Takamura *et al.* by an independent method viz., comparing the climb rate of loops in Al–5% Mg and pure Al. The details are given in our paper* in this proceedings.

* *Proc. Int. Conf. Cryst. Latt. Def. (1962)*: J. Phys. Soc. Japan **18** Suppl. III (1963) 98.

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An Experimental Study on Vacancy-Impurity Interaction in Aluminum

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The recovery of quenched-in extra resistivity has been studied in dilute aluminum alloys, and is explained as the annihilation of supersaturated vacancies. The activation energies of vacancy migration are obtained as 0.47 ± 0.02 eV for Al-0.8×10^{-4} Mg, 0.55 ± 0.04 eV for Al-1.0×10^{-4} Si and 0.55 ± 0.03 eV for zone refined aluminum. The rate of resistivity decrease becomes faster as the content of magnesium increases. These results are explained as easy motion of a magnesium-vacancy pair in aluminum.

1. Introduction

The annealing kinetics of lattice vacancies in face-centered cubic metals have been studied by many workers, and are made clear considerably on pure metals, especially on gold[1] and aluminum[2),3)]. The annealing kinetics of vacancies in alloy, however, has not been well understood yet, and a great deal of attention has been devoted to it recently, especially to determine a binding energy between a vacancy and an impurity atom.

Cattaneo and Germagnoli[4] studied the recovery of quenched-in resistivity in gold-silver alloys, and have obtained a value larger than 1 eV for effective activation energy. They deduced the binding energy between a silver atom and a vacancy in gold to be 0.3 eV, according to the theory developed by Damask and Dienes[5].

Many works have been made on the clustering of solute atoms in several aluminum alloys dealing with the migration of solute atoms aided by vacancies but not that of vacancies themselves.

Panseri, Gatto and Federighi[6] studied the effects of small concentration of magnesium on the annealing kinetics of quenched-in vacancies, by resistivity measurement, and deduced that vacancies can be trapped by magnesium atoms at room temperature but become free at about 80–130°C. But the kinetics of quenched-in vacancies in the alloy was not made clear. Further investigation is necessary to make clear the kinetics of quenched-in vacancies in aluminum-magnesium dilute alloys from the view point of the interaction between magnesium atoms and vacancies in aluminum. It is desirable as proposed by Damask and Dienes[5] to perform the experiments with specimens, to which impurity atoms have been added by controlled amounts, prepared from extremely pure aluminum.

2. Experimental Procedures

The material used in this work was aluminum zone-refined in vacuum, whose ratio of electrical resistivity at room temperature to that at 4.2°K was 6000 or more. Very dilute aluminum alloys were also prepared from this zone-refined aluminum, adding 0.093 and 0.008 atomic per cent magnesium of 99.99 per cent pure and 0.010 atomic per cent silicon of 99.999 per cent pure. A polycrystalline wire of 0.3 mm in diameter drawn from these materials were used as specimens and dummies, and two potential leads of the same material were spot-welded both to the specimen wire and to the dummy wire. The distance between the potential leads was 20 cm. An apparatus of electrical resistance measurement and quenching and ageing treatments were described in detail in the previous paper by the authors[3], so it is described briefly here. Specimens were heated to 550°C for five minutes by passing direct current through them, and lowered the temperature to 350°C by decreasing of current density and kept for five minutes at this temperature, and then quenched into water at 2°C. The temperature of specimens during heating was estimated from their resistances. Just after quenching, specimen was removed into a stirred oil bath regulating the fluctuation of temperature within 0.01°C, and the resistivity measurements were carried out in this oil bath during the room temperature ageing. After the decrease in resistivity at room temperature stopped, the specimen was, further, annealed for ten minutes at 160°C in a silicon oil bath, then their resistivity change by this annealing was measured at room temperature. The precision of measurements was 1×10^{-5} of the total resistance of specimens. The change of electrical resistivity is calculated from the resistance difference between a specimen and a dummy.

3. Experimental Results

1) *Preliminary experiment*

The resistance measurements during ageing near room temperature after the quenching from 350°C were repeated on aluminum wires containing magnesium 0.8×10^{-4} in atomic fraction, to ascertain the reproducibility of the experiment. Typical results for the repetition of quenching and ageing are shown in Fig. 1. It is shown that the rate of resistivity decrease is fast in the first treatment, and becomes slower with repeating of quenching, and finally becomes a constant rate. All experimental results to be described below are obtained in the stabilized state after several repetitions of the quenching and ageing treatment.

