GUINIER-PRESTON ZONE FORMATION IN AL-ZN-MG-(CU,ZR) ALLOYS

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Abstract

The formation of Guinier-Preston (GP) zones in a medium-strength and high-strength Al-Zn-Mg-(Cu,Zr) alloys was investigated by dynamic microhardness tests. In the early stage of natural ageing oscillations were observed in the dynamic microhardness of the alloys indicating plastic instabilities similar to the serrated flow often observed in solid solution alloys. The formation of GP zones suppresses the instabilities, therefore the plastic instabilities disappear at a certain state of decomposition. In the quaternary Al-Zn-Mg-Cu alloy this quasi solid solution state is retained for longer ageing time and the increase of the microhardness is also slower than in the ternary Al-Zn-Mg alloy. This shows that although the addition of Cu increases the supersaturation, it retards effectively the early state of zone formation. In contrast to the Al-Zn-Mg-Cu alloy, in the fine-grained Al-Zn-Mg-Cu-Zr alloy the lifetime of the quasi solid solution state is similar to that of the ternary alloy. Both this similarity and the analysis of the spatial distribution of the hardness in the alloys reveal a dual behaviour in the mechanical properties of the fine-grained Al-Zn-Mg-Cu-Zr alloy, confirming the assumption that the GP zone structure in the vicinity of grain boundaries is different from that in the grain interiors.

Keywords: *Guinier-Preston zones, fine-grained structure, dynamic microhardness, plastic instabilities.*

1. Introduction

High strength Al-Zn-Mg-Cu alloys (e.g. 7075 alloys) are based on the Al-Zn-Mg ternary system with Cu addition which effectively influences the decomposition of the supersaturated solid solution (S.S.S.) [1-4]. The precipitation in these alloys has been the subject of many experiments concentrating mostly on the later stages of precipitation have been investigated. On the early stages of the decomposition in the alloys relatively few experimental results are available.

It is well known that the sequence of the precipitation depends strongly on the composition of the alloy, on the quenching conditions, etc. [4-7]. The addition of small amounts (0.08-0.25%) of Zr can ensure a fine-grained structure [7-9] which is less sensitive to the quenching rate [2,7], but on the other hand Zr addition has been observed to slow down the precipitation, in particular the early stages of the process [10]. As a consequence of the small average grain size the influence of grain boundary segregation, precipitation and precipitate-free zone (PFZ) formation is more pronounced in Zr-containing alloys [1,5,11].

It is also well known that the GP zones forming in Al-Zn and Al-Zn-Mg alloys are three dimensional, often spherical [1-3], while those forming in Al-Cu are two dimensional, plate-like [12-15]. In the Al-Zn-Mg-Cu alloys, although there is evidence that Cu atoms are mostly built in into Zn- and Mg-containing η' and η phases [1], it is not entirely clear what types of GP zones are formed and how the grain boundaries influence the formation of GP zones.

In this work the formation of Guinier-Preston (GP) zones in a medium-strength Al-4.6%Zn-1.2%Mg-0.14%Zr alloy and in high-strength Al-6%Zn-2%Mg-(1.4%Cu,0.14%Zr) alloys is investigated on the basis of dynamic microhardness measurements. The results obtained for fine-grained Al-Zn-Mg-Cu-Zr are compared with those obtained for ternary Al-Zn-Mg and quaternary Al-Zn-Mg-Cu of much larger average grain sizes.

2. Experimental Procedure

Ternary Al-5.7%Zn-1.9%Mg samples (alloy **A**), and samples of the same alloy with 1.4%Cu (alloy **B**) and 1.4%Cu-0.14%Zr (alloy **C**), as well as Al-4.6%Zn-1.2%Mg-0.14%Zr samples (alloy **D**) (compositions are given in wt%) were prepared from 99.99% purity aluminium. After casting, the samples were homogenised for 8 h at 470 °C in air, and then hot extruded to sheets of a cross section of 10 mm x 40 mm. The starting temperature of the hot extrusion was 380 ± 5°C. The specimens were annealed at 470°C for 30 min for solution treatment and water-quenched to room temperature (RT). After this treatment fully recrystallized materials were obtained. It was shown previously [9] that alloys **A** and **B** (no Zr addition) have very similar coarse-grained microstructures with mean grain sizes larger than 150μm. In contrast to this, alloy **C** is extremely fine-grained, with an average grain size of less than 8μm. Alloy **D** has also the same extremely fine-grained structure. The development of the fine-grained microstructure can be clearly attributed to the grain refining effect of the finely dispersed, stable Al_3Zr particles [1,2]. After quenching the samples were directly aged at room temperature or at 60°C where GP zones are forming.

