The Microstructure of Mg\textsubscript{98.5}Zn\textsubscript{0.5}Y\textsubscript{1} Alloy with Long-Period Stacking Ordered Structure

Zhi-chao Xu\textsuperscript{1,*1}, Zhong-xue Feng\textsuperscript{1,*1}, Qing-nan Shi\textsuperscript{2}, Ying-xiang Yang\textsuperscript{1,*2} and Xiao-qi Wang\textsuperscript{1,*2}

\textsuperscript{1}Department of Material Science & Engineering, Kunming University of Science and Technology, Kunming 650093, China
\textsuperscript{2}Research Center for Analysis and Measurement, Kunming University of Science and Technology, Kunming 650093, China

The microstructure of an Mg\textsubscript{98}Zn\textsubscript{0.5}Y\textsubscript{1} alloy prepared by directional solidification (DS), synchronized with a long-period (LPSO) structure were systematically investigated using high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy. The formation of 14H-type LPSO was observed to be accompanied by stacking faults. The lamellar 14H-type LPSO structure and stacking faults were both formed on (0001) scanning transmission electron microscopy. The formation of 14H-type LPSO was observed to be accompanied by stacking faults. The lamellar structure were systematically investigated using high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron microscopy.

Keywords: directional solidification, Mg\textsubscript{98}Zn\textsubscript{0.5}Y\textsubscript{1} alloy, 14H, stacking faults, crystal structure

1. Introduction

Magnesium alloys have attracted considerable attention recently owing to their extraordinarily low density, good damping, and ease of recycling. It can be applied in lots of areas, including automobiles, electronic equipment and aerospace\textsuperscript{1,2}. Kawamura \textit{et al.}\textsuperscript{3} developed an Mg\textsubscript{97}Zn\textsubscript{1}Y\textsubscript{2} alloy by warm extrusion of rapidly solidified powders at 573 K which exhibited a high yield strength of 610 MPa at room temperature. These remarkable properties are found to originate from the ultrafine \(\alpha\)-Mg grains and the formation of a long-period structure (LPSO)\textsuperscript{4–6}. Therefore, different kinds of technology, such as directional solidification and rapidly solidified, have been expended to investigate the structure of LPSO phase\textsuperscript{7}. It has been shown that the LPSO phase formed in directional solidification reveals excellent mechanical properties\textsuperscript{2,8}. In addition, the damping capacity of LPSO phase selected along the directional growth in DS Mg-Zn-Y alloys are 0.22 higher than pure Mg. However, detailed summary on the microstructure and formation mechanism of LPSO in Mg-Zn-Y alloys are limited. For this reason, the crystal structure of LPSO phase was indexed in this paper. The as-cast microstructure of Mg-Zn-Y alloys produced by either conventional casting or rapid solidification processing, various LPSO phases of 10H, 18R, 14H and 24R have been observed in Mg-Zn-Y alloys\textsuperscript{9}. Among these LPSO structures, although the 18R-type LPSO is frequently found in Mg-Zn-Y alloys with different chemical compositions, the 14H-type LPSO is considered as more stable phase\textsuperscript{10}. The 14H-type has a hexagonal structure (\(a = 1.11\) nm, \(c = 4.86\) nm) and its closely packed planes have a \textit{BCBCABABACBCB} sequence\textsuperscript{11}. In addition, this sequence is as same as the sequence of I\(_2\)-type stacking faults. Although extensive research has been carried out on the structure of 14H, no details of orientation relationship between stacking faults, matrix and LPSO structures in DS have been adequately clarified.

In the present study, the 14H-type LPSO phase in Mg\textsubscript{96}Zn\textsubscript{2}Y\textsubscript{1} alloy prepared by DS were investigated, focusing on the formation mechanism, unit cell, respectively. The microstructure formed by the directional solidification were analyzed by X-ray pole figures and transmission electron microscopy (TEM) observations. Taking the stacking faults into account, this paper emphasis on the discussion of the orientation relationship between 14H-type LPSO and matrix. The clearly relationship enable us to acquire the microstructure and chemical feature of the 14H-type LPSO. Based on the direct observations, the clusters inner the building blocks were studied and a physical atomic model was constructed. By comparing the simulated diffraction patterns with the experiment, the structure of atomic model were examined.

