A Resistometric Study of the Configuration of Ag Atoms in Aluminum-1.03 at % Silver Alloy

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An apparatus for the precise measurement of electrical resistivity of aluminum alloys above room temperature has been constructed. The electrical resistivities of pure aluminum and of Al-1.03 at % Ag alloy were measured from room temperature to 500°C in air to investigate the correlation between electrical resistivity and the configuration of Ag atoms in the alloy. The difference in resistivity between the pure aluminum and the Al-Ag alloy changed markedly with the measuring temperature, and the behavior corresponds well to the quasi-equilibrium phase diagram of the alloy including G.P. zones. Furthermore, the result shows that the G.P. zones are formed not only in the presence of supersaturated vacancies but also at the equilibrium vacancy concentration during the slow cooling process.

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I. Introduction

Extensive studies have been made on the clustering of solute atoms in alloys including the precipitation phenomena and the formation or resolution of Guinier-Preston zones (G. P. zones), etc. Most of the work has been dealt with changes in physical properties during the aging process after quenching. Many of the vacancies are frozen-in by the quenching, the supersaturated vacancies cluster by themselves and accelerate the solute clustering. Therefore, both property changes due to solute atoms and vacancies are imposed, and it is difficult to separate from each other. In usual metals such as aluminum, the diffusivities of solute atoms and vacancies are fairly large so the clustering and annihilation of these point defects occur even during the quenching. Then the configuration of solute atoms after the quenching differs from one before the quenching. Especially, in some aluminum alloys, the rate of G.P.

zone formation is too fast to detect the process of zone formation⁽¹⁾.

Therefore, it is interesting to study the process of formation of the G.P. zones and precipitation in the state near the thermal equilibrium at high temperature, in other words, to study the clustering process of solute atoms without the supersaturated vacancies.

The electrical resistance was selected as the physical property which was sensitive to the change in configuration of solute atoms at such high temperatures. However, the greater part of the resistance in metals at high temperatures is due to the lattice vibration, and the contribution from the solute atoms is very small in dilute alloys. Therefore, the highly precise measurements are required to detect the change in configuration of solute atoms. Little has been studied on the behavior of solute atoms in terms of electrical resistivity, except for the work of Hirano *et al.*⁽²⁾⁽³⁾ on Al-Zn and Al-Cu alloys. In their work the electrical resistance was measured as the sample was heated or cooled slowly at a constant rate. They found that the resistance in low temperature regions was a little higher than the one extrapolated from the higher temperature regions, and suggested that the supersaturated vacancy is not necessary to form the G.P. zones.

In order to detect phenomena with slow

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reaction rates, e.g. precipitation, an apparatus with which continuously measure the resistivity with high precision was constructed in the present work. Using the apparatus, the electrical resistance of Al-1.03 at%Ag alloy was measured from room temperature to 500°C in the aim of investigating the change in configuration of Ag atoms in the alloy.

II. Experimental Procedure

1. Specimen and the heat-treatment

Specimens used in this experiment were a zone-refined aluminum (referred to as ZR-Al) and an Al-1.03 at%Ag alloy (referred to as Al-Ag), which were wires 0.3 mm in diameter. Details of the preparation of these wires were described elsewhere⁽⁴⁾⁽⁵⁾.

The length of the specimen was about 140 cm, and both ends were served as the current leads. Two wires of the same material as the specimen were spot-welded to the specimen at intervals of about 27 cm (gauge length) as the potential leads for the measurement of electrical resistance.

In order to reduce the dislocations and the other defects introduced by drawing, the specimens were annealed in air at 500°C for 3 h and cooled down to room temperature in an electric furnace. During the cooling, the resistance of the specimens was measured together with the temperature. The grain size of the Al-Ag specimen was about 0.3 mm after the annealing.

After the furnace-cooling, these specimens were aged for about 1 h at different temperatures between room temperature and 500°C. The aging temperature was raised from room temperature to 500°C step by step at temperature intervals of several or several tens of degrees and then lowered down to room temperature in the same manner. The two processes in which the aging temperature was raised or lowered will be referred to hereafter as the heating process and the cooling process, respectively.

