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Effect of Solute Clusters on Low Temperature Aging in Dilute Al-Ag Alloys

Akira SAKAKIBARA* and Teruto KANADANI**

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Aging of dilute Al-Ag alloys after quenching from low temperatures were studied mainly by electrical resistometry. Maximum resistivity observed in the aging curve of the specimens quenched from high temperature disappeared when the quenching temperature was lowered to 473 or 453K. When the quenching temperature was lowered further to 423K or lower, however, maximum resistivity reappeared. At the temperature lower than or equal to 423K but higher than the GP zone solvus, the alloys were not homogeneous but had clusters of solute atoms or fluctuation of solute concentration. Inhomogeneous distribution of solute atoms may affect the aging behavior after quenching from that temperature.

1. INTRODUCTION

Aging of Al-Ag alloys has been studied extensively, but only after quenching from relatively high temperatures, 673K or higher, because of the high GP-zone-solvus temperature for high concentration alloys. In this paper the aging process of Al-Ag alloys is investigated after quenching from low temperatures. Quenching temperature lower than 623K can be employed by using alloys as dilute as Al-0.5wt%Ag and thus decreasing the solvus temperatures for precipitates and for GP zones. The aging process was followed resistometrically to know whether or not the maximum resistivity appeared.

It is well known that small spherical GP zones, rich in solute atoms, are formed in the initial stages of low temperature aging of Al-Ag and Al-Zn alloys, and that those zones are responsible for age hardening. In the course of the aging of these alloys electrical resistivity increases at first, and then decreases after showing maximum; this phenomenon has been considered to be characteristic of formation and growth of GP zones. On the mechanism of this resistivity maximum many theoretical studies have been made since the suggestive note by Mott (1), and have succeeded in explaining it semiquatitatively (2-4). On the other hand, small-angle X-ray scattering experiments have revealed that the Guinier radius of GP zones observed at the resistivity maximum was almost the same irrespective of quenching and aging temperatures, e.g. about 0.9nm for Al-Zn (5) and about 0.5nm for Al-Ag (6). From this fact, the maximum may be regarded as an index of the extent of the growth of GP zones.

2. EXPERIMENTAL PROCEDURES

Alloys, of which the nominal compositions were Al-0.3, 0.35, 0.45, 0.5wt%Ag (chemical composition in Table 1), were obtained by melting pure metals, 99.99%Al and 99.99%Ag, in high alumina crucibles in air. Ingots, 15mm in

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* Department of Mechanical Engineering

** Department of Mechanical Engineering, Okayama University of Science

diameter and about 150mm in length, were homogenized for 1.8ks at 723K, pealed by a lathe, and forged at 723K to plates of 5mm in thickness. The plates were cold-rolled, with appropriate intermediate annealings, to strips of 0.2 and 0.4mm in thickness.

Table 1 Chemical Composition of the Specimen

Specimen	Ag	Si	Fe	Cu	Al
Al-0.30%Ag	0.303	0.003	0.002	<0.001	Balance
Al-0.35%Ag	0.354	0.002	0.002	0.003	Balance
Al-0.45%Ag	0.447	0.002	0.001	0.004	Balance
Al-0.50%Ag	0.495	0.004	0.003	0.002	Balance

From the 0.4mm thick strip, specimens for resistometry were prepared, of which the shape and size were the same as in the previous paper (7). Only one specimen was repeatedly used throughout the experiment for one composition to avoid errors originated in the measurement of dimensions of the specimen and unavoidable if more than one specimen was used. That the specimen was not damaged in repeated heat treatments was assured by the result in Fig.1, where the data points (closed circles) obtained after several runs of measurements coincide with those in the first run (open circles). The error in the resistivity measurement was less than ±0.02%. Specimens for X-ray measurements, 25mm × 5mm, with four leads for resistometry, was cut out of the 0.2mm thick strip. Aside from a little slower aging rate, the aging curves of these specimens agreed well with those of the 0.4mm thick specimens.

The solution treatment was made at 773K for 3.6ks by inserting a specimen into a slit made of an aluminum block placed in a furnace (8). The specimen was furnace cooled to the quenching temperature, 623K-353K, held there for 3.6ks, and quenched by quick extraction from the slit and immersion into iced water by hand. Aging and annealing were carried out in an ethanol bath at 273K and in a silicon oil bath at the temperature above the solvus for GP zones, respectively, both with accuracy of ±0.1K.

Resistivity was measured by a conventional potential drop method, a specimen and a dummy being immersed in liquid nitrogen. X-ray diffraction (35kV × 15mA) and transmission electron microscopy (200kV) were used to examine the existence of precipitates.

