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Effects of the Fluctuation of Solute Concentration in Al-Zn Alloys on the Aging at Low Temperatures; I. Measurements of Electrical Resistivity

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Synopsis

Aging process in Al-Zn alloys was studied by the measurements of the electrical resistivity when the alloy was quenched from a high temperature, about 300°C (the first quenching temperature), to an intermediate temperature, between 110°C and 230°C (the second quenching temperature), held at this temperature for a time, quenched again into iced water and aged at a low temperature. Variation of the holding time at the second quenching temperature brings about the variation of the isothermal aging curves. Maximum resistivity of the isothermal aging curve, ρ_{max}, decreases at first, passes a minimum and then increases to reach a stationary value as the holding time at the intermediate temperature increases. It is pointed out that this phenomenon is mainly due to the fluctuation of solute concentration and the vacancy concentration decreasing at the intermediate temperature.

1. Introduction

Aging behaviors in Al-Zn alloys have been studied by many authors. In these studies, however, the alloys were quenched from relatively high temperatures, and the homogeneous supersaturated

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solid-solution was assumed to be the starting state of the aging. However, it is known that there are fluctuations of solute concentration in the solid solution (1). Present authors also reported the exixtence of "clusters" in the solid solution, measuring the resistivities of relatively dilute alloy above and below the solvus in the equilibrium phase diagram (2). The term "clusters" is apt to be understood as small aggregates of a few solute atoms, and indeed Guinier et al. (3) explained their results of the small-angle X-ray scattering by means of this model. Previous results of the present authors cannot give the decision whether they are aggregates of solute atoms or fluctuations of solute concentration, but comparing with the results of the concentrated alloys (4~6) they may more reasonably be considered as fluctuations.

When the alloys are quenched from a relatively low temperature, at which such fluctuations exist, and aged at a low temperature, the fluctuation may influence on the formation and growth of G.P. zones and so the aging behavior may show some difference from the case where the alloys are quenched from a higher temperature, for instance above 300°C, and aged at a low temperature. The aging behaviors of Al-Zn alloys quenched from lower temperatures were investigated by means of measurements of electrical resistivity.

2. Experimental Procedures

2. 1 Specimens

Al-Zn alloys, nominal compositions being Al-6.0. 7.0, 8.0, 10.0 and 15.0wt%Zn, were prepared from pure elements of 99.996%Al and 99.999%Zn. The alloy was melted in alumina crucible in air and cast into metallic mold. The ingot was homogenized at 500°C for 50hr, hot-forged to sheets of 5mm in thickness and cold-rolled to strips of 0.4mm in thickness. Specimens for measurements of electrical resistivity were cut from these strips in the shape previously reported (7).

2. 2 Heat Treatments

The specimen was quenched from a usual quenching temperature (first quenching temperature, T_{Q1}) into the silicon-oil bath at an intermediate temperature(second quenching temperature, T_{Q2}) where significant fluctuation was expected to occur and G.P. zones or Y-phase precipitates (8) were not formed. The quenching method was the same as previously reported (9). After holding at the intermediate temperature for a time, the specimen was quenched again into iced water and transfered quickly into liquid nitrogen. Then it was aged isothermally in the liquid bath.

2. 3 Measurements of Electrical Resistivity

Elecrical resistivity was measured by a usual potentiometric method, specimens being emerged in liquid nitrogen. Effect of the temperature change of liquid nitrogen was corrected with a well-annealed dummy of the alloys of the same composition. Resistivity was calculated from the dimention and weight of the specimen, where the average of as-quenched resistivities was used as the reference when the specimen was quenched several times from 300°C into iced water.

3. Results

In Fig.1 isothermal aging curves of the Al-10wt%Zn alloy at 0°C are shown when T_{Q1}=300°C, T_{Q2}=130°C and the holding time at T_{Q2} ($t(T_{Q2})$) was changed. The shape of these curves resemble each other. The process is delayed as $t(T_{Q2})$ increases. The maximum resistivity

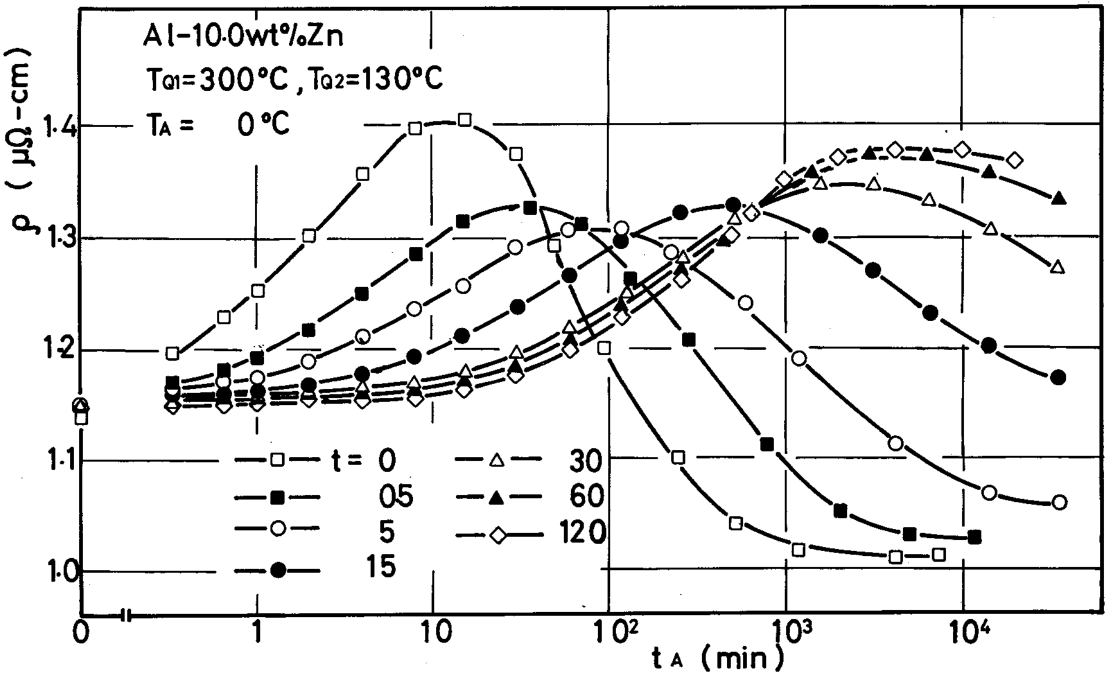

Fig.1 Isothermal aging curves of the Al-10wt%Zn alloy at 0°C when $t(T_{Q2})$ is changed. T_{Q1}=300°C, T_{Q2}=130°C.

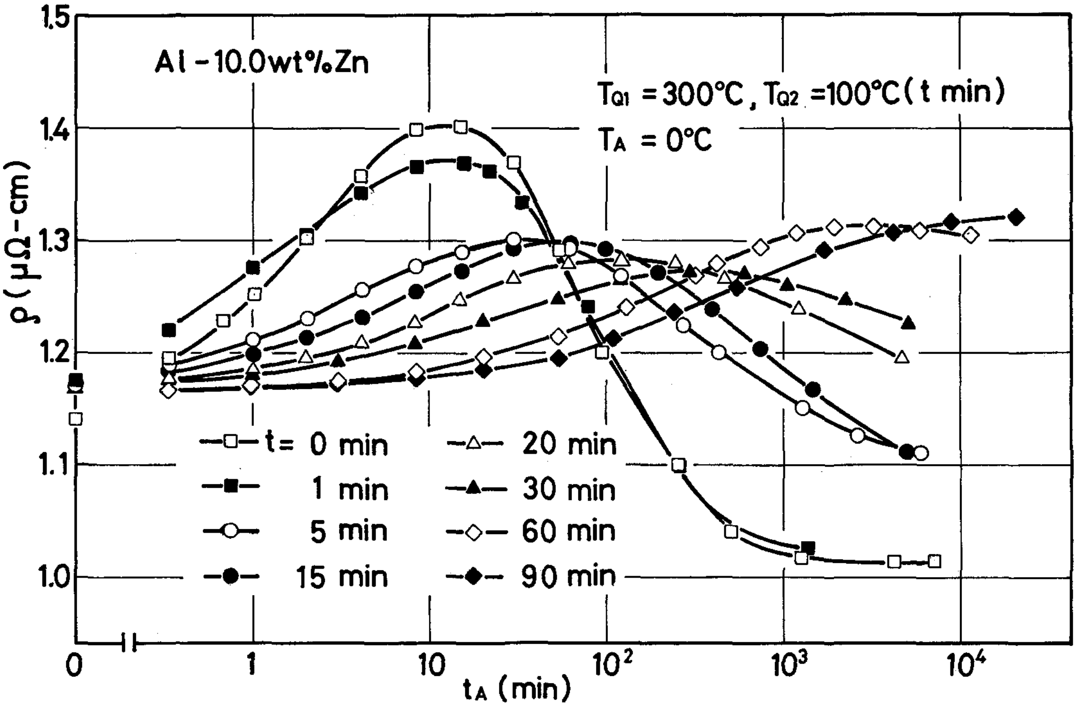

Fig.2. Isothermal aging curves of the Al-10wt%Zn alloy at 0°C when t(T_{Q2}) is changed. T_{Q1}=300°C, T_{Q2}=100°C.

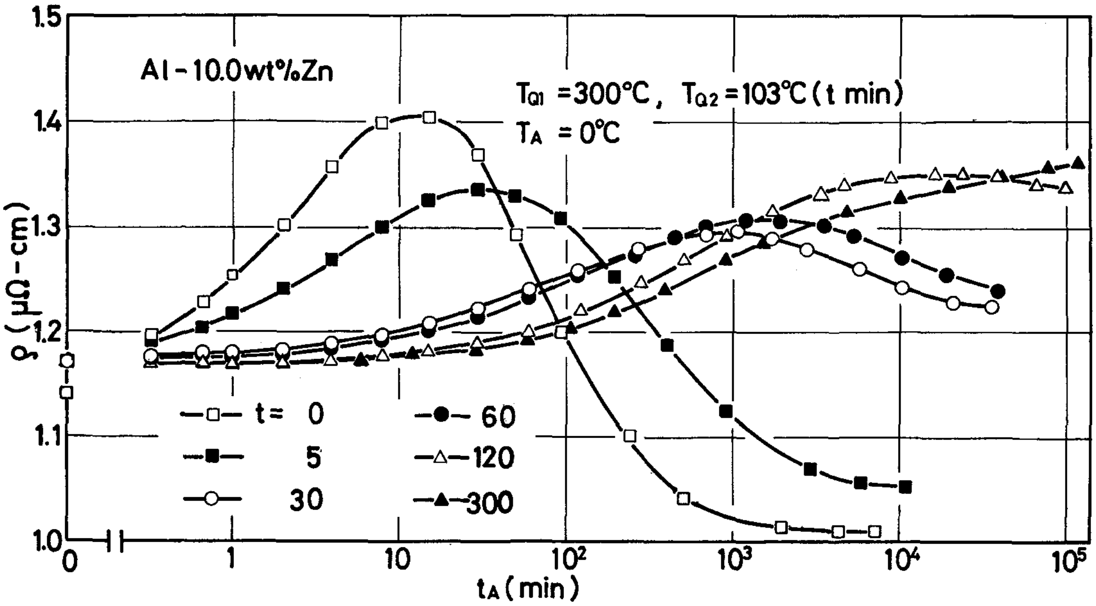

Fig.3 Isothermal aging curves of the Al-10wt%Zn alloy at 0°C when t(T_{Q2}) is changed. T_{Q1}=300°C, T_{Q2}=103°C.

