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## Information on the Early Decomposition Behaviour in Al-Zn(6)-Mg(X) Alloys by an Analytical Description of Isothermal Resistivity Curves

Based on a theoretically derived expression for the extra-resistivity resulting from the formation of GP-Zones

$$\varrho_{\text{ex}} = C \cdot f \cdot \frac{\Omega}{r}$$

isothermal resistivity measurements with Al-Zn(6 at.%)–Mg(0.81; 1.73 at.%) alloys were analysed. A comparison of both expressions  $d(\ln \varrho_{\text{ex}})/dt$  and  $d(\ln f)/dt$  yields statements on the early stage of decomposition behaviour, especially, whether up to a considered time point size growth happened. The evaluated examples lead to the conclusion that size growth is most probably to exclude up to the time point of 4T.

The  $T_a$ -dependence of the maximum value of extra-resistivity is explained by an equilibrium distribution of bigger particles of a smaller number at higher aging temperatures, of smaller particles of a greater number at lower aging temperatures and by the assumption, that the amount of solute atoms inside the GP-zones is decreasing with rise of  $T_a$ .

### 1. Introduction

At the age-hardening Al-alloys with full coherent precipitates (GP-zones) as first decomposition stage at the begin of the decomposition a maximum of the resistivity appears and thereafter the "normal" resistivity decrease follows. That resistivity behaviour was sufficiently explained for the first time by RADOMSKY. Basing on the solution of the BOLTZMANN-equation in the isotropic relaxation time approximation and using theoretical X-ray small-angle scattering (XSAS) intensities quoted by GUINIER in order to describe the interference function of GP-zones an expression for the extra-resistivity caused by spherical GP-zones was derived by RADOMSKY:

$$\varrho_{\text{ex}}^{\text{sph}} = C \cdot f \cdot [\Omega(2k_F r)/r]. \quad (1)$$

$r$  is the so-called effective resistivity radius approximately corresponding with the Porod's radius assuming the size distribution of zones is describable by a lognormal function,  $f$  is the volume fraction of the precipitates related to the total volume of the crystal.

Repeatedly in the literature (see for example WERT and ZENER) a function of JOHNSON-MEHL-AVRAMI-type is used to describe the dependence of  $f$  on time  $t$  during isothermal decomposition

$$f = f_0 \{1 - \exp [-(t/T)^n]\} \quad (2)$$

$f_0$  means the saturation value of the volume fraction, both  $n$  and  $T$  determine the change rate of the volume fraction.  $\Omega$  is a function depending on the effective resistivity radius and the Fermi wave number  $k_F$ . The course of  $\Omega/r$  in dependence on  $r$  is shown

in Figure 1. Finally C stands for the expression

$$C = (\Delta n_f)^2 \frac{\pi^{2/3} \hbar}{3^{2/3} e_0^2 n_0^{8/3}} \quad (3)$$

where

$\Delta n_f$ : difference of the density of conduction electrons between matrix and GP-zones

$n_0$ : average density of conduction electrons in the alloy

$e_0$ : elementary charge

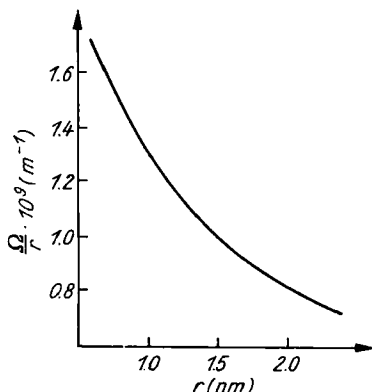


Fig. 1. Course of the  $\Omega/r$ -function in dependence on the particle radius  $r$

(1) makes possible to obtain information on the temporal development of the volume fraction, on the growth law of the zones, and as this paper will show, especially on the question whether up to a certain time point the increase of the volume fraction is mainly caused by increase of the particle density or by size growth of precipitates. This is therefore especially important because direct investigation methods as XSAS and TEM can give only few information on the earliest decomposition happening.

