

On the Formation and Growth of G.P. zones in Al-Zn Alloys above or below the Spinodal Temperature

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Synopsis

Measurements of electrical resistivity and intensity of small-angle X-ray scattering and transmission electron microscopy were made on Al-Zn alloys of several compositions. G.P. zones are formed by the nucleation-and-growth mechanism above the spinodal temperature. The nucleus has a critical size for growth. This size becomes larger when aged at higher temperatures. The sizes of the G.P. zones formed by this mechanism distribute broadly, but those formed by the spinodal decomposition do closely. The spinodal temperatures estimated for Al-10.0, 12.5, 15.0, and 20.0wt%Zn alloys are ~ 95 , ~ 110 , ~ 130 , and $\sim 180^\circ\text{C}$, respectively. The critical temperatures below which G.P. zones are observed in these alloys are ~ 115 , ~ 135 , ~ 160 , and $\sim 210^\circ\text{C}$, respectively.

1. Introduction

It has been confirmed that G.P. zones are formed by spinodal decomposition (S.D.) when Al-Zn alloys are aged at low temperature. Junqua *et al.* (1) determined the spinodal temperature (T_{sp}) precisely, by the measurement of magnetic susceptibility ($129 \pm 1^\circ\text{C}$ for Al-15 wt%Zn alloy), and revealed that G.P. zones are formed by nucleation-and-growth (N.G.) above T_{sp} . It is expected that there is an

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incubation time before initial change of properties, as is usually found in the precipitation, when G.P. zones are formed by N.G.. Delafond *et al.* (2) and the present authors (3) have reported some results on this phenomenon. Mimault *et al.* (4) recently considered theoretically the relation between the change of resistivity and that of the intensity profile of small-angle X-ray scattering (SAXS) which occur when G.P. zones are formed by S.D. or N.G..

In the present paper, some results obtained on the G.P. zone formation investigated mainly by the measurement of electrical resistivity and supplementarily by the measurement of SAXS intensity and the transmission electron microscopy (TEM) are reported.

2. Experimental Procedures

2.1. Specimen

Nominal compositions of the alloys used in this study were Al-10.0, 12.5, 15.0, and 20.0wt%Zn. Metals of 99.996%Al and 99.999%Zn were melt in the high-alumina crucible in air and cast into the steel mold. Ingots of 15 mm in diameter were homogenized for 50 hr at 450°C and hot-forged to the plates of 5 mm thick. These plates were cold-rolled several times, each after an intermediate annealing at 450°C, to sheets of the appropriate thickness for the measurements.

Specimens for the resistivity measurement were made by cutting the strips of 0.4 mm thick into the shape and size previously reported (5). Cold-rolled strips, 50 mm long, 10 mm wide, and 0.1 mm thick, were electropolished and used for the SAXS measurements. Their resistance was measured also, wires of the same alloy spot-welded as leads.

Thin films for TEM were prepared by electropolishing the strips of 0.1 mm thick in HClO_4 -EtOH solution after heat treatments.

2.2. Heat Treatments

Heat treatments were carried out as follows; specimens were set in the electric furnace at 500°C, kept there for 1 hr, furnace-cooled to the first quenching temperature (T_{q1} , 250~400°C), quenched to the second quenching temperature (T_{q2} , 150~200°C) after holding for 1 hr at T_{q1} , held for 1 hr at T_{q2} , quenched again into iced-water, and aged. Purpose of holding at T_{q2} was to slow down the rate of ageing by controlling the vacancy concentration, although the fluctuation of solute concentration may be formed at that temperature (6). Quenching

method was reported previously (5). Silicon oil was used for the quenching medium when the quenching temperature (T_q) was above 100°C, and water bath was used when it was below 100°C. Specimens were annealed in the silicon oil bath.

2.3. Measurements

Measurements of resistivity and SAXS intensity, and TEM were carried out in the same manner as in the previous report (7). Electrical resistivity was measured by the usual potentiometric method, specimens being kept in the liquid nitrogen. SAXS intensity was measured photographically. Specimens were kept nearly at the temperature of liquid nitrogen, and held in a vacuum together with the films during exposure. Measurements of blackness of the films, and evaluation of intensity were the same as described in the previous report (7). For TEM, HU-200E type electron microscope was used and operated at 100 or 200 kV.

3. Experimental Results

3.1. Electrical Resistivity

Fig. 1 shows isothermal ageing curves of the Al-15%Zn alloy at 127°C or 132°C when it was quenched from T_{q1} (400°C) to T_{q2} (150~200°C), held there for 1 hr, quenched again into iced-water at 0°C, and aged. Solid lines represent the ageing at 132°C; the resistivity increases a little for the first 30 sec, reaches a stationary value independent of T_{q2} , remains there for some time and begins to fall after ageing for about 60 min. This period where the resistivity stays at a stationary value can be considered as the incubation time. On the other hand, broken lines, which represent the ageing at 127°C, increase at first, arrive at a maximum and then decrease. The maximum values practically coincide each other. Time to reach the maximum is shorter for a higher T_{q2} and thus the curves were never coincide into one curve. At this ageing temperature G.P. zones are formed by spinodal decomposition (1), and resistivity changes in the same manner as was observed during ageing at a lower temperature than 127°C. Thus ageing behaviour at 127°C differs from that at 132°C.

Fig. 2 shows an isothermal ageing curve of the Al-15%Zn alloy at 100°C when T_{q2} =150°C (in the bottom), and ageing curves when the ageing temperature (T_a) was raised to 132°C on the way of ageing at

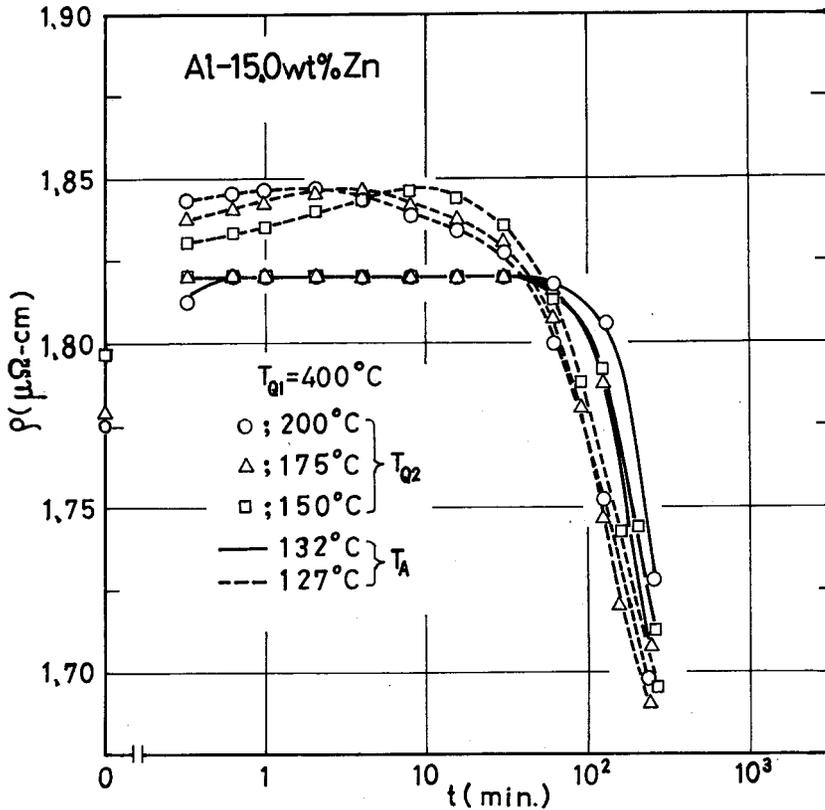


Fig.1 Isothermal ageing curves of the Al-15%Zn alloy at 127°C (dotted line) when quenched from T_{q1} (400°C) to T_{q2} (150~200°C), held at T_{q2} for 60 min and quenched again into iced-water.

100°C (in the top). When aged at 132°C after ageing for about 8 min or less at 100°C, resistivity decreases a little at first, but the curves, after ageing for some time, coincide with the later part of incubation period of the ageing at 132°C without preageing, that is, the curves thereafter are not influenced by the preageing. For the specimen preaged for 12 min at 100°C, resistivity decreases rather rapidly before the end of incubation period of direct ageing at 132°C without staying at a stationary value. When the preageing temperature was changed from 100°C to 127°C, preageing for upto 2 min did not eliminate the incubation period in the ageing curves at 132°C, but after preageing for 4 min or longer the period was not observed as in the several curves in Fig. 2. Fig. 3 shows a result when the ageing temperature, 132°C in Fig. 2, was replaced by 140°C. In this case, preageing for upto 10 min at 100°C did not influence the ageing at 140°C, that is, the ageing curves coincide with the curve without

preageing in the latter part, but preageing for 12 or 15 min did in the same manner as in Fig. 2.

