Memoirs of the School of Engineering Okayama University Vol. 12, February 1978

Fluctuation of the Solute Concentration in Al Rich Al-Zn Alloys

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(Received January 17, 1978)

Synopsis

Several Al-Zn alloys containing 0.041~4.4 at%Zn were studied by means of measurements of electrical resistivity. The results obtained are as follows:

(1) The electrical resistivity increases when the specimen is annealed at temperatures higher than the solvus temperature of the G.P. zones. The increase of the resistivity is due to the formation of fluctuation.

(2) The electrical resistivity of the specimen containing fluctuation is dependent upon annealing temperature only and independent of quenching temperature.

(3) The fluctuation is formed in very dilute alloys as 0.041 at%Zn at temperatures higher than the solvus temperature of the G.P. zones.

(4) The formation energy of vacancy and the migration energy of the Zn atom in the alloys determined by the formation process of fluctuation are in good agreement with those by the formation process of G.P. zones.

(5) In spite of the result (4), it seems that the fluctuation is not the same as the small G.P. zones which are observed in the early stage of aging.

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I. Introduction

Al-rich Al-Zn alloys, in which the difference between radius of a solute atom and a solvent atom is small, are age-hardening alloys and have been studied by many workers. It is well-known that on low temperature aging G.P. zones are rapidly formed and grown immediately after quenching in homogeneous solid solution, in which solute atoms and vacancies are excessive.

Rudman et al. (1,2) reported that in relatively high-concentrated (20~50 at%Zn) Al-Zn alloys, the concentration of Zn is inhomogeneous even in the solid-solution single-phase field at high temperature and that the ratio of Zn atoms at the nearest-neighbor sites for one Zn atom is a little higher than the concentration of the alloy. They called these high-concentrated regions "clusters". They reported also that the degree of clustering is the most prominent in the Al-50 at%Zn alloy.

On relatively dilute (0.3~1.78 at%Zn) alloys Levelut and Guinier (3) indicated by an excellent X-ray method that Zn atoms get together about room temperature higher than the solvus temperature of G.P. zones and that the degree of association increases with increase in both concentration and temperature. On the high-concentrated regions there are several other reports (4~8).

Hori and Hirano (9,10), on the other hand, reported that the solvus temperature of G.P. zones is higher than the α-α' presipitation temperature.

In the present paper, the experimental results obtained on the difference between the high-concentrated regions and G.P. zones, on the extent of the temperature and concentration in which the regions are recognized, and others will be shown.

II. Experimental Procedures

1. Specimens

Nominal composition of the alloys used were Al-0.041, 0.083, 0.21, 0.42, 0.84, 1.3, 1.7, 2.6, 3.5, and 4.4 at%Zn, and pure metals contained in these alloys were 99.996 % Al and 99.999 % Zn. Alloys were casted into metallic mold in air and size of the ingot was about 15 mm in diameter and 100 mm in length. These ingots were homogenized at 450°C for about 30 hr. With respect to the compositions of these alloys, accurate values are not definite because of the absence of analysis. For the Al-4.4 at%Zn alloy, however, when quenching temperature and aging temperature were the same as in a previous report (11), maximum resistivity on the isothermal annealing agrees well with one another. For the other alloys, when as-quenched resistivity for a certain quenching temperature was plotted against its composition, there is only a little difference between the values and the curve obtained. Hence, the deviation from the nominal composition seems to be small.

Ingots were hot-forged at 450°C to sheets of about 5 mm in thickness, and cold-rolled to plates of 0.4 mm in thickness. Specimen for electrical resistivity measurements was produced by cutting-off from the plate, and its shape and size were the same as in a previous report (12). For the relatively dilute alloys, however, the length of the central part was longer.

In addition to the measurements of electrical resistivity, measurements of intensities of small-angle X-ray scattering and transmission electron microscopy were also carried out. These two measurements were carried out to ascertain the presence of presipitates or G.P. zones.

A specimen for small-angle X-ray scattering measurements was produced by cold-rolling to a plate of 0.05 mm in thickness from the central part of a specimen for electrical resistivity measurements. This specimen was heat-treated in the same way as that for electrical resistivity measurements. Electrical resistivity of this specimen was measured and X-ray phatographs were taken at about the temperature of liquid nitrogen after an appropriate annealing.

A specimen for electron microscopy, produced by cold-rolling to a plate of 0.08 mm in thickness, was quenched with the same equipment for heat treatments as one used for the specimen for electrical resistivity measurements. After the heat treatment required, the specimen was thinned by electropolishing in a solution of perchloric acid in alcohol (current density; 0.05 A/cm^2) and then in a solution of nitric acid in alcohol (current density; 1.5 A/cm^2).

2. Heat Treatments

Quenching method was the same as that previously reported (12). All the specimens were solution-treated for 1 hr at 500°C in a furnace installed with an aluminum block to which specimens were attached closely. Then, specimens were cooled in the furnace to the quenching temperature (controlled within ±1°C) and held there for 1 hr. Thereafter, quenching was made by hand by quickly extracting the specimen out of the furnace and immersing it into iced water bath.

Then, it was transferred into liquid nitrogen as quickly as possible. Quenching mediums were silicon oil (above 50°C) and water (below 50 °C). Annealing treatments were made by transferring the specimen into an adequite liquid bath.

3. Measurements

Measurements of electrical resistivity were carried out at liquid nitrogen temperature by a potentiometric method and the errors caused by various electromotive forces were removed by the usual method. The temperature of liquid nitrogen was corrected with a dummy made from the same alloy as the specimen and annealed sufficiently.

The intensity of small-angle scattering of X-rays was measured by a photographic method. The method was the same as that previously reported (13).

The electron microscope used was HU200 type and operated on 100 kV. Its direct magnification was 10^5 times.