## 2. Investigations on the increase of volume fraction

As OETTEL et al. have shown the experimentally obtained extra resistivity is describable in a wide time span by the equation

$$\varrho_{\text{ex}} = \varrho(t) - \varrho_0 = \Delta\varrho \{1 - \exp[-(t/T)^n]\}. \quad (4)$$

$\varrho_0$  is the quenched-in resistivity of the solid solution and  $\Delta\varrho$  is the maximum value of the extra resistivity. The parameters  $\Delta\varrho$ ,  $\varrho_0$ ,  $T$ , and  $n$  can be determined in a proper way as shown by OETTEL et al. likewise.

A comparison of equations (1) and (4) demonstrates that (4) presumes  $\Omega(2k_F r)/r = \text{const.}$  In case of size growth of GP-zones the determination on  $n$  was falsified by the decrease of the  $\Omega/r$ -function: the experimentally obtained value of  $n_{\text{exp}}$  is greater than the true value  $n$  describing the increase of the volume fraction.

In order to decide whether up to the time point  $T$  size growth has taken place or not the expression  $[d(\ln \varrho_{\text{ex}})/dt]_T$  from (1) can be formed by use of (2)

$$\left[ \frac{d(\ln \varrho_{\text{ex}})}{dt} \right]_T = \left[ \frac{d(\ln f)}{dt} \right]_T + \left[ \frac{1}{\Omega/r} \cdot \frac{d(\Omega/r)}{dt} \right]_T = \frac{1}{(e-1)} \cdot \frac{n}{T} + A. \quad (5)$$

In case size growth did not take place up to  $T$  ( $\Omega/r$ ) is constant and therefore  $A = 0$ .

The calculable expression  $(1/(e-1)) \cdot n/T$  and the expression  $[d(\ln \varrho_{\text{ex}})/dt]_T$ , graphically determinable from the plot of the  $\ln \varrho_{\text{ex}}-t$ -curve at time  $T$ , have to be in keeping.

Table 1

Comparison of the values of the calculable expression  $(1/(e-1)) \cdot n/T$  and the expression  $[d(\ln \varrho_{\text{ex}})/dt]_T$  for AlZn(6)Mg(0.81) at  $T_q = 480^\circ\text{C}$  and various  $T_a$  values

| $T_a/^\circ\text{C}$ | $\frac{1}{e-1} \cdot \frac{n}{T}$ | $\left[ \frac{d(\ln \varrho_{\text{ex}})}{dt} \right]$ |
|----------------------|-----------------------------------|--|
| 0                    | 0.0139                            | 0.0137   |
| 10                   | 0.0441                            | 0.0439   |
| 20                   | 0.119                             | 0.118  |
| 30                   | 0.301                             | 0.287  |
| 40                   | 0.614                             | 0.563  |
| 50                   | 1.054                             | 1.031  |
| 60                   | 2.159                             | 2.135  |

In the other case that considerable size growth has taken place up to  $T$  follows  $d(\Omega/r)/dt < 0$  because of the course of the  $\Omega/r$  function and therefore  $A < 0$ . One can expect that the plot graphically determined is considerably smaller than the calculated value  $(1/(e-1)) \cdot n/T$ . In Table 1 both values of the AlZn(6)Mg(0.81) alloys are opposed. The differences are small, they are within of limits of error of the plots graphically determined. Since in case of size growth as already mentioned above  $n_{\text{exp}} > n$  it is to expect that the differences between  $n_{\text{exp}}/T \cdot (1/(e-1))$  and  $[d(\ln \varrho_{\text{exp}})/dt]_T$  will be greater yet and the increase of the volume fraction follows (2) and is to explain by rise of particle density.