2) *Al–0.8×10⁻⁴Mg alloy*

The isothermal annealing curves near room temperature after quenching from 350°C to water at 2°C on the aluminum alloys contain-

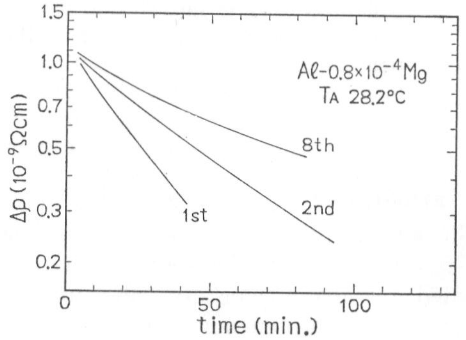

Fig. 1. Resistivity change during isothermal annealing after the repetition of quenching and ageing treatments on aluminum alloy containing magnesium 0.8×10^{-4} in atomic fraction where 1st, 2nd and 8th mean the number of times of the treatments.

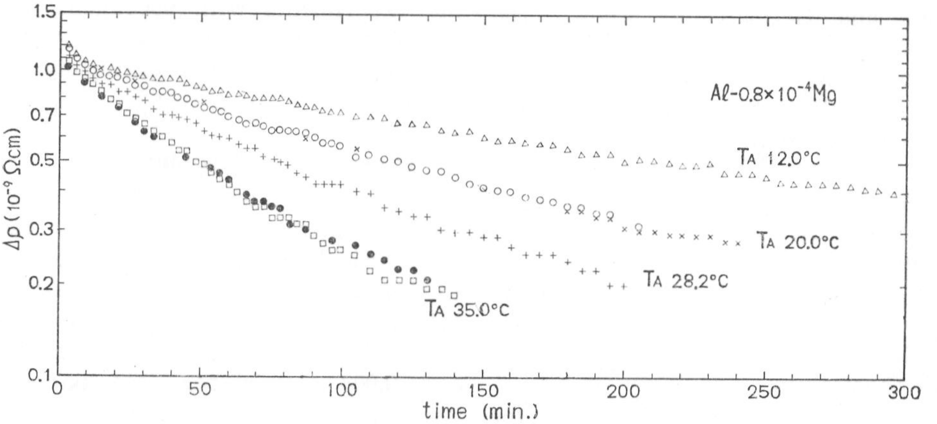

Fig. 2. Resistivity change during isothermal annealing at various temperature after quenching from 350°C on the aluminum alloys containing magnesium 0.8×10^{-4} in atomic fraction.

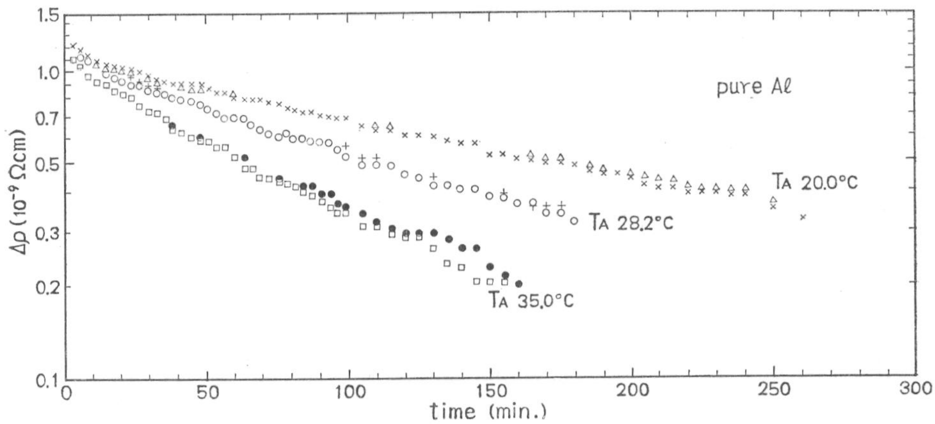

Fig. 3. Resistivity change during isothermal annealing at various temperature after quenching from 350°C on the pure aluminum.

ing magnesium 0.8×10^{-4} in atomic fraction are given in Fig. 2, while the experimental results on pure aluminum are shown in Fig. 3. The following facts are found from these experiments.

a) The quenched-in resistivity roughly decreases exponentially with the time in these isothermal annealings in both pure aluminum and Al–0.8×10^{-4}Mg alloy.

