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Growth twinning behavior of cast Mg−Zn−Cu−Zr alloys

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Abstract: The morphology and orientation of the growth twins formed in the cast Mg−Zn−Cu−Zr alloys aged at 100 °C were characterized using optical microscopy and transmission electron microscopy. It was found that twins were invisible in the as-cast or solutionized Mg−Zn−Cu−Zr alloys while $\{10\bar{1}2\}$ twins were exclusively formed in the aged condition. The twinning behavior was significantly affected by two factors, namely, the Zn content and the heat treatment process. A possible formation mechanism of such growth twins was discussed using the viewpoint of vacancy.
Key words: Mg−Zn−Cu−Zr alloy; Mg alloys; twinning; heat treatment; vacancy

1 Introduction

Mg alloys are the lightest metallic structural materials and have many inherent advantages such as high specific strength and stiffness, good castability and excellent recycle ability. With the growing emphasis on energy consumption reduction and environment conservation, Mg alloys receive much attention and have been increasingly applied in the automotive, electronic and aerospace industries [1]. However, Mg alloys with hexagonal close-packed (HCP) crystal structure exhibit poor ductility and formability due to the limited independent slip systems at room temperature. Therefore, twinning plays an important role in improving the ductility and machinability for more applications of Mg alloys [2,3].

In contrast to numerous theoretical and experimental investigations on deformation twins in wrought Mg alloys [2−6], few works were reported concerning the growth twins formed in cast Mg alloys [7−9]. LUO and ZHANG [7] observed the lens-like laminar $\{01\bar{1}2\}$ twins in the as-cast and homogenized Mg−0.54Zr, Mg−5.68Zn and Mg−5.65%Zn−0.50Zr (mass fraction, %) alloys, which were considered the result of the large heat stress accumulated during the semicontinuous water-cooled casting process. The growth twins were also clearly shown in the aged AZ Mg alloys [8]. Apart from twinning in Mg matrix, AI et al [9] reported the growth twins in the lump-like CaMgSi precipitates of an as-cast Mg−1.0Ca−0.5Si−0.3Zr alloy. Although they have suggested the crystallographic and energetic conditions for the twin formation in the CaMgSi precipitates, the effects of the chemical composition and heat treatment process on the growth twins in Mg matrix were still not well understood.

In this work, the effects of Zn content and heat treatment process on the formation of growth twins in cast Mg−Zn−Cu−Zr alloys were investigated. The morphology and orientation of the twins were carefully characterized by means of both optical microscopy (OM) and transmission electron microscopy (TEM). A possible formation mechanism of such growth twins was proposed on the basis of vacancy theory.

2 Experimental

Mg−Zn−Cu−Zr alloys were prepared by commercially pure Mg (99.95%), pure Zn (99.9%), Mg−28.78Cu and Mg−31.63Zr (mass fraction, %) master alloys. The chemical compositions of the alloys were measured using a Thermo ARL4460 inductively coupled

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plasma spectrometer, as listed in Table 1. The melting was conducted in a stainless steel crucible under a protective atmosphere of SF_6 (0.5%, volume fraction) and CO_2 (Bal.) mixture. After being maintained at 730−750 °C for 30 min, the melt was poured into a preheated permanent mold at 250 °C, and a cast block with dimension of 200 mm×200 mm×40 mm was then fabricated. The cast alloys were solution treated at 430 °C for 24 h, then quenched into the cold water, and finally aged at 100 °C for 3 d in an oil bath.

Optical microstructures were observed on a Leica DMIRM/DFC320 optical microscope, and the specimens were mechanically polished and subsequently etched by a solution of 3 g picric acid, 50 mL ethanol, 20 mL acetic acid and 20 mL distilled water. Thin foils for TEM were prepared by a twin-jet electropolishing method in a solution of 10.6 g LiCl, 22.32 g $Mg(ClO_4)_2$, 200 mL 2-butoxi-ethanol and 1000 mL methanol at about −45 °C and 70 V. TEM characterization was performed using a JEM−100CXⅡmicroscope operated at 120 kV.

Table 1 Chemical compositions of ZC61 and ZC31 alloys

Alloy	*w*(Zn)/%	*w*(Cu)/%	*w*(Zr)/%	*w*(Mg)/%
ZC61	5.69	0.60	0.44	Bal.
ZC31	2.94	0.47	0.45	Bal.

