MEMOIRS OF THE SCHOOL OF ENGINEERING, OKAYAMA UNIVERSITY, Vol. 9, No.1, July 1974

Grouth of G.P. zones in Al-Zn alloy

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Synopsis

Metastable values of electrical resistivity, ρ_E, obtained during isothermal ageing differs in each experimental run even when the conditions of quenching and ageing were carefully kept constant. This phenomenon is considered to result from the competitive growth of G.P.zones. The range of the values of ρ_E under the same conditions of heat treatments were examined, and the results obtained are as follows:
(1) Metastable values of resistivity, ρ_E, during ageing at 70°C after quenching from 300°C were in rather narrow range. On the other hand, the width of the range obtained during ageing at 50°C was wide.
(2) When the specimens were aged at first at 70°C until the maximum values of resistivity, ρ_M, being reached and then aged at 50°C for long time, the metastable values of resistivity, ρ_E*, were obtained. And the width of discrepancy of values of ρ_E* was nearly equal to that of ρ_E which was obtained in the case of isothermal ageing at 70°C after quenching from 300°C.
(3) It may be concluded that the width of discrepancy of values of ρ_E* becomes smaller since the width of discrepancy of the number of G.P.zones for all experiments which can grow through competitive growth is

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made small by 70°C ageing than that immediately after quenching from 300°C.

1. Introduction

There are many studies about ageing phenomena of Al-Zn alloys, and each step of ageing, from initial stage to appearance of α' phase with f.c.c.structure, has been known. They are quite various, that is, the mechanism of precipitation, kind, structure, and state of distribution of formed materials, reversion, and so on. Above all , G.P.zones are studied by various methods and very interesting.

The paper of Panseri and Federighi(1) by the measurements of electrical resistivity is very important. They measured electrical resistivity of Al-10wt%Zn alloy which was quenched from various temperatures and annealed at various temperatures, and evaluated the energies of formation and migration of vacancies in the alloy. In this investigation, they assumed that the number of G.P.zones remains constant during ageing, and all G.P.zones grow with the same rate. And they ascribed the difference of the maximum value of resistivity due to the difference of ageing temperatures to the difference of the number of G.P.zones of critical size.

On the maximum of resistivity, several theorical studies(2)-(6) have been done since Mott(7)'s suggestion. Herman et al.(8,9) measured electrical resistances, Young coefficient, critical shear stress, and small angle scattering of X-ray, and showed that maximum of electrical resistivity corresponds to about 9 Å radius of G.P.zones, and the rate of G.P.zone formation are proportional to the vacancy concentration, and so on. Also they found that increase of resistivity, or decrease of radius of G.P.zones, took place when the specimens were heated at temperatures higher than the reversion temperature for a short time. The concentration of solid solution coexisting by several authors.(10)-(14)

Ohta and Hashimoto(15) determined the highest temperature for several alloys at which the maximum of electrical resistivity in isothermal ageing curves could be observed, and they suggested that these highest temperatures are corresponding to the solvus temperatures for G.P.zones.

On the other hand, Ohta and Hashimoto(16) found that the values of resistivity, ρ_E, of metastable state reached after the maximum of the resistivity had passed are dependent upon the quenching temperatures. They considered that these dependencies are caused by competitive growth of G.P.zones, since the numbers and sizes of G.P.zones existing immediately after quenching must be determined by cooling condition. Also, they found that ρ_E in isothermal ageing are differing each other under the same condition of heat treatments, that is, the same quenching temperature, T_Q, and the same ageing temperature, T_A. They considered that quenching rate is more or less different at every quenching in spite of the same T_Q and the same temperature of liquid for quenching, and that ρ_E are differing each other since the numbers and sizes of G.P.zones formed during quenching are different.

Therefore, it is of great interest how a small number of larger G.P.zones, which have been present before ageing begins, affects to the growth of G.P.zones in the procedure of isothermal ageing. Several experimental results obtained are presented in this article.

2. Experimental Methods

Atomic concentration of the alloy used was Al-4.4at%Zn. The purity of metals from which this alloy was made were 99.996% aluminium and 99.999% zinc. These pure metals were melted in crucibles of high purity almina in air, and cast into the metallic mould. The sizes of ingots were about 15mm in diameter and about 100 mm in length.

