Reversion and Reaging in an Al-2at%Zn-2at%Mg Alloy

By

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Kinetics of reversion and reaging of an Al-2at%Zn-2at%Mg alloy have been studied by resistivity measurements and tensile tests. Perfect reversion occurred only when aged at −20°C. The formation of the transition phase was found to occur in parallel with the dissolution of zones when the specimen aged at 70°C was reverted at 200°C. An incubation period accompanied with initial fast and slow reactions was observed in reaging. When the aging prior to reversion was ceased before the end of fast reaction, the incubation period was not observed, similarly in the case of Al-Cu alloy. It will be clear that the nucleation is necessary for zone formation in Al-Zn-Mg alloys. The initial fast and slow reactions will be explained in terms of the amount of vacancies compared with the number of solute atoms after reversion.

Introduction

In an Al-2at% Zn-2at% Mg alloy, G.P. zones are formed by aging at temperatures below 130°C, after rapid quenching from the solid solution temperature (>380°C)[1]. After a long aging period, the existence of ordered structure in the zone is confirmed by X-ray techniques[2,3]. According to the measurement of resistivity and proof strength[1], the rate of zone formation is hardly influenced by the quenching temperature, but the nucleation of zones was thought to be athermal similarly in other well discussed Al alloys. In this alloy the transition phase formation takes place overlapping to the zone formation in rather wide temperature range(~70°C–~130°C)[4], and hence, the perfect reversion like that in Al-Cu alloy is not observed. When reverted to a somewhat low temperature, the growth of transition phase particle occurs in parallel with the dissolution of zones, then the proof stress shows a shallow valley and the resistivity decreases with two stages. The latter fact suggests that there are two species of zones. If the resistivity increment reaches the value of first aging, it will be considered that the most part of zones are dissolved and the quantity of transition phase formed during reversion is very small, assuming the negligible contribution of transition phase to the resistivity.

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Herman et al.[5,6], have investigated the reaging of Al-Cu and found the incubation period in isothermal aging curves by measurements of resistance and Young's modulus. Their conclusion about the nucleation of G.P. zones is also pertinent to this alloy system.

The purpose of the present paper is to give some experimental information concerning reversion and reaging of Al-Zn-Mg alloys containing Mg to the extent of that in commercial alloy. The temperature dependence of kinetics of reversion is investigated by the measurement of electrical resistivity and 0.2% proof stress. The incubation time and rates of reaging after reversion is also investigated.

Experimental

The wire of 0.75 mm in diameter was prepared from high purity materials. The alloy composition is shown in Table I. Aluminium leads were welded to the specimen of ca. 15 cm long, and wound to the quartz holder to protect points of contact from mechanical shock. All heat treatments were carried out with this specimen assembly. The sepcimens were quenched from 450°C after solution treatment of 30 min. dropping into brine of -20°C. Aging was carried out in a stirred bath of polyethyleneglycol, whose temperature was controlled to $\pm$ 0.5°C. Silicon oil bath was employed for reversion. Electrical resistance was measured at liquid nitrogen temperature by the four probe potentiometric method. Tensile test was performed at room temperature using Instron type machine with the strain rate of 6.67×10^{-4}/sec. The stress at 0.2% plastic strain on the stress-strain curve was taken as a proof stress. Because of the difficulty of small intensity, the X-ray small angle scattering method was applied only to Al-3at.%Zn-lat.%Mg alloy.

Results and Discussions

Figure 1 shows the changes of proof stress with isothermal dissolution treatments at 130°C after -20°C and 70°C agings. In the early stage, softening takes place with dissolution of zones, but the formation of transition phase elevates again the proof stress. So each curve except one which is aged at 70°C for 15 hrs. has a minimum in the range of 10–100 seconds. Although the proof stress of specimens aged at –20°C decreases rapidly near the value of as-quenched state, the minimum

Table 1. Chemical compositions of the specimen. (wt%)

