MICROSTRUCTURE DEVELOPMENT OF Ca-DOPED Mg–Zn ALLOY DURING HOT DEFORMATION

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Abstract

Structure and properties of magnesium can be modified by addition of solutes as well as by the metal working operations. To elucidate the alloying effect on both the deformation and the recrystallization mechanism, the present work compares the development of the microstructures of Mg–4Zn and Mg–4Zn–0.4Ca alloys (in wt.%) processed via two different deformation processes: the uniaxial compression (UC) and the equal channel angular pressing (ECAP). The stress-strain curves exhibited the classic evolution with the strain rate sensitivity slightly higher for Mg–4Zn than for Mg–4Zn–0.4Ca whereas the absolute value of the stress was higher in case of the ternary alloy during two deformation processes. Microstructure analysis showed that the hot deformation resulted generally in formation of the bimodal structure composed of fine grains of several micrometers and coarse unrecrystallized grains. Moreover, lower strain rates condition led to deformation-induced precipitation. The aim of the current work is therefore to better describe the effect of the Ca addition into Mg–4Zn alloy on its deformation as well as to reveal the mechanism(s) of the recrystallization phenomenon observed in such alloys.

Keywords: Magnesium alloys, deformation, recrystallization, microstructure.

1. INTRODUCTION

Advantageous mechanical, physical and chemical properties predetermine magnesium alloys to be promising engineering materials [1–4]. These properties can be modified by both the alloying effect and the metal working operations. For example, zinc is a common alloying element for magnesium exerting solution hardening effect [5]. Moreover, it is supposed that zinc can increase stacking fault energy (SFE) of magnesium and thus affects the mechanism of plastic flow [6]. On the other hand, additions of calcium induce the grain refinement and usually result in precipitation during solidification and hot processing [7]. It is also worth noting that zinc and calcium can be well metabolized since these elements are supplements for human body. This fact also makes the system Mg-Zn-Ca very attractive to biomedical applications [2, 8–10].

Additional improvement of the properties of magnesium alloys can be attributed to refined grain size as well as to the existence of fine precipitates formed by hot deformation and heat treatment [11]. The grain refinement in various magnesium alloys can be achieved by dynamic recrystallization (DRX) activated at various deformation conditions during torsion, uniaxial compression, tension test or equal channel angular pressing [3, 12, 13]. According to the nature of the process, two modes of dynamic recrystallization can be generally distinguished, continuous DRX and discontinuous DRX. The continuous DRX represents continuous absorption of dislocations in subgrain (low-angle) boundaries which eventually reset in formation of new grains separated by the high-angle boundaries. In discontinuous DRX new grains are formed usually by boundary bulging, for example, via strain induced boundary migration [13, 15]. In spite of that
dynamic recrystallization represents complex processes arising during higher temperature deformation. Thus many different effects or mechanisms occurring during DRX are frequently studied such as, for example, twinning [3, 6, 14], activation of slip systems [6] or particle-stimulated nucleation (PSN) [17]. PSN has been studied in more detail in case of aluminium alloys [18]. Its mechanism consists in the rapid sub-boundary migration in the deformation zone characterized by consecutive lattice rotation. Thus misorientation gradient is formed around large hard particles during deformation. This results in creation of new high-angle grain boundaries (HAGBs). The newly formed grain nucleus may grow to produce a recrystallized grain. An important feature of grains nucleated by PSN is that they generally adopt orientations which are different from those produced by other recrystallization mechanisms [17]. Moreover PSN mechanisms can lead to weaken the deformation texture that is also attractive feature in magnesium alloys [17, 19]. An interesting research has been performed by Robson [17] on the influence of precipitates on the recrystallization in Mg–Mn alloy. It was based on idea that precipitates either promote or suppress the recrystallization depending on their size, spacing and fraction as found in aluminium alloys. In case of the Mg–Mn alloy, Robson concluded that precipitates do not represent principal sites for nucleation of the new grains during hot deformation. However, this kind of nucleation can be more probable in the Mg-Zn-Ca system.

The present paper is focused on refinement of the microstructure of magnesium alloys by plastic deformation, uniaxial compression and equal channel angular pressing. The investigation was focused on the relationship between the deformation parameters and the microstructure resulting from dynamic recrystallization with respect to the effect of Ca addition into Mg–4Zn alloy.