III. Experimental Results

Figs. 1~7 show the plots of the as-quenched resistivity ρ_0 for each alloy quenched into iced water against the quenching temperature T_Q. When T_Q is above 300°C, ρ_0 increases with T_Q for all alloys used. This increase is caused by the excess vacancies quenched and the G.P. zones formed during quenching, but for the alloys < 1 at%Zn G.P. zones probably make little contribution to this increase. For all alloys used as-quenched resistivity increases as T_Q decreases when T_Q is below 200°C. This increase of ρ_0 may be due to the fluctuation of concentration, which has been present at T_Q and remains still after quenching. Particularly, it should be noted that ρ_0 increases even for such dilute alloys as 0.041 at%Zn when T_Q is low. Black dots in these figures represent values to which resistivity reaches when annealed at various temperatures higher than the solvus temperature for G.P. zones after quenching into iced water from 300 °C. These values fall on the extention of the ρ_0-T_Q curve. It may be considered that the minimum value of ρ_0 is caused by the two reasons above, which increase ρ_0 as T_Q increases, and by the contribution of the fluctuation which decreases as T_Q increases. T_Q at which the minimum resistivity occurs decreases as the concentration of the alloy decreases.

Figs. 8 and 9 show the isothermal annealing curves at 30°C after quenching from various temperatures. For all curves the saturated

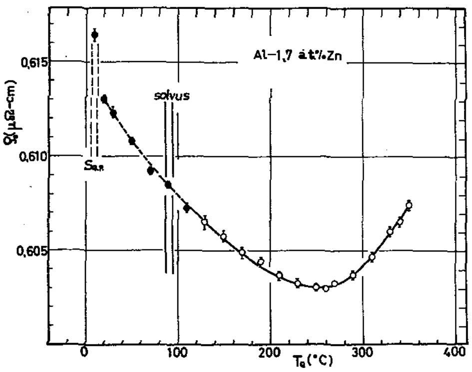

Fig.1 A plot of ρ_0 against T_Q for the Al-1.7 at%Zn alloy.

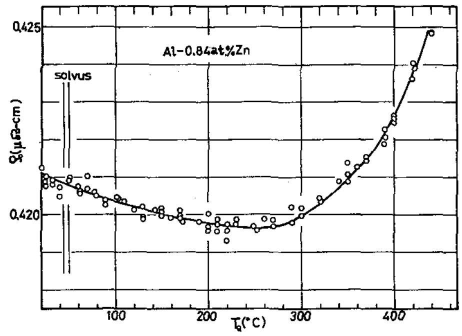

Fig.2 A plot of ρ_0 against T_Q for the Al- 0.84 at%Zn alloy.

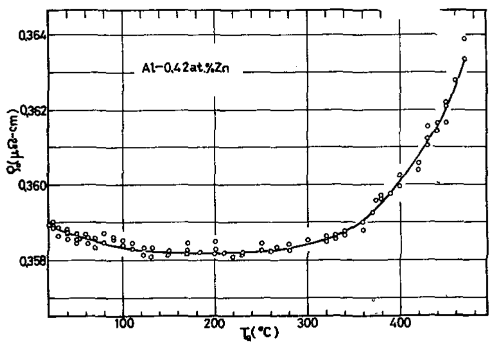

Fig.3 A plot of ρ_0 against T_Q for the Al-0.42 at%Zn alloy.

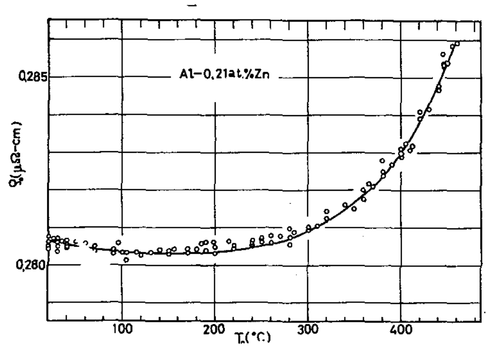

Fig.4 A plot of ρ_0 against T_Q for the Al-0.21 at%Zn alloy.

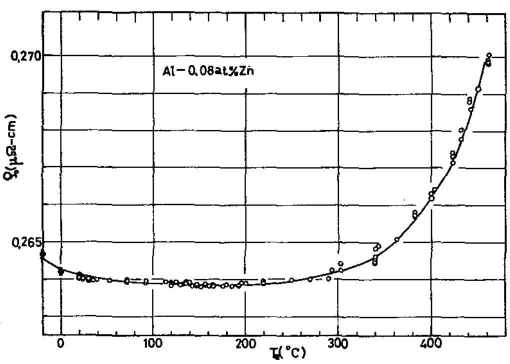

Fig.5 A plot of ρ_0 against T_Q for the Al-0.083 at%Zn alloy.

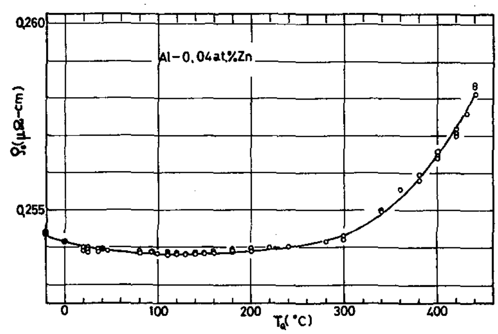

Fig.6 A plot of ρ_0 against T_Q for the Al-0.041 at%Zn alloy.