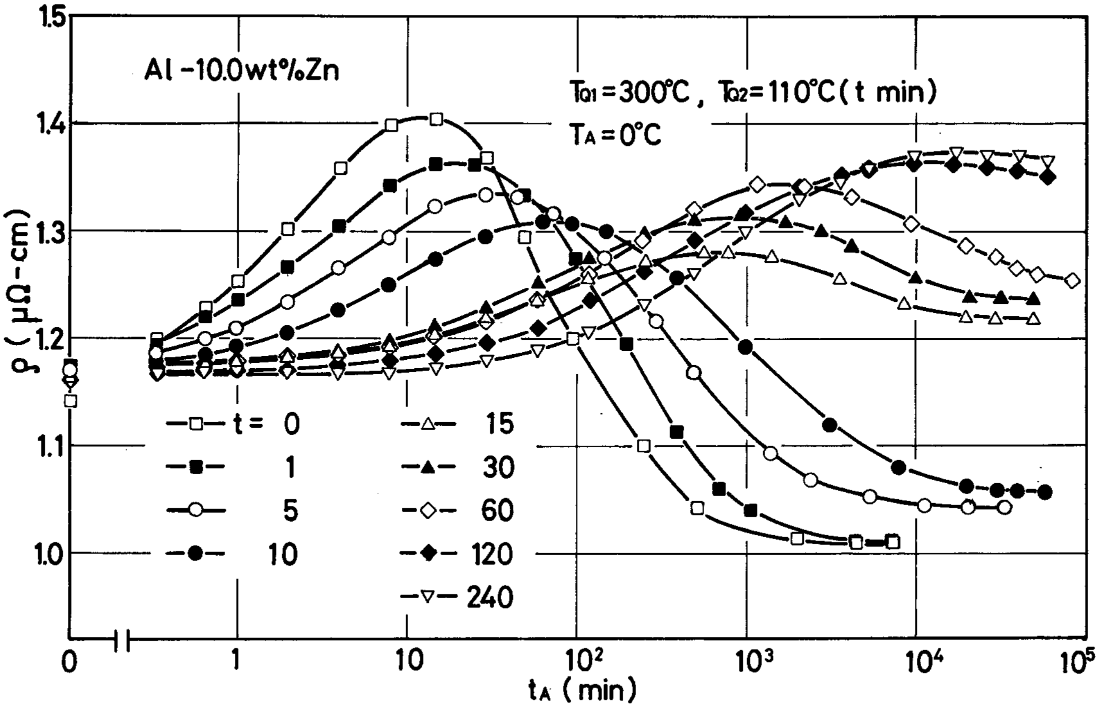

Fig.4 Isothermal aging curves of the Al+10wt%Zn alloy at 0°C when t(T_{Q2}) is changed. T_{Q1}=300°C, T_{Q2}=110°C.

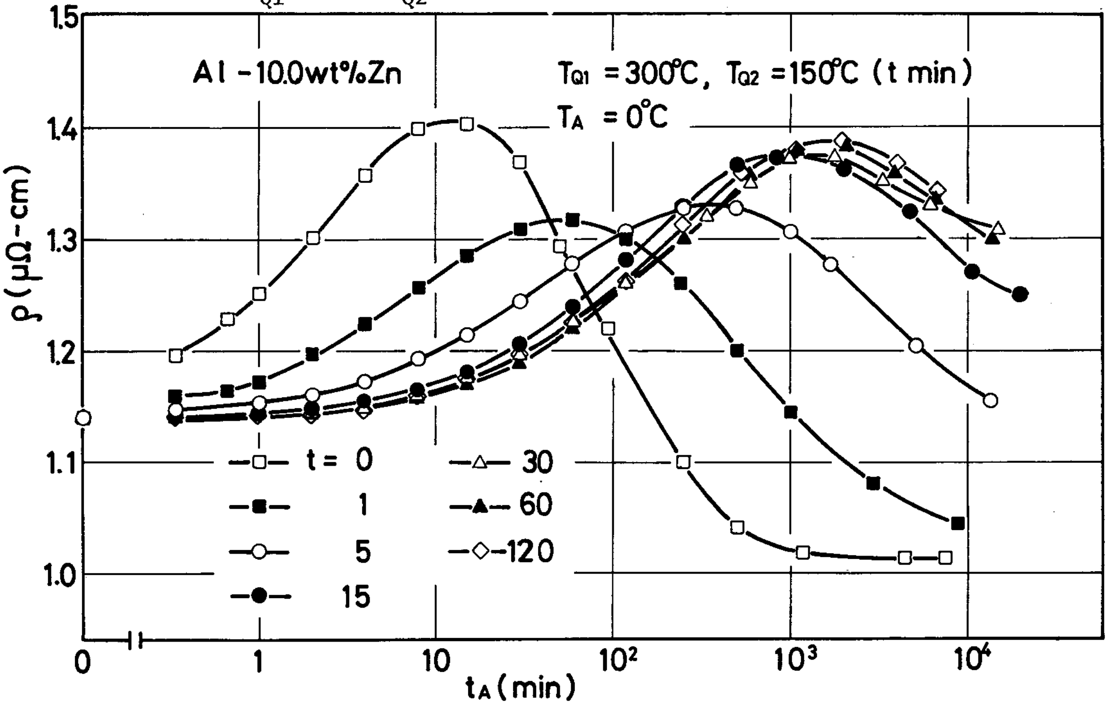

Fig.5 Isothermal aging curves of the Al+10wt%Zn alloy at 0°C when t(T_{Q2}) is changed. T_{Q1}=300°C, T_{Q2}=150°C.

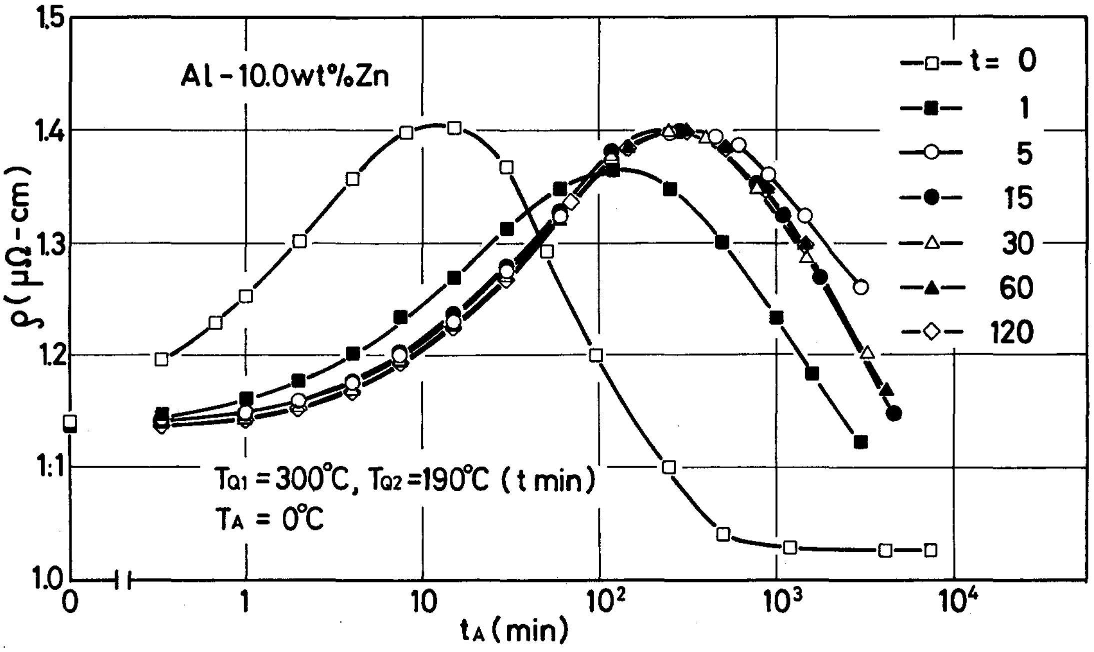

Fig.6 Isothermal aging curves of the Al-10wt%Zn alloy at 0°C when $t(T_{Q2})$ is changed. T_{Q1}=300°C, T_{Q2}=190°C.

ρ_{max} decreases at first and then increases to a stationary value as $t(T_{Q2})$ increases. In Figs. 2~6, aging curves similar to those in Fig.1 are shown when T_{Q2}=100, 103, 110, 150, 190°C. The aging curves vary in the same manner as in Fig.1 when $t(T_{Q2})$ is changed. Variation of the resistivity maxima with $t(T_{Q2})$ is shown in Fig.7 for several T_{Q2}.

Isothermal aging curves at 40°C for several T_{Q2} are shown in Figs. 8~13 when T_{Q1}=300°C. Maximum resistivity ρ_{max} is plotted against $t(T_{Q2})$ in Fig.14. These curves, on the whole, resemble those of T_A=0°C. In the case where T_{Q2} is low and ρ_{max} reaches a stationary

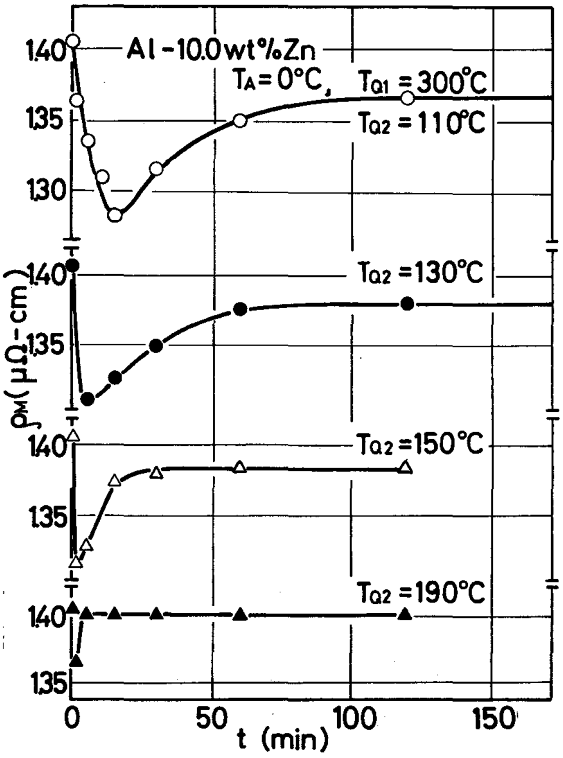

Fig.7 ρ_{max} vs. $t(T_{Q2})$ plots.

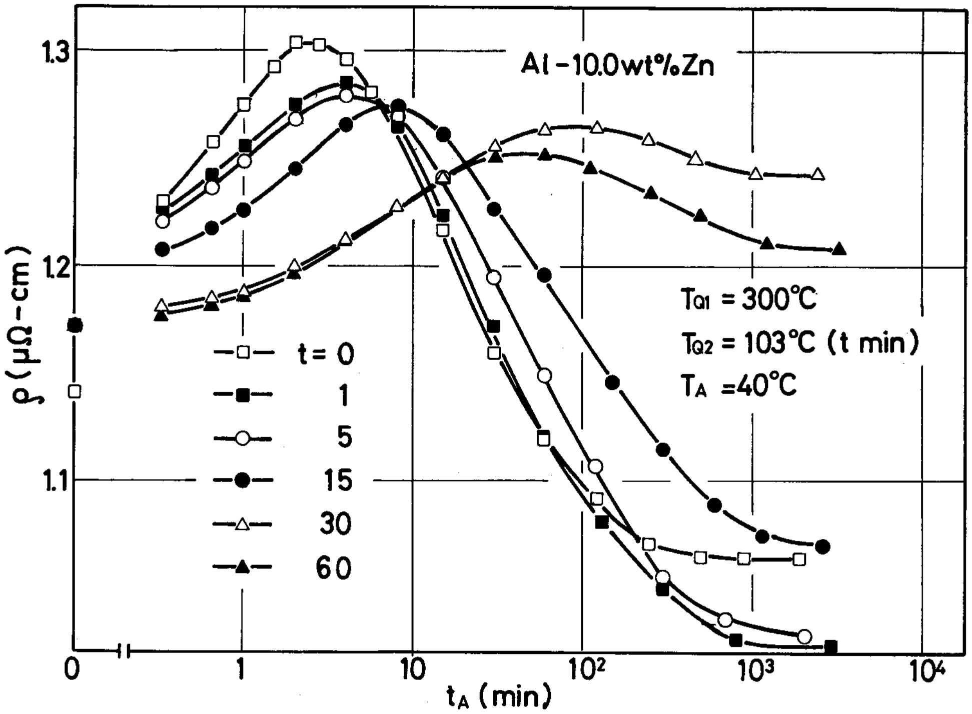

Fig.8 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=300°C. T_{Q2}=103°C for t min.