Fig. 4 shows isothermal ageing curves of the Al-15%Zn alloy at a temperature 110~175°C after quenching from 400°C. Each curve decreases at first, then shows a gentle slope or a plateau and decreases again. The higher the ageing temperature is, when it is below 145°C, the larger the resistivity at the gentle slope is. On the other hand, when the ageing temperature is higher than 150°C, the higher the ageing temperature, the smaller the resistivity at the plateau is. SAXS intensity from the alloy aged at 132°C upto the stages each indicated by an arrow in the curve was measured and Guinier radius was obtained from the scattering intensity curve. G.P. zones could not be recognized in the alloy aged for 20 sec. Guinier radius was about 27 Å after ageing for 40 sec. The specimen aged for 20 sec at 127°C was also examined to compare and G.P. zones whose Guinier radius of about 43 Å were recognized. Guinier radius

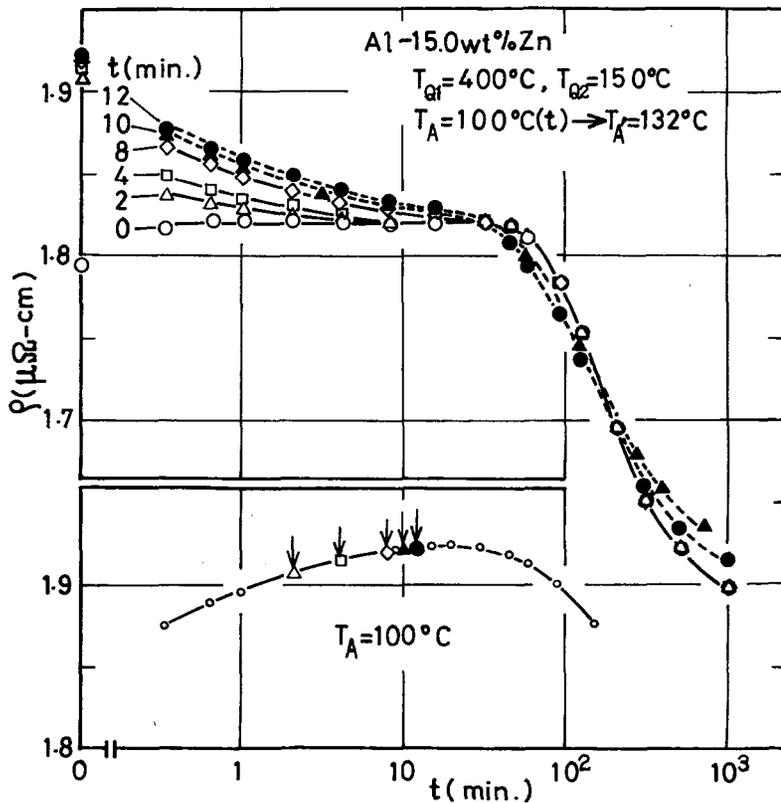


Fig.2 Isothermal ageing curve of the Al-15%Zn alloy at 100°C when $T_{q1} = 400^\circ\text{C}$, $T_{q2} = 150^\circ\text{C}$ and the holding time at T_{q2} is 60 min (in the bottom), and isothermal ageing curves at 132°C after ageing at 100°C

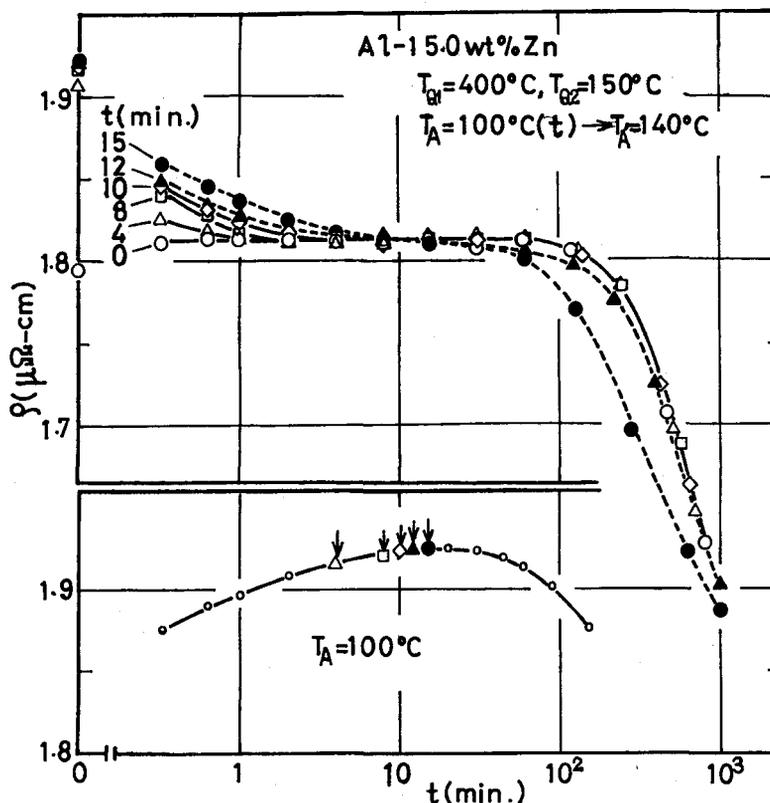


Fig.3 The same as Fig.2 but $T_a=140^{\circ}\text{C}$ instead of 132°C .

of the G.P. zones, present in the alloy aged at 132°C at the stage where the resistivity changed gently, was about 36 \AA and 40 \AA for 4 min and 30 min of ageing, respectively. Measurement of SAXS intensity of the alloy aged further has not been carried out. It was expected that the G.P. zones then would be grown further and that they would become ellipsoidal in shape when their radii were larger than 35 \AA (8). Therefore, it was not reasonable to evaluate Guinier radius, in such a case, from SAXS scattered by a polycrystalline specimen. Fig. 5 shows also ageing curves of the same alloy quenched from 300°C . Resistivity at the gentle slope increases with T_a below 145°C and decreases above 145°C , in the same manner as in Fig. 4.

Fig. 6 shows isothermal ageing curves of the Al-15%Zn alloy at 132°C when the alloys were quenched from various temperatures ($250\sim 500^{\circ}\text{C}$) to the ageing temperature. Resistivity in all curves decreases, rapidly at first, then gently and again rapidly. The value of resistivity at the gentle slope depends remarkably upon the quenching temperature and is lower for higher quenching temperature upto 400°C .

The resistivity for 500°C is larger than that for 400°C, inversely to the other, probably because the process of formation and growth of G.P. zones more or less modified by quenched vacancies of higher concentration.

Fig. 7 shows isothermal ageing curves of the Al-15%Zn alloy when the alloy was aged at a temperature 140~175°C after quenching from various temperatures. In the ageing curves at 175°C, the value of resistivity was constant and independent of T_q from 10 min upto the longest ageing time. When $T_a=150^\circ\text{C}$, it was also constant and independent of T_q upto 4000 min but began to decrease thereafter. There exist stages of gentle change in resistivity when $T_a=142^\circ\text{C}$ or 140°C , but the values of resistivity depend on T_q . At 132°C , G.P. zones are obviously formed and it can be deduced from Figs. 6 and 7 that the significant dependence of resistivity at the gentle slope on quenching temperature may be an evidence of the formation of G.P. zones. Difference in the value due to T_q is smaller for higher ageing temperature. Figs. 8~10 show also ageing curves of the alloy at 145, 127 and 110°C .

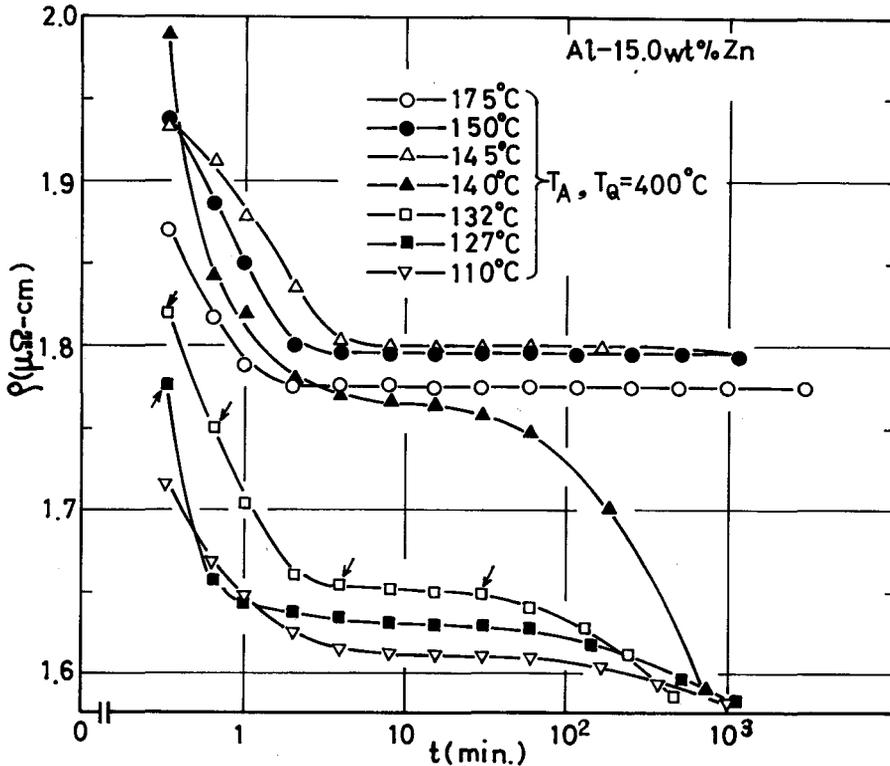


Fig.4 Isothermal ageing curves of the Al-15%Zn alloy at various temperatures after quenching from 400°C.