The microhardness measurements were made immediately after aging on an electroytically polished cross section of the sample. The experiments were carried out by using a Vickers microhardness indenter in a dynamic ultramicrohardness testing machine (Shimadzu DUH 202). In the depth sensing hardness measurements the indentation depth (h), and the load (F) were recorded as a function of time (t) by a computer. During the tests the load was increased at a constant loading rate of 14 *mN/s*. The load was increased up to 20 or 2000 *mN*.

3. Results

3.1 Effect of Natural Aging - Plastic instabilities

Typical indentation depth-load (h-F) curves obtained on the four alloys in the early stage of natural aging (at room temperature, RT) are shown in Fig.1. It can be clearly seen that at the beginning of the natural aging (within 20 min after quenching) characteristic steps appear in the h-F curves for each of the alloys investigated. The step formation is a typical plastic instability effect similar to the Portevin-Le Châtelier effect or to jerky flow.

With increasing aging time the steps occur less frequently and they become more irregular and above a certain time, t_i, they disappear completely. The values of t_i are given in Tab.1. In the samples based on Al–6%Zn–2%Mg alloys (samples **A**, **B** and **C**) the t_i is longest in the Cu-containing alloy **B** (t_i>100min), while in the ternary alloy **A** and in the Cu and Zr containing fine-grained alloy **C** the instability steps disappear within about 30 - 60 minutes. In the lower concentration alloy **D** the steps are retained for much longer, for more than 150 minutes.

The occurrence of plastic instabilities is caused by the interaction of diffusing solute atoms with moving dislocations, a phenomenon often called dynamic strain aging (DSA) [16,17]. This implies that the occurrence of the load-indentation depth steps, that is of the plastic instabilities during indentation is connected to a certain concentration of alloying elements in the solid solution phase of the alloys.

The increase in the microhardness (see Fig.2) indicates GP zone formation immediately after quenching (within 5 minutes). The occurrence of the instability steps at this stage of the process indicates that the GP zones are not strong enough to suppress the DSA effect. The occurrence of the steps, therefore, characterizes the transition (at the aging time t_i) from the solid solution state to a decomposition state with solid solution and GP zones, when the interaction of GP zones with moving dislocations suppresses the effect of DSA.

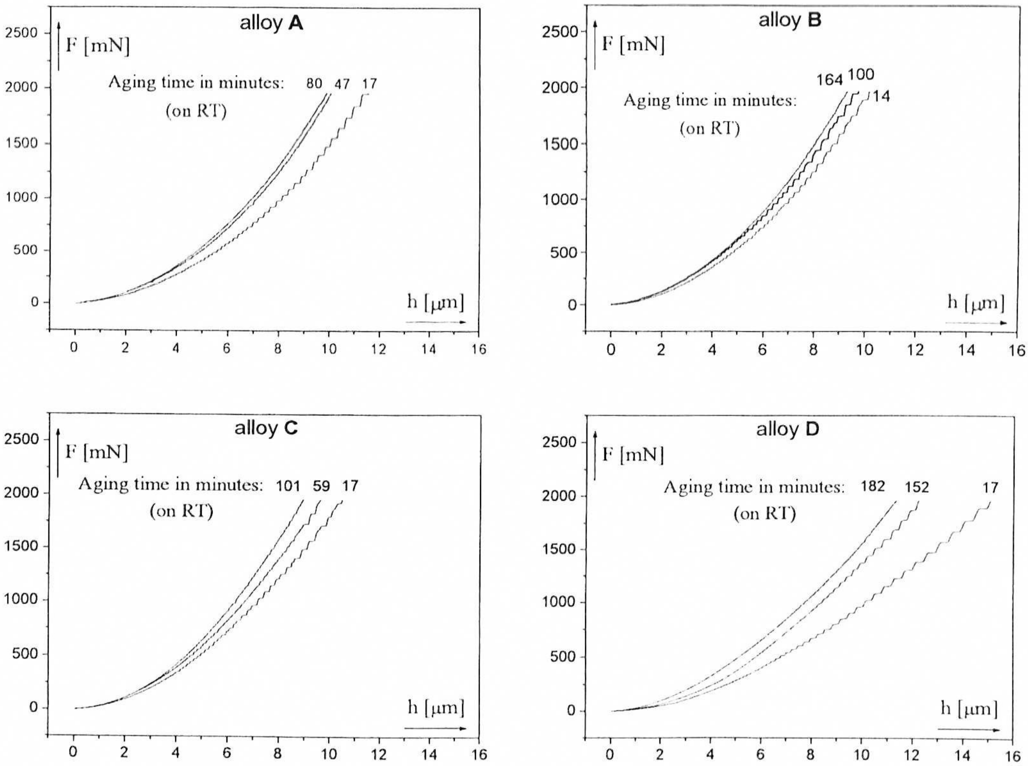

Fig. 1: The effect of the natural aging on the indentation depth-load curves taken by dynamic microhardness tests

Alloy	t_i [min]
A	**< 30**
B	**> 100**
C	**< 60**
D	**> 150**

Tab.1: The time t_i of the natural aging for disappearance of the steps on the indentation curves

The value of the aging time, t_i (see Tab.1) gives us important information about the effect of Cu and Zr additions on the formation of GP zones in the AlZnMg alloys (cf. t_i for alloys **A**, **B** and **C**). The lifetime t_i is longest in alloy **D** (t_i>150min.), which can be explained by taking into account the fact that this alloy contains the lowest solute concentration, therefore the thermodynamic driving force for GP zone formation is the smallest in this alloy.