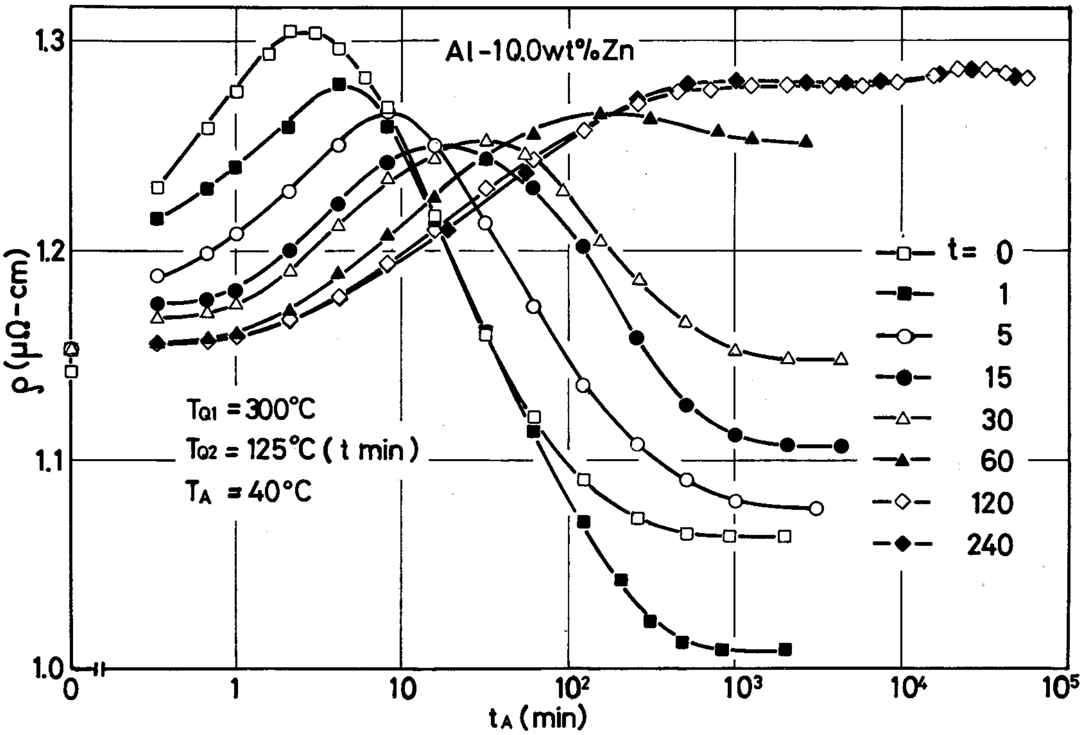

Fig.9 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=300°C. T_{Q2}=125°C for t min.

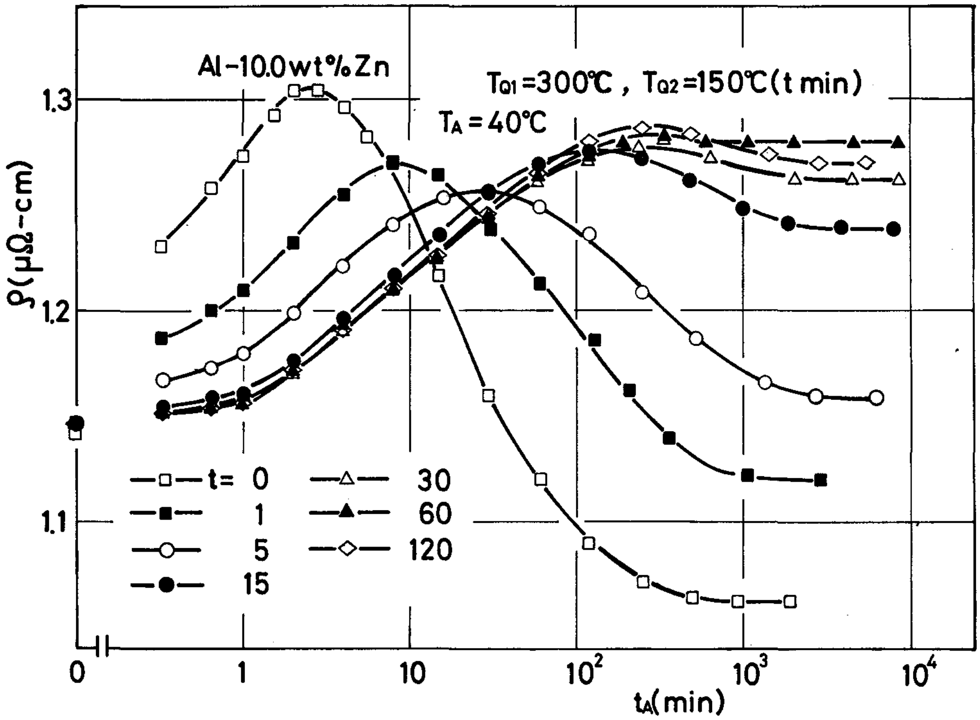

Fig.10 Isothermal aging curves of the Al-10wt%Zn alloy at 40°C when t(T_{Q2}) is changed. T_{Q1}=300°C, T_{Q2}=150°C.

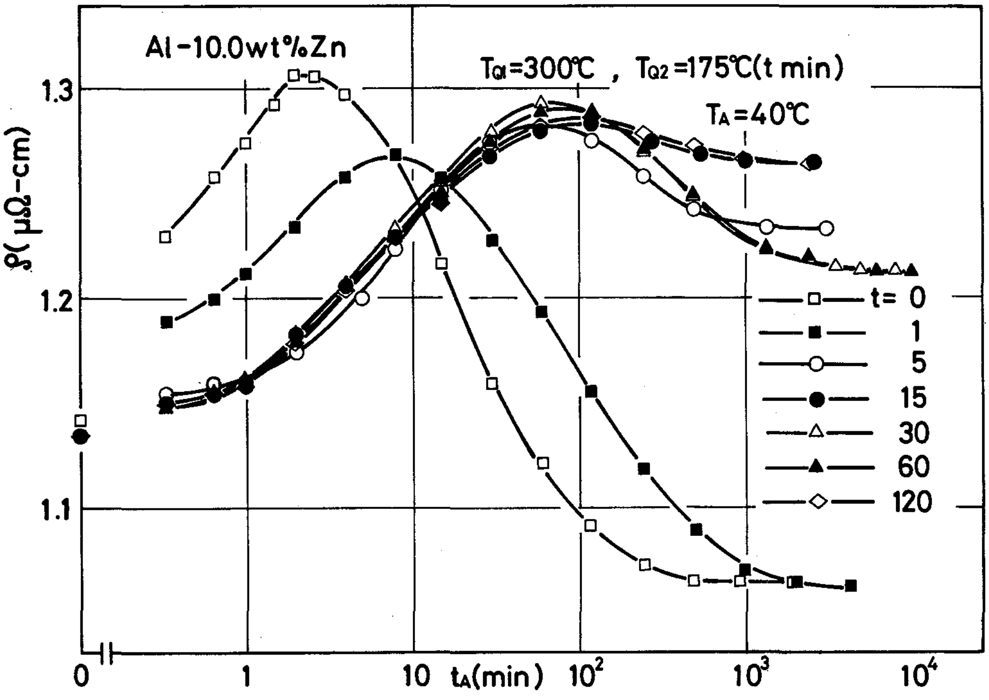

Fig.11 Isothermal aging curves of the Al-10wt%Zn alloy at 40°C when t(T_{Q2}) is changed. T_{Q1}=300°C, T_{Q2}=175°C.

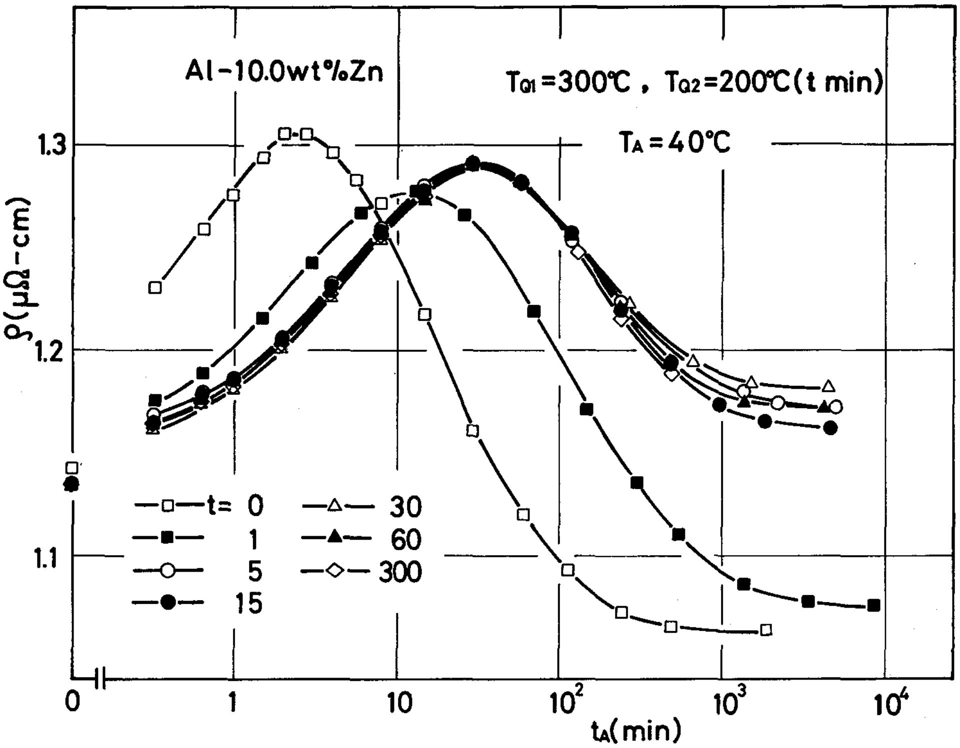

Fig.12 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=300°C. T_{Q2}=200°C for t min.

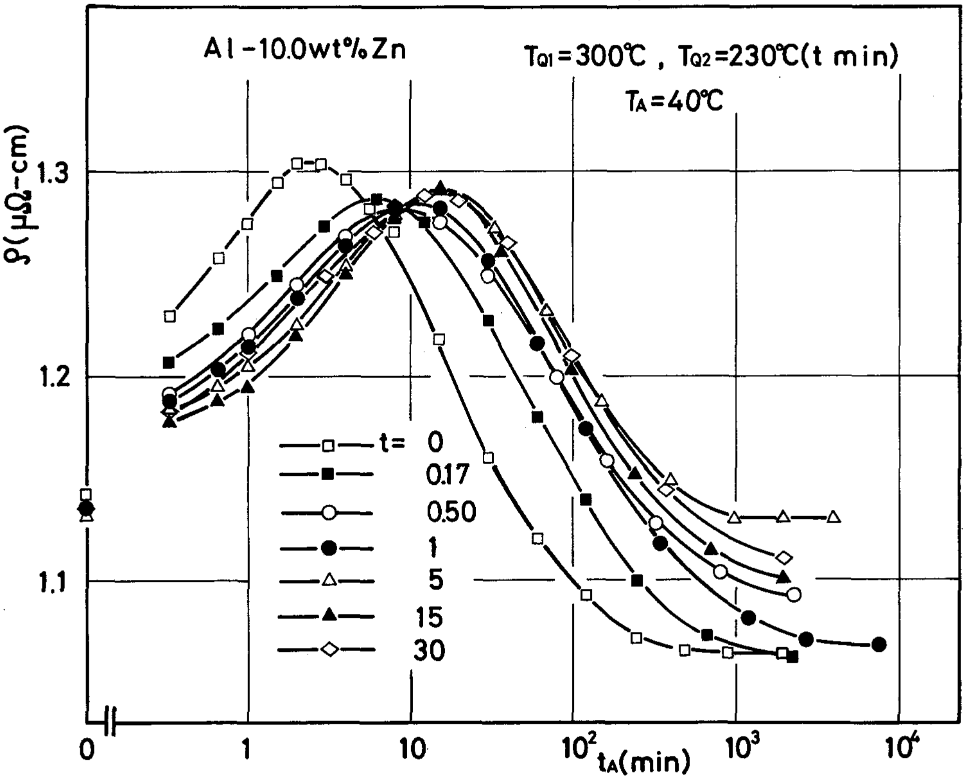

Fig.13 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=300°C. T_{Q2}=230°C for t min.

value with long $t(T_{Q2})$, resistivity increases rapidly at first, temporarily reduces the rate of increasing, then increases rapidly again and decreases after the maximum value. Isothermal aging curves at 40°C, when T_{Q2} is kept constant(125°C), but T_{Q1} is 250°C or 400°C, are shown in Figs. 15 and 16 respectively, and corresponding ρ_{max}-$t(T_{Q2})$ plots are shown in Fig.14(a). It is clearly observed that $t(T_{Q2})$ corresponding to the minimum of ρ_{max} becomes longer at higher T_{Q1}.