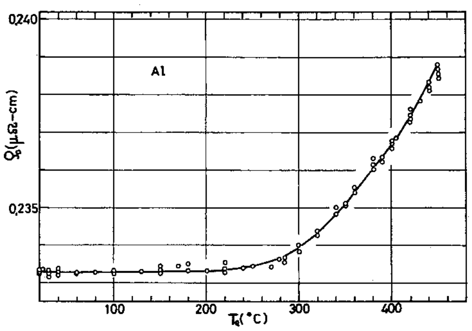

Fig.7 A plot of ρ_0 against T_Q for pure Al.

values of resistivity are nearly the same. As to a certain alloy, such values are dependent upon annealing temperature only and independent of quenching temperature. This is different from the case that the metastable values of resistivity which are obtained after the resistivity maximum, vary remarkably with quenching temperatures when G.P. zones are formed during isothermal aging.

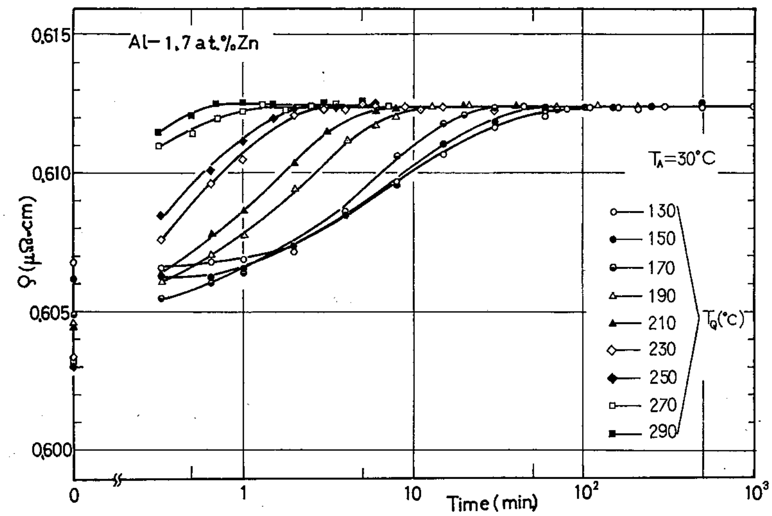

Fig.8 Isothermal annealing curves at 30°C after quenching from various temperatures for the Al-1.7 at%Zn alloy.

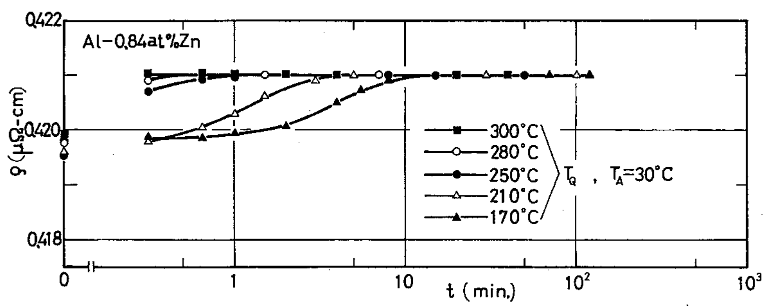

Fig.9 Isothermal curves at 30°C for the Al-0.84 at%Zn alloy

Fig. 10 shows a logarithmic plot of the time required to reach a saturated value of resistivity against $1000/T_Q$ for the Al-0.84 at%Zn alloy quenched from various temperatures and annealed isothermally. The activation energy obtained from the slope of this straight line is 0.72 ±0.05 eV. This value is in good agreement with the value 0.70 ± 0.05 eV which Panseri and Federighi (11) found for the formation of G.P. zones in Al-10 wt%Zn alloy, and corresponds to the formation energy of vacancies in Al-Zn alloys.

Fig. 11 shows isothermal annealing curves of the Al-0.84 at% Zn alloy at several temperatures (-50~30°C). Quenching temperature T_Q is 300°C (when $T_A \geqq 0$°C) or 340°C (when $T_A < 0$°C). Isothermal annealing curves at -20, -30 and -40°C have been previously reported (6). The form of the curves for $T_A \leqq -40$°C differs from that for the other temperatures and, especially at -40°C, the curve is apparently of two-step aging. In the cases at -45 and -50°C, the first step of the curves becomes a little obscure as the temperature declines, but can be recognized. It is considered that the first step is due to the formation of the fluctuation and that the second step is due to the formation and growth of the G.P. zones. The growth in

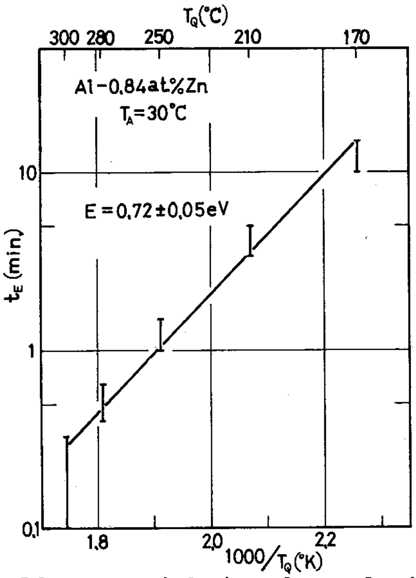

Fig.10 Logarithmic plot of time t_E(the time required to reach a saturated value of resistivity) against $1000/T_Q$ for the Al-0.84 at%Zn alloy quenched from various temperatures.