Similar considerations and investigations can be made for time points after  $T$ , too. From equation (2) follows

$$\left[ \frac{d(\ln f)}{dt} \right]_t = \frac{1}{[1 - \exp \{- (t/T)^n\}] \exp \{- (t/T)^n\}} \left( \frac{t}{T} \right)^n \cdot \frac{n}{t}. \quad (6)$$

For some experimentally obtained curves that can be fitted with a constant parameter  $n$  up to the saturation value both expressions  $[d(\ln f)/dt]_t$  and  $[d(\ln \varrho)/dt]_t$  were found for time points  $t = x \cdot T$ ,  $x > 1$ .

The results are shown in Table 2.

Table 2

Comparison of the values of the expressions  $[d(\ln f)/dt]_t$  and  $[d(\ln \varrho_{\text{ex}})/dt]_t$  for two different AlZn(6)Mg(x) alloys and various  $t_a$ ,  $T_q$ ,  $t$  values

| alloy           | $T_q/^\circ\text{C}$ | $T_a/^\circ\text{C}$ | $t$ | $\left[ \frac{d(\ln f)}{dt} \right]_t$ | $\left[ \frac{d(\ln \varrho_{\text{ex}})}{dt} \right]_t$ |
|-----------------|----------------------|----------------------|-----|--|--|
| AlZn(6)Mg(0,81) | 360                  | 0                    | T   | 0.0106                                 | 0.0105   |
|                 |                      |                      | 2T  | 0.0029                                 | 0.0028   |
|                 |                      |                      | 4T  | $3.33 \cdot 10^{-4}$                   | $3.22 \cdot 10^{-4}$                                     |
|                 | 415                  | 60                   | T   | 2.125                                  | 2.050  |
|                 |                      |                      | 2T  | 0.738                                  | 0.747  |
|                 |                      |                      | 4T  | 0.234                                  | 0.222  |
| AlZn(6)Mg(1,73) | 360                  | 30                   | T   | 0.121                                  | 0.120  |
|                 |                      |                      | 2T  | 0.031                                  | 0.034  |
|                 |                      |                      | 4T  | 0.0049                                 | 0.0051   |
|                 | 480                  | 90                   | T   | 2.794                                  | 2.791  |
|                 |                      |                      | 2T  | 0.782                                  | 0.779  |
|                 |                      |                      | 4T  | 0.126                                  | 0.101  |

The errors of the graphically obtained values  $[d(\ln \varrho)/dt]_t$  increase with rising  $x$  because the resistivity changes are decreasing with rising aging time. The proposed results lead to the conclusion, that considerable size growth does not yet start even up to times  $t = 4T$  with the investigated alloys.

### 3. Conclusions with regard to particle density, particle size, and particle composition in the early stage of decomposition

In Figure 2 the normed measure of the maximum value of the extra resistivity  $\varrho_{\max}$  due to the formation of GP-zones is plotted versus the aging temperature  $T_a$  for an Al-Zn(6)-Mg(0.81) alloys. As already known from former investigations of other authors (PANSERI, FEDERIGHI)  $\varrho_{\max}$  decreases with rise of  $T_a$ . But the reason of this fairly steep decrease of  $\varrho_{\max}$  is rather uncertain till now, i.e. it is unknown in which

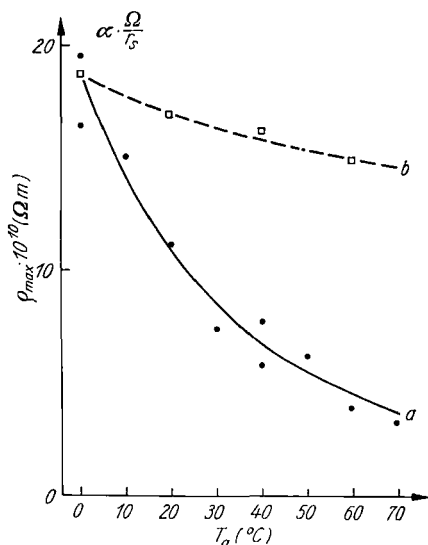


Fig. 2. Curve a: Experimentally obtained maximum values of the extra resistivity  $\Delta\varrho_{\max}$  in dependence on the ageing temperature  $T_a$  (full line); curve b:  $\Omega/r_s$  from the experimentally obtained "starting radii" (XSAS measurement) in dependence on  $T_a$  fitted to the curve a at 0° C. (dashed line)