In Figs. 17~20, isothermal aging curves of the 10%Zn alloy are shown when T_{Q1}=350°C, T_A=40°C and T_{Q2} is changed.

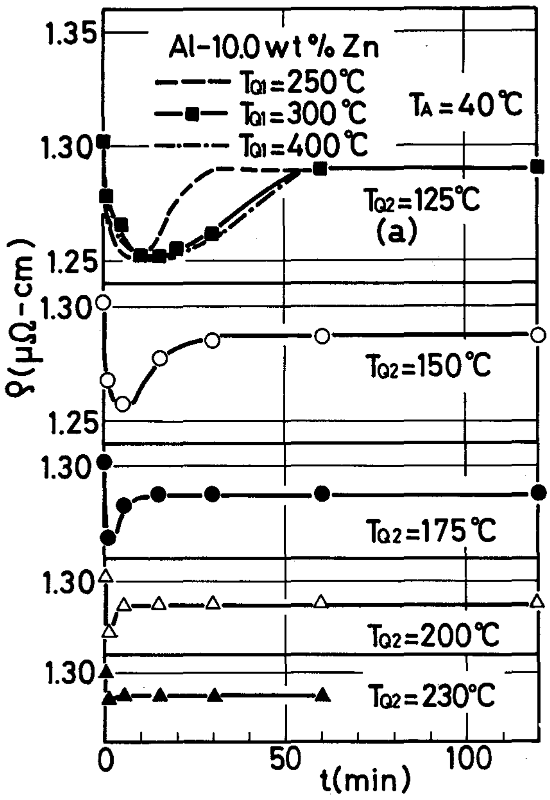

Fig.14 ρ_{max} vs. $t(T_{Q2})$ plots.

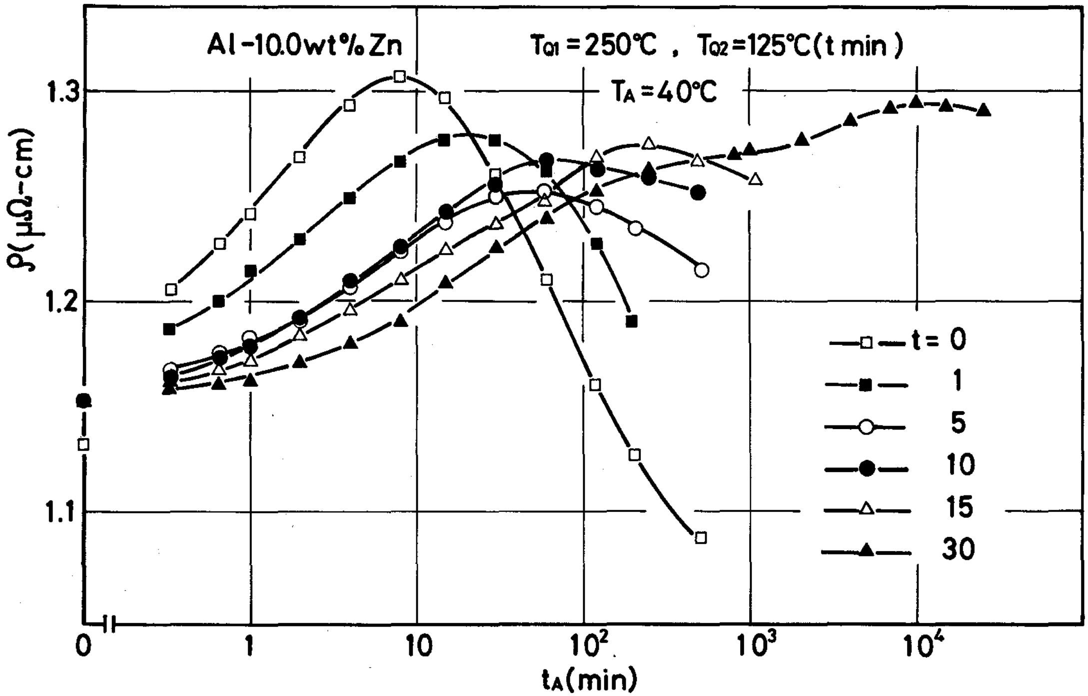

Fig.15 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=250°C, T_{Q2}=125°C for t min.

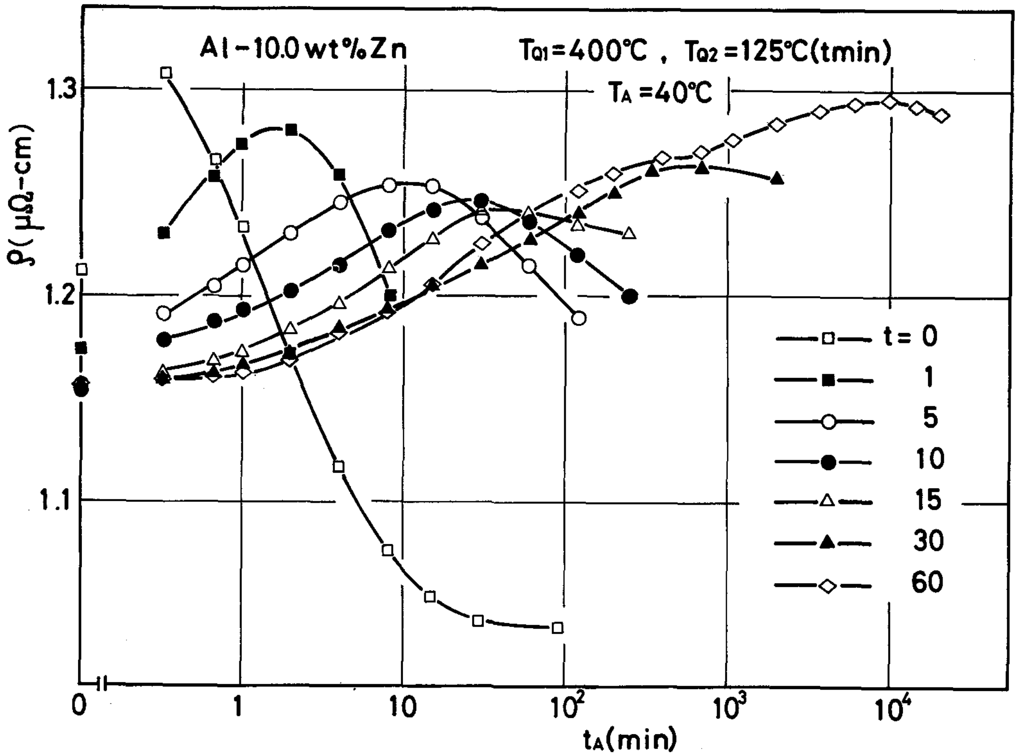

Fig.16 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=400°C. T_{Q2}=125°C for t min.

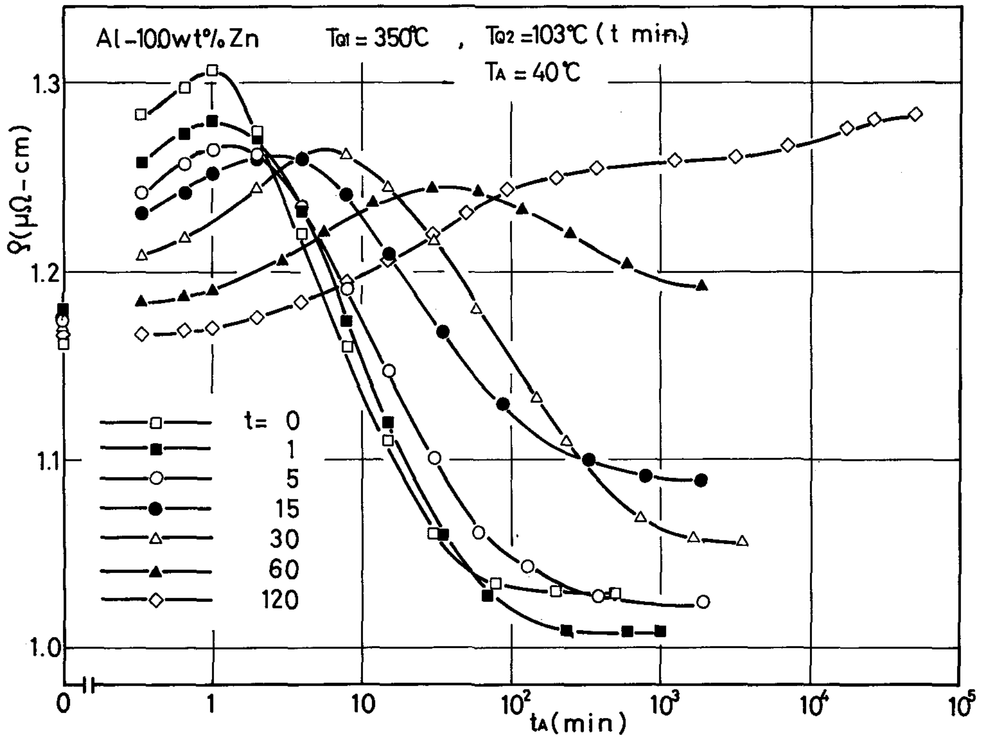

Fig.17 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=350°C. T_{Q2}=103°C for t min.

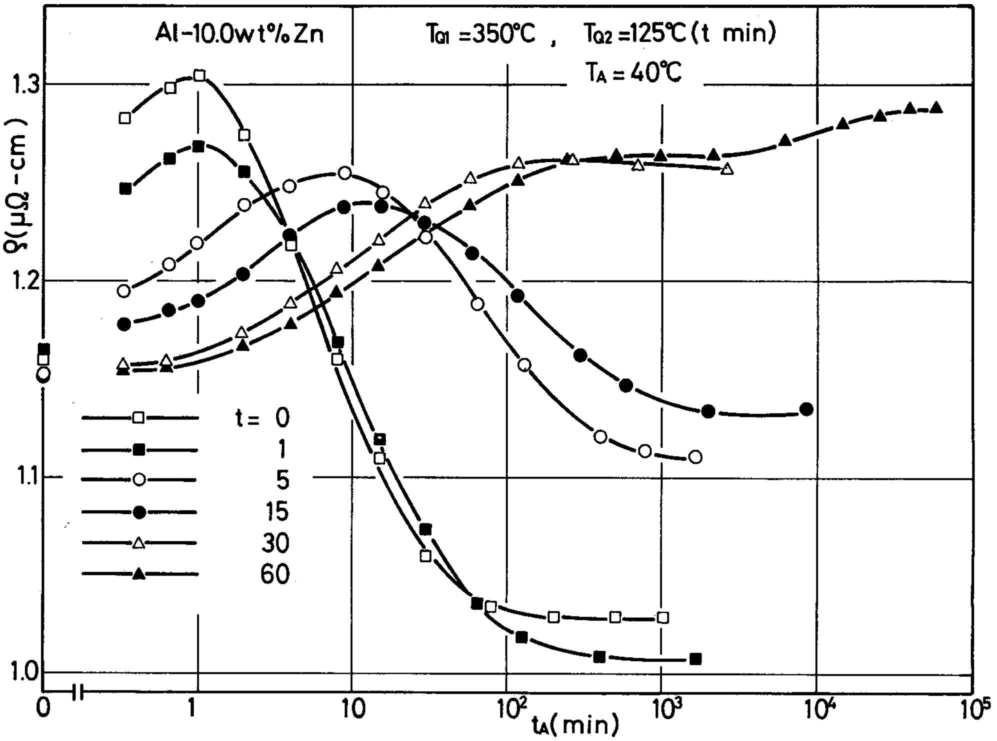

Fig.18 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=350°C. T_{Q2}=125°C for t min.