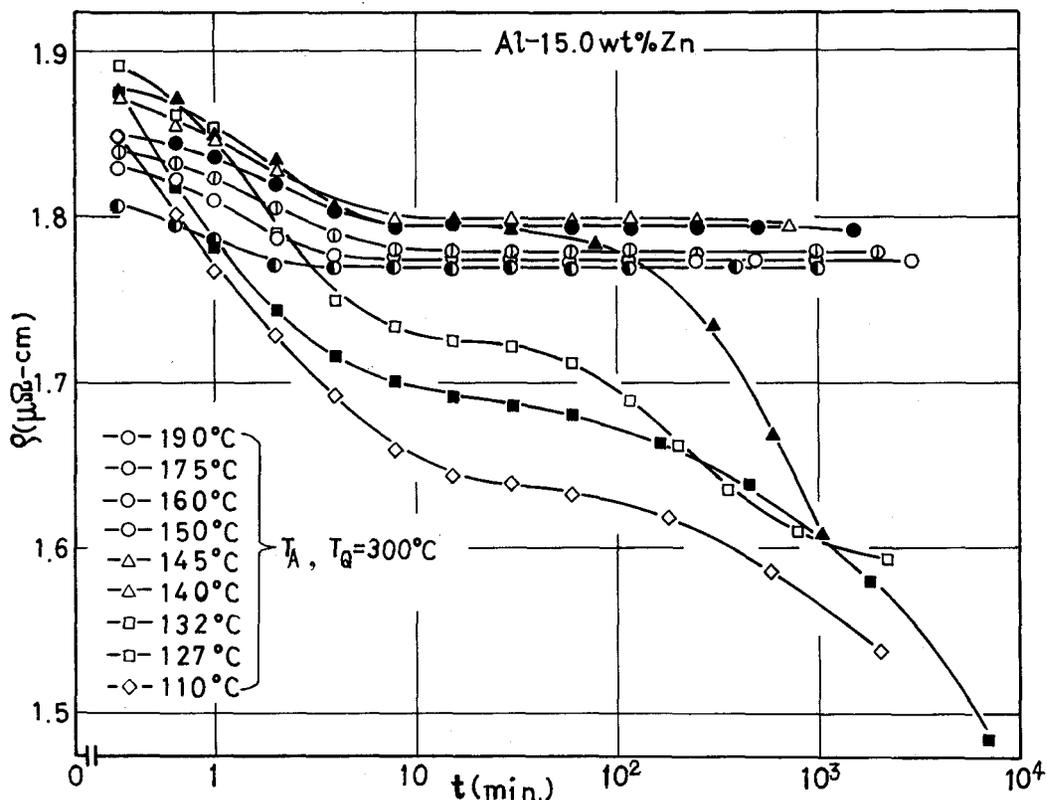


Fig.5 Isothermal ageing curves of the Al-15%Zn alloy at various ageing temperature after quenching from 300°C.

Fig. 11 shows isothermal annealing curves of the Al-15%Zn alloy at several temperatures after ageing for 2 min at 132°C (●,▲,■). Resistivity decreases after increasing for a while when annealed at 140°C or 150°C. When annealed at 160°C, however, it does not decrease and after a while coincide with that of annealing at 160°C without preageing (□). This means that G.P. zones are not formed at 160°C.

Fig. 12 shows isothermal ageing curves of the Al-20%Zn alloy at various temperatures when $T_{q2}=210^{\circ}\text{C}$. When T_a is lower than 170°C, resistivity increases in 20 sec, and decreases gradually thereafter. The increment at the beginning is larger for lower T_a and the ageing curves do not coincide each other. On the other hand, when T_a is higher than 180°C, resistivity increases a little in the first 20 sec, then stays at a stationary value thereafter, and begins to decrease after long ageing. The curves obtained when T_a is lower than 170°C, correspond probably to the stage after the maximum in

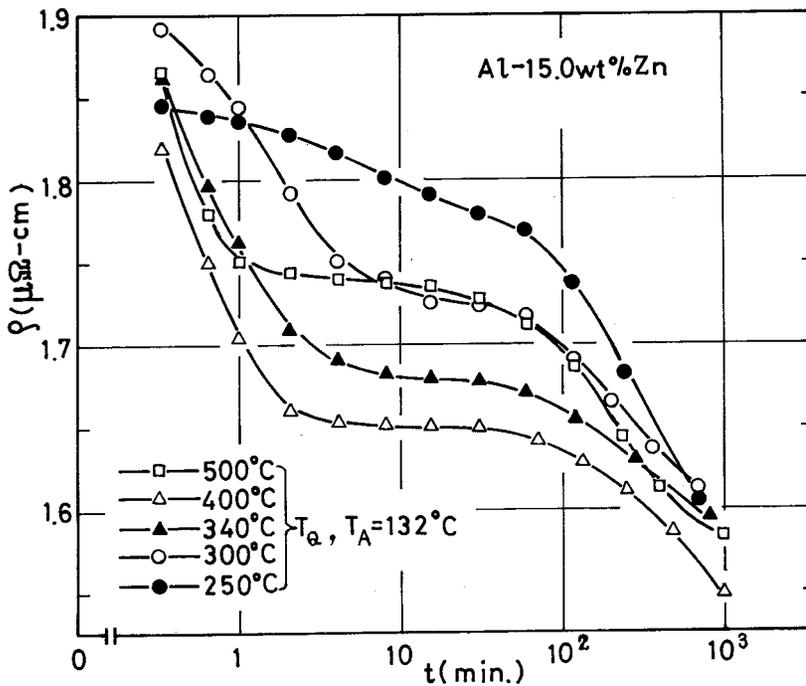


Fig.6 Isothermal ageing curves of the Al-15%Zn alloy at 132°C when quenched from various temperatures to the ageing temperature.

resistivity, the maximum being missing because of very rapid spinodal decomposition. The Al-10, 12.5 and 15%Zn alloy were also examined in the same way and the result of the 12.5%Zn alloy is shown in Fig. 13, for example. The maximum, missing in Fig. 12, was then present when the ageing temperature was not so high, because of the low concentration of the alloys. The ageing temperature above which maximum in resistivity is no longer observed was $\sim 95^\circ\text{C}$ and $\sim 110^\circ\text{C}$ for the 10%Zn and 12.5%Zn alloy, respectively.

Isothermal ageing curves of the Al-20%Zn alloy at $180\sim 210^\circ\text{C}$ are shown in Figs. 14~17 when T_q 's are varied. Similar results to those in the ageing of the 15%Zn alloy can be obtained, but the period in which the resistivity stays at a stationary value extends several hundred of minutes in this case, much longer than that in Fig. 7. The same examination as this was carried out on the 12.5%Zn and 10%Zn alloy and the results are shown in Figs. 18~23 and Figs. 24~27. Similar results to those in Fig. 7 were obtained. The temperature, which corresponds to 150°C in Fig. 7 was 125°C and 105°C for the 12.5 %Zn and 10%Zn alloy, respectively.

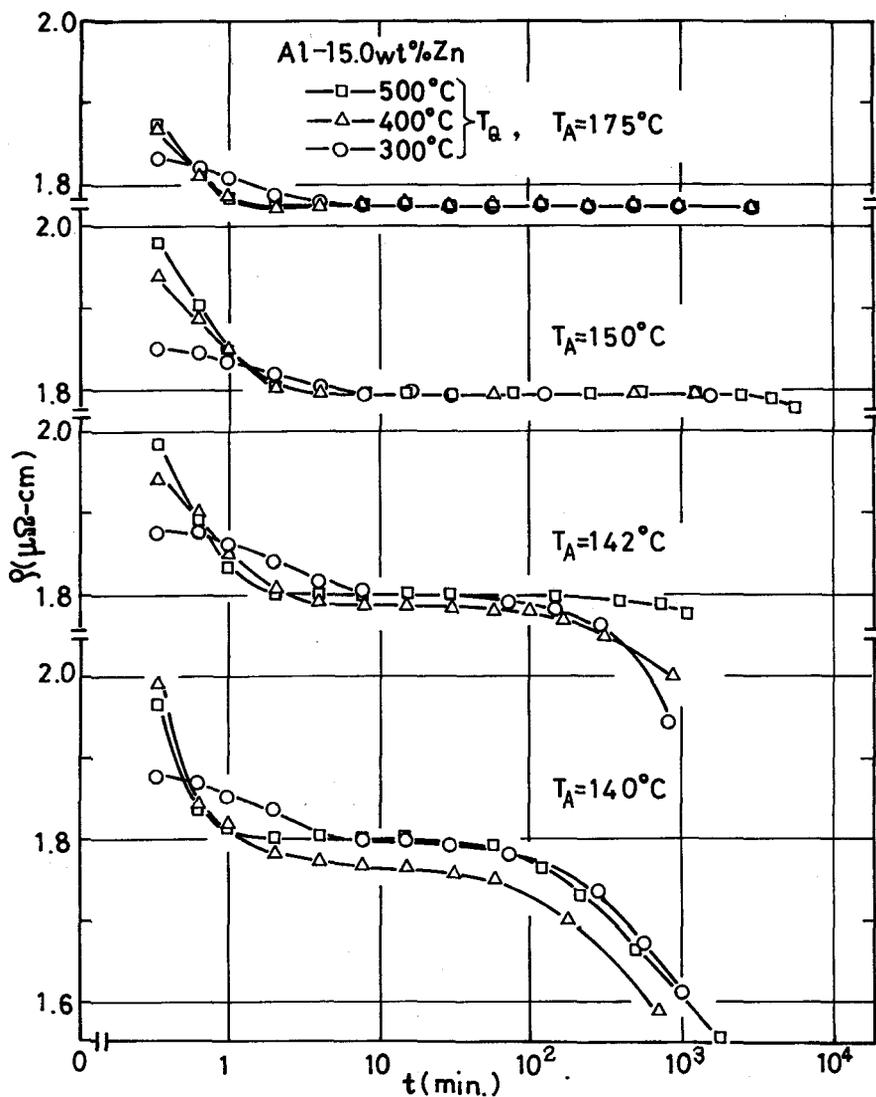


Fig.7 Isothermal ageing curves of the Al-15%Zn alloy at 175°C, 150°C, 142°C and 140°C after quenching various temperatures