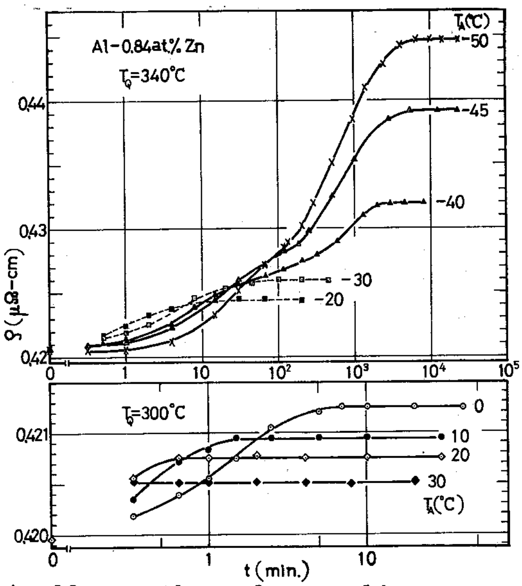

Fig.11 Isothermal annealing curves of the Al-0.84 at% Zn alloy at several temperatures after quenching from 340 or 300°C.

the second step seems to stop on the way. This can be interpreted as in the previous paper (6). Both the saturated values of resistivity due to the formation of the fluctuation and those due to the G.P. zones seem to be dependent on T_A and independent of T_Q in this experiment. The forms of the isothermal annealing curves for $T_A \geq 0°C$ after quenching from 300°C, resemble one another closely and these curves saturate to the values simply dependent on T_A. This value increases as T_A decreases. Therefore, it is considered that the state corresponding to this value varies with T_A. Because the state, to which the resistivity saturation corresponds, varies with T_A (when $T_A \geq 0°C$), a logarithmic plot of the time required to reach the saturated value of resistivity against $1000/T_A$(K) is not appropriate to obtain the activation energy for this process. By the use of the same experimental equation for the initial rate of isothermal aging as Perry's (4), the initial rate of annealing was obtained. Fig. 12 shows a logarithmic plot of this initial rate against $1000/T_A$. The activation energy obtained was 0.43 ± 0.05 eV. This value is in good agreement with that Panseri and Federighi (11) found in Al-10 wt%Zn alloy. Ohta et al. (6) also have found the same value. These values previously obtained have been thought as the activation energy for the formation of G.P. zones or the migration of a Zn atom. Because of the agreement of the activation energy, it is considered that the fluctuation is also formed by the migration of Zn atoms.

Fig. 13 shows the determination of the migration energy of a Zn atom

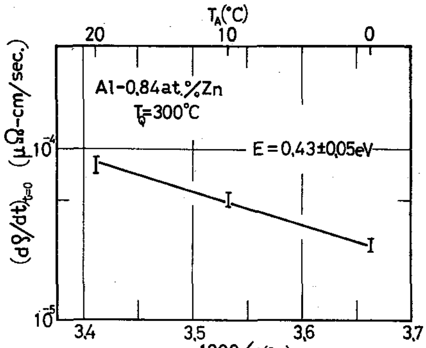

Fig.12 Logarithmic plot of initial rate of annealing against $1000/T_A$ for the Al-0.84 at%Zn alloy.

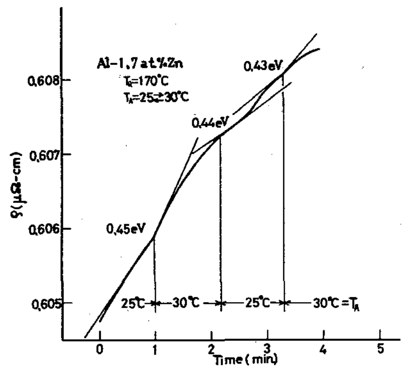

Fig.13 Determination of the migration energy of a Zn atom in the Al-1.7 at%Zn alloy by the ratio-of-slopes method.

in the Al-1.7 at%Zn alloy (quenched from 170°C and then annealed at 25 and 30°C), by the ratio-of-slopes method. The activation energy obtained is 0.45 ± 0.05 eV and agrees well with that in Fig. 12.

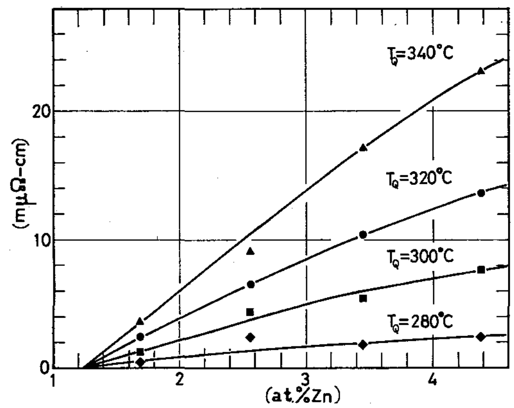

Fig.14 A plot of $\Delta\rho_0=\rho_0-\rho_{0-min}$ against the concentration of alloys. (ρ_{0-min}: The minimum value of ρ_0 in Figs.1 and 2)

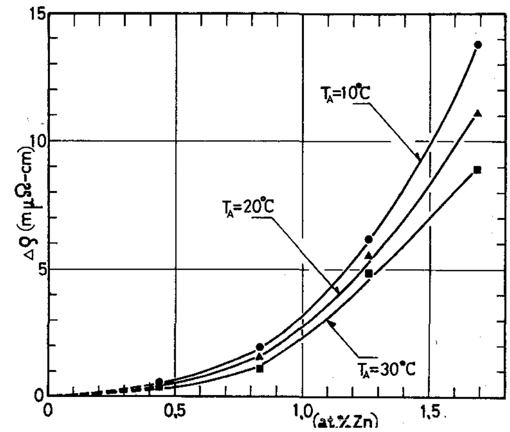

Fig.15 A plot of $\Delta\rho$ against the concentration of alloys. ($\Delta\rho$: The total increase in resistivity after quenching from 300°C)

Fig. 14 shows a plot of $\Delta\rho_0$($\Delta\rho_0=\rho_0-\rho_{0-min}$) against the concentration of alloys in the case of high quenching temperatures for the relatively high concentrated alloys. G.P. zones are formed during quenching from the high temperature in the high concentrated alloys, which causes the increase in ρ_0. As seen in Fig. 14, extrapolation of those curves to the low concentration region turns out that $\Delta\rho_0$ = 0 at about 1.3 at% for each curve. As previously described, ρ_{0-min} has no significance because the effect of the various factors which influence on the value of ρ_{0-min} varies independently with the concentration. Therefore, $\Delta\rho_0$ is nothing but only one criterion, but the results shown in Fig. 14 are related to the presence of the solvus of the G.P. zones (6).