Fig.2 shows also the influence of natural aging on the Vickers microhardness (HV) of the alloys. The maximum (2 N) load was applied for these hardness measurements, and the size of the indenter pattern on the samples was about 30-40 μm which is much larger than the average grain size in alloys **C** and **D**.

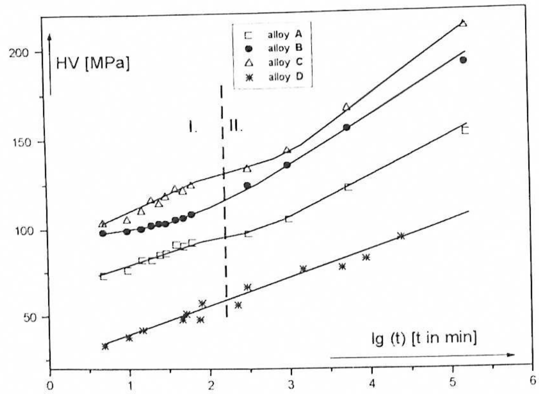

Fig.2: The influence of the natural aging on the Vickers hardness

Owing to the strengthening effect of GP zones the microhardness of the alloys increases continuously during RT aging after quenching. The initial rate of hardening is highest in the ternary Al-Zn-Mg alloy (alloy **A**) (see stage I (t< 1 h) of hardening). This rate is strongly decreased by the addition of copper (alloy **B**). The effect of Cu in the Al-Zn-Mg system was studied by several authors with controversial results concerning the question whether the addition of Cu accelerates or retards the formation of GP zones [18-20]. After the initial stage the strengthening introduced by the formation of GP zones takes place at a higher rate in the Cu-containing than in the ternary Al-Zn-Mg alloy. The mentioned controversy in the literature may originate from observations in different stages of the aging process. In the Cu- and Zr-containing fine-grained alloy **C** in the initial stage of natural aging - in contrast to the behaviour of alloy **B** - the retarding effect of Cu on the strengthening can not be observed. In this alloy - similarly to alloy **A** (without Cu) - GP zones start to form immediately after quenching. These remarks confirm the results obtained for the lifetime, t_i in alloys **A**, **B** and **C**. In the Cu containing alloy (alloy **B** with large grain size) addition of Cu retards the formation of GP zones, and therefore, t_i is relatively long.

The small amount of Zr in alloy **C** is present in the form of coherent Al_3Zr particles [1,2], which probably have little direct influence on the GP zone formation. It can be concluded, therefore, that the fast zone formation observed in stage I of the natural aging, as well as the relatively shorter t_i lifetime in this sample are related to the fine-grained structure of this Cu-containing alloy.

3.2 Spatial distribution of the microhardness in the samples

Vickers microhardness was also measured on the samples aged at 60 °C for 2 hours. These hardness tests were made with low (e.g. F=20mN) loads so that in this case the size of the indenter pattern is between 3 and 5 μm which is smaller than the average grain size (8μm) of alloys **C** and **D**. Consequently the hardness-values determined with this extremely low load reflect the local "microscopic" hardness of the alloy. Therefore, in this case instead of the average hardness the distribution of the local hardness was determined. Fig.3 shows the distribution curve of the local Vickers hardness obtained on the different alloys. The curves in this figure indicate the relative frequency (in %) at which, in a series of about 300-400 measurements made on a given sample, the results fall within an interval of ±10 MPa around HV. It can be clearly seen that the HV distribution curve of alloy **C** has two peaks indicating two most frequent microhardness values (Fig.3c). This reflects a characteristic spatial inhomogenity in the microstructure of this alloy. In Figs.3a, 3b and 3c it can be seen clearly that the lower and higher most frequent microhardness values of alloy **C** coincide with those of alloys **A** (without Cu, Fig.3a) and **B** (Cu-containing, Fig.3b), respectively. Therefore, from the point of view of the local "microscopic" behaviour, alloy **C** behaves partly like alloy **A** and partly like alloy **B**. In the case of the similarly fine-grained, but not Cu-containing alloy **D** - in contrast to the behaviour of fine-grained and Cu-containing alloy **C** - only one Gaussian curve can be observed. Taking into account this fact the dual behaviour of alloy **C** must be a consequence of the fine-grained structure, i.e. of the high fraction of sample volume near grain boundaries and of the Cu addition, as well.