2. EXPERIMENTAL DETAILS

The alloys were prepared from pure Mg (~ 99.99 %), pure Zn (~ 99.96 %) and a Mg10Ca (wt. %) master alloy by induction melting (Balzers VSG-02 vacuum furnace) in a carbon crucible under argon atmosphere and followed by casting into a steel mould. The composition of the Mg–4Zn and Mg–4Zn–0.4Ca alloys (in wt. %) was verified by XRF analysis.

The ingots were annealed 24 h at 340 °C, quenched into water and machined into billets (10 mm ×10 mm × 60 mm) for ECAP (INSTRON 5882) and into cube (10 mm ×10 mm × 10 mm) for compression tests (SCHENCK servohydraulic compression machine). The characteristic angles of ECAP die were $\Phi = 90^\circ$ and $\Psi = 45^\circ$. The two processes were realized at 240 °C with the final equivalent Von Mises strain close to 1 and the process rate of 5 mm/min in case of ECAP, and at three different constant strain rates 0.001, 0.03 and 1 s⁻¹ in case of the UC tests. Before experiments, the samples were held at the processes temperature for 10 min. After these processes they were quenched into water to freeze microstructure for subsequent observation.

The microstructure was observed by light microscope (Olympus GX51) and scanning electron microscope (Jeol JSM-6500F). The samples were mechanically ground, polished and finally etched. The linear intercept method was used for measuring of the grain size.

3. RESULTS

3.1 Deformation

Fig. 1 shows the stress–strain curves of the alloys Mg–4Zn (a) and Mg–4Zn–0.4Ca (b) for uniaxial compression deformation at three different strain rates and the temperature equal to 240°C. The typical behaviour of a material undergoing DRX can be seen there: after initial work hardening a peak stress is attained and followed by work softening. Moreover, the strain rate dependence of the stress-strain curve can be distinguished similarly to other Mg alloys such as AZ31 [20].
The work softening is more obvious in case of the binary alloy deformed at the higher strain rate. On the other hand almost no stress peak is observed for low strain rate.

Calculated strain rate sensitivity $(m = \frac{\partial \ln(\sigma)}{\partial \ln(\dot{\varepsilon})})$ is slightly higher for the Mg–4Zn $(m=0.11)$ than for Mg–4Zn–0.4Ca $(m=0.08)$ whereas the absolute value of the stress was higher in case of ternary alloy during both deformation processes.

3.2 Microstructure

Before processes of deformation, the as-cast alloys were annealed 24h at 340°C to homogenize their structures. Besides, large precipitates (with the size of units to tens µm and various shape) with almost uniform dispersion were present in case of the ternary alloy. The grain size of these annealed alloys was at the level of hundreds µm.

After the deformation processes both alloys showed similar, highly heterogeneous structures (Fig. 2). A mix of fine and coarse grains forms a “necklace structure” where the recrystallized grains are concentrated along the original boundaries. Furthermore the deformation led to the extensive twinning and new fine grains were created also within the twins (Fig. 2 (c)) as well as within the shear bands which were formed more obviously in case of as-ECAP samples (Fig. 2 (d)). Let us mention that the phenomenon of doubled twinning [3, 14] was also observed. In some cases voids occurred at edges of the mentioned shear bands or the grain triple junctions, and were more significantly induced by the deformation of the binary alloy.
Moreover, the hot deformation of both alloys led to formation of fine precipitates in course of the DRX. These precipitates were present at the grain boundaries and also inside the new grains (Fig. 2 (b)). On the other hand, no precipitation was observed inside the remaining initial grains.

The size of the new grains as well as the volume fraction of DRX was influenced (i) by the type of the deformation, (ii) by the change of the strain rate and (iii) by presence of big precipitates before the deformation. Average grain size decreased with increasing strain rate and was slightly lower (1–2 µm) in case of the ternary alloy. On the other hand, the volume fraction of fine grains was lower in case of the binary alloy and of the samples deformed by CT as compared to ECAP.

The distribution of the precipitates in case of the ternary alloy was more obviously influenced by formation of the shear bands during deformation by ECAP in comparison to UC (Fig. 2 (d)).