Fig. 15 shows a plot of $\Delta\rho$, the total increase of resistivity, against the concentration of alloys on annealing at 30, 20 and 10°C after quenching into iced water from 300°C. Though the as-quenched resistivity is a little larger than the ρ_{0-min} of each alloy because of quenched vacancies, the difference is small. Resistivity after annealing at a temperature is also in good agreement with the as-quenched resistivity after quenching from the temperature. Therefore $\Delta\rho$ in this figure corresponds to $\Delta\rho_0$ in Fig. 14. However, $\Delta\rho_0$

differs from $\Delta\rho$ in the following point; $\Delta\rho_0$ consists mainly of the contribution due to the formation of G.P. zones while $\Delta\rho$ due to the presence of fluctuation of concentration. As seen in Fig. 15, the increase of resistivity due to the fluctuation, $\Delta\rho$, decreases as the concentration of the alloy decreases and extrapolation of each curve turns out that $\Delta\rho$ = 0 at zero concentration. When Fig. 14 is compared with Fig. 15, dependence of $\Delta\rho_0$ and $\Delta\rho$ on the quenching and annealing temperature, respectively, is opposite each other, that is, $\Delta\rho_0$ increases as the quenching temperature increases while $\Delta\rho$ increases as the annealing temperature decreases. This suggests that the fluctuation is not formed during cooling. Moreover, each part of the curves in these figures extrapolated to low concentration differs extremely one another. This suggests that there is no solvus line for the fluctuation.

Figs. 16～28 show isothermal annealing curves of various alloys at several temperatures after quenching from several temperatures. Their details are the same as those in Fig. 11.

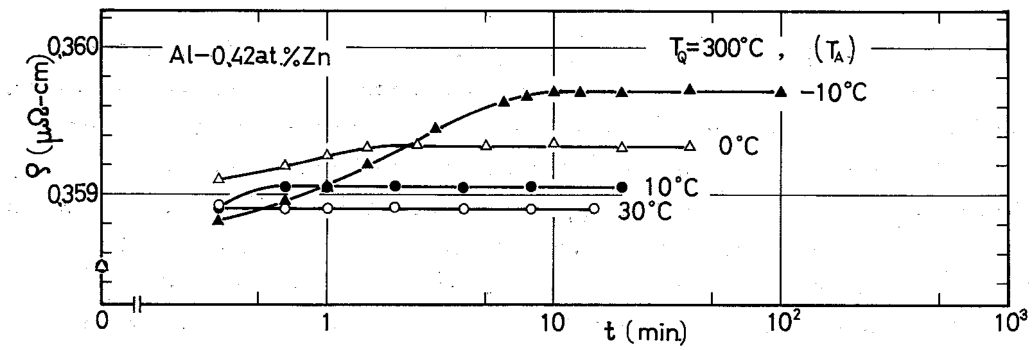

Fig.16 Isothermal annealing curves of the Al-0.42 at%Zn alloy at several temperatures after quenching from 300°C.

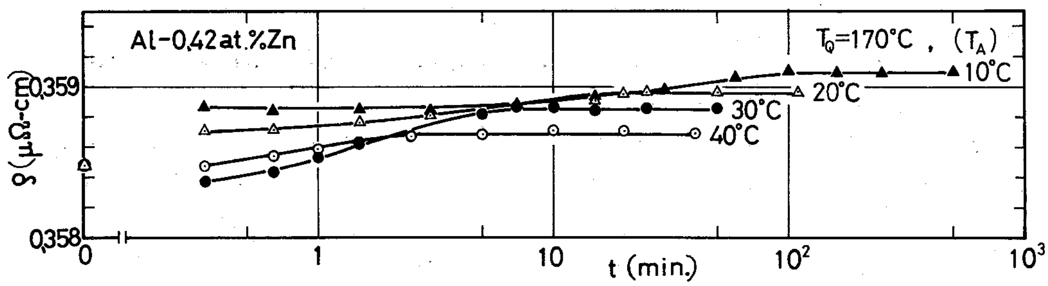

Fig.17 Isothermal annealing curves of the Al-0.42 at%Zn alloy at several temperatures after quenching from 170°C.

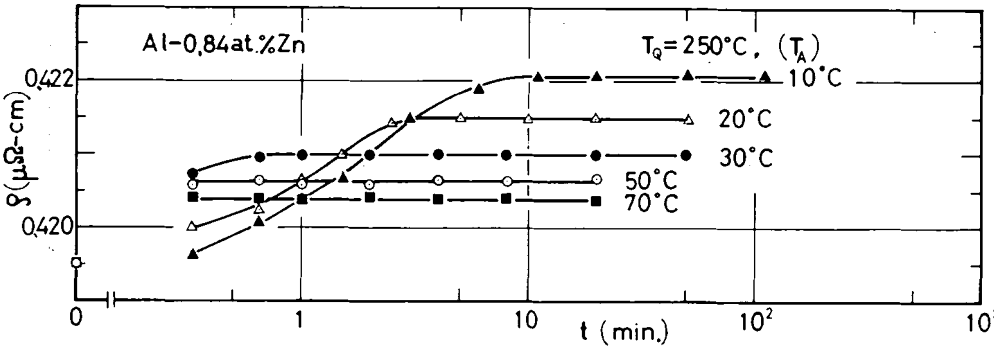

Fig.18 Isothermal annealing curves of the Al-0.84 at%Zn alloy at several temperatures after quenching from 250°C.