These ingots were homogenized for about 50 hours at 350°C, and then were forged at the same temperature, and then cold-rolled to the strips of 0.4mm in thickness with appropriate annealing. The shapes and sizes of specimens are the same as those which were reported by one of the present authors,(17) and shown in Fig.1.

Each specimen was annealed for about an hour at 500°C, cooled to quenching temperature in the furnace, held for an hour at that temperature, and then quenched into a liquid nitrogen bath.

The quenching temperature was 300°C and ageing temperatures were 20°C, 30°C, 40°C, 50°C, and 70°C. Isothermal ageings were repeated several times at each temperature mentioned above. Another series of experiments were double ageings, that is, the specimens were aged at a temperature until the maximum of electrical resistivity being reached at first, and then successively aged at another temperature. The ageing temperatures in these cases were 70°C and 50°C. Ageing was carried out in liquid baths whose medium were methyl alcohol

(20°C), water(30°C, 40°C, and 50°C), and silicon oil(70°C).

The electrical resistance was measured with Yokogawa's auto recording and measuring apparatus(its precision was 1/10^4). Resistivity was calculated from the shape and sizes of the specimen. The electrical resistance was measured keeping the specimen in the liquid nitrogen bath until the electrical resistance arriving at the constant value, ρ_E or ρ_E^*.

The temperature of liquid nitrogen was corrected with a dummy made from the same alloy as the specimen and its shape is shown in Fig.1.

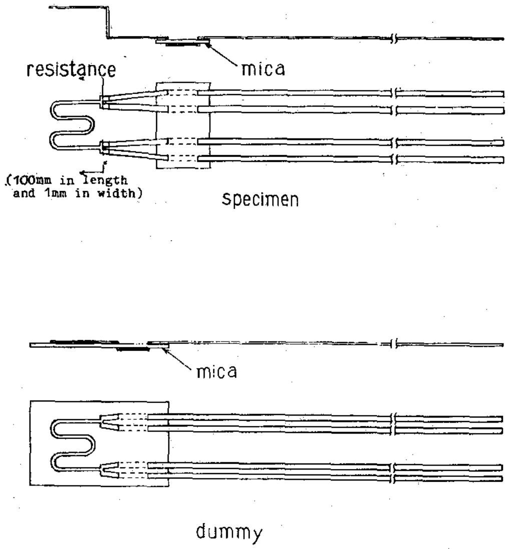

Fig.1 Shapes of specimen and dummy

3. Results

3 - 1 Isothermal Ageing

Isothermal ageing curves at 20°C, 30°C, 40°C, 50°C, and 70°C after quenching from 300°C into ice-water, 0°C, are shown in Fig.2 (a), (b), (c), (d), and (e). In each figure, the maximum values of resistivity, ρ_M, and the time having elapsed before the maximum resistivity being reached, t_M, agree in all measurements, but metastable values of resistivity after long ageing, ρ_E, differ fairly in each other. Width of discrepancy of values of ρ_E for a certain ageing temperature, T_A, is dependent upon T_A, that is, the width for T_A=70°C is the smallest, and the width for T_A=40°C is largest.

3 - 2 Double Ageing

Fig.3 shows the results obtained when the specimens are quenched from 300°C and aged at 50°C after ageing at 70°C until ρ_M being reached. In this figure, the maximum resistivity in the second ageing, ρ_M^*, and the time having elasped before this maximum resistivity being reached, t_M^*, agree in all measurements. Comparing this ρ_M^* and t_M^* with ρ_M and t_M in isothermal ageing curves when T_Q=300°C