2. Experiment Procedures

The alloys with the nominal compositions were prepared by induction melting pure Mg (>99.8 mass%), pure Zn (>99.8 mass%), Mg-25%Y (mass%) in the boron nitride (BN) coated graphite under a dynamic argon gas atmosphere. To prepare DS polycrystal whose crystal growth directions were oriented along the solidification direction, the ingots were directionally solidified using the power down method with a cooling rate of 1°C/min under an Ar atmosphere. The microstructure and crystal structure after the directional solidification were analyzed with a transmission electron microscope. Phase identification were performed by X-ray diffraction (XRD, Rigaku D/max-2500PC) using a copper target with a scanning angle from 10° to 90° and a scanning speed of 2°/min. The bright-field TEM images were obtained.
from a JEOL JEM 2100F FEGTEM instrument operating at 200 KV.

3. Results and Discussion

The crystal structure of the LPSO phase and the microstructure in the as-DS-grown Mg_{85}Zn_{6}Y_{9} and Mg_{75}Zn_{10}Y_{15} crystal were examined and described in detail in a previous paper. The Mg_{85}Zn_{6}Y_{9} DS crystal was confirmed to almost only consist of the 18R-type LPSO phase and the Mg_{75}Zn_{10}Y_{15} was confirmed to exhibit the 10H structure. In this section, the microstructure and crystal structure of the Mg_{95.5}Zn_{0.5}Y_{1} DS crystal are described. Figure 1 (a) and (b) show the OM image of a typical microstructure in as-DS-grown Mg_{95.5}Zn_{0.5}Y_{1} and as-cast Mg_{95.5}Zn_{0.5}Y_{1}. As seen in the figures, the crystal growth direction in the DS alloy exhibited a peculiar regularity. Figure 1 (a) presents that the crystal growth direction were elongated along the solidification direction. As shown in Fig. 1 (b), the crystal growth direction were randomly oriented. Figure 2 presents the XRD patterns of Mg_{95.5}Zn_{0.5}Y_{1} DS crystal. The square represent the $\alpha$-Mg and the triangle represent the Mg_{12}ZnY. The profile for Mg_{95.5}Zn_{0.5}Y_{1} alloy includes peaks from $\alpha$-Mg matrix and Mg_{12}ZnY (LPSO). The XRD patterns reveals that the DS polycrystal mainly consisted of the $\alpha$-Mg and LPSO phase.

For further analysis of the LPSO phase, the microstructure was clarified by the bright-field TEM image in Fig. 3. These lamellar structure had a different width, as shown in Fig. 3 (a). Figure 3 (b) shows that the [1030] selected-area electron diffraction (SAED) patterns of the LPSO in the as-DS-grown state, thirteen diffraction spots were observed in the (a *) reciprocal-lattice row. The diffraction spots were distributed evenly between the incident beam and the (0002) fundamental reflection of the hcp unit cell. These diffraction spots indicates that the LPSO phases in these crystals exhibited the 14H structure. Besides, it should be noted that the ordered diffraction spots were somewhat diffuse, as indicated by the arrows. These features are similar to those observed in as-DS-grown Mg_{75}Zn_{10}Y_{15} alloy and will be explained later. Figure 3 presents the 14H-LPSO directly formed in as-DS-grown Mg_{95.5}Zn_{0.5}Y_{1} alloy, the growth direction showed regularity and the microstructure was uniformed.

To see more structural details of the as-DS-grown 14H-LPSO order, atomic-resolution HRTEM images are performed and shown in Fig. 4. Looking carefully at the atomic-resolution in the TEM image, it is found that the brightest spots basically occurred at the striped contrast which is building block. Each building block had two adjacent bright atomic columns. According to the theory that intensity is proportional to the square of the atomic number in the HRTEM image, it can be concluded that these two bright atomic layers were enriched in Y and/or Zn atoms (atomic number is 39 for Y, 30 for Zn, and 12 for Mg). This phenomenon demonstrated a chemical order in the structure. Inspection of the image in Fig. 4 (a) reveals immediately that the 14H-LPSO contained two building blocks and the length of each 14H-LPSO was 3.65 nm, as indicated by the white arrows. Figure 4 (b) is an enlarged image of Fig. 4 (a), where the stacking sequence of ABABCA/ACACBA was clearly recognized, as shown by the letters inserted. The two adjacent bright atomic columns existed in twin-related building blocks (ABCALBA and ACBA-type). These two building blocks had the opposite shear direction which measured as 68.7°. The two twin-related building blocks in the unit cell were separated by three close-
ly packed planes of \(\alpha\)-Mg. The distribution Y and Zn atoms in the B and C segregation layers was the same. The cluster of Zn6Y8 which considered as the optimized structure inner the building blocks can improve the density and stability\(^{12,13}\). That is, the cluster effectively promote the formation of building blocks. Carefully analysis of these diffraction patterns indicate that the 14H phase had an ordered hexagonal structure with lattice parameters \(a = b = 11.168 \text{ Å}, c = 36.408 \text{ Å}, \alpha = \beta = 90^\circ, \gamma = 120^\circ\).

