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Effect of processing strain rate and temperature on interfacial segregation of zinc in a magnesium alloy

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ABSTRACT

We show that, while interfaces formed in a Mg-3Zn-0.5Y (at%) magnesium alloy by severe plastic deformation (SPD) by high pressure torsion (HPT) at room temperature (RT) are segregated with Zn (without aid of any thermal treatment), only a small fraction of grain boundaries are segregated when extruded at 573 K (300 °C). We have examined the effect of strain rate and temperature on the diffusion behavior and segregation of zinc in magnesium alloys. At first, we have established the driving force for segregation by evaluating segregation energy and the interface energy gain by density functional theory calculations. The mechanism of segregation is established through calculation of excess vacancy concentration and critical dislocation velocity as a function of strain rate. It is estimated that Zn atoms are transported by SPD induced vacancy flux in case of HPT at RT, whereas the Zn atoms are dragged by equilibrium vacancies and dislocations on extrusion at 573 K (300 °C). The amount of segregation to the different twins and grain boundaries with different interfacial energies have been calculated by thermodynamic parameters and found to be in the range of 1–8 at% of Zn for the case of HPT process and 0.7–1.6 at% of Zn for extrusion processed specimens. These estimates correspond to the solute concentrations determined experimentally.

1. Introduction

Magnesium (Mg) alloys have attracted considerable interest in automotive and aerospace industries because of their high specific strength and stiffness [1,2]. However, the applications of Mg alloys are limited, due to low ductility, poor creep and corrosion resistance and low forming capability due to the small number of independent slip systems in the low symmetry hcp structure at low temperatures. The occurrence of unfavorable deformation textures and incompatibility stresses among the grains are the other major negatively influencing factors limiting the applications of Mg alloys for structural applications [3]. The most effective method of improving the properties of magnesium alloys is by refining the grain size. Very fine grain size, of the order of nanometer, can be achieved by severe plastic deformation, such as by equal channel angular extrusion and high pressure torsion (HPT) [4–6]. Furthermore, to strengthen the magnesium alloys effective barriers need to be created in order to block the motion of dislocations, twin boundaries and grain boundaries. Due to lack of sufficient slip systems in magnesium, strains are accommodated in the 'c' direction mainly through deformation twinning. There are two types of common twins in magnesium alloys, the $\{10\bar{1}1\}\langle 10\bar{1}2\rangle$ twins and the $\{10\bar{1}2\}\langle 10\bar{1}1\rangle$ twins which deform c axis in compression and tension, respectively [7,8].

A high volume fraction of interfaces, however, can reduce the stability of the alloys because of long range elastic stresses and enhanced free volume, which can lead to grain growth at very low temperatures. Addition of suitable additional alloying elements can stabilize the grain boundaries by solute enrichment and solute drag at the boundaries. In all previously reported cases, a thermal treatment was applied to obtain the solute enrichment or segregation at the grain boundaries [9–13] and twin boundaries [14,19]. However, Meng. et al. [15] reported grain size stabilization due to precipitation at grain boundaries in a Mg-Zn alloy during HPT processing at room temperature (RT). Furthermore, Basha et al. [16] have reported on segregation of Zn at newly formed interfaces, including twin boundaries, during RT HPT processing of a Mg-3.0Zn-0.5Y (at%) alloy [17] without any annealing. This alloy contains a quasicrystalline icosahedral (I-) phase and, in a wrought form, is known to have ultra-high strength and moderate ductility due to very fine grain size and weak texture [18]. This segregation is thus driven by strain rate [16].

We present here an analysis of the effect of temperature and strain rate on segregation of zinc to various interfaces. For this purpose three experimental data points of Mg-3at%Zn-0.5at%Y alloy are taken, after

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HPT process and extrusion, which give three strain rates and two different temperatures. The amounts of zinc segregation at various boundaries are determined experimentally. The driving force for segregation is established through first principles calculations, in which interfacial energy and segregation energies are evaluated. The dominant mechanisms of diffusion at RT and a higher temperature are evaluated by establishing generation of excess vacancies and critical dislocation velocities as a function of strain rate. Generation of vacancy-solute complexes and their diffusion coefficient is also considered. Variation in the amount of solute concentration at various boundaries is estimated through a thermodynamic model.

2. Experimental procedure

The alloy of nominal composition Mg-3at%Zn-0.5at%Y studied here was synthesized by melting high purity metals under inert atmosphere. The cast ingot was caliber rolled to form into a rod. Annealing at 573 K for 24 h was performed on the rod, which dissolved the binary Mg-Zn precipitates (but not the ternary phases), removed the strain due to rolling, and resulted in grain growth to a grain size of 10 μm (hereafter called ST sample). High pressure torsion (HPT) was performed on discs of 10 mm diameter and 0.85 mm thickness sliced from the ST rod. HPT processing was conducted at room temperature under a load of 5 GPa. The lower anvil rotated at a speed of 1 rpm, producing a strain rate of the order of $10^{-1}s^{-1}$. Samples were processed with number of rotations N = 0, 1/4, 1/2, 1 and 5. Samples were extracted carefully at a distance of 2–3 mm from the center of the disk for microstructure investigations. A part of the cast ingot was also extruded at 573 K with a strain rate of the order of $0.25 \times 10^{-3}s^{-1}$ in order to compare with the HPT processed specimens.

X-ray diffraction (XRD) was performed on a 'Rigaku Smart Lab' machine with CuKα target at 45 kV and 200 mA. Samples for transmission electron microscopy (TEM) were prepared by an ion milling (Gatan, model 600) after mechanical grinding to 80 μm. Microscopy was performed on Tecnai G2 F30 microscope, operated at 300 kV, equipped with energy dispersive X-ray spectroscopy (EDS). EDS was performed in scanning TEM (STEM) mode with a probe size of 2 nm. Fischione model 3000 HAADF detector was used for STEM high angle annular dark field (HAADF) images (camera length 80 cm) and low angle annular dark field (LAADF) contrast images (camera length > 80 mm). More details are given in an earlier report [17].