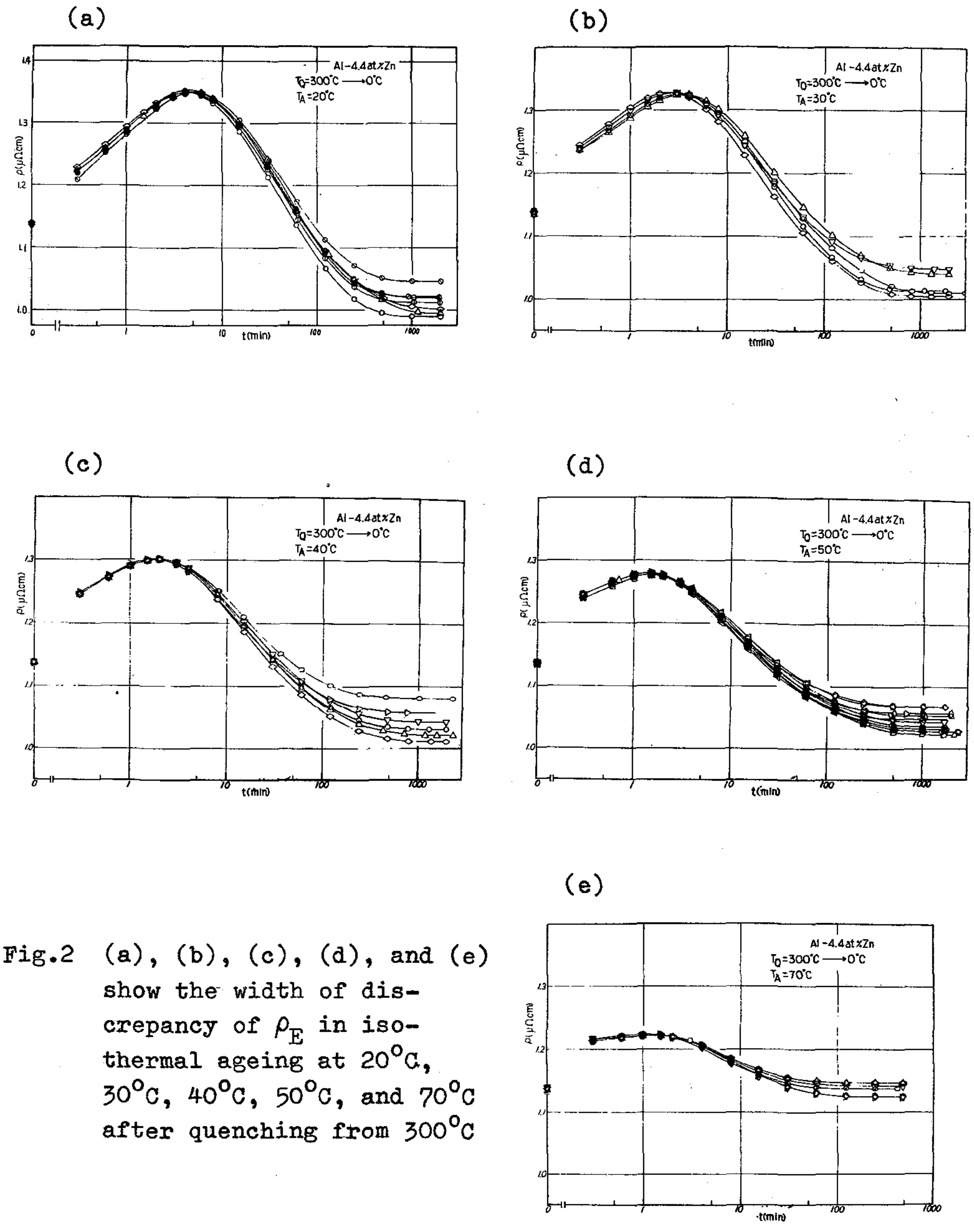

Fig.2 (a), (b), (c), (d), and (e) show the width of discrepancy of ρ_E in isothermal ageing at 20°C, 30°C, 40°C, 50°C, and 70°C after quenching from 300°C

and T_A=50°C, ρ_M* is lower than ρ_M, that is, $(\rho_M{}^*-\rho_o)=0.85(\rho_M-\rho_o)$, where ρ_o is as quenched resistivity, and t_M* is longer than t_M, that is $t_M{}^*=t_M+1$ (minute).

Table 1 Resistivity data, average value, and width of discrepancy of ρ_E in isothermal ageing after quenching from 300°C

ageing temperature: T_A(°C)	20	30	40	50		70
resistivity data for ρ_E (μΩcm)	1.0455	1.0480	1.0808	1.0675	1.0677	1.1462
	1.0215	1.0394	1.0570	1.0565	1.0559	1.1461
	1.0195	1.0130	1.0425	1.0504	1.0502	1.1372
	1.0120	1.0095	1.0310	1.0428	1.0336	1.1247
	1.0013	1.0046	1.0210	1.0308	1.0227	1.1245
	0.9948		1.0112	1.0232		
	0.9890					
average value of ρ_E (μΩcm)	1.0119	1.0229	1.0406	1.0460		1.1365
width of discrepancy of ρ_E ($\times 10^{-4}$μΩcm)	565	434	696	445		217