	Zn	Mg	Cu	Si	Fe	Al
wt. %	5.24	2.08	0.002	0.007	0.003	bal.
at. %	~2	~2				

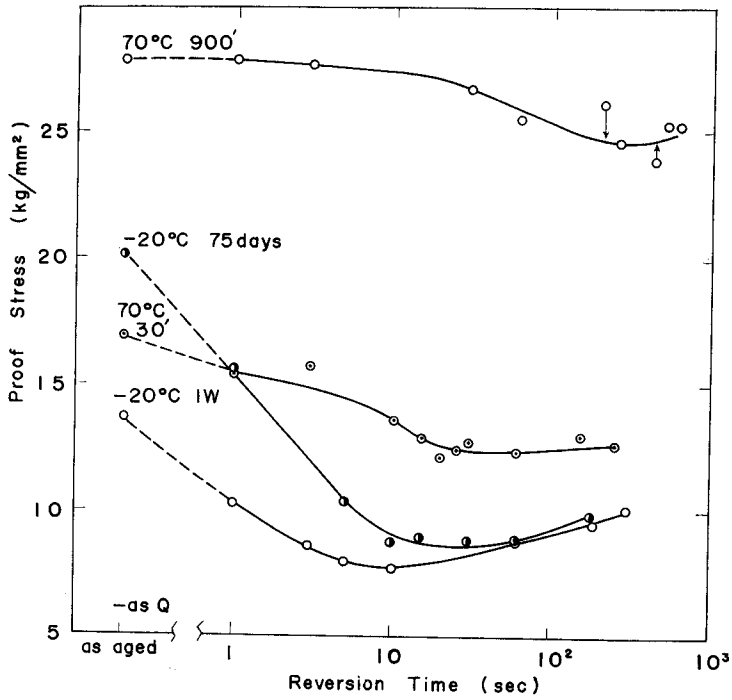

Fig. 1. Change in proof stress with isothermal reversion at 130°C.

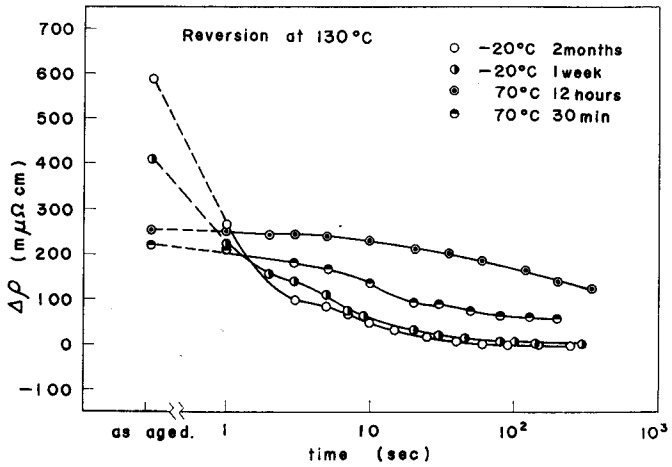

Fig. 2. Resistivity change with the same heat treatment as Fig. 1.

values in specimens aged at 70°C are higher than the as-quenched value. These observations can be explained by the larger zone size and the more advanced nucleation of transition phase during aging at higher temperature for a longer period[7].

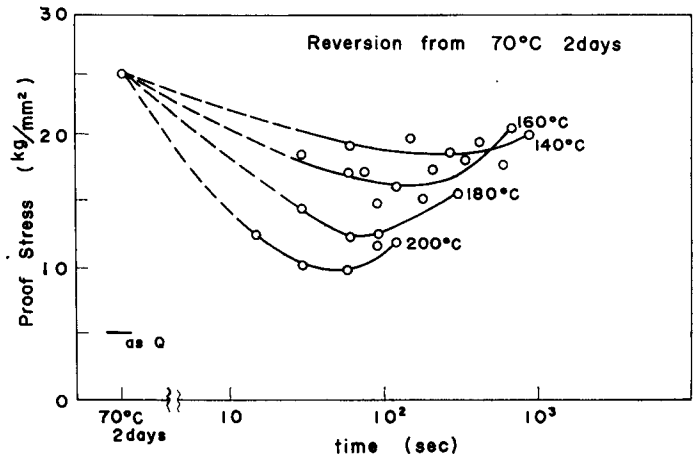

Fig. 3. Change in proof stress with isothermal reversion at several temperatures after aging at 70°C for 2 days.