3. RESULTS AND DISCUSSION

Fig.1 shows aging curves of the Al-0.3wt%Ag alloy aged at 273K after quenching from various temperatures, $T_q \geqq 453K$. The curves for T_q from 523K to 623K have a feature of GP zone formation; resistivity increases at first,

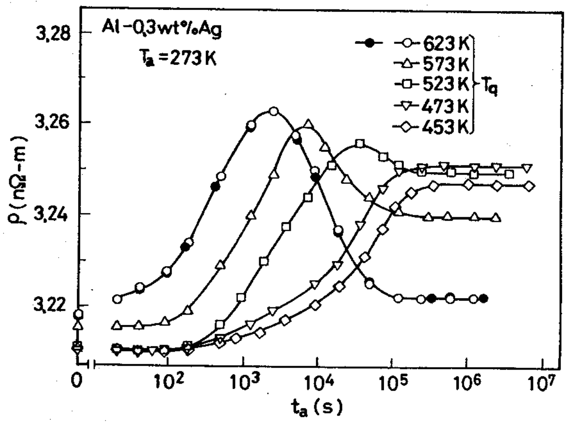


Fig.1 Aging curves of Al-0.3wt%Ag alloy at 273K after quenching from various temperatures; ● ○ 623K, △ 573K, □ 523K, ▽ 473K, ◇ 453K.

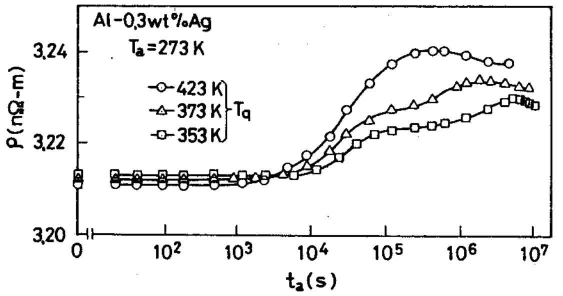


Fig.2 Aging curves of Al-0.3wt%Ag Alloy at 273K after quenching from various temperatures; ○ 423K, △ 373K, □ 353K

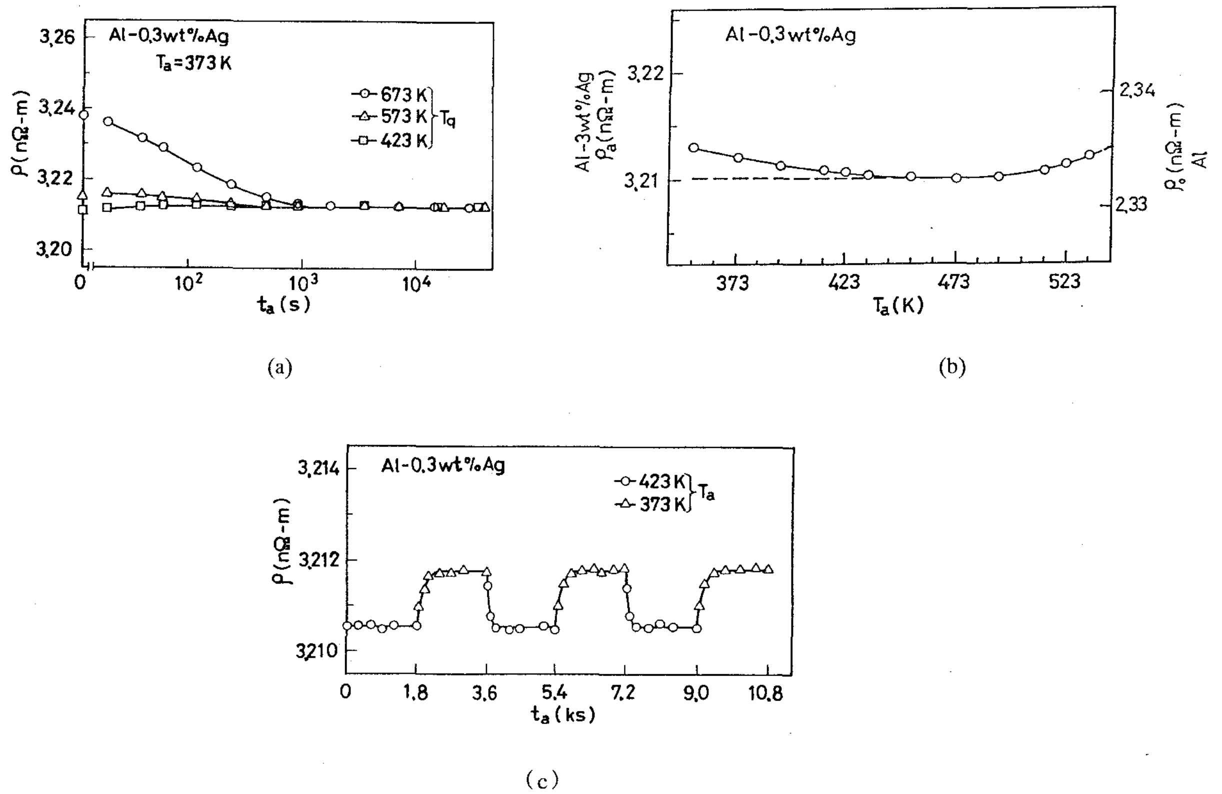
decreases after the maximum (ρ_m) and reaches the quasi-equilibrium value (ρ_e). The value of ρ_m decreases with decreasing T_q. Meanwhile the value of ρ_e increases with decreasing T_q, contrary to the result obtained for T_q higher than 623K (9). As a result of decreasing ρ_m and increasing ρ_e, the resistivity maximum becomes obscure and is not observed when T_q=473K and 453K.