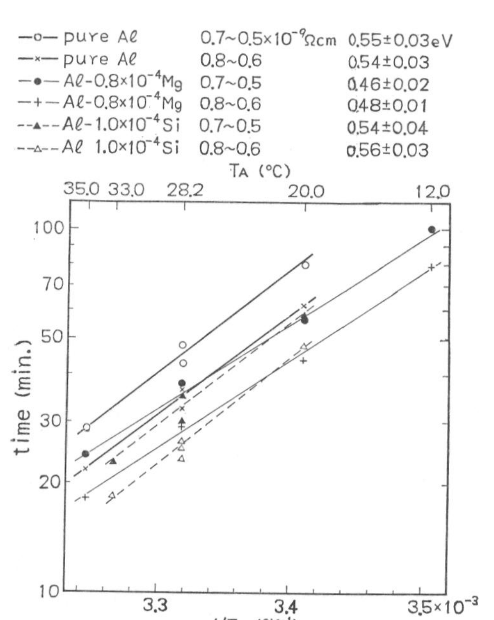

Fig. 4. Semilogarithmic plot of ageing time with the reciprocal of the absolute ageing temperature. The activation energies of ageing are shown with its resistivity range in which the activation energies are estimated on pure aluminum and various dilute alloys.

b) The increments of resistivity due to the quenching are almost the same in amount in both cases, and its value is about $1.2\times10^{-9}\Omega$ cm.

c) The activation energies of the process of decreasing resistivity after quenching are estimated to be 0.47 eV for Al–0.8×10^{-4} Mg alloy and 0.55 eV for pure aluminum as shown in Fig. 4.

d) The rate of decrease in resistance after quenching for Al–0.8×10^{-4} Mg alloy is slightly faster than that for pure aluminum.

e) No decrease in resistivity is found in the annealing at 160°C for ten minutes subsequent to the room temperature ageing in both cases.

3) *Al–0.93×10^{-3} Mg Alloy*

The same experiment as described above for the Al–0.8×10^{-4} Mg alloy was carried out for the aluminum alloy containing a magnesium 0.93×10^{-3} in atomic fraction, and the result is given in Fig. 5. The decrement of resistance due to the ageing at room temperature after quenching is somewhat smaller than that in pure aluminum and Al–0.8×10^{-4} Mg alloy, and no decrease in resistance due to the annealing at 160°C for ten minutes subsequent to the room temperature ageing was also found. The rate of decrease in resistivity at room temperature is faster than that in Al–0.8×10^{-4} Mg alloy.

4) *Al–1.0×10^{-2} Si Alloy*

The same experiment was carried out also for the aluminum alloy containing silicon 1.0×10^{-4} in atomic fraction, and the result

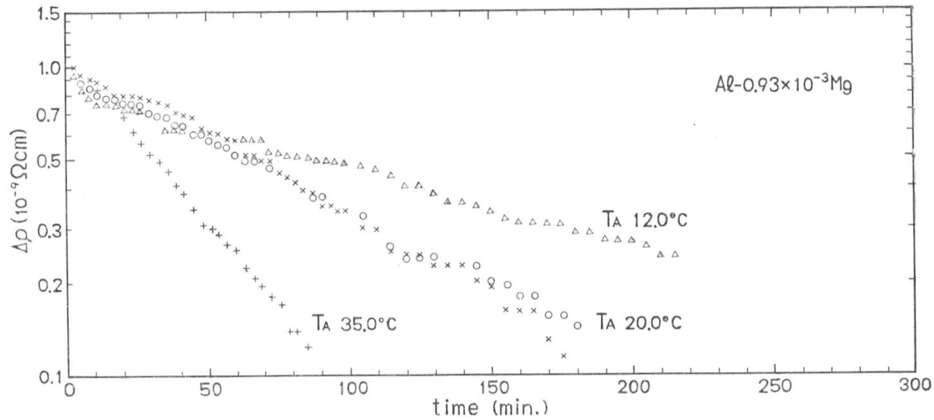

Fig. 5. Resistivity change during isothermal annealing at various temperature after quenching from 350°C on the aluminum containing magnesium 0.93×10^{-3} in atomic fraction.