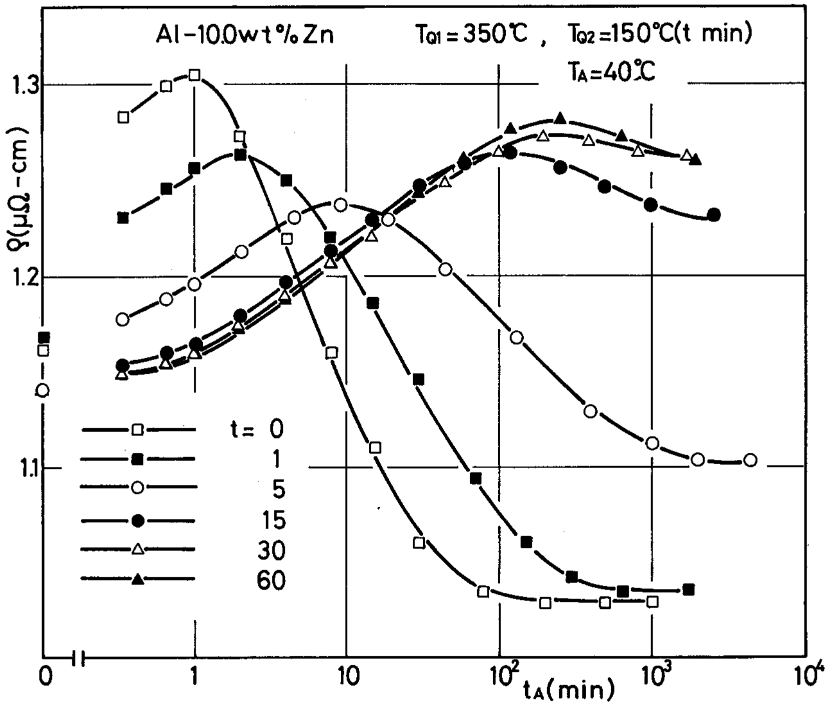

Fig.19 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=350°C. T_{Q2}=150°C for t min.

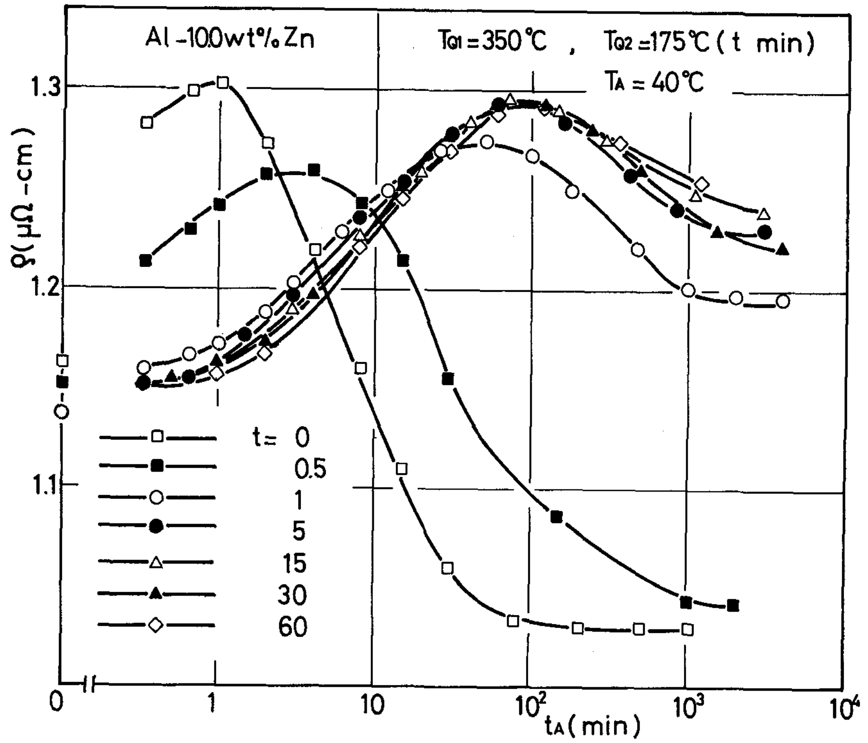

Fig.20 Aging curves of the 10%Zn alloy at 40°C. T_{Q1}=350°C. T_{Q2}=175°C for t min.

Results of the alloys other than 10%Zn are shown in Figs. 21~39. For the alloys of 6 and 7%Zn, ρ_{max}-t(T_{Q2}) plot does not take minimum when the aging temperature is rather high.

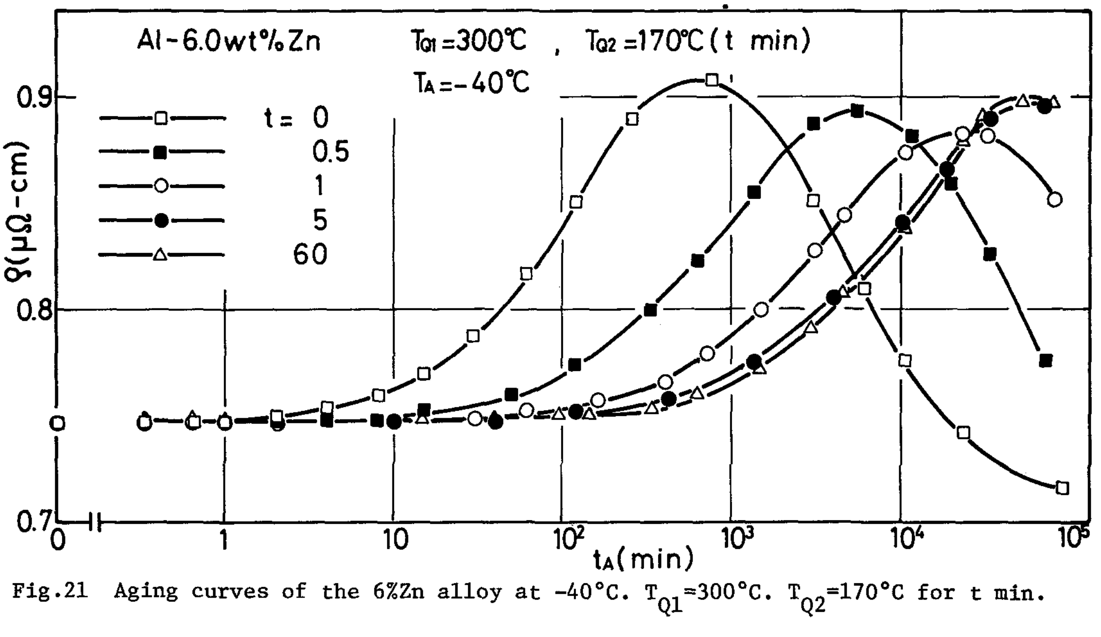

Fig.21 Aging curves of the 6%Zn alloy at -40°C. T_{Q1}=300°C. T_{Q2}=170°C for t min.

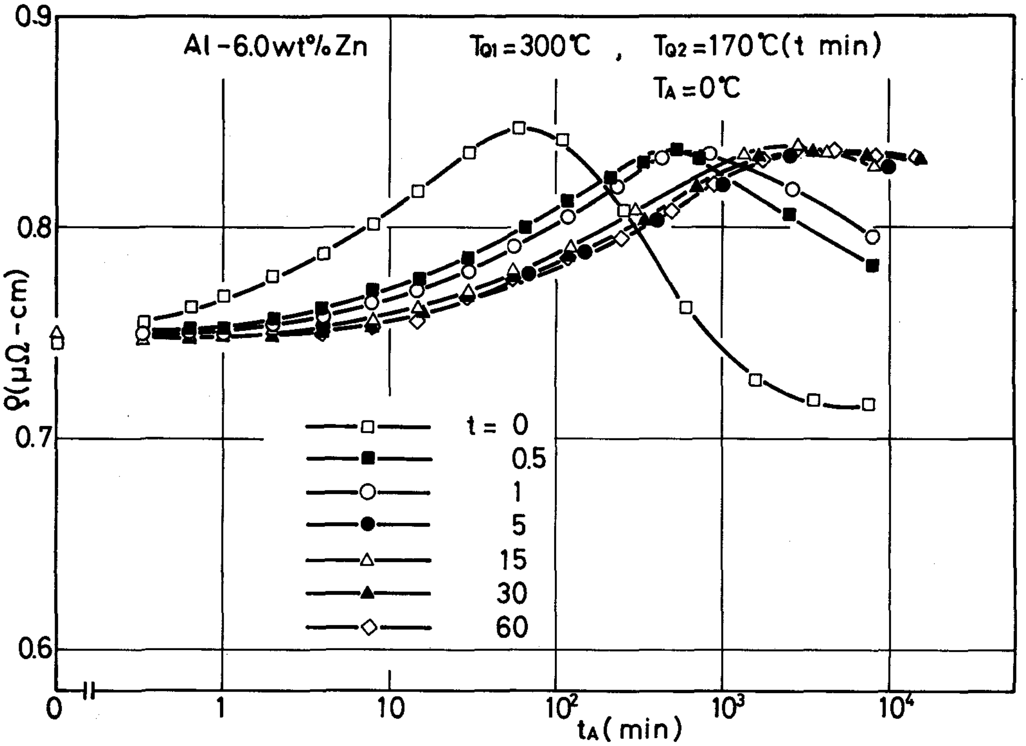

Fig.22 Aging curves of the 6%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=170°C for t min.

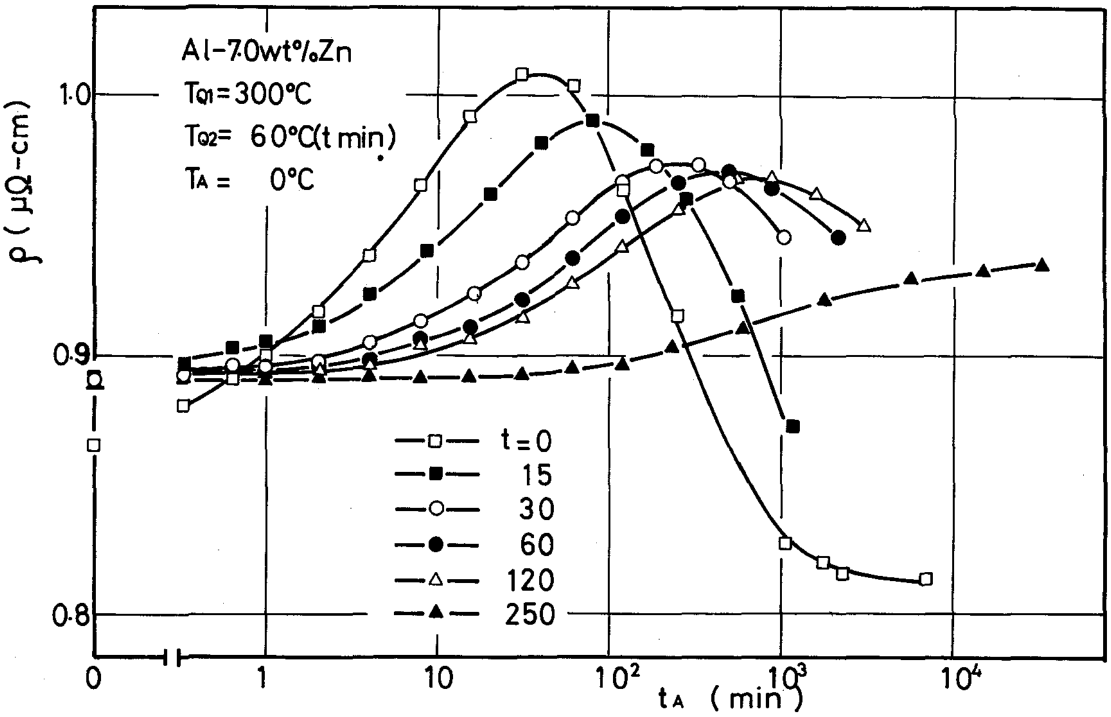

Fig.23 Aging curves of the 7%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=60°C for t min.