In the Al-3wt%Ag alloy and several Al-Zn alloys, the average size of GP zones at the quasi-equilibrium stage, measured by small-angle X-ray scattering, decreased according as the difference between ρ_m and ρ_e became small (6,10). Therefore it is considered that the variation of the aging curves with decreasing T_q shown in Fig.1 is caused by the virtual interruption of GP zone growth owing to the impoverishment of retained vacancies (10).

Fig.2 shows aging curves at 273K for T_q's lower than those in Fig.1. These curves again show the maximum which once disappeared in Fig.1 when T_q was decreased down to 473K. This phenomenon that the maximum once lost when T_q was lowered reappears for T_q lowered further was also observed for aging temperatures from 273K to 323K and compositions from 0.35 to 0.5wt%Ag.

No precipitates were found, by transmission electron microscopy and X-ray diffraction, in the specimen which was quenched from 373K and aged until the resistivity decreased after showing the maximum. Accordingly the fall of resistivity observed after the maximum is considered to be due not to the precipitation which frequently follows GP zone formation, but to the continuation of zone growth caused by lowering T_q.

On the assumption that the reappearance of the maximum in the aging curves was originated in the initial state of aging, i.e. as-quenched state, the state at T_q was examined. Fig.3(a) shows annealing curves of the Al-0.3wt%Ag alloy at 373K quenched from various temperatures. At the annealing temperature (T_a) above the GP zone solvus, where GP zones do not form, resistivity values, different from each other at the beginning, converged to a certain



(a)

(b)

(c)

Fig.3 (a) Annealing curves of Al-0.3wt%Ag alloy at 373K after quenching from various temperatures; ○ 673K, △ 573K, □ 423K. (b) Plot of quasi-equilibrium resistivity (ρa) against the annealing temperature (Ta) for the quenching temperature673K. (c) Annealing curve at 423K(○) and 373K(△) alternately changed.

value, ρ_a, that was determined by T_a. The same result as this was obtained for other annealing temperatures (T_a).

These values of ρ_a are plotted against T_a in Fig.3(b). The dashed line in the figure shows the result of pure aluminum (99.99%) as a reference. For T_a's higher than 473K the variation in ρ_a of the alloy with T_a accords well with that of pure aluminum. However, for lower T_a's the values of ρ_a of the alloy increase with decreasing T_a while that of pure Al decreases slightly. An increase in resistivity with increasing T_a may certainly be ascribed to the increase in the number of equilibrium vacancies at T_a. On the other hand, the increase in resistivity with decreasing T_a observed below 473K is considered to be due to the short-range clustering or the local fluctuation of solute concentration that has been observed in Al-Zn, Al-Cu and Al-Mg alloys (11-15). Further, the increase in resistivity due to this phenomenon is different from that due to GP zone formation. If GP zones were formed, the quasi-equilibrium value of resistivity, should depend remarkably on T_q. This is not the case.

Fig.3c shows an annealing curve in resistivity when the Al-0.3wt%Ag alloy was annealed alternately at 423K and 373K after quenching from 623K and quasi-equilibrium value was attained at 423K. On changing T_a, r changed in a short time to the stationary value for the new T_a. Such a reversible change in r as this was not observed when GP zones were formed (16). This result suggests again that the state corresponding to r_a did not involve GP zones, but involve only short-range clustering of solute atoms.

From the results in Fig.3, it is considered that aging of the alloy quenched from the temperatures below 423K, as is the case in Fig.2, did not start from the state of a homogeneous solid solution but from the one which involved short range clustering or solute fluctuation. Therefore it may be thought that in spite of the lower concentration of vacancies in the case T_q<423K than in the case T_q=473K and 453K, competitive growth may have proceed further because GP zones formed in the region of short-range clustering or higher solute concentration in the fluctuation were able to grow more easily than in the other regions. Thus the maximum of resistivity reappears in the aging curve when T_a becomes lower than or equal to 423K. A detailed study, however, is required further in the future.

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