2. Temperature control

Specimens were settled in an aluminum block which is shown in Fig. 1, to reduce the fluctuation of temperature, the contamination of

Fig. 1 Aluminum block in the furnace A: Thermocouple TC1, B: Small hole, C: Thermocouple TC2, D: Thermocouple TC3, E: Specimen ZR-Al, F: Specimen Al-Ag, G: Potential leads for ZR-Al, H: Potential leads for Al-Ag.

Fig. 2 Schematic diagram of the electric furnace, the temperature controller and the circuit for electrical resistance measurement.

specimens and the deformation due to their thermal contraction or expansion. The specimens were insulated from the aluminum block by alumina insulating tubes (0.8 mm in inside diameter). The block was inserted into the electric furnace as shown in Fig. 2. The connecting point at which the two specimen wires (ZR-Al and Al-Ag) were connected by spot-welding was placed about 30 cm apart from the furnace and maintained at room temperature to eliminate the thermoelectromotive force in the current circuit and to suppress the diffusion of Ag atoms into ZR-Al from the Al-Ag alloy.

The temperature of specimens was controlled by an automatic temperature controller consisting of reference input elements, a multi-position controller and a regulator for the electric power to the furnace as illustrated in Fig. 3. The apparatus constructed by us could control

Fig. 3 Block diagram of the temperature controller.

the aging temperature by regulating the alternating current flowing into the furnace and automatically changing the aging temperature. The mechanism of temperature control is described below in details in connection with the construction and functions of the apparatus.

The temperature in the furnace was determined by a thermoelectromotive force V_{TC1} of a chromel-alumel thermocouple TC1 which was placed in a small hole of the groove at the surface of the aluminum block as shown in Fig. 1. The voltage V_{TC1} was compared with the standard voltage V_s which corresponded to the desired temperature. The voltage V_s was given from a standard voltage generator and was automatically changed using a program controller. The difference ($V_s - V_{TC1}$) was transmitted to the multi-position controller with a sensitivity of $1 \mu V$, which consisted of a dc amplifier, a digital voltmeter and a digital comparator, as shown in Fig. 3. In the multi-position controller, the difference ($V_s - V_{TC1}$) was amplified with the dc amplifier and converted to a digital form in the digital voltmeter. The converted digital form which was the number of pulses was compared with three levels of voltage (0, low, high) set up manually in the digital comparator. Based on the result of the comparison, one of the corrected signals (negative, low, middle or high signal) was transmitted to a power regulator which regu-

Photo. 1 Wave form of the alternating current to the heater. Wave forms (a), (b), (c) and (d) correspond to the corrected signals high, middle, low and negative, respectively.

lated the alternating current to the heater in the furnace. The power regulator contained a gate-controlled semiconductor switch whose conduction time was determined by the number of alternating cycles per unit time which corresponded to the corrected signal as shown in Photo. 1. To reduce the noise in the usual phase control method, the alternating cycle was started from zero degree in the phase angle as seen in the photograph. To obtain the uniform temperature distribution in the furnace, the heater was separated into three parts (H-1, H-2, H-3) as shown in Fig. 2 and the power to each heater was regulated independently.

Using the apparatus, the temperature of the specimen was maintained within $\pm 0.05^\circ C$ during the aging, and the temperature difference between both ends of the gauge length of specimen was less than $0.1^\circ C$.

3. Measurements of temperature and electrical resistance

The temperature around the specimen was measured with two chromel-alumel thermocouples whose voltages were referred to as V_{TC2} and V_{TC3} respectively. Two thermocouples were mounted near both ends of the gauge length of the specimen in the aluminum block, as shown in Figs. 1 and 2.

Electric current through the specimen was about 80 mA supplied from a dc constant-current source. The precise value of the current was determined by the measurement of the voltage V_{ST} of a standard resistor, which was connected in series with the specimen and

Fig. 4 Block diagram of the apparatus for voltage measurement.

placed in an oil bath as shown in Fig. 2.