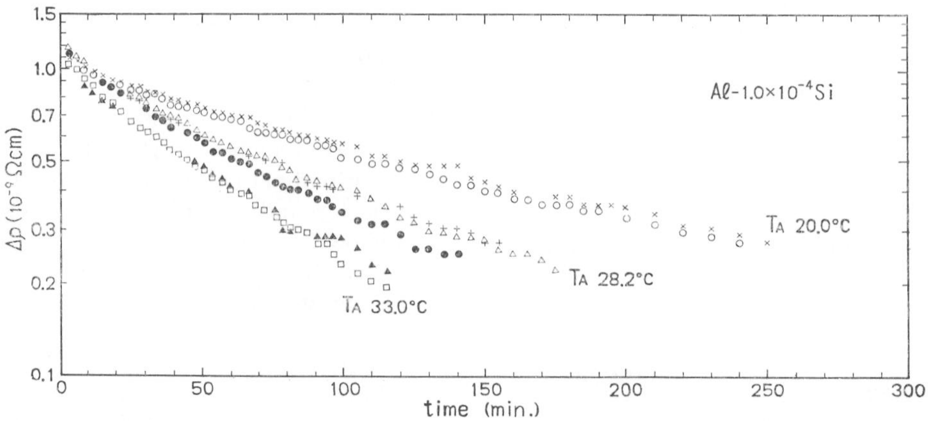

Fig. 6. Resistivity change during isothermal annealing at various temperature after quenching from 350°C on the aluminum alloy containing silicon 1.0×10^{-4} in atomic fraction.

is given in Fig. 6. It is found that the decrement of resistivity due to the ageing is the same amount as that in pure aluminum, and that the quenched-in resistivity roughly decreases exponentially with ageing time similarly to pure aluminum. The activation energy of the process are estimated as 0.55 eV as shown in Fig. 4.

4. Discussion

The quenched-in resistivities in Al–0.8×10^{-4} Mg alloy and Al–1.0×10^{-4} Si alloy decrease in almost the same way as in pure aluminum in the following three points: 1) the total amount of resistivity decrease, 2) exponential decay of resistivity in the isothermal annealing and 3) no decrease in resistivity by the annealing at 160°C. Therefore, the resistivity decrease after quenching from 350°C in these dilute alloys seems to be caused only by the annihilation of quenched-in vacancies as in the case of pure aluminum. However, activation energies of the process are 0.55 eV in pure aluminum, 0.47 eV in Al–0.8×10^{-4} Mg alloy and 0.55 eV in Al–1.0×10^{-4} Si alloy. The difference in activation energy between pure aluminum and Al–0.8×10^{-4} Mg alloy will be explained as follows.

It was proposed recently by Peryman[7] and by Panseri *et al.*[6] that the magnesium atoms in aluminum are able to trap vacancies at room temperature. It seems that an attraction acts between a magnesium atom and a vacancy in aluminum, and that the vacancy in the aluminum together with a magnesium atom migrates to a sink, in the manner as shown in Fig. 7, exchanging its site for that of magnesium atom or an aluminum atom

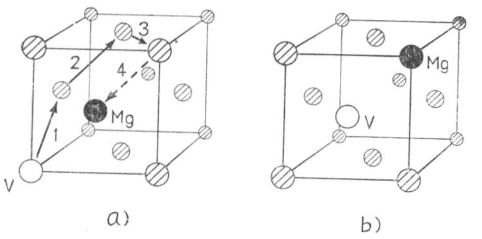

Fig. 7. An example of migration of a vacancy-magnesium pair. a) shows the initial stage. A vacancy V (○) exchanges its site for the aluminum atom (◉) three times and finally exchanges, its position for the magnesium atom Mg (●). b) shows the final stage.

at the nearest neighbour of magnesium atom. The low activation energy in Al–0.8×10^{-4} Mg may be explained as the result of easier motion of a vacancy near a magnesium atoms due to the relaxation of lattice around a magnesium atom.

Activation energy of the range 0.27 to 0.47 eV was given from the strain ageing of aluminum magnesium alloys by Westwood and Broom[8], and the high activation energy, 0.47 eV, was explained as the migration of magnesium atoms aided by the vacancies produced during the prior strain. This value coincides well with one obtained in the present experiment. From this fact that the activation energy of vacancy migration coincides with that of solute migration in dilute aluminum magnesium alloy, the proposed model for vacancy migration as a pair with a magnesium atom is assured. Low activation energies for solute clustering obtained in several aluminum alloys[9),10),11)] can also be explained by this model. It can also be understood from the above consideration