4. DISCUSSION

Microstructure analysis shows that the new grains were formed in the vicinity of the original boundaries. It indicates that the imposed strain caused gradual accumulation of dislocations in these regions. As a result, continuous bulging of the initial grain boundaries (Fig.2 (b)) and rearrangement of dislocations accumulated near the grain boundaries by dislocation climb could cause nucleation of the recrystallized grains. Since the processing at an intermediate temperature used in this work allows the deformation twinning to occur easily, it competes to the non-basal slip [11]. Twin domains possess much higher stored deformation energy compared to the matrix and are therefore favourable nucleation sites for DRX [21] (Fig. 2 (c)). Extensive twinning can be also expected as a result of the very large initial grain size (hundreds of µm) [23]. Formation of twins was more obvious in samples deformed at higher strain rates than in case of lower ones like in the work of Xu on AZ91 [3].

As expected, addition of calcium into Mg–4Zn alloy usually results in precipitation. Thus in case of the Mg–4Zn–0.4Ca alloy, big precipitates are present in the structure. These precipitates can act as obstacles for dislocation motion, accumulate the dislocations and create new nucleation sites for DRX. Moreover, growth of the twins is limited by presence of big precipitates. Consequently the grains are subjected to high stress because the imposed strain cannot be accommodated by them. This high stress state also enables nucleation of the new twins within the grains to accommodate applied strain similarly as was mentioned above. As a result the absolute value of the stress can be increased in case of the ternary alloy during the deformation processes. On the other hand higher amount of sites with high stress state can increase the volume fraction of DRX. Other consequence of these obstacles can be found in more acceptable distribution of the imposed stress within the sample. Finally, considerably fewer voids can be observed in comparison
with binary alloy as well as the work softening accompanied by dynamic recovery and dynamic recrystallization is more gradual (Fig.1 (b)).

Nevertheless, in both binary and ternary Mg alloys the applied deformation processes caused formation of fine precipitates (Fig.2 (b)). The precipitation as the aging process can start within 100 s even at temperatures above 200°C in Mg–Ca–Zn alloys [7]. It was supposed in another study on microstructure evolution of a Mg–2.4 at. % Zn alloy during extrusion at 210°C [22] that fine precipitates form before the deformation due to preheating of the samples for 30 min. Contrary, fine precipitates were observed predominantly in the vicinity of the original grain boundaries, the twin boundaries and within the DRX grains. The corresponding BSE images in Fig. 2 (b) reveal clearly the distribution of fine precipitates. The mentioned sites possess higher concentration of strain probably due to higher dislocation densities which can provide nucleation sites for precipitation. These precipitates act as obstacles for motion of dislocations and grain boundaries produced during subsequent deformation and as a result the growth of the new DRX grains is limited during hot deformation. The average DRX grain size in case of both alloys is comparable. On the other hand the precipitation on the twin boundaries diminishes initially the driving force for recrystallization at the same site. Further precipitation induces the pinning forces retarding the twin boundary mobility [24].

5. CONCLUSION

The microstructural changes taking place during the hot deformation of Mg–4Zn and Mg–4Zn–0.4Ca magnesium alloys were investigated. It was found that the coarse primary grains are gradually replaced by the new fine recrystallized grains arranged into the heterogeneous “necklace” structure. The two applied processes – UC and ECAP – were accompanied by the extensive twining, formation of shear bands and fine precipitation.

The UC tests were carried out at three different strain rates level which influenced the average DRX grain size and the volume fraction of DRX. The high strain rate led to extensive formation of twins, finer recrystallized grains and presence of voids. On the other hand the average size of the recrystallized grains in the samples processed by UC at low strain rate was comparable to that found in the samples after application of the ECAP.

The addition of Ca into the binary Mg–4Zn alloy results in formation of big precipitates with various shapes. They act as obstacles for dislocation motion, growth of twins and the imposed stress can be accumulated in their vicinity. Thus new grains were rarely formed in vicinity of big precipitates. In spite of that, potential PSN mechanisms in case of ternary alloy should be more investigated. Based on that, it could be possible to find deformation conditions leading to more homogenize the deformation structure of Mg-Zn-Ca. Moreover, better identification of the nature of the recrystallization phenomena observed in such alloys should be obtained by EBSD analysis which is in progress.

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