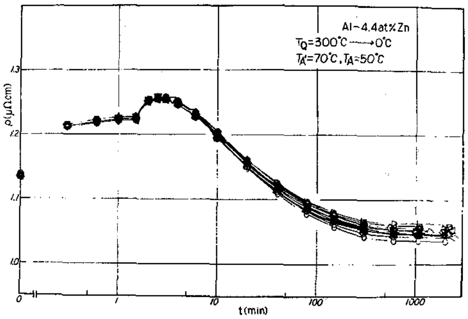

Fig.3 Width of discrepancy of ρ_E* when aged first at 70°C, and secondarily at 50°C after quenching from 300°C

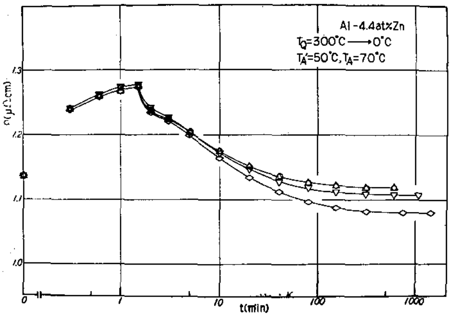

Fig.4 Width of discrepancy of ρ_E+ when aged first at 50°C, and secondarily at 70°C after quenching from 300°C

Metastable values of resistivity after long second ageing of double ageing, ρ_E*, also differ in each other. However, the width of discrepancy of ρ_E* is much smaller than that of ρ_E at T_A=50°C, and a little larger than that of ρ_E at T_A=70°C. The mean value of ρ_E* is

Table 2 Resistivity data, average value, and width of discrepancy of $\rho_E{}^*$ and $\rho_E{}^+$ in double ageing after quenching from $300^\circ C$

ageing temperature	$T_A{}'=70^\circ C$, $T_A=50^\circ C$	$T_A{}'=50^\circ C$, $T_A=70^\circ C$
resistivity data for $\rho_E{}^*$ and $\rho_E{}^+$ ($\mu\Omega$cm)	$\rho_E{}^*$ 1.0633 1.0569 1.0560 1.0559 1.0558 1.0552 1.0515 1.0492 1.0482 1.0475 1.0470 1.0471 1.0464 1.0455 1.0449 1.0429 1.0414 1.0359	$\rho_E{}^+$ 1.1182 1.1180 1.1060 1.0794
average value of $\rho_E{}^*$ and $\rho_E{}^+$ ($\mu\Omega$cm)	1.0503	1.1054
width of discrepancy of $\rho_E{}^*$ and $\rho_E{}^+$ ($\times 10^{-4}\mu\Omega$cm)	274	388

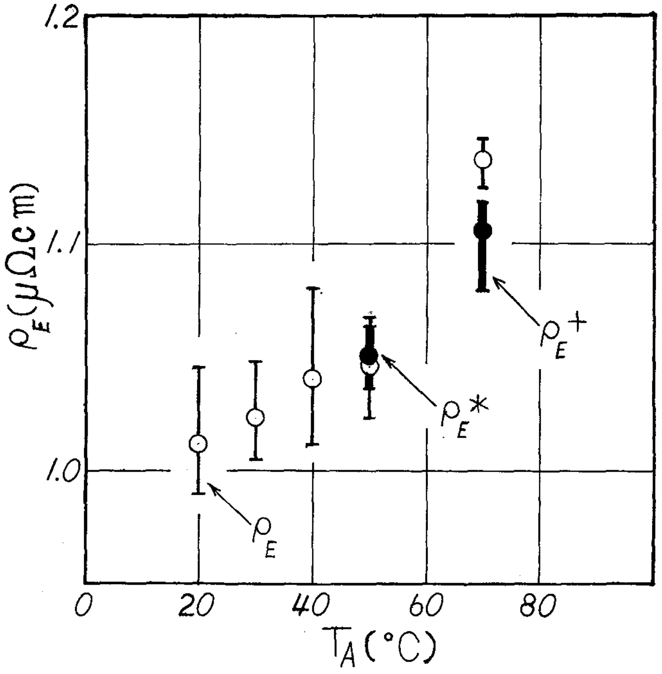

Fig.5 Mean value and width of discrepancy of ρ_E, $\rho_E{}^*$ and $\rho_E{}^+$ are protted versus T_A which are obtained in isothermal ageing and double ageing. $\rho_E{}^*$ and $\rho_E{}^+$ are described with black circle and pole versus second ageing temperature.

nearly equal to or slightly larger than that of ρ_E at $T_A=50^\circ C$.