It has been reported that the formation of LPSO are divided into two steps\(^{14}\). Firstly, the stacking faults have to be formed, then the rare earth atoms and Zn atoms should be gather around the stacking faults. However, the details of the orientation relationship of the stacking faults with \(\alpha\)-Mg matrix in as-DS-grown \(\text{Mg}_{98.5}\text{Zn}_{0.5}\text{Y}_{1}\) alloy have not been clarified yet, so as the LPSO phase. With this in mind, we employed the HRTEM to elucidate the orientation relationship. As shown in Fig. 5 (a), the as-DS-grown 14H-LPSO precipitated along the (0001)\(_{\alpha\text{-Mg}}\) and grew along the \([12\overline{1}0]\) direction. Figure 5 (b) is the diffraction spot pattern of 14H-LPSO observed in the Fig. 5 (a), we can directly derive that \([4\overline{5}1\overline{0}]\)\(_{14\text{H}}\) was parallel to \([1\overline{2}\overline{1}\overline{0}]\)\(_{\alpha\text{-Mg}}\) and \((0001)\)\(_{14\text{H}}\) was parallel to \((0001)\)\(_{\alpha\text{-Mg}}\).

Figure 6 shows HRTEM images of the microstructures of the \(\text{Mg}_{98.5}\text{Zn}_{0.5}\text{Y}_{1}\) alloy. The straight line represent the atom layer. These images demonstrate that the atoms below the A layer translated some displacement along the \([1\overline{2}\overline{1}0]\) direction. By the analysis of the orientation relationship, it is noted that the stacking faults formed in \((0001)\)\(_{\alpha\text{-Mg}}\) and extended along the \([1\overline{2}\overline{1}0]\) direction. These features indicate that the growth direction of stacking faults was parallel to the growth direction of 14H-LPSO. From the above research, we can directly derive that there was a connection between the stacking faults and the 14H-LPSO. First, the stacking faults and 14H-LPSO were all formed on \((0001)\)\(_{\alpha\text{-Mg}}\) plane and grew or extended along \((\overline{1}\overline{2}\overline{1}0)\) direction. Secondly, both of them had the same stacking sequence. The stacking sequence of 14H-LPSO which considered as more stable phase was ABABCAACACBABC. Besides, the 14H-LPSO unit had
two ABCA-type building blocks arranged in opposite shear directions. The stacking sequence of the common intrinsic stacking faults of I2 was ....ABABABABCACAB....15). The 14H-LPSO can be considered as periodic arrangement of stacking faults of I2. Based on the above relationship, it can be concluded that the stacking faults played an important role in the formation of as-DS-grown 14H-LPSO. The total energy of alloys are decreased due to the formation of stacking faults. It has been reported that Y element can largely decrease the energy of stacking faults. However, Zn element can increase the energy of stacking faults. Considering the magnitude of the change, it can be concluded that Y element make a major contribution to form stacking faults16). When the alloy is solidified, the stacking faults can be easily formed due to the segregation of Zn and Y happened around the interdendritic space and grain boundary. The 14H-LPSO may nucleate and grows through stacking faults. Based on the above research, we propose the stacking faults nucleation assumption in as-DS-grown Mg98.5Zn0.5Y1 alloy. It can be described as follows: the LPSO nucleated at the edge of stacking faults, then continuously formed a step which led to crystal growth. In the light of the above assumption, the stacking fault is considered to be a second–phase embryo. According the classical nucleation, the change of total free energy of stacking faults can be expressed by

\[ \Delta G = n[\Delta G^{Ch} + \Delta G^{E}] + 2\sigma(n) \]  

(1)

