# PRECIPITATION AND GP- ZONE STRUCTURES IN AlZnMg(Cu,Zr) ALLOYS

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Precipitation processes taking place in high trenght AlZnMg alloys (7xxx series) were investigated by compression tests TEM and EDX.

The results show that addition of Cu changes strongly the temperature of GP - zone  $\rightarrow$  intermediate phase transition.

The addition of Zr leads to an extremly fine-grained structure and in the AlZnMgCuZr alloy a "duplex" GP-zone structure is formed, causing a "duplex" behaviour of this alloy.

## 1. INTRODUCTION

The high strength Al-Zn-Mg-Cu Alloys (e.g. 7075 alloys) are based on the AlZnMg ternary system with Cu addition wich influences effectively the decomposition of the Supersaturated solid solution (S.S.S.S) [1,2]. It is well known that the decomposition of the S.S.S.S. takes place generally according to the following sequence [1-3]

SSSS  $\rightarrow$  GP zone  $\rightarrow$  Intermediate ( $\eta$ ) phase  $\rightarrow$  Stable ( $\eta$  and sometime T) phases

To better understand the physical and mechanical properties of these alloys it is important to know the precipitation structure belonging to each step and the temperature intervals where these steps are occurring. The sequence of the processes, however, depends strongly on the composition of the alloy, on the quenching conditions, etc.[3-5]. The addition of small amounts (0.08 - 0.25%) of Zn can ensure a fine - grained structure [6-8] which is relatively less sensitive to the quenching rate [2,6]. In the case of these alloys, however, the effect of grain boundaries is enhanced, enhancing thereby also the influence of precipitates at grain boundaries and precipitate free zones (PFZ) [1,4].

It is also well known that the GP-zones which form in Al-Zn and Al-Zn-Mg alloys are spherical, while those forming in Al-Cu are plate-like [1,2,9,10]. In the Al-

Zn-Mg-Cu alloys although there are evidences that Cu atoms are mostly built into Zn and Mg containing  $\eta^4$  and  $\eta$  precipitates [1], it is not entirely clear what types of GP-zones are formed.

In this paper the effect of GP-zone formation and precipitation processes on the mechanical properties of AlZnMg(Cu,Zr) alloys was investigated.

## 2. EXPERIMENTAL PROCEDURE

The precipitation and work hardening processes of ternary Al5,7Zn1,9Mg samlpes ( alloy A ), as well as samples of the same alloys with 1.4% Cu ( alloy B ) and 1.4% Cu, 0.14% Zr ( alloy C ) addition ( compositions given in wt% ) have been investigated by compression tests, TEM and EDS investigations. After solution treatment and quenching into room temperature water the samples were directly aged in the temperature region of 20 to  $240^{\circ}$ C.

The alloys were prepared from 99,99% purity aluminum. After casting the samples were homogenised for 8 h at 470°C in air, and then hot extruded to sheets of  $10x40 \text{ mm}^2$  cross section. The starting temperture of the hot extrusion was  $380\pm5^{\circ}$ C. For solution treatment the specimens were annealed at 470°C for 30 min and waterquenched to room temperature. After this treatment fully recrystalised materials were obtained. It was shown previously [8] that alloys A and alloys B with no Zr addition have very similar coarse - grained microstructure with mean grain size larger than 150 $\mu$ m. In contrast to this the microstructure in alloy C is extremly fine - grained, with an average grain size of less than 8 $\mu$ m. The development of this microstructure can be clearly attributed to the grain refining effect of the finely dispersed, stable Al<sub>3</sub> Zr partiecles [1,2].

#### 3. **RESULTS AND DISCUSSION**

Figure 1 shows the influence of 2 h ageing temperature,  $T_a$  on the 0.2% proof stress,  $\sigma_p$ . It can be seen that the effect of Cu addition is conspicuous. The Cu



Fig. 1. The effect of ageing on 0.2% proof stress

content at each temperature increases effectively the value of  $\sigma_p$ . Furthermore, the results show that the Cu addition has strongly changed the temperature of GP-zone  $\rightarrow$  intermediate phase transition. While for the pure ternary AlZnMg alloy (alloy A) 120°C was determined for the maximum temperature of GP-zone formation, in the Cu-containing alloys (B and C) the process of zone formation is extended to higher temperatures. It is interesting that the alloy C shows a "duplex" behaviour. Below 140°C the  $\sigma_p$  obtained for this alloy changes in the same way as that for alloy A. The value of  $\sigma_p$  increases up to 120°C and it decreases abruptly at about140°C...

Above this temperature it seems that there is no difference between the properties of alloys C and alloys B, the formation of metastable and stable phase particles determines mainly the strength of the alloys.

Figure 2 shows the microstructure of alloy C after 2 h ageing at 220°C. Due to this ageing well developed precipitate structure in the grain interiors with characteristic PFZs along grain boundaries can be observed. The equal strength of alloys C and alloys B must be explained by the similar precipitate structure- where Cu atoms are probably built into Zn- and Mg-containing phases [1]- Of these alloys. In this temperature region ( $\geq 140^{\circ}$ C) the fine-grained structure and the high amount of PFZs in alloy C seem to have no significant influence on the  $\sigma_{p}$ .