3.2. TEM

Photo 1 shows transmission electron micrographs of the Al-15%Zn alloy when it was quenched from 400°C to 150°C, held there for 60 min, and then aged for 600 min at 132°C and 127°C. G.P. zones with very different sizes were observed and larger ones of them appear to be oblate ellipsoidal of 70~80 Å in radius, when the alloy was aged for 600 min at 132°C. Density of G.P. zones in the case was

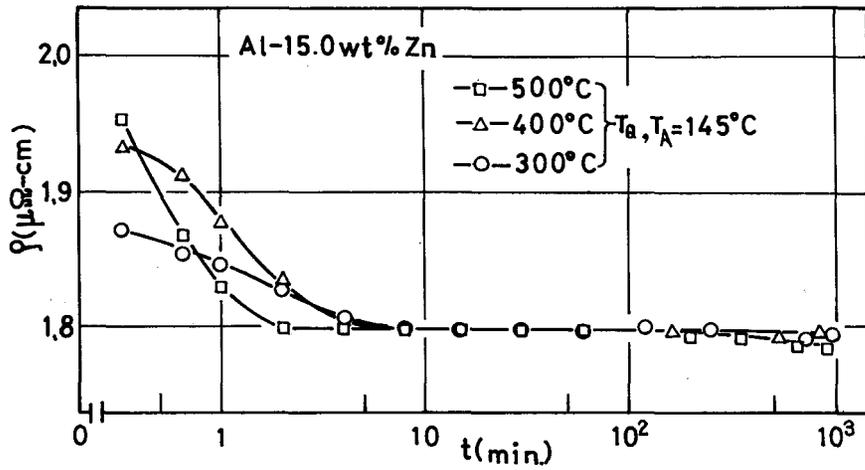


Fig.8 Isothermal ageing curves of the Al-15%Zn alloy at 145°C after quenching from various temperatures

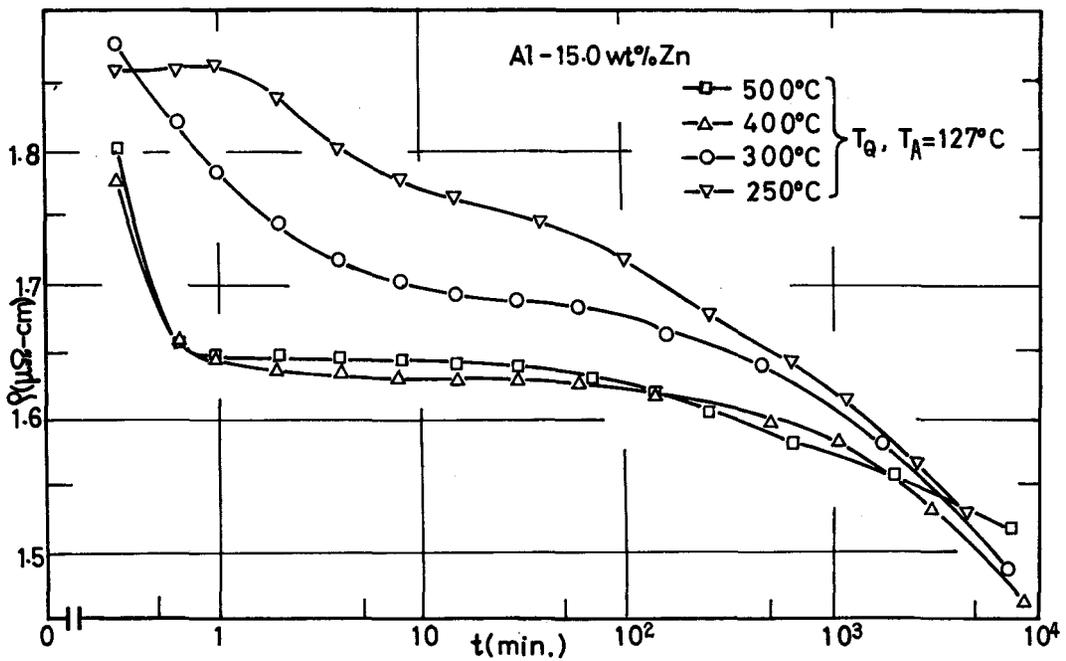


Fig.9 Isothermal ageing curves of the Al-15%Zn alloy at 127°C after quenching from various temperatures

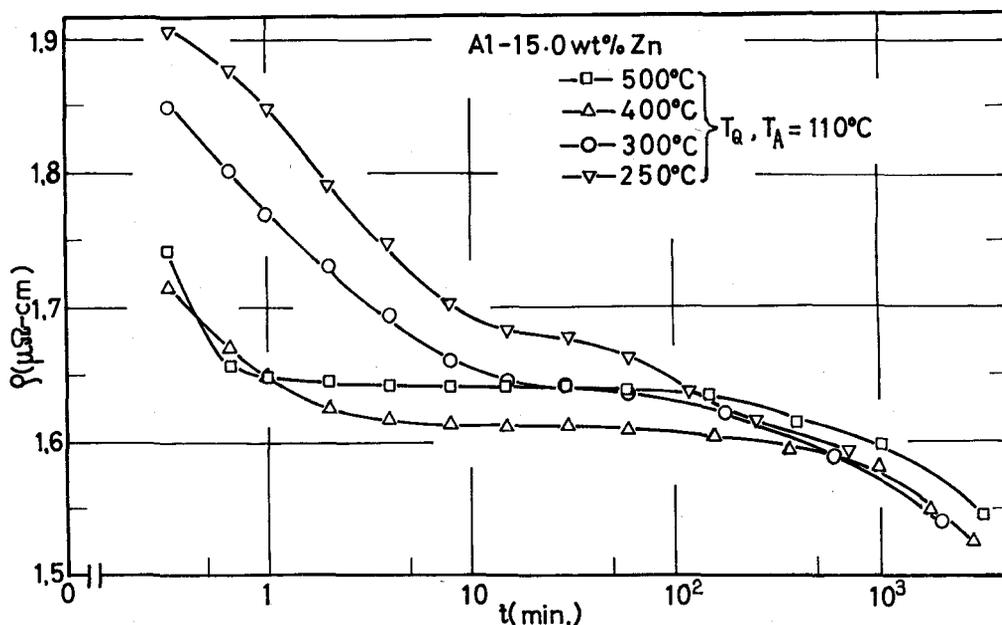


Fig.10 Isothermal ageing curves of the Al-15%Zn alloy at 110°C after quenching from various temperatures

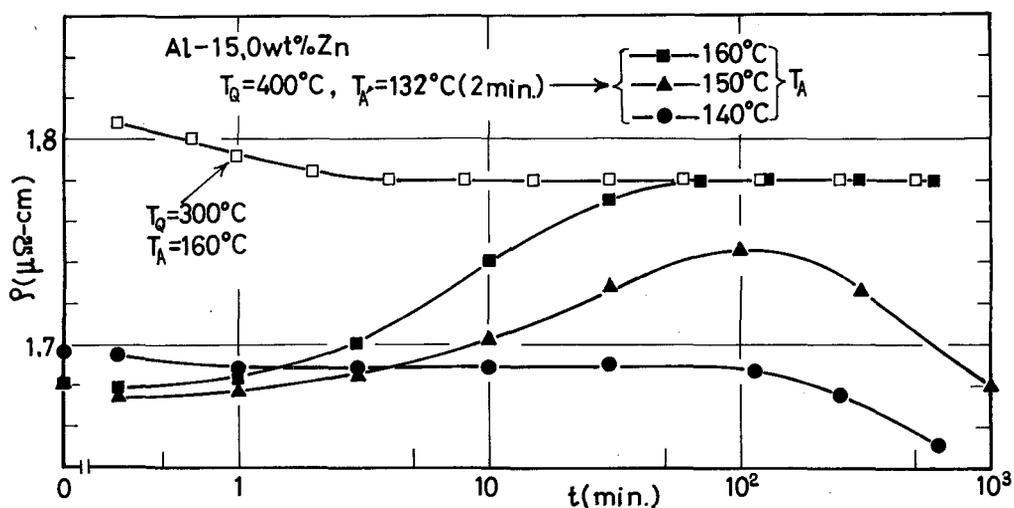


Fig.11 Isothermal annealing curves of the Al-15%Zn alloy at 140°C, 150°C and 160°C after ageing for 2 min at 132°C (●,▲,■), and isothermal annealing curve of the Al-15%Zn alloy at 160°C after quenching from 300°C.

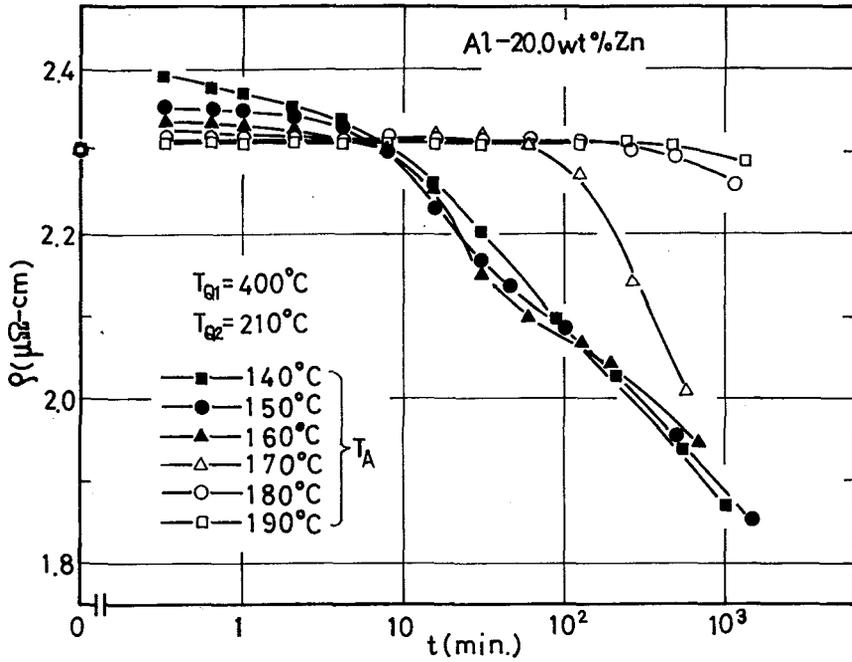


Fig.12 Isothermal ageing curves of the Al-20%Zn alloy at various temperatures when quenched from 400°C to 210°C, held there for 60 min and quenched again to 0°C.