Where \( \Delta G^{Ch} \) is the chemical free energy, \( \Delta G^{E} \) is the elastic strain energy, and \( \sigma(n) \) is the interfacial energy. Actually, \( \sigma(n) \) is just the generalized stacking fault energy \( \gamma \). Therefore, eq. (1) can be modified to be

\[ \Delta G = n[\Delta G^{Ch} + \Delta G^{E}] + 2\gamma(n) \]  

(2)

When \( \Delta G \leq 0 \), the embryo will grow up spontaneously. \( \Delta G^{Ch} \) can be expressed by

\[ \Delta G^{Ch} \leq -\left(\frac{\Delta G^{E} + 2\gamma(n)}{n}\right) \]  

(3)

Equation (3) presents the relationship between stacking faults \( \gamma \) and chemical driving forcing (\( \Delta G^{Ch} \)). The lower the stacking faults energy is, the smaller chemical driving force needed to overcome the resistance. Therefore, the embryo will grow easily. From the thermodynamics point of view, it can be concluded that the 14-LPSO may nucleate directly through stacking faults. The stacking faults nucleation were firstly proposed by J.W.Christian17) in explaining the martensitic transformation. It was verified by M.Cohen18) through a series of experiment and simulation calculation.

On the basis of the lattice, the orientation relationship we mentioned above and further analysis of as-DS-grown 14H-LPSO on atomic scale, an atomic model was established19). As shown in Fig. 7 (a), the atomic model consisted

Fig. 5 (a) High resolution atomic image of the lamellar LPSO (b) SAED pattern of the lamellar LPSO structure observed inner the \( \alpha - Mg \) matrix of the alloy prepared by directional solidification.

Fig. 6 High resolution atomic image and SAED pattern of stacking fault in the Mg98.5Zn0.5Y1 alloy prepared by directional solidification.
of 168 atoms and viewed along [0\bar{1}0] direction. The yellow ball represent the Y atom, the pink ball represent the Mg atom and the blue ball represent Zn atom. The unit cell included two building blocks which have the opposite shear direction. The angle was 68.7º. The height of unit cell was 3.647 nm and the atomic composition of this proposed crystal structure was Mg\textsubscript{142}Zn\textsubscript{12}Y\textsubscript{16}. The Fig. 7 (b) shows the 14H-LPSO unit cell viewed along [001] direction. Figure 7 (c) shows the 14H-LPSO unit cell viewed along [111] direction.

Based on the proposed 14H unit cell, electron diffraction patterns were computed using single crystal software. The diffraction patterns of $[10\bar{3}0]_{4\text{TH}}$ zone axes are shown in Fig. 8. The simulated patterns were consistent with the experimental patterns in Fig. 3(b).

However, the electron diffraction patterns in Fig. 3(b) shows that Mans line appeared along the (0001) direction. This can be explained by the occurrence of dislocation along the (0001) direction. There was no such phenomenon in simulated diffraction patterns because of the ideal state.

4. Conclusion

The microstructure of as-DS-grown 14H-LPSO of Mg\textsubscript{98.5}Zn\textsubscript{0.5}Y\textsubscript{1} alloy were investigated using directionally solidified (DS), and the nucleation mechanism were analyzed. The results can be summarized as follows:

1) The as-DS-grown Mg\textsubscript{98.5}Zn\textsubscript{0.5}Y\textsubscript{1} crystal was confirmed to exhibit the 14H structure. The grains showed lamellar shapes.

2) The orientation relationship between the 14H and a-Mg matrix was $[4\bar{5}10]_{4\text{TH}}/\{\overline{1}2\overline{1}0\}_{\alpha-\text{Mg}}$ and (0001)$_{14\text{H}}$// (0001)$_{\alpha-\text{Mg}}$. The unit cell of the 14H structure contained two ABCA-type building blocks arranged in opposite shear direction, which measured as 68.7º.

3) The stacking faults formed in (0001)$_{\alpha-\text{Mg}}$ and extended along the $[\overline{1}2\overline{1}0]$ direction. These features indicate that the growth direction of stacking faults was parallel to the growth direction of 14H-LPSO. With regard to two-dimensional nucleation, the stacking faults nucleation was considered to be priority.

4) The 14H structure has an ordered hexagonal structure ($a = 1.112$ nm, $c = 3.647$ nm). The cluster which is Zn\textsubscript{6}Y\textsubscript{8} effectively promote the formation of building blocks. The atom model of as-DS-grown 14H-LPSO indicate that Mg\textsubscript{142}Zn\textsubscript{12}Y\textsubscript{16} composition is commonly accepted in the literature.

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