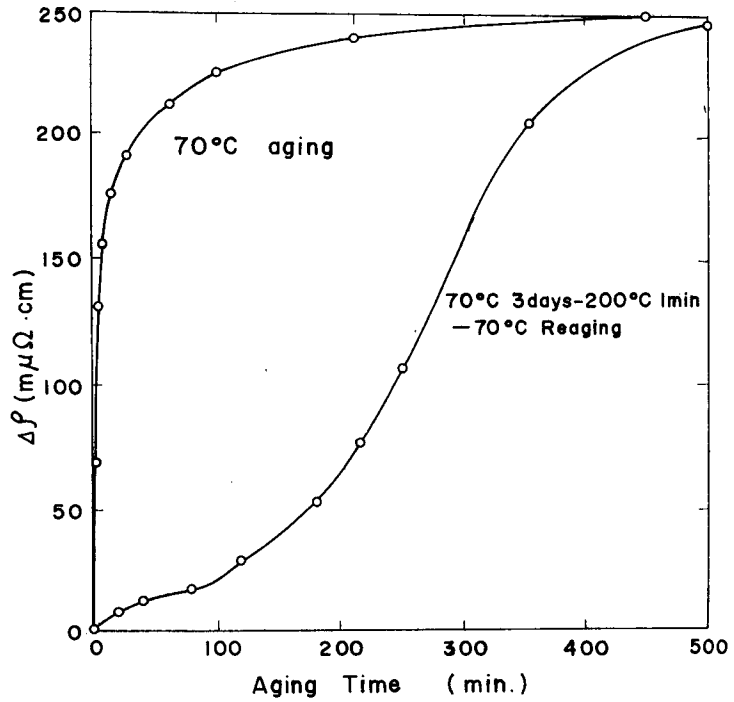

Fig. 4. Change in resistivity vs. time of aging and reaging at 70°C. Reaging was carried out after aging at 70°C for 3 days and reversion at 200°C for 1 min.

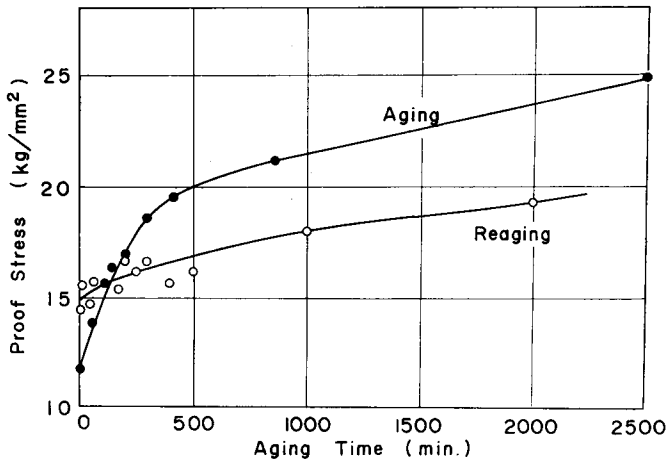

Fig. 5. Change in proof stress vs. time. Heat treatments are same as Fig. 4.

This viewpoint is supported by the results of resistivity measurement shown in Figure 2. The resistivity increase in −20°C aging is larger than that in 70°C aging, but easily reverted to the as-quenched value. In the case of 70°C aging, the resistivity decreases very slowly with reversion and hardly reaches the as-quenched value. Figure 3 shows the change in proof stress during isothermal reversion at several temperatures after aging at 70°C for 2 days. The minimum value in the curves becomes smaller the higher the temperature of reversion, though it does not reach to the as-quenched value even in 200°C reversion.