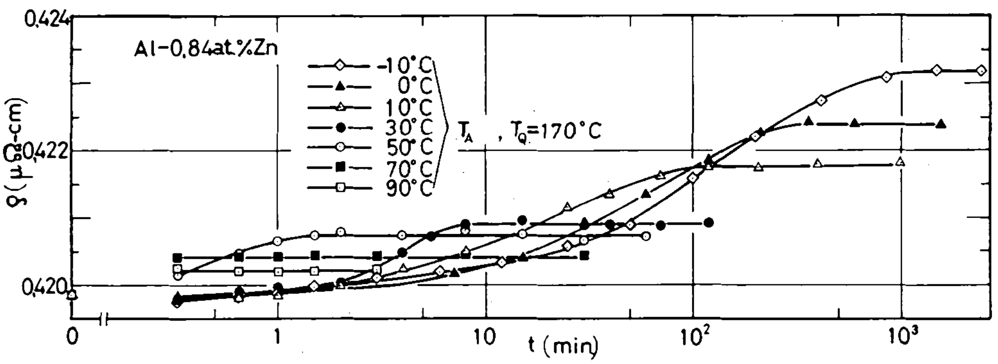

Fig.19 Isothermal annealing curves of the Al-0.84 at%Zn alloy at several temperatures after quenching from 170°C.

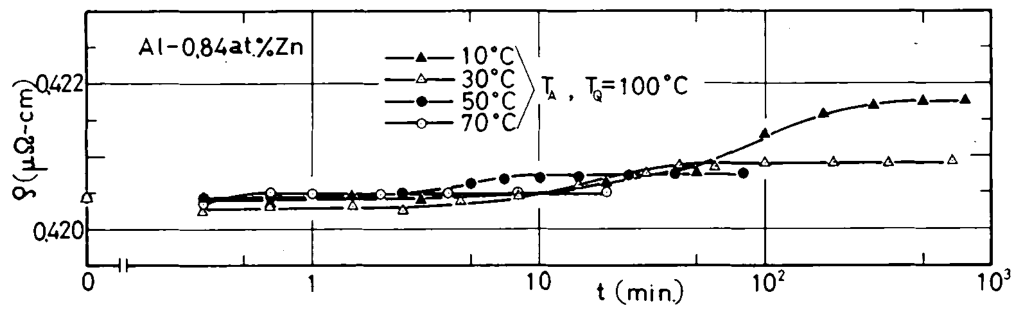

Fig.20 Isothermal annealing curves of the Al-0.84 at%Zn alloy at several temperatures after quenching from 100°C.

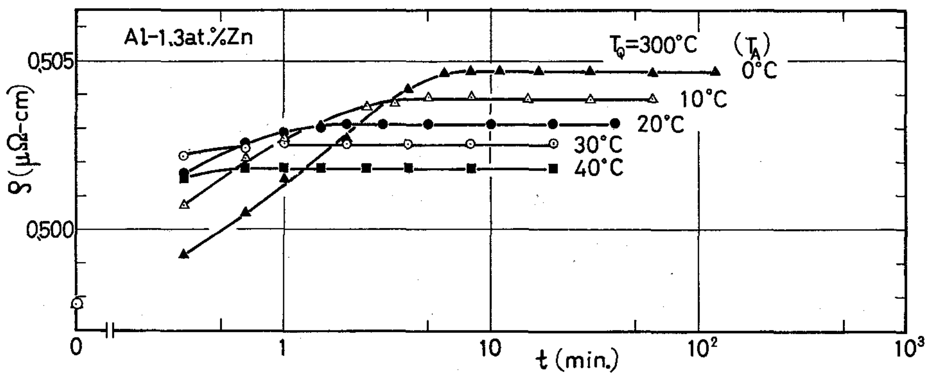

Fig.21 Isothermal annealing curves of the Al-1.3 at%Zn alloy at several temperatures after quenching from 300°C.

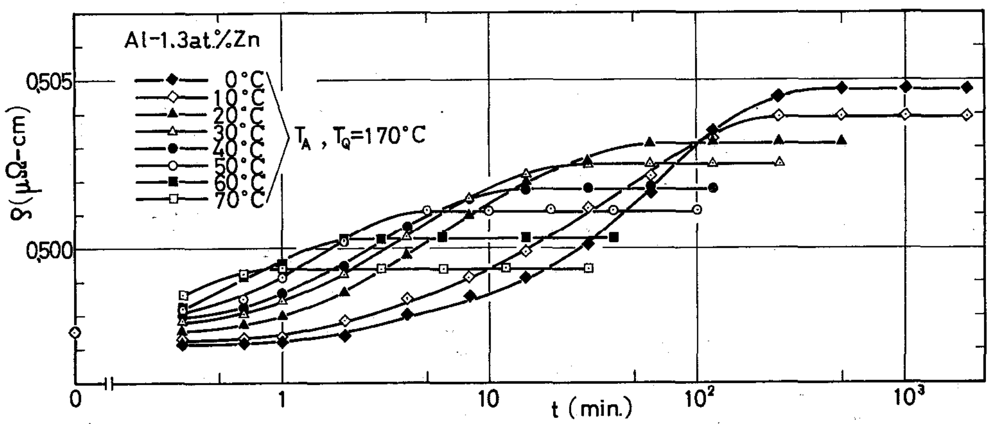

Fig.22 Isothermal annealing curves of the Al-1.3 at%Zn alloy at several temperatures after quenching from 170°C.

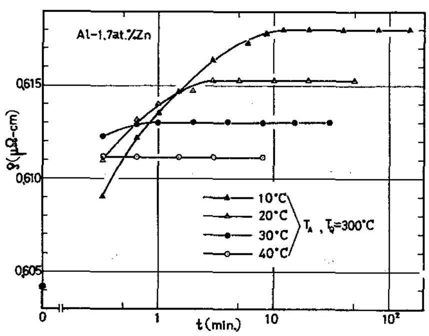

Fig.23 Isothermal annealing curves of the Al-1.7 at% Zn alloy at several temperatures after quenching from 300°C.