Fig.4 shows the results obtained when specimens are quenched from $300^\circ C$ and aged at $70^\circ C$ after ageing at $50^\circ C$ until ρ_M being reached. It is obvious from this figure that metastable values of resistivity after long second ageing, ρ_E+, differ fairly. The width of discrepancy of ρ_E+ is larger than that of ρ_E at $T_A=70^\circ C$, and a little smaller than that of ρ_E at $T_A=50^\circ C$. And the mean value of ρ_E+ is smaller than that of ρ_E at $T_A=70^\circ C$, and larger than that of ρ_E at $T_A=50^\circ C$.

All the results are summarized in Fig.5 whose numerical values are given by Table 1 and 2. It is clear that the values of ρ_E^* are coinciding fairly well in each other in the case of double ageing.

4. Discussion

The value of resistivity in the metastable stage of ageing depends upon the mean size of G.P.zones(15). When the mean size is large, the resistivity is small, and vice versa.

Number of zinc atoms contained in G.P.zones formed during isothermal ageing is determined by the difference, $\Delta C=C_1-C_s$, where C_s is the concentration of solid solution coexisting with G.P.zones at T_A and C_1 is the concentration of the alloy(16). Curve indicating C_s against temperature is called "solvus" for formation of G.P.zones, and shown in Fig. 6. When the specimen is being cooled in water by quenching, G.P.zones maybe formed under the temperature shown by the solvus for G.P.zones. This formation of G.P.zones will continue to the temperature where zinc

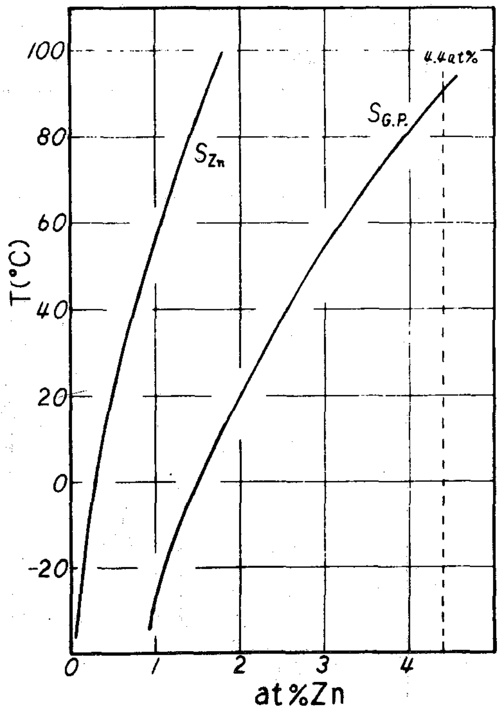

Fig.6 $S_{G.P.}$:Solvus curve for G.P.zone in Al-Zn alloy
S_{Zn}:Solvus curve for zinc in Al-Zn alloy

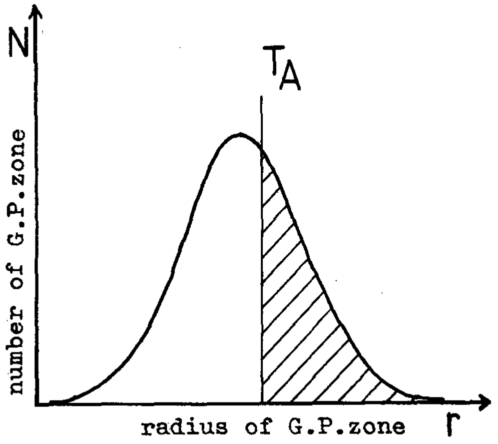

Fig.7 A schematical illustration of the relation between sizes and numbers of G.P. zones formed during quenching. The shaded part shows G.P.zones which can grow at T_A.