3 Results and discussion

3.1 Optical microstructures of Mg−Zn−Cu−Zr alloys

Figure 1 shows the optical microstructures of ZC61 and ZC31 alloys in various treatment conditions. The two as-cast alloys exhibit a typical non-equilibrium solidification microstructure, i.e., α-Mg matrix with dendritic intermetallics dispersed mostly along the grain boundaries and a few inside the grains, as shown in Figs. 1(a) and (d). After a 24 h solution treatment at

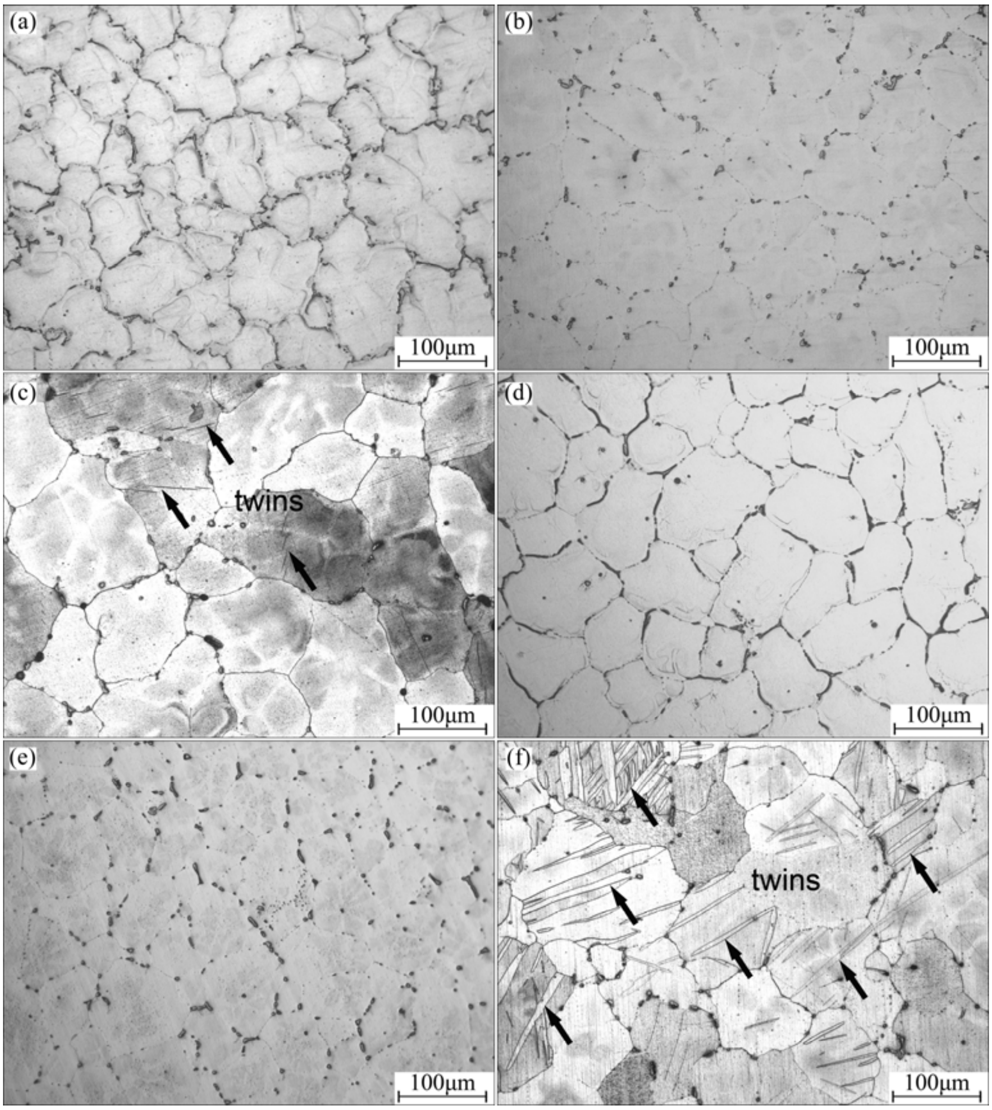

Fig. 1 OM images of ZC61 alloy and ZC31 alloy in various treatment conditions: (a) As-cast ZC61 alloy; (b) Solutionized ZC61 alloy; (c) Aged ZC61 alloy; (d) As-cast ZC31 alloy; (e) Solutionized ZC31 alloy; (f) Aged ZC31 alloy

430 °C followed by a water quenching, the grain boundaries of the alloys become discontinuous along with most of the intermetallics dissolving into the α-Mg matrix. Besides, some fine particles precipitate inside the grains possibly due to the alloying elements exceeding the solid solubility limit in the α-Mg matrix, as shown in Figs. 1(b) and (e). It is noted that twins are formed in both the aged ZC61(Fig. 1(c)) and ZC31(Fig. 1(f)) alloys, but with a much larger number of twins occurring in the ZC31 alloy than that in the ZC61 alloy, thus making the microstructures of the two aged alloys easily distinguishable.

3.2 TEM observation of twins in aged Mg−Zn−Cu−Zr alloys

Figure 2 shows the TEM images and the selected area diffraction pattern of a representative twin in the aged ZC31 alloy. The electron beam was oriented approximately parallel to $[1\bar{2}10]_M$ and $[\bar{1}2\bar{1}0]_T$ as indexed in Fig. 2(c) (M and T represent matrix and twin, respectively), thus showing a composite diffraction pattern $[1\bar{2}10]_M // [\bar{1}2\bar{1}0]_T$. These two sets of diffraction patterns were symmetric to each other with respect to the vectors $(10\overline{12})_M$ and $(10\overline{12})_T$. This indicates that the observed twin was $\{10\bar{1}2\}$ tension twin which was the most universal twinning mode due to the lowest shear associated with Mg [10]. Many twins of the same type were also observed in other grains of ZC31 alloy, and in ZC61 alloy as well.