The "duplex" behaviour of alloy C has also been revealed by other compression and DSC measurements. With the addition of Zr the AlZnMgCuZr alloy behaves as the ternary AlZnMg when the ageing temperature,  $T_a$  is below 120°C and it behaves like the quaternary AlZnMgCu alloy in the case of  $T_a > 120°C$ . It has been supposed that the "duplex" property of alloy C is the consequence of a "duplex" GPzone structure, i.e. the formation of two types of GP-zones at  $T_a \le 120°C$  in this alloy. One type of GP-zones is similar or equivalent to those in a ternary AlZnMg alloy, the other type contains also Cu.



Fig. 2: Microstructure of alloy C aged at 220oC for 2h

The GP-zones without Cu are denoted as  $\alpha_1$  type, the zones containing Cu are denoted as  $\alpha_2$  type. (It should be noted that these  $\alpha_1$  and  $\alpha_2$  type zones are not the same as GPZI and GPZII type zones which can be formed in ternary AlZnMg alloys at different temperatures and correspondingly they represent two versions of the  $\alpha_1$  type zones. ). Furthermore, the effect of these two types of zones on  $\sigma_p$  is denoted as  $I(\alpha_1)$  and  $I(\alpha_2)$  numerical quantities respectively. With these denotation it is evident that in the ternary AlZnMg alloy only  $\alpha_1$  type zones can be formed If  $T_a > 120^{\circ}C \alpha_1$ type zones can not be formed,  $I(\alpha_1)$  becomes zero. It has been shown that in the quaternary AlZnMgCu alloy both of  $\alpha_1$  and  $\alpha_2$  type zones can be found, but the effect of  $\alpha_1$  type zones on  $\sigma_p$  is considerably smaller in comparison to the effect of  $\alpha_2$  type zones (I( $\alpha_1$ ) << I( $\alpha_2$ ).) In the AlZnMgCuZr alloy, however the effect of  $\alpha_1$ type zones is comparable with that of  $\alpha_2$  type zones (I( $\alpha_1$ ) = I( $\alpha_2$ )). This can be explained in the following way. It has to be taken into account that in the AlZnMgCuZr alloy most of Zr atoms are incorporated in Al<sub>3</sub>Zr phase particles which are stable even at relatively high temperatures. The fine dispression of these Al<sub>3</sub>Zr precipitates developing mainly in the course of the high temperature manufacturing processes ( rolling, extruding, etc. ) ensures a fine - grained microstructure. The average grain size of this alloy is less than 8 µm, where as alloys A and alloy B both have very similar coarse - grained structure with mean grain size larger than 150 µm. It has also to be taken into account that the Cu atoms can diffuse relatively quickly into the grain boundaries [12]. The diffusion of Cu atoms results in that for the Cucontaining alloys (B and C) in the vincinity of grain boundaries there are regions which are depleted in Cu, so in these regions the density and therefore the effect of  $\alpha_1$  type zones is dominant. Inside grains the concentration of Cu atoms and consequently the effect of  $\alpha_2$  type zones is small fraction of grain boundaries, the average (macroscopically) effect of  $\alpha_1$  type zones is small in comparison to that of  $\alpha_2$ 

type zones ( $I(\alpha_1) \ll I(\alpha_2)$ ). In alloy C, however because of the fine-grained structure the volume of the Cu-depleted regions can be comparable with that of the interior of grains. This means that the effect of the two types of GP-zones is comparable with each other, ( $I(\alpha_1) = I(\alpha_2)$ ). The model described above is shown schematically in figure 3.

The interpretation described above seems to be confirmed by the results of EDS-microanalysis tests. The sample shown in figure 4, for instance, was aged for one week at RT and for 3 h at 80°C to obtain well developed GP-zone structure. The EDS-microanalysis measurements show that going from a grain boundary towards the interior of the grain the Cu-concentration is increasing, confirming the decrease in Cu concentration in the vicinity of grain boundaries.



Fig. 3: Schematic GP-zone structure in the alloys investigated

## 4. CONCLUSIONS

The results show that addition of Cu changes strongly the temperature of GPzones  $\rightarrow$  intermediate phase transition.

The addition of Zr leads to an extremly fine-grained structure and in the AlZnMgCuZr alloy a "duplex " GP - zone structure is formed, causing a "duplex " behaviour of this alloy.

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Fig. 4: Sample of alloy C in state of Q+RT week  $+80^{\circ}$ C 3 h (the small points with relatively high density are Al<sub>3</sub>Zr particles. Numbers show the Cu concentration relative to the bulk Cu concentration in the sample)



Fig. 4: Sample of alloy C in state of Q+RT week  $\pm 80^{\circ}$ C 3 h (the small points  $\times$  relatively high density are Al<sub>3</sub>Zr particles. Numbers show the Cu concentration relative to the bulk Cu concentration in the sample)

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