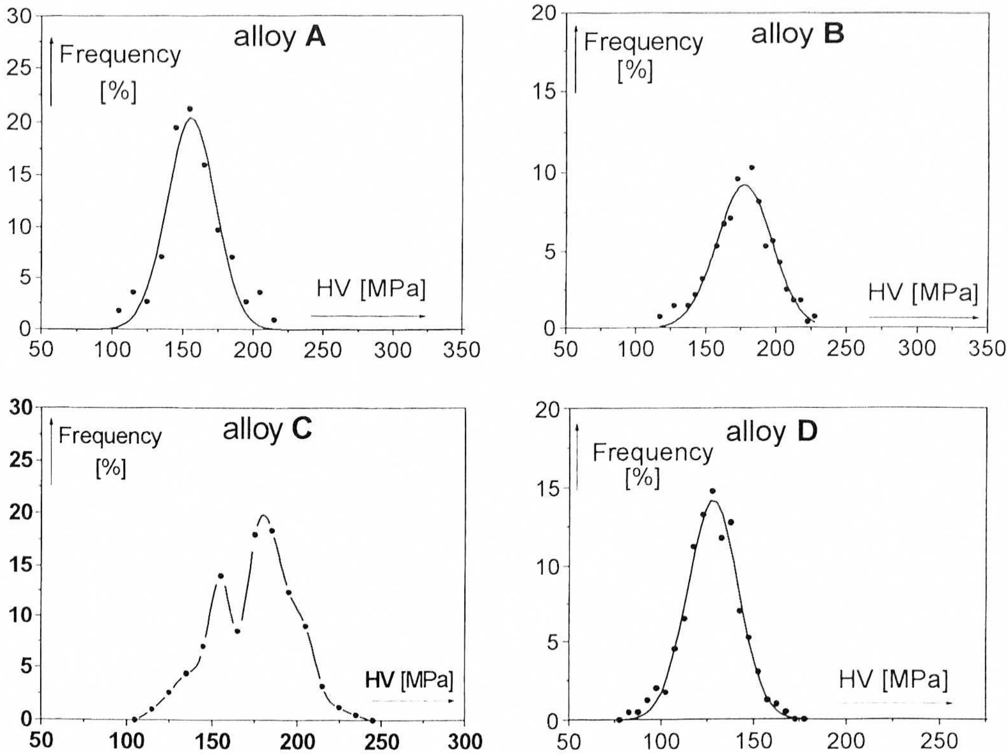

Fig. 3: Hardness distribution curves of the alloys aged on 60 °C

Because of the small average grain size in alloys **C** and **D** the Hall-Petch effect [21,22] could also yield a contribution to the strength and hardness of these samples. The only one peak of the frequency curve obtained on alloy **D** (see Fig.3d), as well as previous results [23] indicate that the contribution of the Hall-Petch effect is negligible compared to that of the precipitate microstructure.

Results obtained for both RT and 60°C agings confirm an earlier assumption [22] that in fine-grained, Cu-containing Al-Zn-Mg-Cu-Zr alloy (alloy **C**) the GP zone structure in the vicinity of grain boundaries is different from that in the grain interiors. In the vicinity of grain boundaries there are regions depleted in solute atoms, but mainly in Cu, so in these regions the density and therefore the effect of the ternary zones (without Cu) is dominant. In the interior of the grains the concentration of solute atoms remains uninfluenced and consequently the effect of Cu-containing zones is considerable.

4. Conclusions

The formation of Guinier-Preston (GP) zones in a medium-strength and in high-strength Al-Zn-Mg-(Cu,Zr) alloys was investigated by dynamic microhardness tests. The main results can be summarized as follows

1) In the early stage of natural ageing besides the formation of GP zones, plastic instabilities characteristic of the behaviour of solid solutions occur in the alloys.

2) In the coarse-grained samples (d≈150μm) the addition of Cu retards the formation of GP zones, but in the Al-Zn-Mg-Cu alloy grain-refined by Zr (d≈8μ), the rate of the initial zone formation was as fast as in the pure ternary Al-Zn-Mg alloy.

3) Results obtained confirm an earlier assumption that in fine-grained, Cu-containing Al-Zn-Mg-Cu-Zr alloy (alloy **C**) the GP zone structure in the vicinity of grain boundaries is different from that in the grain interiors.

Acknowledgements: This work was supported by the Hungarian National Scientific Research Fund under contract numbers OTKA-022976 and OTKA-014987. The authors are grateful to Mr. Heiko Haschke from Rostock University who carried out the microhardness measurements during his summer training in Budapest.

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