The voltage between gauge length of specimens and thermocouples were measured quickly (0.5 s/time) with a digital voltmeter (Takeda Riken Industry Co., Ltd. TR-6515) and continuously recorded with a digital recorder as shown in Fig. 4. The voltage to be measured was selected automatically with a change-over switch constructed by us and transmitted to the digital voltmeter. The direction of the current through the specimen circuit was reversed by the change-over switch to reduce the thermoelectromotive force in the circuit in the following way. Firstly one of the voltages V_{TC2} , V_{TC3} , V_{ST} , V_P , V_A was selected by the change-over switch in the order at intervals of 3~14 s. Then the direction of the current through the specimen was reversed, and the voltage measurements were made in the opposite order, and the mean value of both measurements were used as the correct value for each voltage. One set of these voltage measurements required 24 s at least.

The accuracy of the voltage measurements in this system was 0.01 % of readings plus or minus 1.5×10^{-6} V, and it was possible to detect the temperature variation of 0.05°C.

The conversion of the electrical resistance into the electrical resistivity was made in a similar way described before⁽⁵⁾. The value used as the resistivity at 300 K, $\rho(300 \text{ K})$, of the specimen was $2.733 \mu\Omega\text{cm}$ and $3.172 \mu\Omega\text{cm}$ for ZR-Al and Al-Ag, respectively. In order to obtain the value of $R(300 \text{ K})$ for each specimen, the specimens were annealed at 500°C for 3 h and furnace-cooled. During the furnace-cooling, the resistance of the specimen was

measured together with the temperature. The value of $R(300 \text{ K})$ of each specimen was determined from a relation $R(T) = R(300 \text{ K}) [1 + \alpha \cdot \Delta T]$ using the values of the resistance $R(T)$ at the temperature near 300 K, where α was the temperature coefficient of resistivity, which was 4.14×10^{-3} and $3.54 \times 10^{-3} \text{ deg}^{-1}$ for ZR-Al and Al-Ag, respectively.

III. Experimental Results

The electrical resistivity of ZR-Al and Al-Ag alloy after aging for about 1 h are plotted against the aging temperature T_A between room temperature and 500°C for both heating and cooling processes in Fig. 5. One set of the measurements of the temperature and the resistance of specimen was carried out at intervals of two minutes during the aging. Aging temperature T_A was changed at intervals of several or ten degrees. Aging temperature T_A was changed at intervals of several tens of degrees, but the resistivity change against T_A was similar to that in Fig. 5.

Figure 5 shows that the resistivity of ZR-Al, ρ_p , changed monotonously against T_A , and the

Fig. 5 The electrical resistivities plotted against the aging temperature T_A on ZR-Al and Al-1.03 at% Ag alloy after 1 h aging at T_A .

values of ρ_p in the heating process agreed well with those in the cooling process. On the other hand, the resistivity of Al-Ag, ρ_A , was larger than ρ_p for all the aging temperatures T_A , and showed a complicated behavior in comparison with ρ_p . The characteristic feature was recognized in each region of the aging temperature which was region I (lower than 150°C), region II (between 150 and 350°C) and region III (above 350°C). The temperature coefficient of ρ_A was slightly larger than that of ρ_p in region I. In the region III, the resistivity difference ($\rho_A - \rho_p$) was considerably larger than that in region I, while the temperature coefficient of ρ_A was almost the same as that of ρ_p .

In region II, ρ_A changed markedly with T_A , and a considerable change in ρ_A was observed during the 1 h aging. For example, two open circles at 240°C in Fig. 5 show the initial and final values of ρ_A during the aging for 1 h. Furthermore, hysteresis was observed between the heating and cooling processes. Now, the resistivity difference, $\Delta\rho = \rho_A - \rho_p$, was considered to be the contribution from Ag atoms in the alloy, and so $\Delta\rho$ is plotted against T_A

Fig. 6 The resistivity difference $\Delta\rho$ between ZR-Al and Al-1.03 at% Ag versus T_A . Vertical line shows the change in $\Delta\rho$ during 1 h aging and arrow shows the direction of the change.

in Fig. 6. Vertical lines connecting two points in the figure show the changes in $\Delta\rho$ during aging for 1 h, except the aging at 280°C and 150°C in the cooling process in which the aging times were 4 and 2 h, respectively.

It can be seen in Fig. 6 that the variation in $\Delta\rho$ with T_A in region II was quite large in contrast with that in regions I and III. In region I, the value of $\Delta\rho$ increased slightly with T_A from room temperature to 150°C, and the value of $\Delta\rho$ in the heating process were almost the same as that in the cooling process. The value of $\Delta\rho$ in region III rather decreased with T_A in both heating and cooling processes.