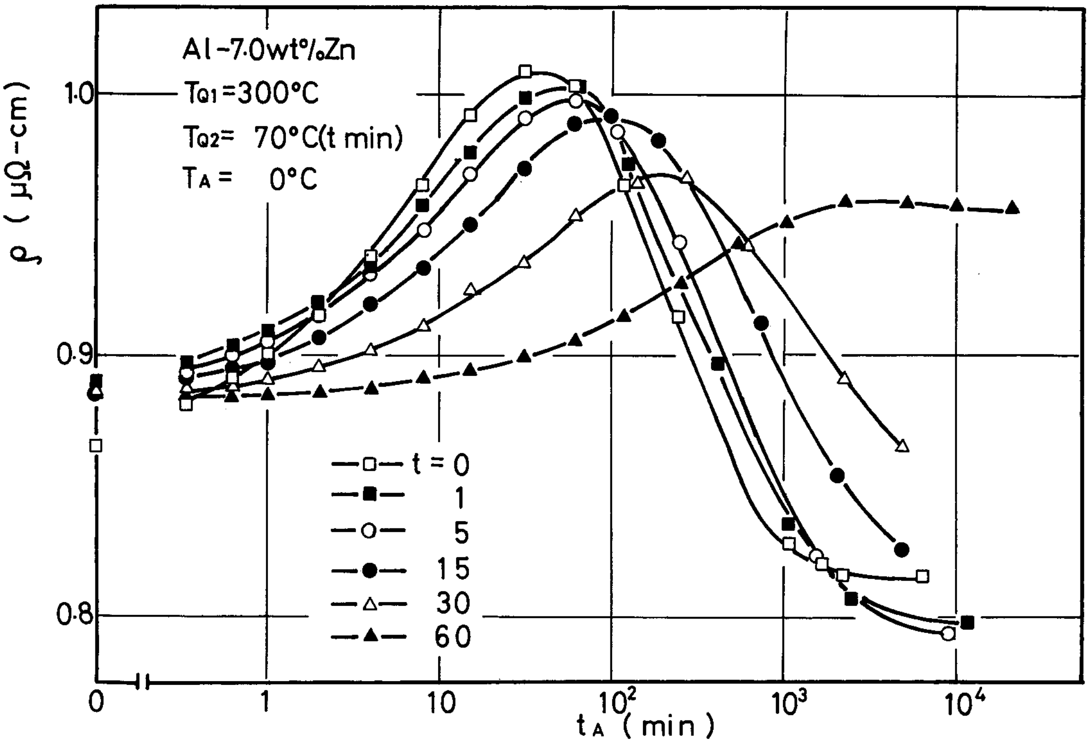

Fig.24 Aging curves of the 7%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=70°C for t min.

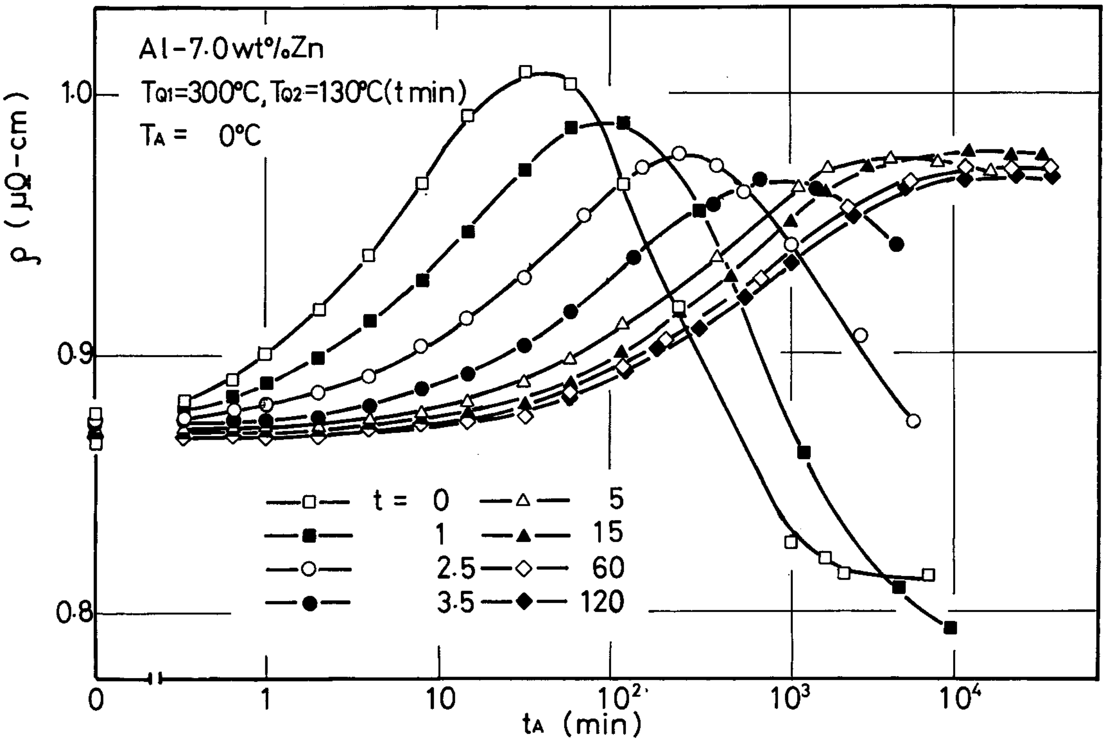

Fig.25 Aging curves of the 7%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=130°C for t min.

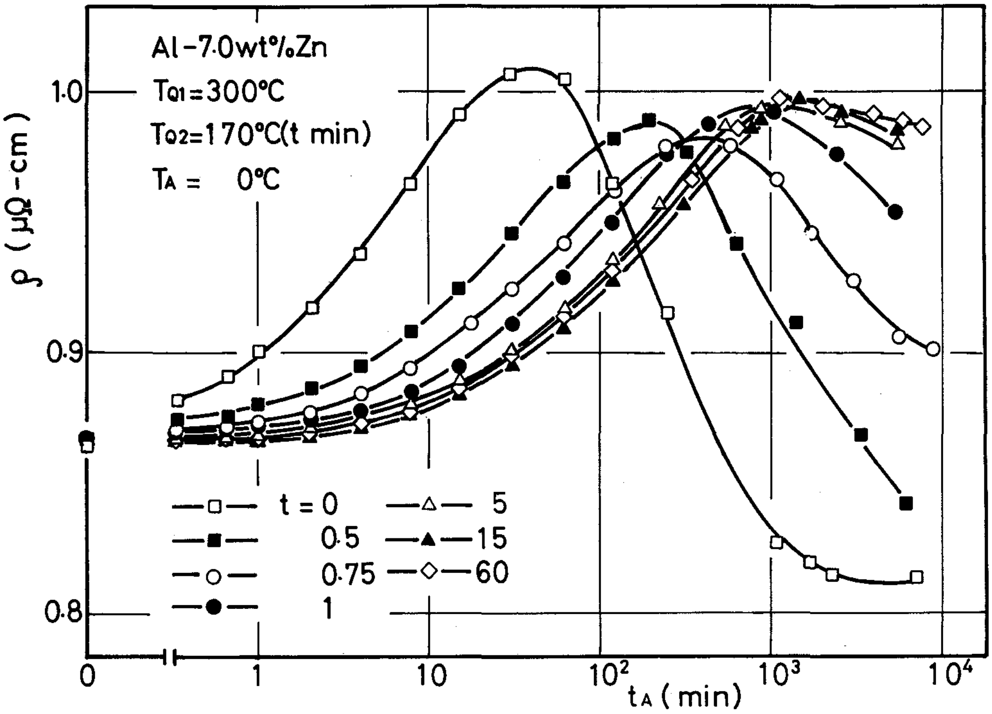

Fig.26 Aging curves of the 7%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=170°C for t min.

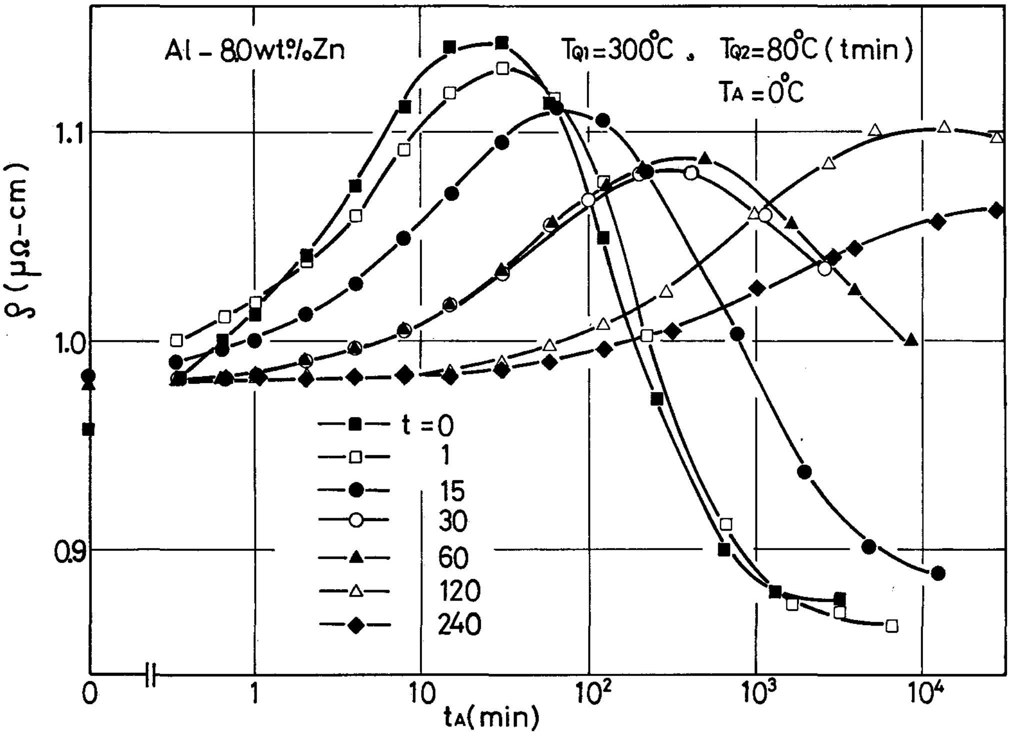

Fig.27 Aging curves of the 8%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=80°C for t min.

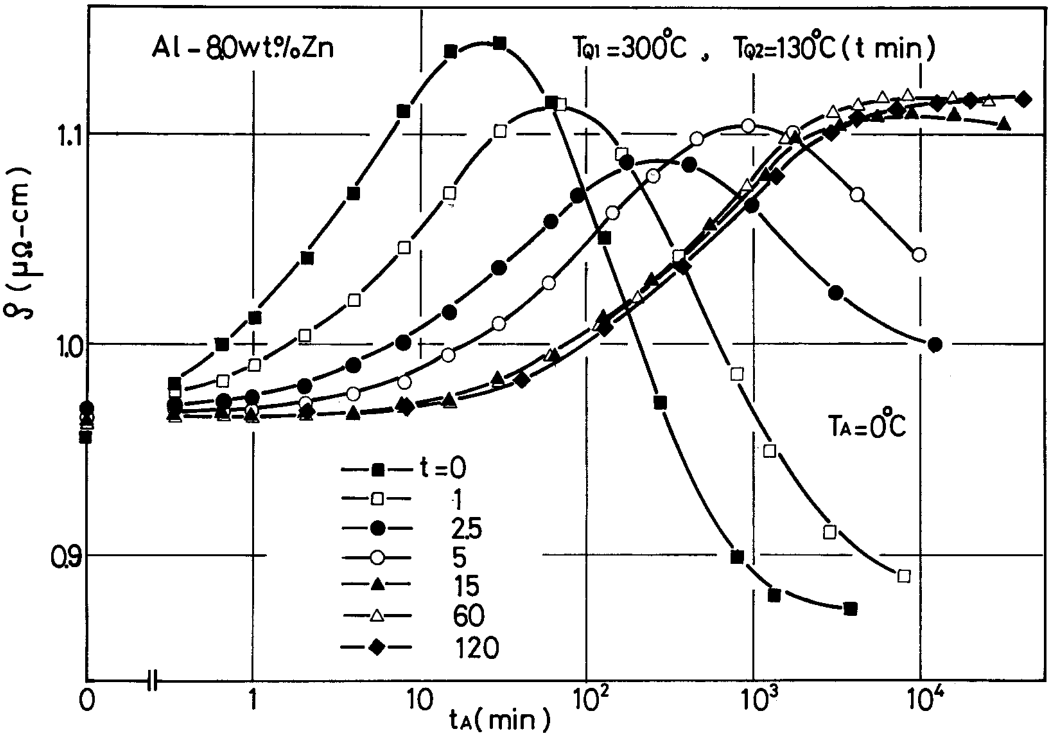

Fig.28 Aging curves of the 8%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=130°C for t min.

