for your important comments.

Sines, G.: Intuition makes me doubt that vacancy-foreign atom binding energies can be so high. W. Grupen suggests that a supersaturated vacancy atmosphere can be attracted to and temporarily held near to clusters by the elastic interaction. The gradual dissolution of such atmospheres would greatly enhance the diffusion.

Hasiguti, R. R.: I was also at first surprised by the large value of the binding energy. But it is true that the ageing process of Al-Cu alloys is extraordinarily retarded by the addition of small amount of tin, which suggests the strong trapping effect of vacancies by tin atoms. The binding energy was also obtained from the analysis of retarding effect of G-P zone formation in Al-Cu-Sn alloy (Kimura and Hasiguti: *Acta Met.* **9** (1961) 1076) which turned out to be 0.4 eV or even larger. The properties and behaviors of tin atoms in aluminum are considered to be quite different from those of copper atoms or magnesium atoms, which have the binding energy of about 0.2 eV. The extremely small solubility of tin in aluminum is an example. In conclusion, we consider that the value 0.4 eV is really the binding energy, and that we should find the origin of the large value in particular properties of tin atoms.

Brandon, D. G.: Can you tell us under what conditions solute-solute interactions can be neglected?

Hasiguti, R. R.: We simply neglected them, because our alloys are dilute alloys.