Variation of $\Delta\rho$ with T_A was remarkable in region II. The temperature at which $\Delta\rho$ increased was higher in the heating process than that in the cooling process. In the temperature range from 150 to 240°C, $\Delta\rho$ rapidly increased and decreased in the heating and cooling processes, respectively. The changing rate of $\Delta\rho$ with T_A was slightly larger in the temperature range from 200 to 240°C than that in the range below 200°C in both processes. At higher temperatures in region II, the value of $\Delta\rho$ in the heating process decreased with T_A to a minimum at $T_A = 300^\circ\text{C}$ and then increased rapidly with T_A up to 350°C, while in the cooling process $\Delta\rho$ decreased gradually with decreasing T_A . Therefore, a remarkable difference in $\Delta\rho$ was observed between the cooling process and the heating process in the temperature range from 260 to 350°C, and it was the most remarkable hysteresis in the $\Delta\rho$ - T_A curve.

As described already, $\Delta\rho$ changed during the aging as seen in Figs. 7 and 8 for the heating and cooling process, respectively. In general, $\Delta\rho$ changed monotonously in these processes. However, for the aging at 251°C in the heating process, $\Delta\rho$ increased initially and then decreased monotonously as shown in Fig. 7.

To clarify the change in $\Delta\rho$ with the aging time t_A , the differences ($\Delta\rho_t - \Delta\rho_{t=0}$) between the three representative aging time t_A , i.e., 10, 20 and 30 min, and $t_A = 0$ are plotted against T_A for both processes in Fig. 9. The number in the figure shows the aging temperature at which $|\Delta\rho_t - \Delta\rho_{t=0}|$ is small after the aging for 30 min.

From these results, the temperature region where $\Delta\rho$ shows the characteristic behavior

Fig. 7 The resistivity change during isothermal aging in the heating process.

Fig. 8 The resistivity change during isothermal aging in the cooling process.

against T_A and t_A is classified as region I (room temperature $\sim 150^\circ\text{C}$), IIa ($150\sim 205^\circ\text{C}$), IIb ($205\sim 240^\circ\text{C}$), IIc ($240\sim 260^\circ\text{C}$), IId ($260\sim$

Fig. 9 The resistivity changes during isothermal aging at 10, 20 and 30 min after the temperature changes. Symbol (●) shows overlapping of two symbols (○) and (●), and means that the resistivity did not change during the aging.

310°C), IIe ($310\sim 350^\circ\text{C}$) and III ($350\sim 500^\circ\text{C}$) in the heating process, and the region III' ($500\sim 320^\circ\text{C}$), II'e ($320\sim 250^\circ\text{C}$), II'c ($250\sim 240^\circ\text{C}$), II'b ($240\sim 200^\circ\text{C}$), II'a ($200\sim 150^\circ\text{C}$) and I' ($150^\circ\text{C}\sim$ room temperature) in the cooling process.

IV. Discussion

The resistivity change in ρ_A during aging can be explained by the change in configuration of Ag atoms in the alloy. In the regions III and III' Ag atoms are resolved in the alloy, because $\Delta\rho$ is almost constant over the region, and furthermore $\Delta\rho$ at a given aging temperature does not change during the isothermal aging. This is well understood from the phase diagram by Rotherham and Larke⁽⁶⁾, as shown in Fig. 10. In the diagram, the solvus of the Al-Ag alloy intersects the line for 1.03 at%Ag at 328°C . In the present experiment, however, the temperature at which $\Delta\rho$ attains to a constant value is 350°C in the heating process and 320°C in the cooling process, which deviates from 328°C . It is considered that the deviation arises from superheating or supercooling. Now, the small decrease in $\Delta\rho$ above 350°C seems to be a temperature dependence of the resistivity due to the isolated Ag atoms, that is, a deviation from Matthiessen's rule. A similar temperature dependence has been observed at temperatures below 300 K in a quenched Al-1.03

Fig. 10 The same figure as in Fig. 6 with the solubility limit (solid line), the solvus of G.P. zone (dotted line) and the temperature regions classified in text.