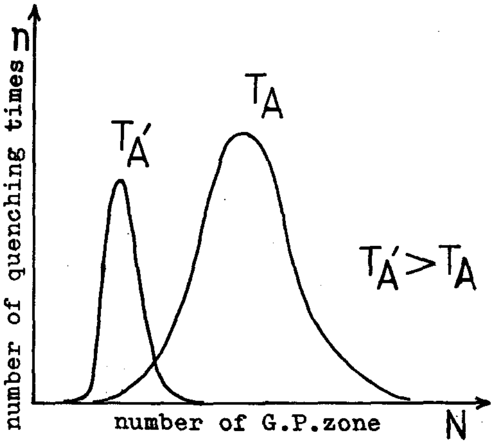

Fig.8 Showing the variation of the number of G.P.zone which can grow at T_A with T_A(schematic)

aotms can diffuse, perhaps about -50°C during being cooled in liquid nitrogen. This range of temperature is from ~90°C to ~-50°C. The relation between sizes and numbers of G.P.zones with each size formed during cooling are shown schematically as in Fig.7. On the other hand, cooling rates of the specimen may be different in every quenching even if T_Q and the temperature of liquid for quenching are controlled as carefully as possible. Therefore, the curve of distribution in Fig.7 may slide on horizontal axis changing its height and breadth.

When the specimen is annealed at T_A, G.P.zones which are larger than a certain size can grow, and those smaller than that size will revent. This size will be dependent upon T_A, and larger when T_A is higher. The shaded part in the curve of Fig.7 shows G.P.zones which can grow at T_A. The number of G.P.zones in the shaded area in Fig.7 is protted against the number of quenching times schematically in Fig.8. On the other hand, many G.P. zones are formed newly in solid solution at T_A, and the size of these G.P.zones must be smaller than those which have been existing immediately after quenching and are growing at T_A.

In the early stage of ageing, G.P.zones of both kinds grow and reach the critical size. Since the concentration of a G.P.zone to the electrical resistivity is not very sensitive to the size of zone near the critical size, it may be possible that the difference of sizes of two kinds of G.P.zones do not make large difference of resistivity if the total number of zones is nearly equal. Furthermore, it is considered to be probable that all zones can grow and competitive growth will not occur until a little after the stage where the maximum resistivity is reached, since the isothermal ageing curves for every measurement agree with each other very well.

In the later stage of ageing, the competitive growth must be the main mechanism of growth of G.P.zones. In these cases, the distribution of sizes of G.P.zones is very important. The ratio of the number of larger G.P.zones to the number of smaller G.P.zones is dependent upon the number of G.P.zones which are formed during quenching and do not revert at the ageing temperature. The number of these large G.P.zones may be different in every experiment under the same experimental conditions. If the annealing temperature is higher, larger number of G.P.zones formed during quenching will be desolved, and small number of these zones will remain and grow. The difference of the number of these remaining G.P.zones in each experiment might be small. And these zones would play a role in the competitive growth. This is the case of ageing at 70°C. When the ageing temperature is not so high, the number of G.P.zones which do not revert at the initial stage of ageing is fairly large, and the number may be different largely in each experiment. In these cases, the number of G.P.zones which can grow is different in each experiment in the stage of the competitive growth. This is the case of ageing at 50°C.

The first ageing at $T_A'=70^\circ C$ of double ageing is all the same as isothermal ageing at $T_A=70^\circ C$ written above, and two kinds of zones are formed and grow. After resistivity reached ρ_M at $T_A'=70^\circ C$, ageing temperature was changed down to 50°C, and second ageing was carried out successively at that temperature. When the ageing temperature is changed suddenly down to 50°C, G.P.zones which are formed during quenching and growing at 70°C and formed at 70°C and growing do not revert. They continue to grow at $T_A=50^\circ C$. On the other hand, new G.P.zones are formed and grow at 50°C. Therefore, there are three kinds of G.P.zones, that is, (1) formed during quenching and their size largest, refered as zones(1), (2) formed at $T_A'=70^\circ C$ and size medium, zones(2), (3) formed at $T_A=50^\circ C$, size smallest, zones(3).

When the competitive growth takes place, zones(1) and (2) can grow and zones(3) will be eaten by larger zones. The total number of zones(1) and (2) will not change so largely as the number of zones which can grow in single ageing at 70°C. Therefore, the first ageing at 70°C until the maximum resistivity being reached can make the width of discrepancy of values of $\rho_E{}^*$ obtained by the second ageing at 50°C narrower than that of ρ_E obtained by ageing at 50°C only. The final mean size of G.P.zones by the double ageing may be determined by ΔC at 50°C, thus the value of ρ_E in this case is nearly the same as that obtained by the simple ageing at 50°C.

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