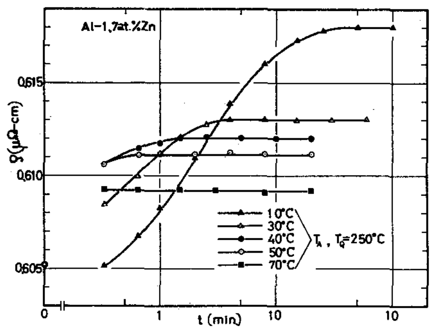

Fig.24 Isothermal annealing curves of the Al-1.7 at% Zn alloy at several temperatures after quenching from 250°C.

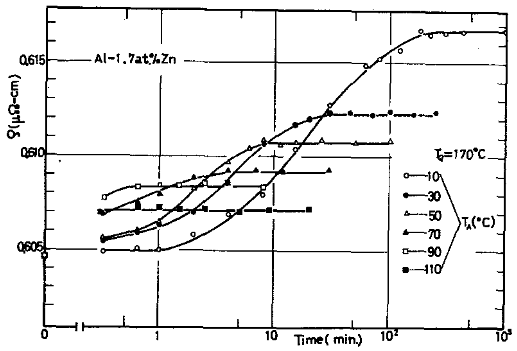

Fig.25 Isothermal annealing curves of the Al-1.7 at% Zn alloy at several temperatures after quenching from 170°C.

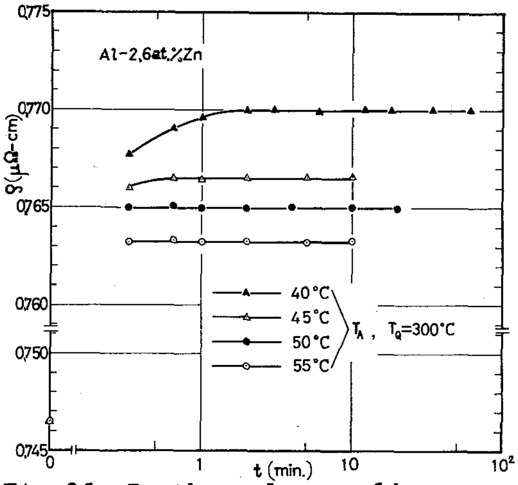

Fig.26 Isothermal annealing curves of the Al-2.6 at% Zn alloy at several temperatures after quenching from 300°C.

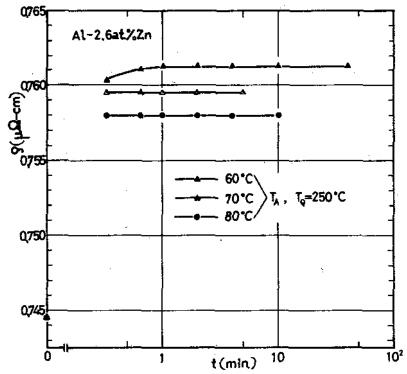

Fig.27 Isothermal annealing curves of the Al-2.6 at% Zn alloy at several temperatures after quenching from 250°C.

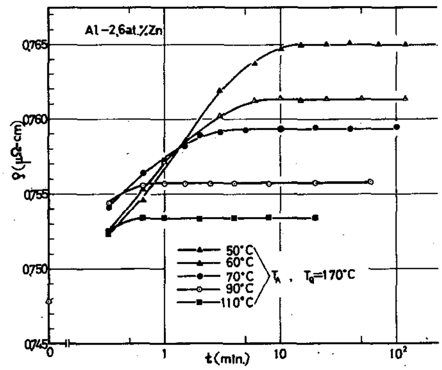

Fig.28 Isothermal annealing curves of the Al-2.6 at% Zn alloy at several temperatures after quenching from 170°C.

Fig. 29 shows a logarithmic plot of the time required to reach the resistivity saturation on the annealing at various temperatures after quenching from 170°C against $1000/T_A$ for several alloys. Two points are noticed; When annealing temperature T_A is constant, the time required to reach the saturated value of resistivity increases with the concentration of alloy. The slope of the straight line obtained for each alloy decreases with the concentration of alloy.

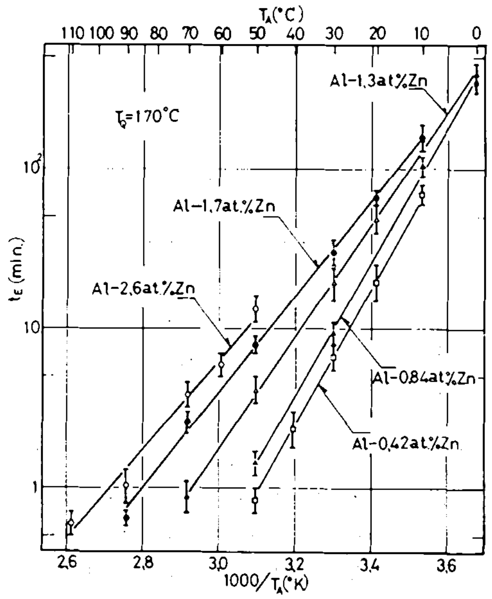

Fig.29 Logarithmic plot of t_E for several alloys quenched from 170°C against $1000/T_A$.

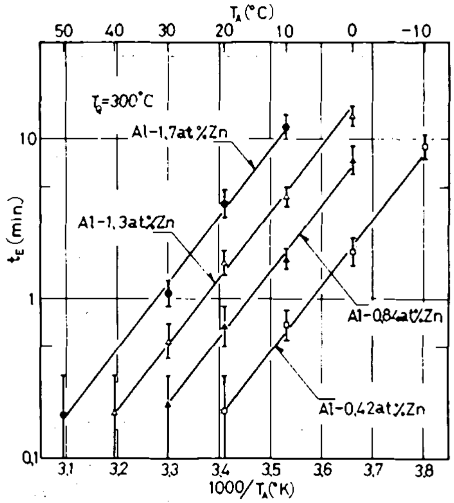

Fig.30 Logarithmic plot of t_E for several alloys quenched from 300°C against $1000/T_A$.