at%Ag alloy, and explained by the deviation from Matthiessen's rule⁽⁷⁾. Thus, the regions III and III' correspond to the state of solid solution in the phase diagram. However, the region below 350°C, especially the rapid decrease in $\Delta\rho$ during the early stage of isothermal aging, cannot be explained simply by the precipitation of the γ phase from the α solid solution or *vice versa*. It is necessary to take into account the formation and resolution of small solute clusters and the G.P. zones in the process of precipitation and resolution of γ -phase from α -phase or *vice versa*. Especially, the rapid increase in $\Delta\rho$ with T_A which is observed in the regions IIb and IIc in the heating process is explained by resolution of the G.P. zones. Similarly, the rapid decrease in $\Delta\rho$ with T_A which is observed in regions II'b and II'c in the cooling process is attributed to the formation of the G.P. zones. Figure 10 shows part of the metastable miscibility gap of Al-Ag alloys determined by Baur and Gerold⁽⁸⁾, together with the equilibrium phase diagram. Baur and Gerold have reported that the G.P. zones are in the η -state characterized by an ordered ar-

rangement of atoms below 175°C and are in the ε -state characterized by a disordered arrangement above 220°C.

Now, let us consider the configuration of Ag atoms in the temperature regions I and II. The solvus line of the γ -phase intersects the line for 1.03 at%Ag at 328°C as seen in Fig. 10, so the precipitates (γ -phase) are formed in the temperature region II'e in the cooling process. In the region II'e, the decay rate of $\Delta\rho$ versus t_A is slow as seen from the isothermal aging curve at 250°C in Fig. 8, so the precipitation rate seems to be slow. Abbott and Haworth have pointed out that a prolonged aging time is necessary to establish the equilibrium composition of the α and γ -phases⁽⁹⁾. Therefore, the rapid decrease of $\Delta\rho$ observed in the region II'c cannot be explained without the formation of the G.P. zones. In other words, the alloy achieves a supercooled state in the region II'e in the cooling process, and the supersaturated Ag atoms in the α -phase start abruptly to form the G.P. zones as the temperature is lowered below 245°C. Such a rapid decrease of $\Delta\rho$ is observed not only in the case in which it takes about 30 h to cool down the specimen from 500 to 245°C as described above, but also in the case in which it takes about 4 h as seen in Fig. 11.

Furthermore, $\Delta\rho$ during the isothermal aging shown in Figs. 7 and 8 approaches to constant value in the regions IIb and II'b, but in the regions IIa and II'a such a tendency does not observed. In the regions I and I' $\Delta\rho$ hardly changes as seen in Fig. 9. These facts consist with the following conclusions in the X-ray study for quenched Al-Ag alloy by Baur and Gerold⁽⁸⁾. The concentration of Ag atoms in the G.P. zones changes rapidly as the aging temperature changes above 100°C, and the transformation between η -state and ε -state occurs between 175 and 220°C. Then, it is concluded that the G.P. zones in the region I(I') is the η -state, and one in the region IIb(II'b) is the ε -state, and that the transformation between η -state and ε -state occurs in the region IIa(II'a).

The rapid increase in $\Delta\rho$ between 240 and 260°C in the heating process in Fig. 10, i.e. the region IIc in Fig. 9, is explained by the resolution of the G.P. zones. This process is also

Fig. 11 Changes in resistivity difference $\Delta\rho$ and temperature during furnace cooling (F.C.) from 500°C to each aging temperature.

seen in the isothermal aging curve at 251°C in the heating process in Fig. 7.

Furthermore, the decrease in $\Delta\rho$ in the region II_d corresponds to the precipitation of super-saturated Ag atoms to form the γ phase and the increase in $\Delta\rho$ in the region II_e is attributed to the resolution of the precipitates.

As described above, the resistivity change in the Al-Ag alloy is understood taking into account the formation and resolution of the

G.P. zones during the aging at such high temperature. During such a slow cooling process in which vacancies are almost in thermal equilibrium, the G.P. zones are formed around 245°C, and almost all of them remain as the zones during the aging at lower temperatures. However, the transformation between ε -state and η -state occurs at the regions II_a and II'_a. The zones resolve again by the heating above 245°C.

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