When specimens are reverted at 200°C after the same aging as Figure 3, the resistivity change is too fast to observe the stagnancy near the as-quenched value which is apparent in 130°C reversion. In Figures 4 and 5, specimens are reaged at 70°C, after aging at 70°C for 3 days and reversion at 200°C for 1 min. compared with the primary aging at 70°C. The rate of reaging becomes small, but the increment in resistivity from the as-reverted state is almost comparable to that of the primary aged specimen. Hence, it is considered that the zones are almost perfectly dissolved by reversion, and newly formed by reaging. The kinectics of resistivity change, as shown in Figure 4, exhibits the reaction with incubation period which suggests the existence of the nucleation process, in addition to the fast and slow reaction at the first stage. Figure 5 shows the change in proof stress, comparing the reaging treamtent with aging one. The existence of incubation period is not clear from this result, but the hardening is disticntly slowed in reaging.

The two stage increase in resistivity can be devided into the fast and slow reactions, namely the first stage and the second stage with incubation period. There

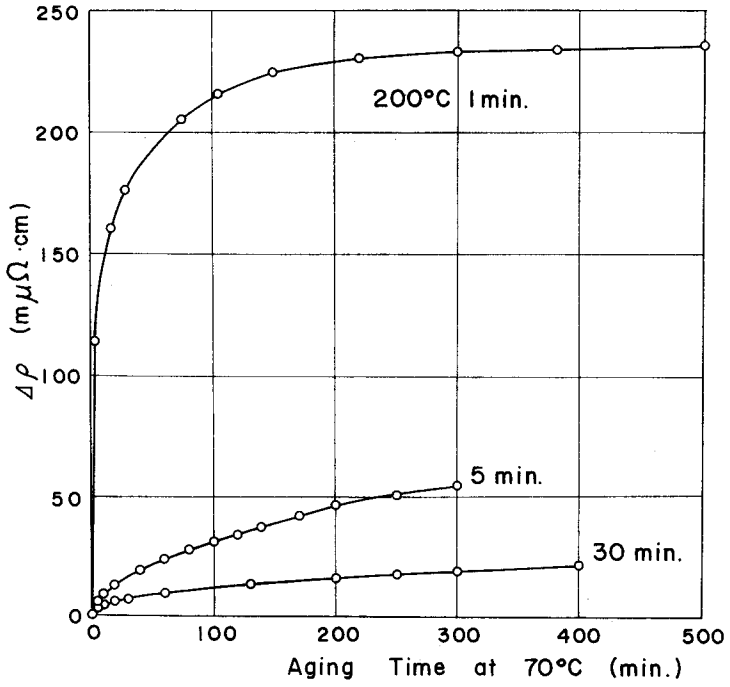

Fig. 6. Change in resistivity vs. time at 70°C after aging at 200°C for various periods.

are two cases to be considered which depend upon whether the nucleation of G.P. zones is athermal or not. If the athermal nucleation is pertinent also to the present case, the increase in the second stage will come from the existence of particles of transition phase which are so fine as to be able to contribute to the resistivity increase, and need the nucleation process before growth. But it is more plausible to consider that the nucleation is necessary also to G.P.zone formation, and the incubation period may have not been observed because of a too large rate of nucleation. To examine the relation between slow rate of reaction and incubation, primary aging in heat treatments prior to reaging was omitted. Namely, the specimen was aged at 200°C immediately after quenching and then aged at 70°C. Figure 6 shows results of resistivity measurements. Aging at 200°C for 1 min. shows little effect on the kinetics of successive aging at 70°C. Prolonged aging at 200°C lowers the resistivity increase by reaging at 70°C, but every curve shows the typical fast and slow reactions and no two stage increase, just as shown in Figure 4, is observed. Even after the aging at 200°C for 30 min., the resistivity increases more than 20 $m\mu\Omega$cm. This result suggests that the cause of the incubation phenomenon is not