3. Results

The XRD patterns of the HPT processed samples at different revolutions showed mainly peaks corresponding to hexagonal close packed (hcp) Mg phase Fig. 1(a). The diffraction pattern of the rolled alloy in ST condition showed very strong peaks corresponding to $\{10\bar{1}0\}$, $\{10\bar{1}1\}$ and $\{11\bar{2}0\}$ planes, in accordance with basal texture formed by rolling. After the compression (N = 0) the intensity of the 0002 peak was significantly enhanced and becomes more dominant than the other peaks, attributed to formation of twins. Again, after application of different amount of torsional strain, there was an increase in the intensities of $10\bar{1}0$ and $10\bar{1}1$ peaks at the expense of intensity of 0002 peak due to re-crystallization and randomization of grain orientations. The strain developed in the matrix is obtained using the Hall-Williamson method as 0.115% for N = 0 specimen and 0.128% for N = 5 specimen, respectively. The strain developed in the matrix of the extruded sample was calculated to be 0.110% from XRD peaks Fig. 1(b).

Fig. 2(a) shows a LAADF micrograph (camera length CL = 200 mm) acquired from $\{10\ \bar{1}\ 2\}$ type of deformation twin in N = 0 HPT (compressed only) sample. The diffraction pattern inset shows both the matrix and the twin to be in $\langle 11\bar{2}0\rangle$ zone axis, with a coinciding set of $\{10\ \bar{1}\ 2\}$ spots (along dashed line). The HAADF image and STEM-EDS maps acquired from the same region show the segregation of Zn and Y at the twin boundary (Fig. 2(c-e)). Fig. 2(f) shows STEM-EDS line scan across the twin boundary marked by a line in Fig. 2(c). The amount of Zn and Y solute segregation at the twin boundary measured by nano-probe EDS spot analysis are 1.5 ± 0.5 at% and 0.5 ± 0.3 at%, respectively. Here, it should be emphasized that there are only a few boundaries where yttrium segregation has been observed; the reason might be the local temperature or strain variation near the boundary. In other observations only zinc segregation was observed at the boundary. There was also a special boundary observed, which was analyzed to be a $\{11\ \bar{2}\ 0\}$ type of twin. Segregation of zinc on this boundary was also observed.

Fig. 3(a) shows microstructure of N = 5 HPT processed sample. The bright field image shows a recrystallized region of the sample. The diffraction pattern shown Fig. 3(b) is acquired from same the region and exhibits ring pattern which indicates formation of high angle boundaries. Fig. 3(c) shows a STEM HAADF image acquired with CL = 80 mm from another region of the same sample. In this HAADF image, segments of bright contrast are observed at the grain boundaries, which indicates solute segregation. The thickness of these segments is in the range of 1–3 nm. Shown in Fig. 3(d) is a LAADF image acquired with CL = 200 mm from the same region shows individual recrystallized grains due to the additional diffraction effects. The average grain size is estimated to be 150 ± 20 nm [16]. Inset in this figure is a STEM-EDS mapping of Zn from a region marked with a square, confirming zinc segregation at high angle grain boundaries. Local composition at these grain boundaries was shown to be in a range of 2–4 at% by spot-EDS analysis. No segregation of yttrium was detected at the boundaries. The amount of Zn solute segregated measured from STEM-EDS spot analysis at three type of boundaries, averaged over 20 different measurements for each type, are listed in Table 1.

In order to know the effect of processing, the results obtained from HPT processed specimens have been compared with an alloy of same composition extruded at 573 K. Fig. 4 shows the HAADF images acquired with camera lengths of 80 mm and 200 mm from Mg-3Zn-0.5Y alloy extruded at 573 K. The HAADF image acquired with 80 mm indicates the segregation of Zn phase on only a small segment of grain boundaries which is marked by an arrow. This can be attributed to the larger grain size compared to the diffusion length of Zn atoms and higher solubility at high temperature 573 K. The amount of concentration of zinc measured at grain boundary from STEM-EDS analysis is 2–3 at%. The HAADF image acquired with camera length of 200 mm showed the typical grain size of the alloy to be 500 ± 30 nm. The zinc solute composition measured on 20 different grain boundaries by STEM-EDS analysis is found to be 1.8 ± 0.5 at%.

4. Discussion

In the present alloy composition, primary ternary phase is the quasicrystalline Mg_3Zn_6Y I-phase, but some amount of cubic $Mg_3Zn_3Y_2$ W-phase also forms. Since yttrium has very low level solubility in Mg, almost all yttrium can be retained within the ternary phases. Even though both zinc and yttrium have some solubilities in magnesium at high temperatures, the composition of the α-Mg matrix on annealing at higher temperatures also depends on the phase equilibrium at that temperature. For example, it has been reported that at 700 K, W-phase of composition $Mg_{25}Zn_{60}Y_{15}$ is in equilibrium with α-Mg of composition Mg-3at%Zn (no yttrium) in an alloy of composition Mg-35Zn-5Y [20]. In another alloy of composition Mg-40Zn-10Y, W-phase of composition $Mg_{25}Zn_{60}Y_{15}$ and I-phase of composition $Mg_{37}Zn_{53}Y_9$ are again in equilibrium with α-Mg of composition Mg-3at%Zn (at 700 K) [20]. A reaction between W and I phase is described as L (liquid) + W ⇌ α − Mg + I (at 721 K) [21]. The I phase can form phase equilibria with α-Mg, W phase and Mg-Zn binary phases [21].