degree the change of both, volume fraction  $f$  and "starting radius" with  $T_a$  will influence  $\varrho_{\max}$ . The aim is to contribute in clarifying this open problem by means of both, eq. (1) and XSAS-data. From eq. (1) follows

$$\varrho_{\max} = C \cdot f_0 \cdot \frac{\Omega}{r}. \quad (7)$$

For a first rough interpretation we assume both  $C$  and  $f_0$  are independent on  $T_a$ . Therefore the course of  $\varrho_{\max}$  with  $T_a$  is caused by the change of the  $\Omega/r$ -function.

In Figure 1 the course of the  $\Omega/r$ -function in dependence on  $r$  is shown. After that the values of the  $\Omega/r$ -function are decreasing with rise of  $r$ . Taking into account the decrease of  $\varrho_{\max}$  with rise of  $T_a$  most probably the  $r$ -values are increasing. Obviously within the frame of the initial decomposition on equilibrium distribution of precipitates puts in, which is characterised by a greater number of smaller particles at lower aging temperatures and by a smaller number of bigger particles at higher aging temperatures.

For a more detailed interpretation the "starting radii"  $r_s$  of the GP-zones from XSAS-measurements done with this alloys after direct quench to  $T_a$  (KABISCH,

ZOCH) can be taken. From both, the  $r_s$  and the  $\Omega(2k_F r_s)$  values, the change of  $\Omega(r_s)/r_s$  with  $T_a$  can be calculated. The result is drawn in Figure 2 by the dashed line fitted to the experimentally obtained resistivity curve at 0 °C.

The course of  $\Omega/r$  with  $T_a$  determines the  $r$ -dependence of  $\rho_{\max}$ .

Figure 2 shows that this course does not fit the measured  $\rho_{\max}$ -curve. That means other influences on  $\rho_{\max}$  have to be taken into account as for example the change of both zinc and magnesium content of the zones and the change of the saturation value of the volume fraction  $f_0$  with  $T_a$ . In order to get accordance between both curves in Figure 2 one can use the assumption that both,  $C$  and  $f_0$ , depend on  $T_a$  in the following manner:

$$(Cf_0)_{T_{a1}} > (Cf_0)_{T_{a2}} \quad \text{for} \quad T_{a1} < T_{a2}.$$

A numerical estimate on the basis of both experimentally obtained  $r_s$  and  $\rho_{\max}$  values leads to the result that these influences are fairly strong. Most probably the amount of solute atoms inside the GP-zones is decreasing with rise of  $T_a$  as well known from the Al-Zn alloys (DLUBEK et al.). From this can be concluded:

1. The difference of the density of conduction electrons between matrix and GP-zones  $\Delta n_f$  due to the changes of solute concentration in the zones as well as the matrix and in connection with eq. (3)  $C$  is decreasing with rise of  $T_a$ , i.e.  $C(T_{a1}) > C(T_{a2})$ .
2. The saturation value of the volume fraction  $f_0$  increases with  $T_a$ , i.e.  $f_0(T_{a1}) < f_0(T_{a2})$ . Of course the total amount of solute atoms inserted into the zones decreases with increase of  $T_a$ , but the solute concentration of the zones decreases more with rise of  $T_a$ .
3. The change of  $f_0$  is smaller than the change of  $C$ .

More combined XSAS and resistivity investigations are necessary to clarify this problem above all the composition of the zones in dependence of  $T_a$ .

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