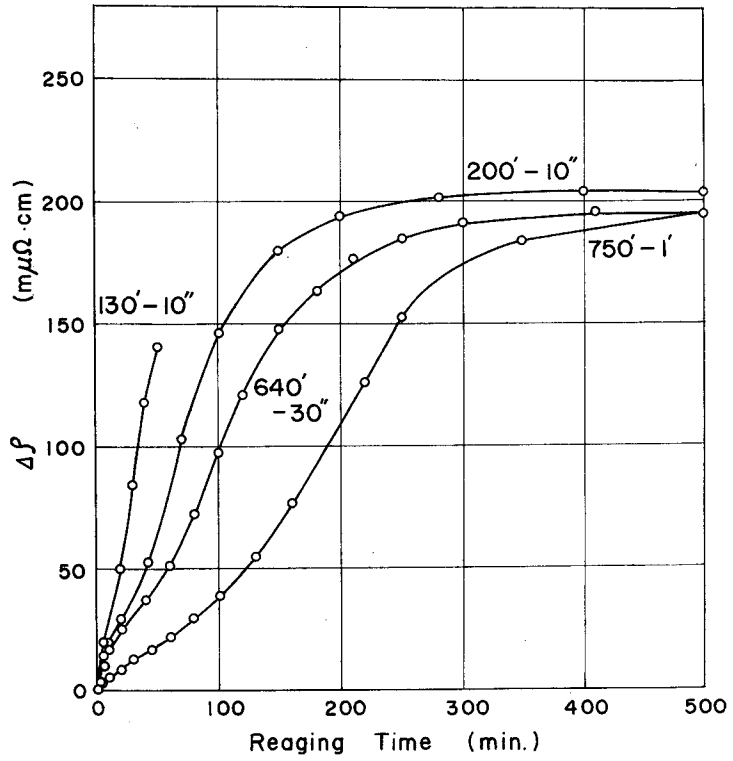

Fig. 7. Change in resistivity vs. reaging time at 70°C after various period of primary aging at 70°C and reversion at 200°C. Pairs of hyphenated figures means the primary aging time and reversion time, respectively.

set up by the process occurring at 200°C, and the reaction in primary aging at 70°C must influence the reaging even after the reversion treatment at 200°C.

Then, aging time at 70°C is reduced to examine the time necessary for the achievment of constitutional change which gives rise to the incubation period in reaging. Results are shown in Figure 7. The two stage increase in resistivity is observed to be the primary aging for 130 min. at 70°C, and the rate of reaging is most influenced by the aging time at 70°C. The longer the primary aging time is, the later the second increase begins. But in every cases, the first increase ceases at nearly equal value of $\Delta\rho$, namely ca. $30 m\mu\Omega$cm.

As there is a possibility of transition phase formation at 70°C, the first aging and reaging are carried out at 40°C. Still the incubation period is observed, as shown in Figure 8.

Higher Zn/Mg ratio is necessary to estimate the size or the volume fraction of zones, because the intensity of X-ray small angle scattering due to zones is lowered

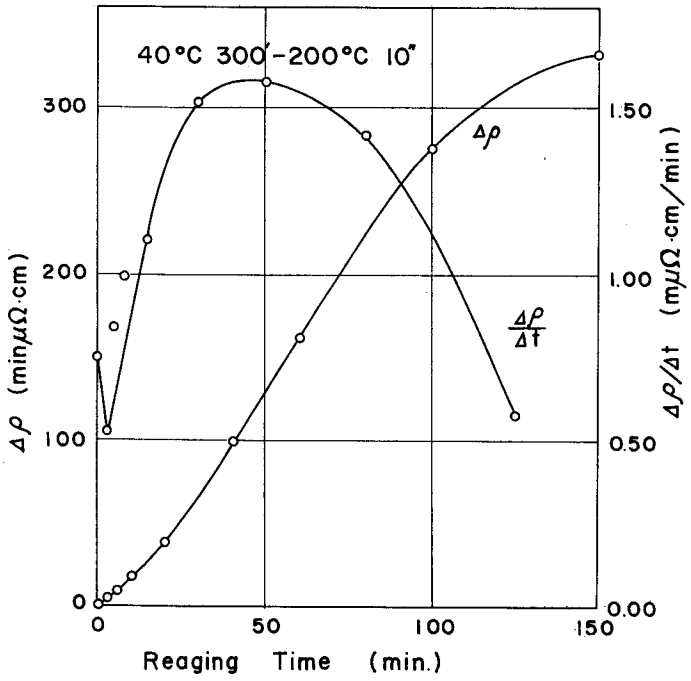

Fig. 8. Isothermal reaging curve at 40°C. Differential curve is also shown.