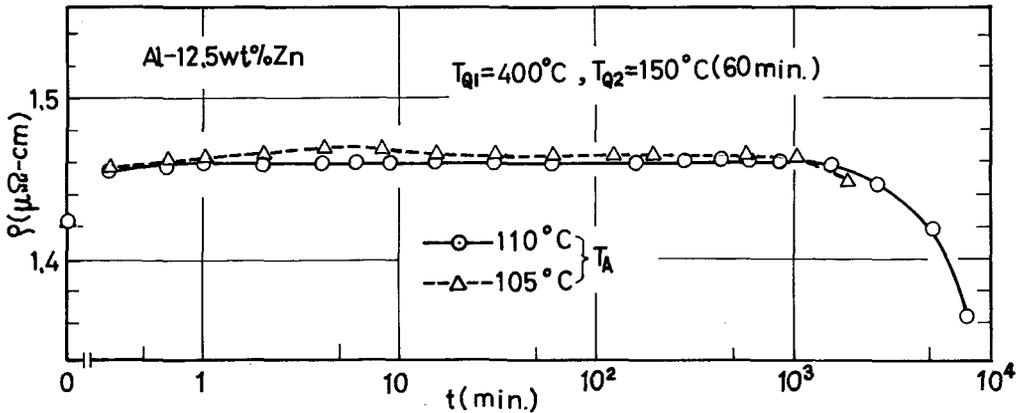


Fig.13 Isothermal ageing curves of the Al-12.5%Zn alloy at 105°C and 110°C when quenched from 400°C to 150°C, held there for 60 min and quenched again to 0°C. Maximum, missing in Fig.12, can be observed.

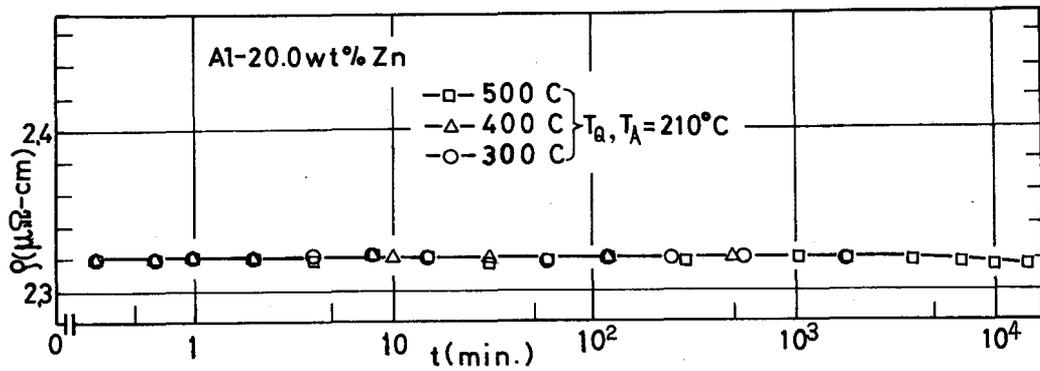


Fig.14 Isothermal ageing curves of the Al-20%Zn alloy at 210°C after quenching from various temperatures

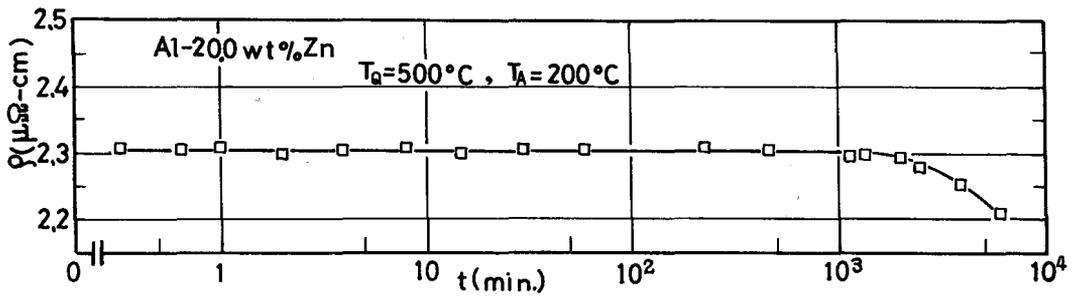


Fig.15 Isothermal ageing curves of the Al-20%Zn alloy at 200°C after quenching from various temperatures

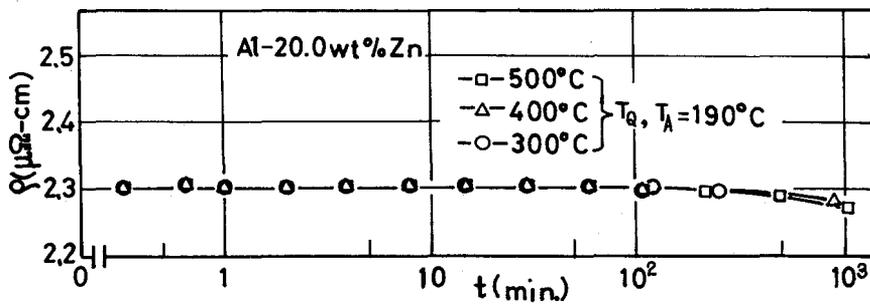


Fig.16 Isothermal ageing curves of the Al-20%Zn alloy at 190°C after quenching from various temperatures

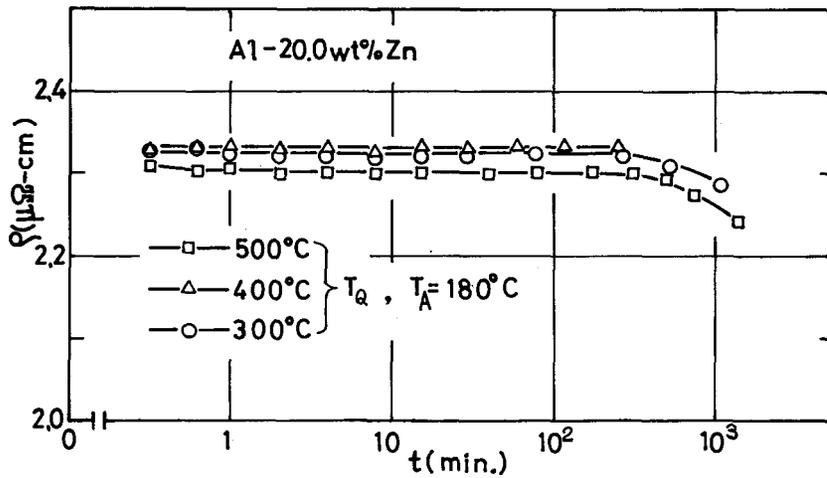


Fig.17 Isothermal ageing curves of the Al-20%Zn alloy at 180°C after quenching from various temperatures

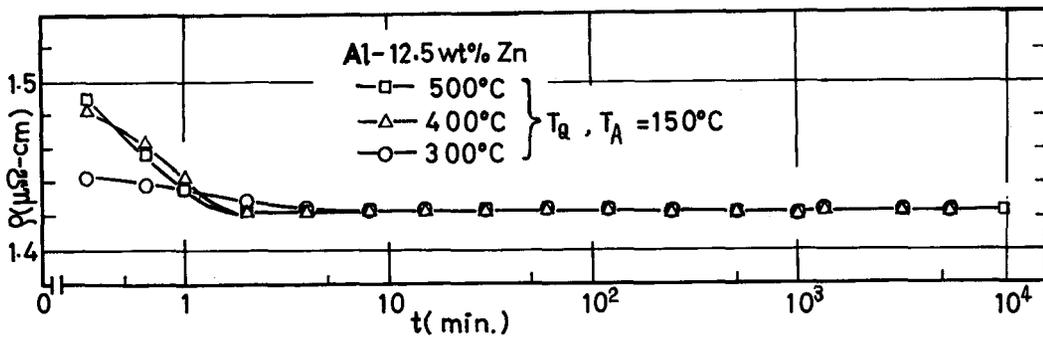


Fig.18 Isothermal ageing curves of the Al-12.5%Zn alloy at 150°C after quenching from various temperatures

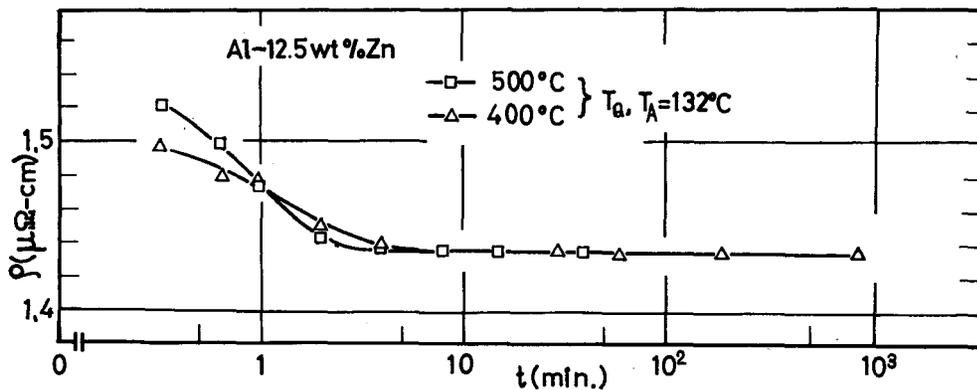


Fig.19 Isothermal ageing curves of the Al-12.5%Zn alloy at 132°C after quenching from various temperatures