Fig. 30 shows the same plot as that in Fig. 29 except that T_Q = 300°C. It is the same tendency as in Fig. 29 that the time required to reach a saturated value of ρ increases with the concentration of alloy when the annealing temperature is constant. However, all the slopes of the straight lines obtained about each alloy are the same and these straight lines are parallel one another. This differs from the case in Fig. 29.

The photographs of small-angle scattering of X-rays were taken about the Al-4.4 at%Zn alloy. Specimen was annealed at 130°C for 60 min after quenched into 130°C from 300°C and was transferred into liquid nitrogen. Then, it was mounted on the same apparatus as described in a previous paper (5). Specimen was kept nearly at the temperature of liquid nitrogen during the period of exposure. The voltage used to generate X-rays was 40 kV and the current 15 mA. Exposures were carried out for 200 hr with CuKα radiation monochromatized by a curved crystal of quartz. When the tube voltage and current were the same as described above, the scattering by the small G.P. zones formed in the early stage of aging at 20°C in the same alloy, of which radius were about 9 Å, was able to be observed by the exposure for about 25 hr. Since the time of exposure is about eight times as long in the present case, it seems that the scattering by the G.P. zones of smaller size or lower concentration can be detected. Such scattering, however, was not detected at all.

Electron microscopy was carried out about the specimen which also had been annealed at 130°C for 60 min after quenching into 130°C from 300°C. As the temperature of the specimen was nearly room temperature during electropolishing, mounting and observation, aging may proceed to some extent in this period. The resolution of the electron microscope used is alway about 6 Å and G.P. zones 17 Å in diameter can be detected on the film. In the present case, however, precipitates such as G.P. zones or Y phases were not detected.

IV. Discussions

The results corresponding to some part in Figs. 1∼8, and 10 are found also in the paper (4,5) described previously. In all alloys used, the electrical resistivity increases when the specimen is annealed at temperatures a little higher than the solvus temperature of the G.P. zones. This increase is not dependent on T_Q but on the concentration of alloy and T_A. The higher the concentration is and the lower T_A is, the larger this increase is. Precipitates such as G.P. zones or Y phase were not detected during this annealing. Therefore, it seems that the above increase in resistivity is the same as Perry found (4) and that it is due to the fluctuation of salute concentration.

The formation energy of a vacancy and the activation energy of the migration of a Zn atom, determined by the isothermal annealing curves for various T_Q and T_A and others, are in good agreement with those determined by the formation of G.P. zones (11). However, because the temperature range of the experiment is different each other, it can not be considered that the concentrated regions in fluctuations are the same as G.P. zones. Fig. 31 shows a plot of metastable values, which resistivity reached in Fig. 11, against T_A. Solvus temperature of G.P. zones for this alloy may be between -40°C and -30°C. The chane line and full line in the figure correspond to the formation of G.P. zones and fluctuations,

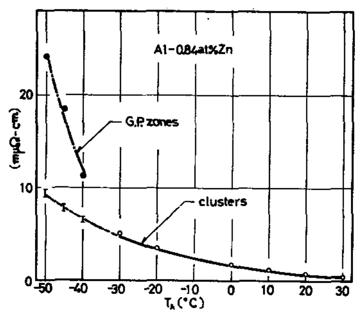

Fig.31 A plot of Δρ for the Al-0.84 at%Zn alloy quenched from 340 or 300°C against annealing temperatures T_A.

respectively. The broken line is a plot of the first stage shown in Fig. 11, and is almost on the extention of the full line. The increase in resistivity due to the formation of the fluctuation lies on a different curve from that due to the G.P. zones, which suggests that the G.P. zones are not the same as the concentrated regions in the fluctuation.

It has been suggested (15) that fluctuation of concentration exists in the metastable field higher than the spinodal temperature and that the mean-square of the amplitude increases as the temperature declines. This is the same tendency as in the experimental results by Levelut and Guinier (3) and accords with the dependence of the increase in resistivity on the temperature in the present experiment. The association of Zn atoms or the clusters described in the previous papers (1∼3), which has been suggested merely as one model and not emphasized, may be related to the fluctuation.

The difference of experimental conditions in Fig. 29 and Fig. 30 is only in T_Q. In Fig. 29, the slope of the straight line obtained at T_Q = 170°C decreases with concentration of alloy. On the other hand, in Fig. 30 the straight lines obtained at T_Q = 300°C are all parallel. In case of Fig. 29, in concentrated alloys fluctuations may already exist considerably at T_Q because T_Q is low. Therefore, during the annealing process a state of fluctuation changes to another state of fluctuation. Hence the slopes of the curves become small, but details are not clear at present. The slopes of the straight lines with 0.42 and 0.84 at%Zn alloy in Fig. 29 and all the straight lines in Fig. 30 correspond to the activation energy of about 0.82 eV. In these cases, because T_Q is high or the concentration of alloy is low, nearly random and homogeneous solid solution are obtained immediately after quenching and, thereafter, fluctuations are formed in the random solid solution. This value (about 0.82 eV) is, however, abnormally large compared with the migration energy of a Zn atom, 0.43 eV. This may be due to the difference among the final states obtained at each annealing temperature. This apparent activation energy being constant regardless of the concentration of alloy suggests a certain relation existing among the metastable states in alloys of different concentration when T_A is constant. At present, however, because details of the fluctuation are not clear, reasonable interpretation of the results above is difficult, and there is necessity for still more works.

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