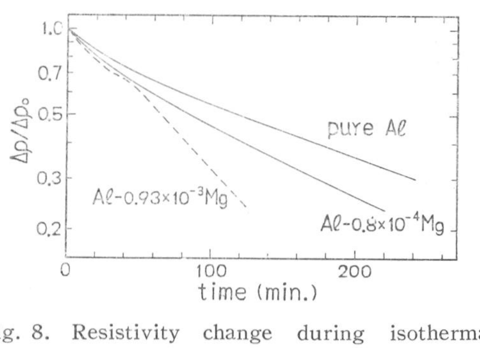

Fig. 8. Resistivity change during isothermal annealing at 20.0°C after the quenching from 350°C on pure aluminum, Al-0.8×10^{-4} Mg alloy and Al-0.93×10^{-3} Mg alloy.

that the rate of resistivity decay becomes faster with increasing magnesium concentration as shown in Fig. 8.

The effective number of jumps made by the vacancy during its life for Al–0.8×10^{-4} Mg alloy is estimated as about ten times of that for pure aluminum. It is explained as follows. Effective one jump of vacancy-magnesium pair needs three exchanges of a vacancy site with an aluminum atom occupying a nearest neighbour of magnesium atom and one exchange of a vacancy with a magnesium atom as shown in Fig. 7 for example. The number of exchange necessary for a jump of a pair increases more if the exchange of a vacancy with a magnesium atom is more difficult than that with one of the four aluminum atoms which are nearest neighbours to both the vacancy and the magnesium atom.

Activation energy of the process in Al–0.93×10^{-3} Mg alloy can not be calculated because isothermal annealing curves have jumps, but the roughly estimated value from Fig. 5 is about 0.45 eV, and is the same as one obtained for Al–0.8×10^{-4} Mg alloy.

On the other hand, from the fact that the activation energy estimated in aluminum-silicon alloy is the same value 0.55 eV as one of the activation energy obtained in pure aluminum, it may be considered that a silicon atom has little interaction with the vacancy in aluminum. If this is true, it may be thought that the interaction between a solute atom and a vacancy in aluminum is caused mainly by lattice strain due to the difference of atomic size, and not by the electro-static force.

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DISCUSSION

Elbaum, C.: Activation energies for vacancy migration in pure aluminum of about 0.55 eV were given in this work. Recent studies of self-diffusion in aluminum give a value of vacancy migration energy of about 0.7 eV. I wonder whether anyone would care to comment on this discrepancy.

Kino, T.: The discrepancy may be caused by the existence of divacancies in our experiment.

Sosin, A.: Since the previous papers have dealt with quenching of dilute aluminum alloys, I would like to report some data on the quenching of Al-10^{-3} Zn. Pure aluminum and alloy samples were quenched simultaneously by dropping from a furnace into a calcium fluoride bath maintained at about −40°C. Measurements were made in a liquid helium bath. We have observed the following.

1. The increment of resistivity in pure aluminum is greater than reported by others (Panseri and Federighi, Bradshaw and Pearson, De Sorbo and Turnbull) but less than implied by the high temperature work of Simmons and Balluffi.

2. The increment of resistivity in the alloy is greater than in the pure aluminum and the difference increases with increasing quench temperature.

3. We have studied annealing only isochronally. It does not appear that there is notable difference between alloy and pure sample. This implies that the binding energy between zinc and vacancy is small and that few vacancies are not bound immediately after the quench.

4. Contrary to the reports just reported by the other investigators in other aluminum alloys, the resistivity due to a vacancy bound near a zinc atom is not so much less than in the bulk to lower the observed value of quenched resistivity in the alloy below that in the pure metal.

Blandin, A. P.: Experimental interaction energies of Mg and Si impurities with vacancies agree in sign, but are larger than the values predicted by Friedel, Déplanté and me. So, pure valence effects are somewhat understood, particularly their sign. Opposite to the case of valence effects, the situation is much less clear for impurities belonging to different periods of the Mendeleiev table, tin for example.

Simmons, R. O.: The difficult experiment on self-diffusion in aluminium using a radioactive tracer technique has been reported by Lundy and Murdock (J. Appl. Phys. **33** (1962) 1671) at Oak Ridge National Laboratory. They found an activation energy of 1.46 eV. This value is in excellent agreement with the sum of the monovacancy formation energy of 0.76 to 0.79 eV (determined by an equilibrium method by Simmons and Balluffi and by quenching of zone-refined aluminum by De Sorbo and Turnbull) and of the monovacancy migration energy of 0.65 eV (determined in the annealing of zone-refined aluminum quenched from relatively low temperatures by De Sorbo and Turnbull).