by Mg atoms in zones. Therefore, the sheet of Al-3at.%Zn-lat.%Mg alloy was prepared. It is confirmed that the incubation in resistivity change with reaging at 80°C also occurs in this alloy, as shown in Figure 9. Figure 10 shows the relation between scattered intensity and scattering angle after several heat treatments. The curves in upper position mean larger volume fraction of G.P. zones in specimen. It is clear that zones formed by 80°C aging is dissoluted by the reversion at 200°C for 1 min. and that zones are reformed by reaging.

In agreement with the proof stress change during reversion treatment, curve(3) suggests that some zones larger than average size still remain after reversion at 200°C. So far as judging from the curves of primary aging(2) and reaging(4), the zones show no difference except in number or by volume fraction.

Figure 11 shows a schematic representation of two stage increase in resistivity during reaging. The observed curve is divided into reaction I of simple fast and slow reactions and reaction II including incubation period. The fast and slow reaction (reaction I) which is not reported in Al-Cu alloy[5,6], is characteristic of reaging of Al-Zn-Mg alloy.

The zone size and the integrated scattering intensity in the Al-3at%Zn-lat%

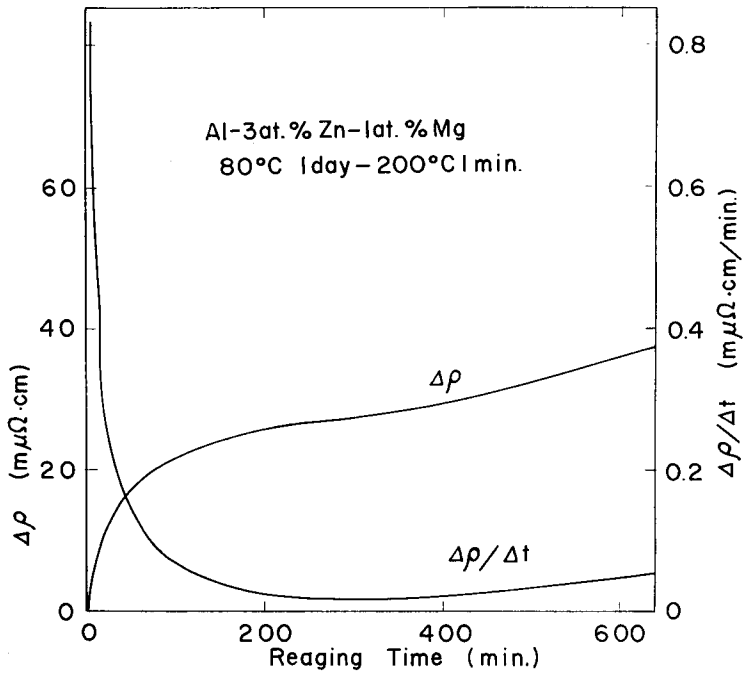

Fig. 9. Reaging curve at 80°C of the Al-3 at.% Zn-1 at.% Mg alloy. Specimen aged at 80°C for 1 day and reverted at 200°C for 1 min.

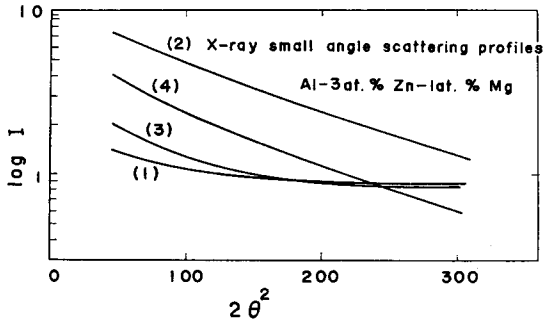

Fig. 10. X-ray small angle scattering profiles of Al-3 at.% Zn-1 at.% Mg alloy after several heat treatments.