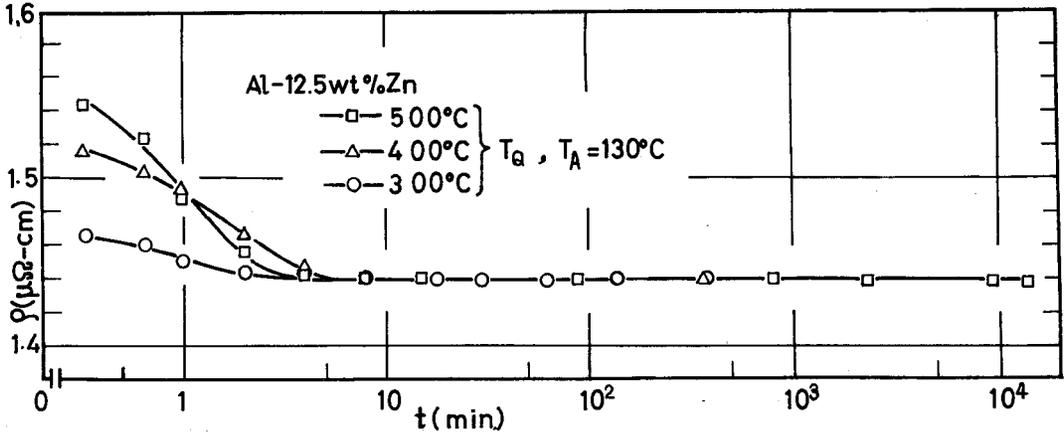


Fig.20 Isothermal ageing curves of the Al-12.5%Zn alloy at 130°C after quenching from various temperatures

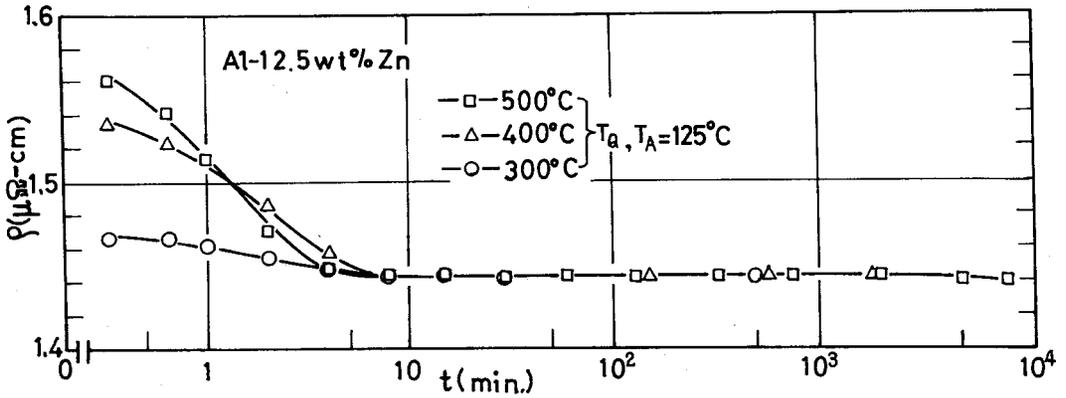


Fig.21 Isothermal ageing curves of the Al-12.5%Zn alloy at 125°C after quenching from various temperatures

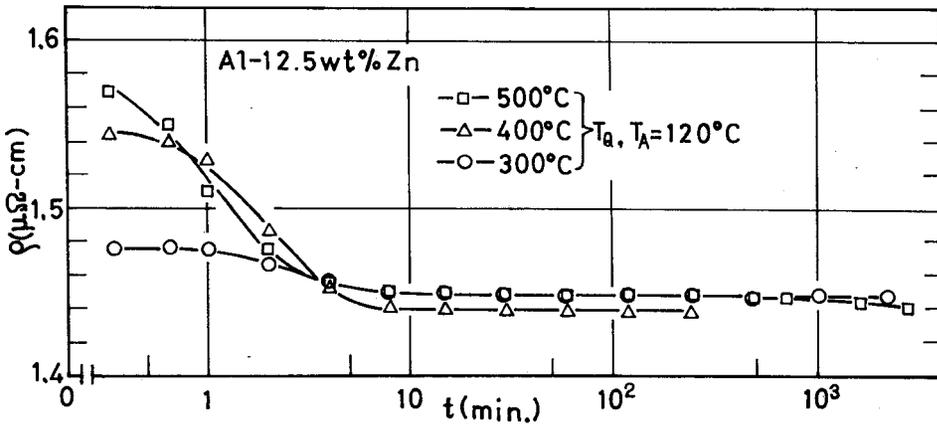


Fig.22 Isothermal ageing curves of the Al-12.5%Zn alloy at 120°C after quenching from various temperatures

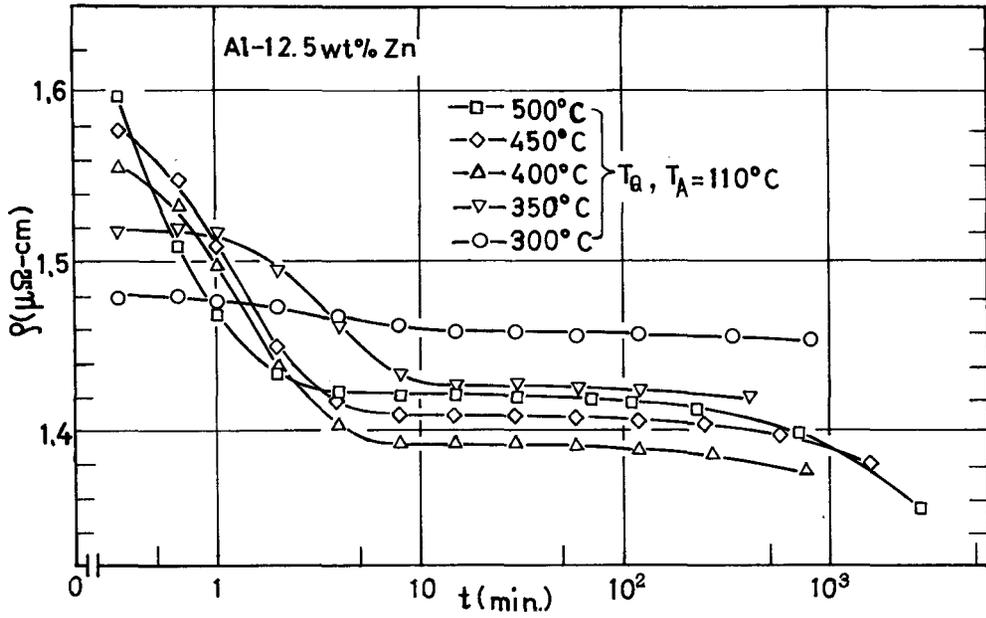


Fig.23 Isothermal ageing curves of the Al-12.5%Zn alloy at 110°C after quenching from various temperatures

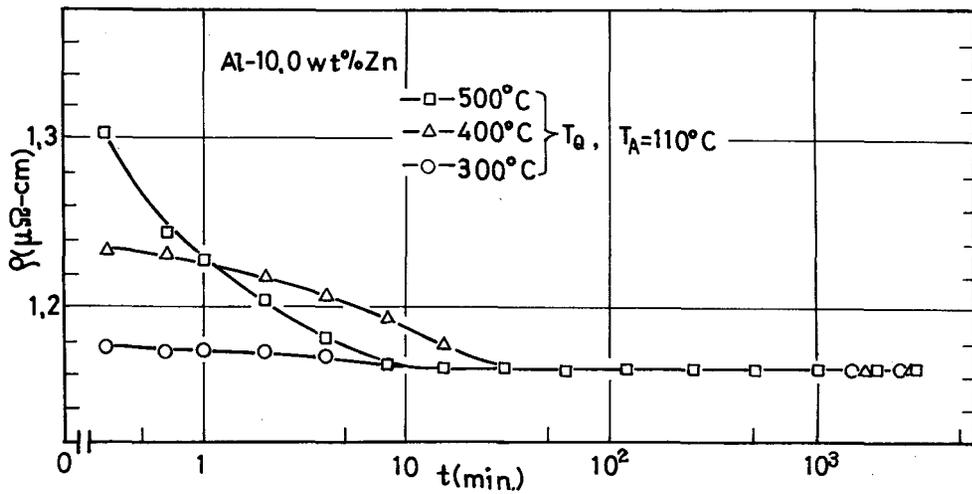


Fig.24 Isothermal ageing curves of the Al-10%Zn alloy at 110°C after quenching from various temperatures