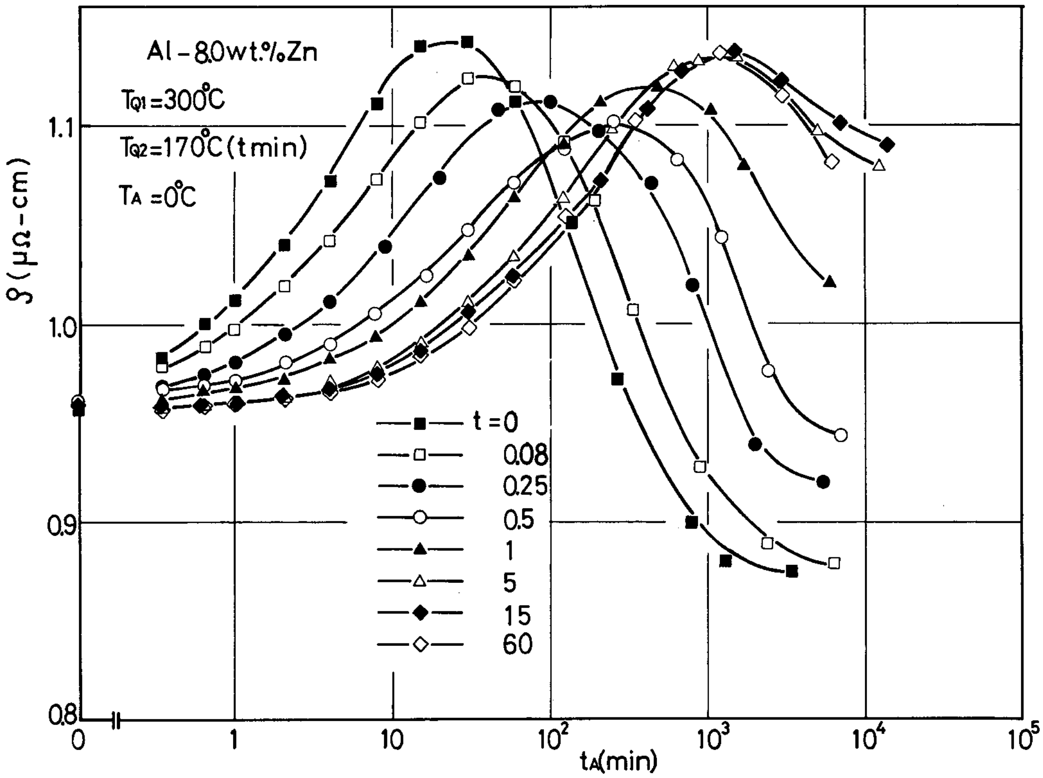

Fig.29 Aging curves of the 8%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=170°C for t min.

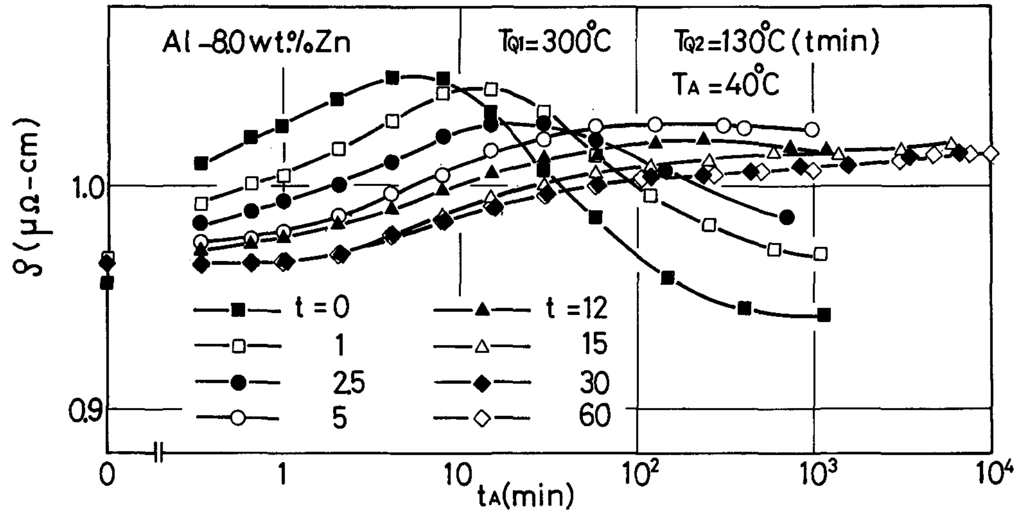

Fig.30 Aging curves of the 8%Zn alloy at 40°C. T_{Q1}=300°C. T_{Q2}=130°C for t min.

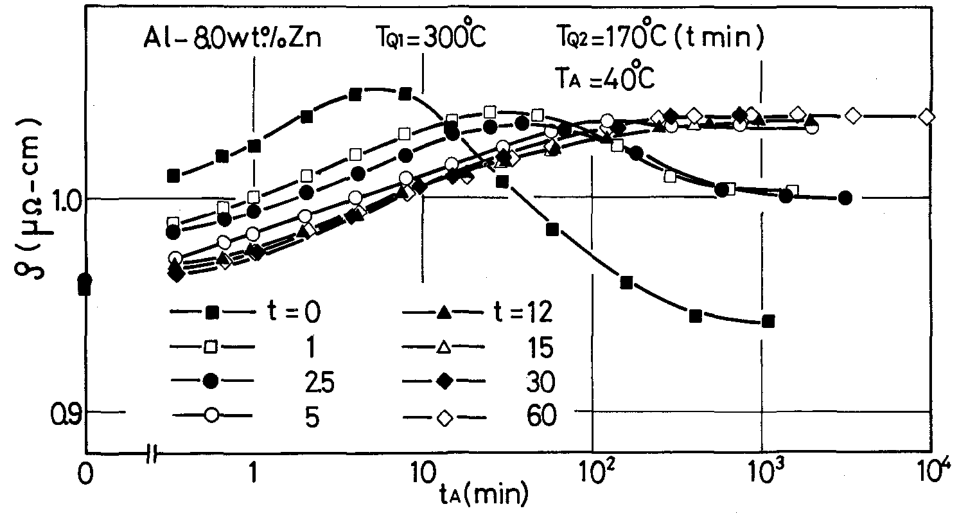

Fig.31 Aging curves of the 8%Zn alloy at 40°C. T_{Q1}=300°C. T_{Q2}=170°C for t min.

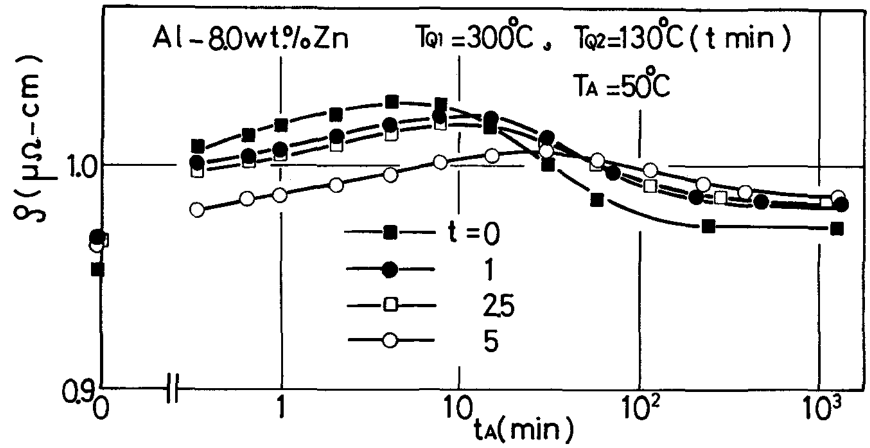

Fig.32 Aging curves of the 8%Zn alloy at 50°C. T_{Q1}=300°C. T_{Q2}=130°C for t min.

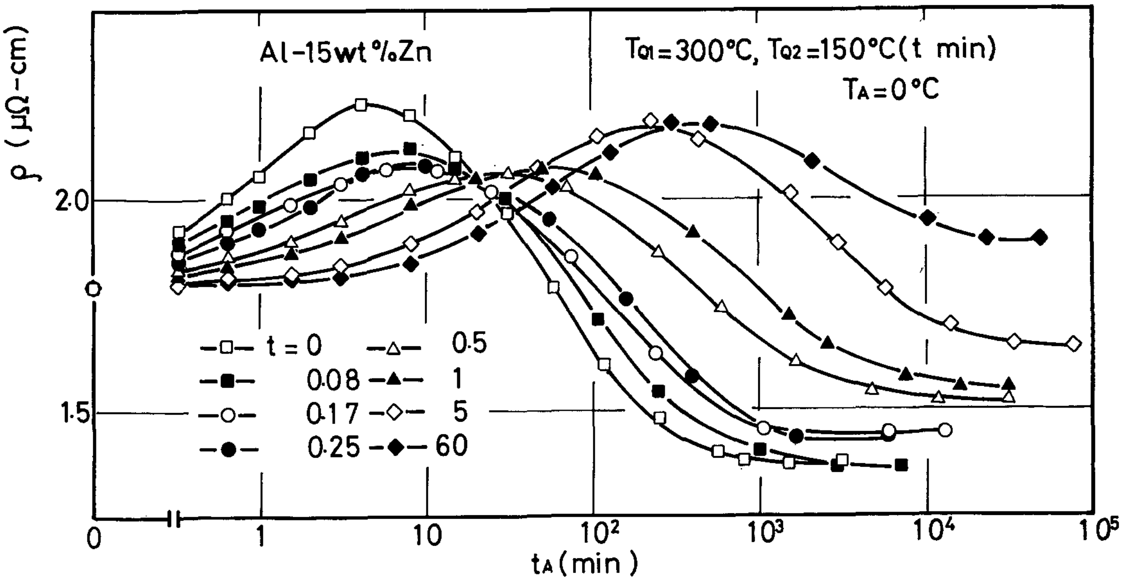

Fig.33 Aging curves of the 15%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=150°C for t min.