(1) as quenched
(2) quenched and aged at 80°C for 65 hrs.
(3) reverted at 200°C for 1 min. after (2).
(4) reaged at 80°C for 46 hrs. after (3).

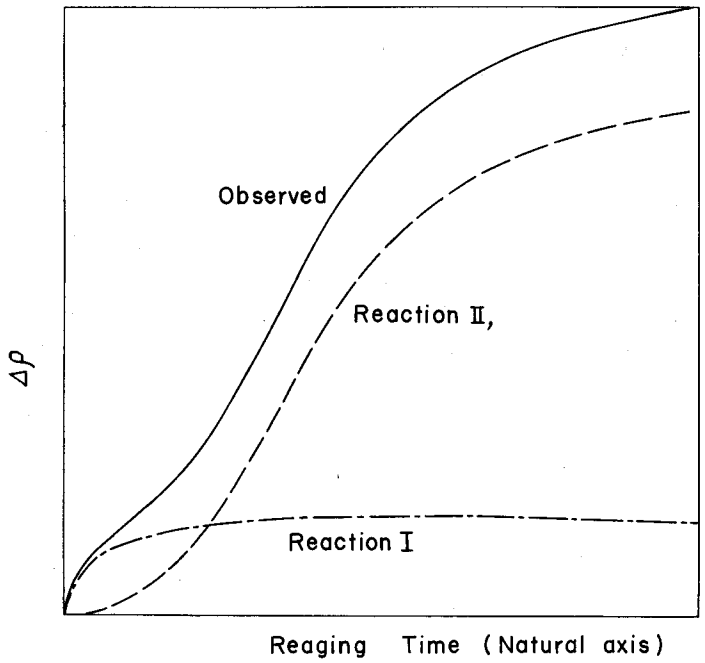

Fig. 11. Schematic representation of reaging curve.

Table 2. The zone size (R) and integrated scattering intensity (Q) in the Al-3at%Zn-1at%Mg alloy after some heat treatments.

Heat treatments	R(Å)	Q(arbitrary units)
Aging at 80°C for 65 hrs.	20.8	96
Reversion at 200°C for 1min.	(19)	—
Reaging at 80°C for 24 hrs.	22.0	—
Reaging at 80°C for 46 hrs.	22.5	48
Reaging at 80°C for 64 hrs.	22.3	59

Mg alloy were estimated from scattering curves and shown in Table 2. The zone sizes in the reaged specimens are larger than that in the primary aged specimens, and the growth of zones is scarcely observed in the reaging. But in the integrated intensity, the value of the reaged specimen is almost one half of that of the primary aged specimen, similarly to the Al–Zn alloy[7].

Conclusions and Comments

The reversion in present alloy strongly depends upon time and temperature of aging, in agreement with the results in Al-Zn-alloy[7]. Perfect reversion of age-

hardening is not observed in 70°C aging. It is considered that in addition to size of the zones the vacancy concentaration released at the reversion temperature influences the rate of reversion.

Because the incubation period has been observed only in non-ideal zone formation[6,7], reaction II can be related to the zones of ordered structure reported in present alloy system[4]. The reason why the incubation period is not observed in the sequence of heat treatments without primary aging, is given by the fact that the vacancy annihilation occurs mainly at the primary aging. In reaging, the ratio of concentration of movable vacancies to that of solute atoms is less than some critical values which govern the nucleation process of G.P.zone formation. Namely, with plentiful vacancy concentration the spherical zones which have a disordered structure will be formed without nucleation at initial stage of reaging, but the vacancy concentration is lowered soon during reaging. Then the further zone formation has to be continued at lower vacancy concentration, and the nucleation process becomes observable.

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