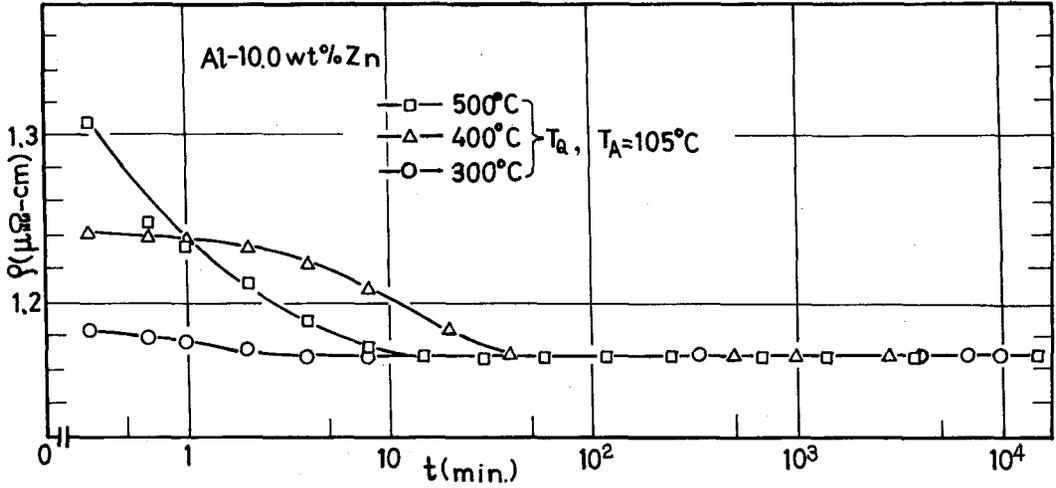


Fig.25 Isothermal ageing curves of the Al-10%Zn alloy at 105°C after quenching from various temperatures

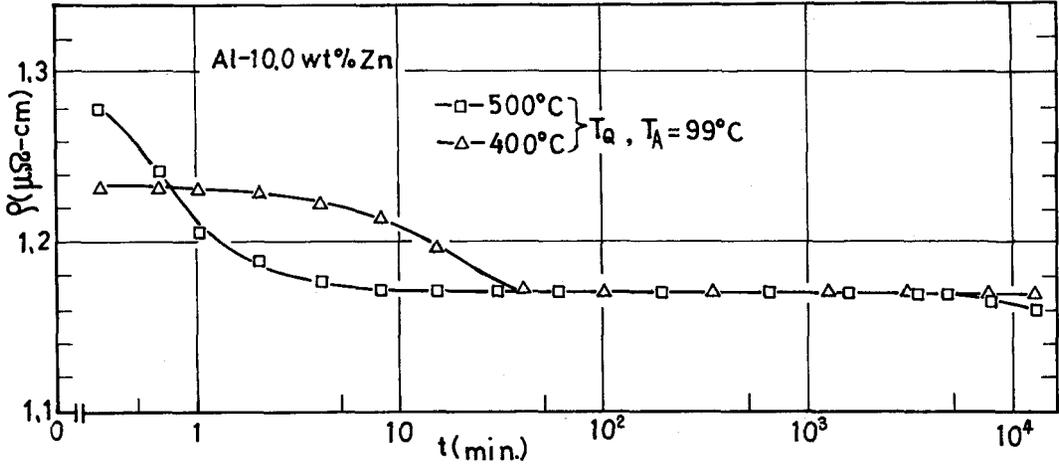


Fig.26 Isothermal ageing curves of the Al-10%Zn alloy at 99°C after quenching from various temperatures

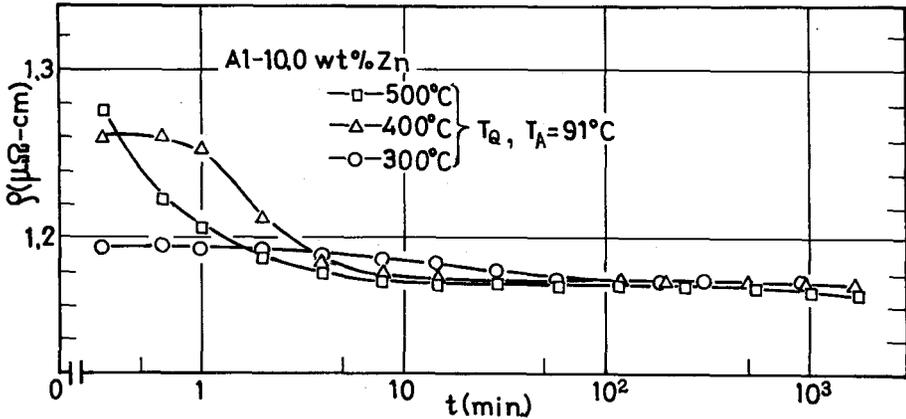
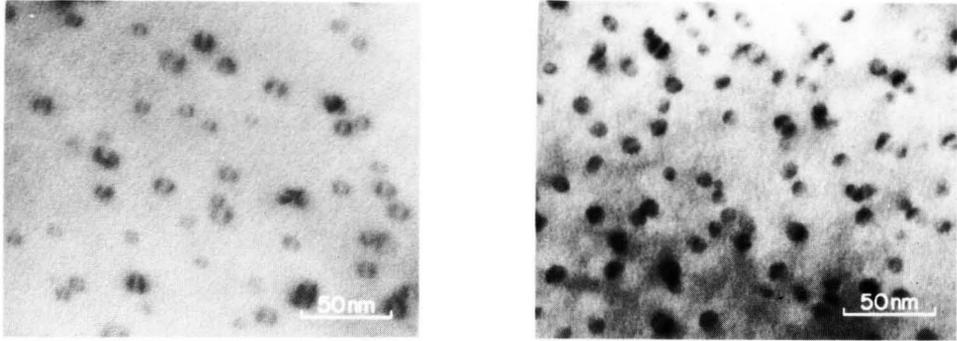


Fig.27 Isothermal ageing curves of the Al-10%Zn alloy at 91°C after quenching from various temperatures



$T_a = 132^\circ\text{C}$

$T_a = 127^\circ\text{C}$

Photo 1 Transmission electron micrographs of the Al-15%Zn alloy aged at 132°C and 127°C for 600 min when the specimens were quenched from 400°C to 150°C and held there for 60 min.

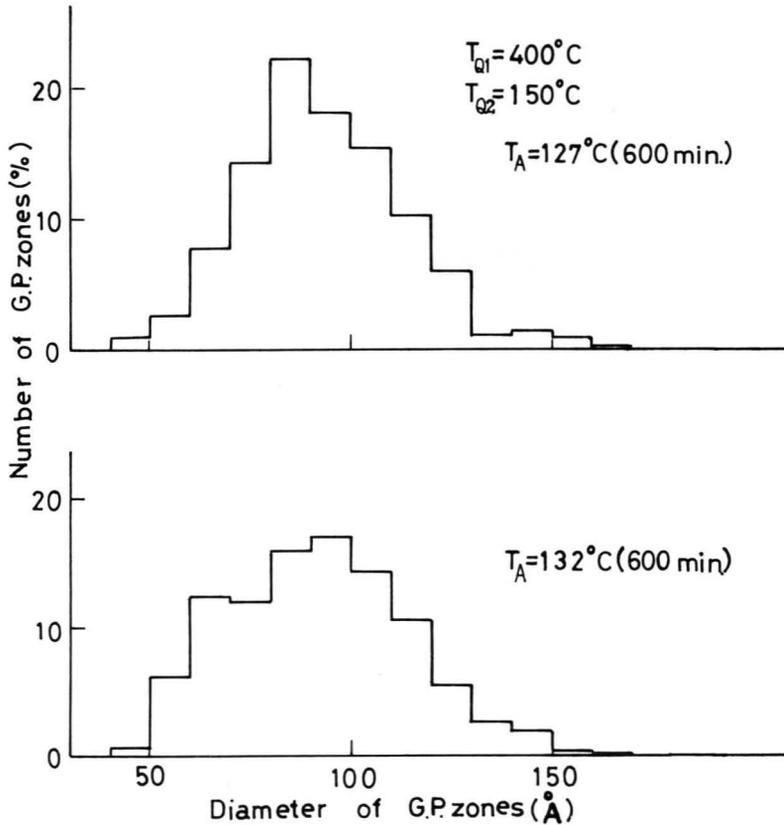


Fig.28 Size distribution of G.P. zones obtained from Photo 1

$3.2 \times 10^{15} \text{ cm}^{-3}$. On the other hand, when the alloy was aged for 600 min at 127°C , large number of G.P. zones nearly of the same size, $40 \sim 50 \text{ \AA}$ in radius, were observed and their density was $2.2 \times 10^{16} \text{ cm}^{-3}$. Specimen aged for a short time (10~15 min) at 132°C or 127°C was examined by TEM but G.P. zones could not be found.

Size distribution of the G.P. zones was examined in 640 G.P. zones from each of the Photo 1. The histograms obtained are shown in Fig. 28. Size distribution of G.P. zones is broad when the alloy was aged for 600 min at 132°C , and is narrow when aged for 600 min at 127°C .

Y-phase (9) was observed, but has not yet been investigated in detail because it does not seem to have important effects on the present processes. TEM was carried out also in the case that the Al-20%Zn alloy was aged for about 1000 min at 190°C or 200°C after quenching from 400°C directly to the ageing temperature, but the photographs are omitted. In this case small number of G.P. zones were observed for the ageing at 190°C and no G.P. zones but heterogeneous precipitation on dislocations was found for the ageing at 200°C .

4. Discussions

Murakami *et al.* studied on T_{sp} by SAXS and determined T_{sp} for Al-15wt%Zn alloy to be $120 \sim 130^\circ\text{C}$ (10). This value was confirmed by Junqua *et al.* with the measurement of magnetic susceptibility and others (1). Kabisch *et al.*, on the other hand, determined this temperature for Al-18wt%Zn alloy to be $\sim 110^\circ\text{C}$ by practically the same method, and deduced that T_{sp} for Al-15wt%Zn alloy would be relatively low, 60°C or so (11). Their study, however, was lack in strict consideration to the integrated intensity and others. Rundman *et al.* reported that S.D. had already been over during quenching or before the first measurement (12). Yamaguchi *et al.* also has recently reported on T_{sp} (13). The value of T_{sp} obtained by Murakami *et al.* and Junqua *et al.* is considered as far to be reliable.