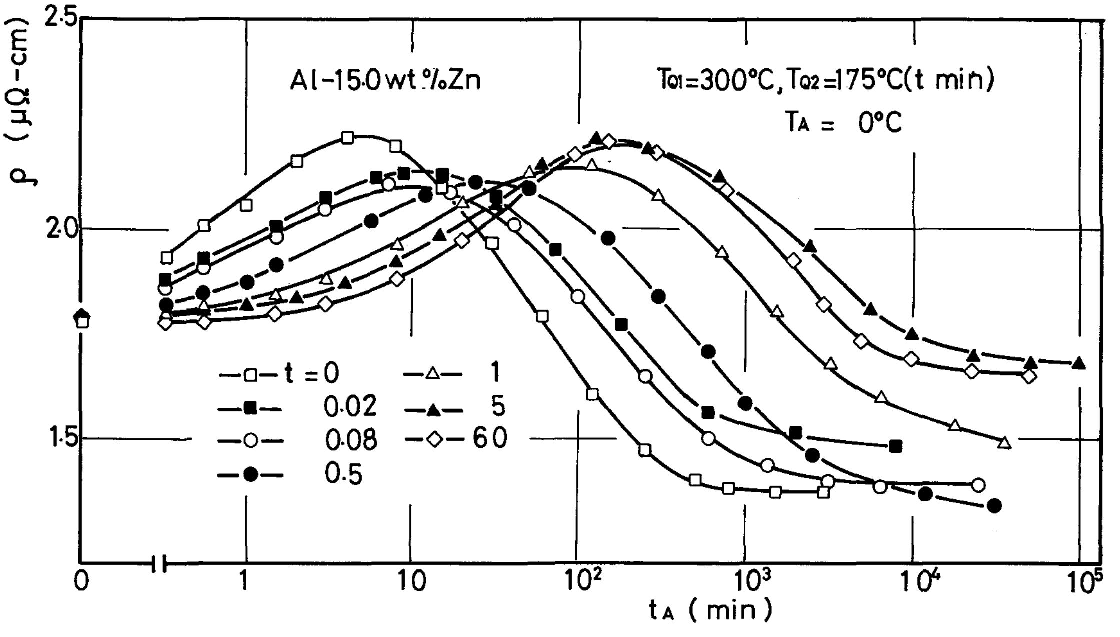

Fig.34 Aging curves of the 15%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=175°C for t min.

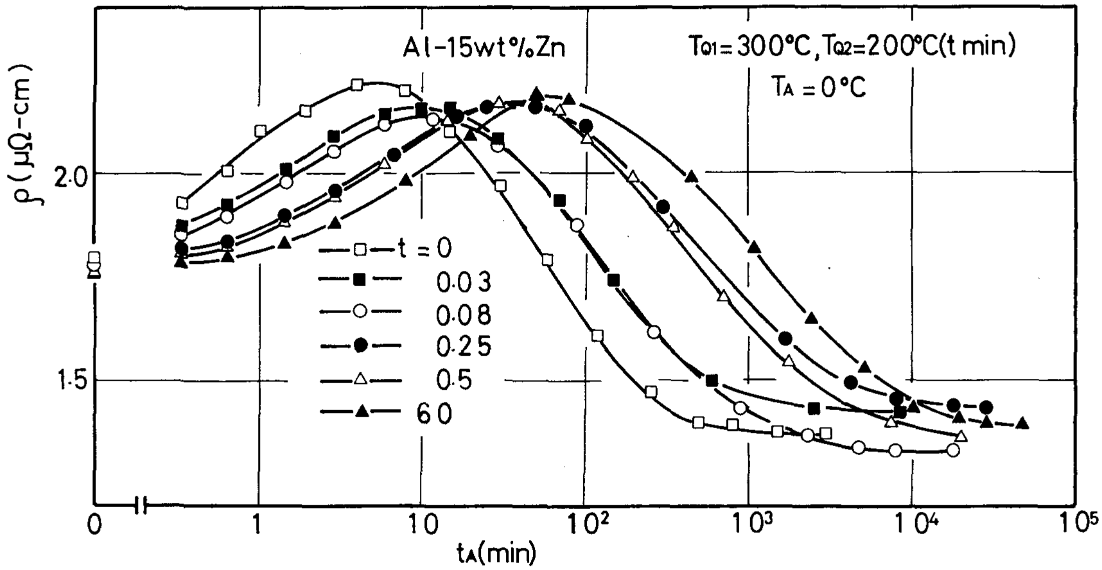

Fig.35 Aging curves of the 15%Zn alloy at 0°C. T_{Q1}=300°C. T_{Q2}=200°C for t min.

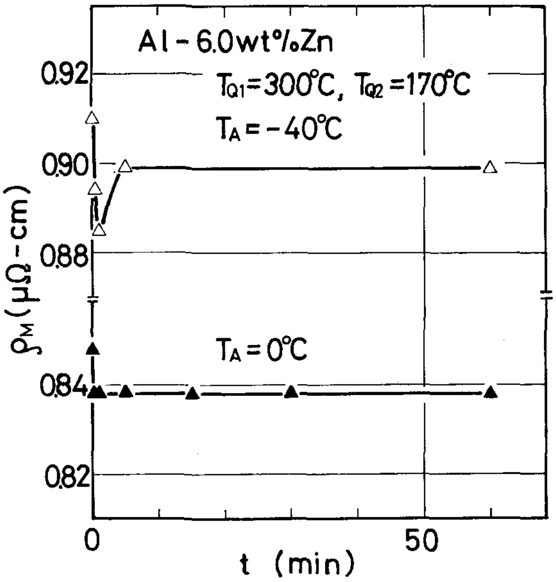

Fig.36 ρ_{max} vs. t(T_{Q2}) plots for the 6%Zn alloy (from Figs. 21 and 22).

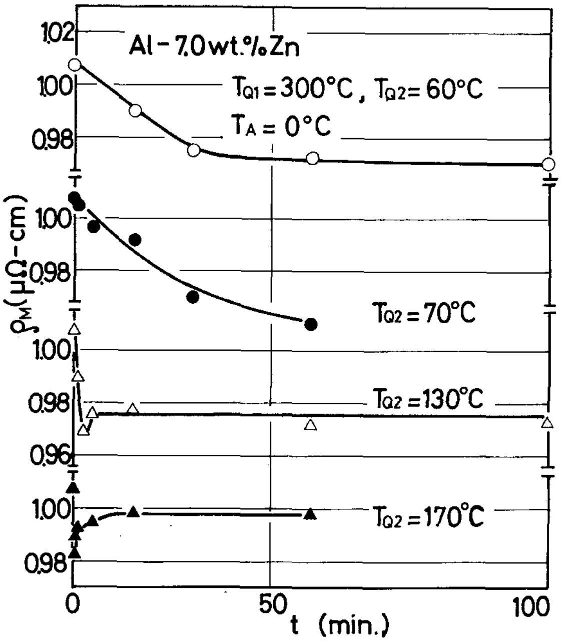

Fig.37 ρ_{max} vs. t(T_{Q2}) plots for the 7%Zn alloy (from Figs. 23~26).

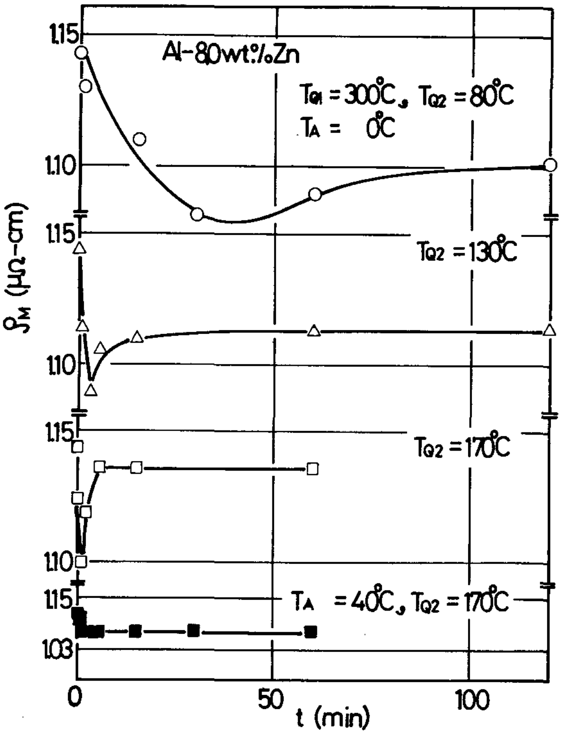

Fig.38 ρ_{max} vs. t(T_{Q2}) plots for the 8%Zn alloy (from Figs. 27~29 and 30).

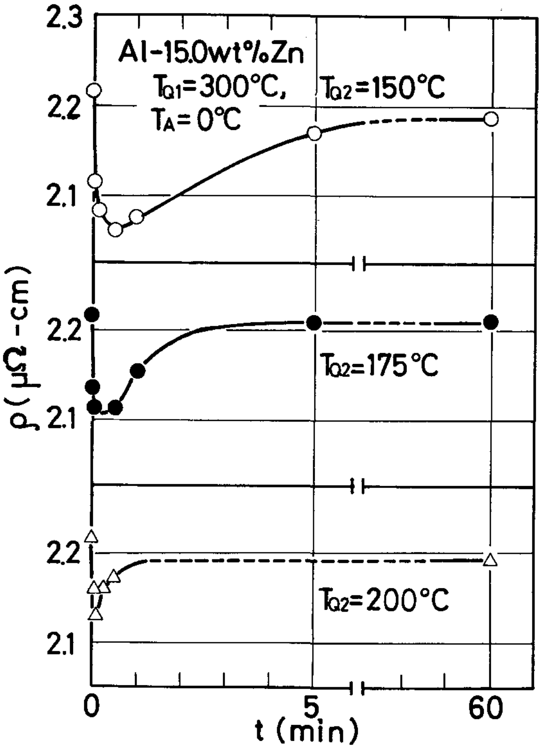

Fig.39 ρ_{max} vs. t(T_{Q2}) plots for the 15%Zn alloy (from Figs. 33~35).

4. Discussions

Previous studies on the fluctuation of solute concentration have been mostly carried out with the alloys of rather high concentration and at high temperatures. Therefore, details are not clear of such dilute alloys at low temperature (c.a. 150°C) as in the present case. However, as previously reported (2), it is reasonable to consider that there exist fluctuations also in dilute alloys.

Variation of ρ_{max} with t(T_{Q2}), shown in Figs. 7 and 14, may be due to the fluctuation affecting the isothermal aging process. This variation is more significant when T_{Q2} is lower.

When quenched from T_{Q1} to T_{Q2}, the fluctuation would reach its quasi-equilibrium state at T_{Q2} in a short time. According to Ohta and Hashimoto (10), resistivity reached a stationary value in a minute or so and remained at the value for more than 1000min when Al-10wt%Zn alloy was annealed at 110°C after quenching from 270°C into iced water. This fact indicates that, with the above treatment, fluctuation reaches its quasi-equilibrium state in less than a minute. In a previous report of the present authors (2), though being on the alloys of lower concentration than those in the present experiments, there are plots of the time to reach the quasi-equilibrium state for the alloys of various concentrations. If these plots are extrapolated to higher concentration, it is expected that the fluctuation should reach its quasi-equilibrium state in less than 0.2min in the present case. Holding times at T_{Q2}, in the present experiment, are all much longer than this period, and hence fluctuation was expected to have reached the quasi-equilibrium state already. Therefore, varying the holding time at T_{Q2} corresponds to varying the vacancy concentration which is decreasing from the equilibrium concentration of T_{Q1} to that of T_{Q2}, under the same state of fluctuation.

This interpretation agrees well with the result in Fig.14(a). The holding time corresponding to the minimum of ρ_{max} becomes longer as T_{Q1} increases. If T_{Q2} and T_A are the same, the resistivity values of minimum ρ_{max} are almost the same for all T_{Q1}, and the aging time to reach ρ_{max} is about 45min, irrespective of T_{Q1}. Hence, in spite of the different T_{Q1}, the state at the start of aging, i.e., the state reached after holding at T_{Q2}, may be considered to be almost the same in the case of minimum ρ_{max}. If a certain state of fluctuation varying during T_{Q2} were corresponding to this initial condition, the time to reach this state should be shorter as the vacancy concentration increased, which is contrary to the present results. If this corresponds to the state of a certain vacancy concentration, the time to reach this state will be longer as the vacancy concentration at the beginning of the holding at T_{Q2} increases, i.e., as T_{Q1} becomes high. The present experimental results that the holding time at T_{Q2} which corresponds to the minimum ρ_{max} increases with increasing T_{Q1} agree with this interpretation.

Appearance of the minimum in the variation of ρ_{max} with $t(T_{Q2})$ may be related also to the degree of supersaturation of solute in the alloy, which was suggested by the fact that the minimization was not found when the alloys of relatively low concentration were aged at relatively high temperatures.

Further discussions will be made in the following report.

The authors wish to record their thanks to Messrs. A. Shimizu, Y. Yamagata and T. Kondoh for assistance in the preparation of this paper.

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