G.P. zones are formed by N.G. above T_{sp} , as shown by Junqua *et al.* with susceptibility measurements (1), and it is expected that, in case of N.G., incubation time may be recognized by the measurement of resistivity. Delafond *et al.* reported that the incubation period was recognized and the resistivity decreased relatively monotonically

after this period above T_{sp} (2). Quenching temperature in their experiment was mainly 180°C . In the present study the incubation period was clearly observed and the effects of the quenching temperature were investigated. Although T_q was sometimes low, G.P. zones, as is known from Fig. 7, was not formed during the holding time. Therefore, only the fluctuation of solute concentration must be taken into consideration. Influence of T_q , in addition to the results reported by Delafond *et al.* (2), can be recognized in Fig. 1 when the alloys are aged at the temperature several degrees above or below T_{sp} . Fluctuation of solute concentration at T_q should be taken into consideration because T_q then was relatively low. The higher the T_q is, the smaller the value of ρ_0 (as-quenched resistivity) is. These results are mainly due to the fluctuation of solute concentration at the quenching temperatures, and do not correspond to the vacancy concentration (6). Spinodal decomposition then occurs either in the concentrated and dilute region of the fluctuation and ageing curves suffer a change more or less (7). It has not been known experimentally whether the fluctuation alters T_{sp} value or not. But it may be assumed that T_{sp} was not affected considerably, because important change, *e.g.* appearance of the incubation period, was not brought in the ageing curves for $T_a < T_{sp}$. The small but rapid increase in ρ , observed in Fig. 1 at the beginning of the ageing at 132°C , is a transition from the state of fluctuation at T_q to that at 132°C and the period thereafter where ρ remains constant is an incubation. Length of this period does not change with T_q . Ageing curves at 127°C are essentially similar in their behaviour to those at a lower ageing temperature. These curves are much affected by T_q and the ageing proceeds more rapidly as T_q becomes higher; change in ρ starts immediately after quenching and rate of the change is influenced by the concentration of quenched vacancies. It is considered from these results that the ageing processes at 127°C and 132°C are different; the former is a formation and growth of G.P. zones by S.D. and the latter is by N.G.. The value of T_{sp} obtained in a similar way, for example, from Figs. 12 and 13, was $\sim 95^{\circ}\text{C}$ for the Al-10%Zn, $\sim 110^{\circ}\text{C}$ for the Al-12.5%Zn, and $\sim 180^{\circ}\text{C}$ for the Al-20%Zn alloy.

G.P. zones formed by S.D. and N.G. in Al-15wt%Zn alloy were observed with TEM by Laslaz *et al.* (14). The present authors payed attention to size distributions of G.P. zones formed by either mechanism. It is expected that width of the size distribution of G.P. zones formed by S.D. is relatively narrow because large number

of zones of nearly the same size are formed and grown simultaneously. In the case of the formation by N.G., it is expected, size distribution becomes broader than that of S.D., because nuclei which reach the critical size at the ageing temperature are grown successively. Histograms in Fig. 28 show the tendency in accord with the prospect.

The results in Figs. 2 and 3 suggest an increase of the critical size of G.P. zones for N.G. with ageing temperature. As ageing proceeds by S.D. in a dilute alloy, G.P. zones for which Porod's approximation holds in SAXS intensity come to be recognized (15). These zones revert in the same temperature range as the zones formed by N.G. (15), and thus they can be considered to be the same in their thermal stability. It may be true that in the present study also G.P. zones which have been formed by S.D. and grown to a certain extent, can play the role of nuclei for N.G.. Therefore, the above mentioned inference on the size of nuclei may be possible.

Figs. 4~7 show the results of the experiments which were performed to obtain the upper limit temperature of the formation of G.P. zones in the Al-15%Zn alloy. Figs. 4 and 5 show results of the ageing of a fixed T_q and various T_a 's. ρ is likely to show plateau at the later stage of ageing in both cases, S.D. and N.G.. Even in the later stage also, G.P. zones sometimes, depending on T_q and T_a , grow and increase their sizes, as was described above. This stationary value of ρ , denoted by ρ_E , increases with T_a , but contrarily, when T_a becomes higher than 150°C, it decreases with T_a . It is considered that ρ takes a value corresponding to the state which includes a fluctuation at these higher temperatures. These results are the same as has been obtained in more dilute alloys (6). Figs. 6~10, each shows ageing curves of a fixed T_a and various T_q 's. It may be seen in these figures that ρ_E depends on T_q when the alloys contain no G.P. zones but fluctuation of solute concentration at the temperature. Dependence of ρ on T_q at the stage of such a gentle change may be, therefore, regarded as one of the evidences for the formation of G.P. zones. Furthermore, the critical temperature below which G.P. zones are formed ($T_{G.P.}$) may be evaluated when it is ascertained that the resistivity does not begin to fall again on further ageing as long as possible. It was inferred that the temperature for the Al-15%Zn was ~160°C. A result obtained in almost the same experiment was reported on Al-15wt%Zn alloy by Takahashi *et al.* (16, 17) and their value agrees well with the present result. They plotted ρ_{flat} (ρ_E in the present paper) against T_a and assign the

temperature above which ρ_{flat} remains a stationary value to the limit temperature of G.P. zone formation. The present authors have employed the method above mentioned because (1) $\rho_E(\rho_{\text{flat}})$ decreases more or less with ageing time and (2) ρ_E takes considerably different values depending on the combination of T_G and T_a (18). The result on $T_{\text{G.P.}}$, however, agrees well with that of Takahashi *et al.*. They reported that ρ_{flat} did not depend on T_a higher than $T_{\text{G.P.}}$, but in the present result ρ_E decreases with T_a , a little as it is. When T_a was higher than 100°C in the present experiment, the specimen was once quenched

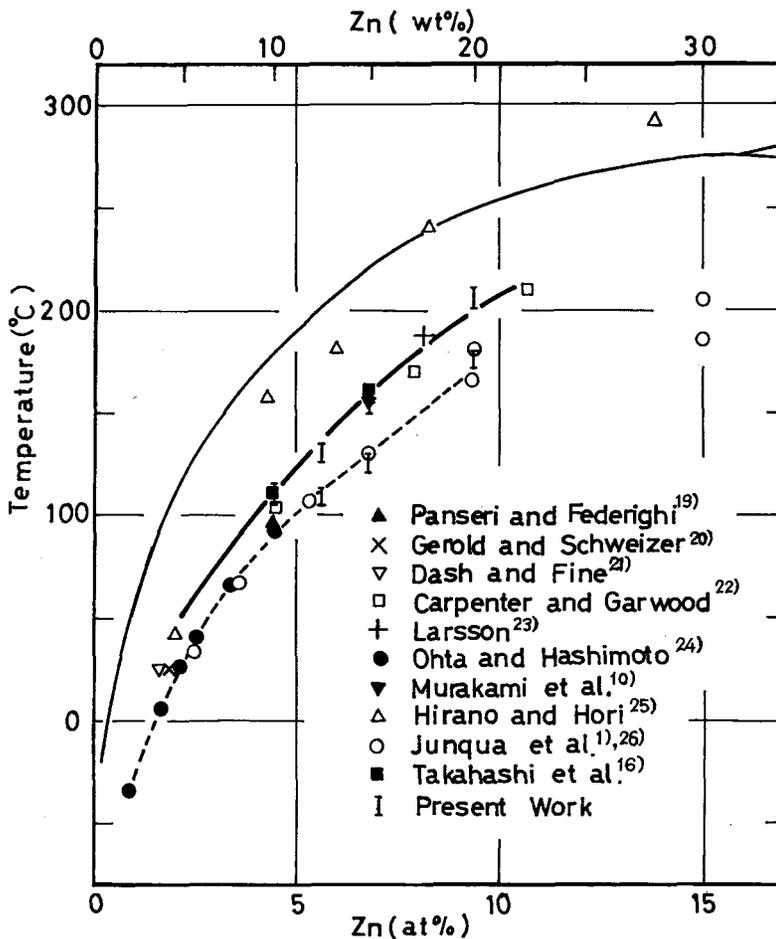


Fig.29 Phase diagram of Al-Zn

----- : Spinodal curve for G.P. zones in Al-Zn alloy

———— : The highest temperatures below which G.P. zones are formed

———— : Solvus curve for zinc in Al-Zn alloy (27)

from T_a into iced-water and was transferred quickly into liquid nitrogen before each resistivity measurement. If the specimen was quenched directly into liquid nitrogen, the results coincident with those of Takahashi *et al.* was obtained in authors' laboratory. G.P. zones may possibly be formed during the slow cooling in liquid nitrogen. The value of ρ thus measured is larger than the present value and seems to be independent of T_a .

The result in Fig. 11 agrees with that of Murakami *et al.* (10), although G.P. zones in the present study have been formed at 132°C by nucleation-and-growth in contrast to the fact that G.P. zones in their study were formed at room temperature by spinodal decomposition.

Figs. 14~17, 18~23 and 24~27 show respectively the results of the Al-20%Zn, 12.5%Zn and 10%Zn alloy, in which the same results as those observed for the Al-15%Zn alloy are found. $T_{G.P.}$ obtained by such a method are ~115°C, ~135°C and ~210°C for the 10, 12.5 and 20% Zn alloy, respectively. These values, with the values of T_{sp} obtained above, are plotted in the phase diagram in Fig. 29. The present results agree practically well with the previous ones.

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