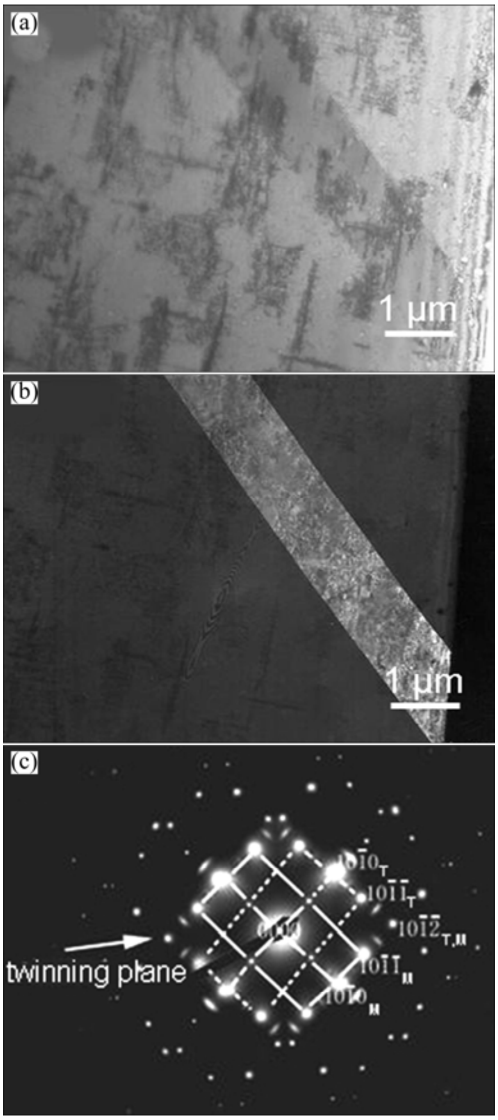

Fig. 2 TEM bright-field image (a), dark-field image (b) and selected area diffraction pattern (c) of a twin plate in aged alloy

3.3 Formation mechanism of growth twins in aged Mg−Zn−Cu−Zr alloys

To understand the twinning behavior, the vacancy produced in the alloys was particularly taken into account. According to the traditional metallurgical principles [11], a high density of vacancies can be produced in metals by rapid quenching from a high temperature. However, such vacancies are generally unstable. As a result, some vacancies could cluster into larger groups while the others would migrate or even vanish at the existing sinks such as grain boundaries, dislocations, voids and inclusions shortly after quenching. In this study, the Cu atoms possess a high binding energy and a strong affinity with vacancies [12]. Consequently, numerous vacancies could be bound to the Cu atoms and retained to a considerable extent even in excess of the equilibrium concentration at room temperature, thus forming vacancy clusters. According to the findings associated with HCP materials [13,14], those vacancy cluster platelets exceeding a certain size are liable to precipitate on the close-packed plane under a greater thermodynamic driving force caused by the subsequent aging treatment, which is energetically favorable to collapse to produce dislocation loops and stacking fault by the vacancy collapse mechanism. Furthermore, a perfect dislocation occurring in the large prismatic dislocation loops can easily dissociate into two partial dislocations separated by a strip of stacking fault.

Twinning is generally considered to be greatly associated with the stacking faults that can serve as the heterogeneous twin nuclei [9,10,15,16]. That is, the embryonic twins tend to be generated by rearranging these stacking faults and subsequently grow into large twins. Specifically, this process proceeds substantially by rearranging the stacking sequence of atoms in the stacking fault strips on the consecutive {0001} basal plane of Mg matrix, as shown in Fig. 3. By analogue to the deformation twinning, here the twinning elements are defined, so as to distinctly elucidate the atomic displacement situation. The four twinning elements are K_1, η_1, K_2 and η_2 according to the traditional twinning theory [10]. The left part in the solid line indicates the normal stacking of the {0001} basal plane, while the right part in the dashed line represents the atomic stacking of the basic plane after twinning. The driving force is the thermal stress triggered by the artificial aging in the present study.

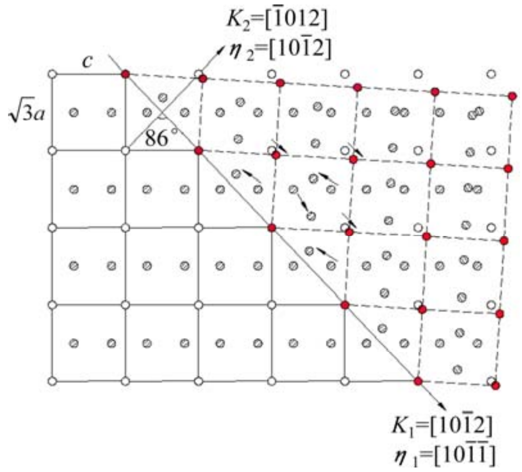

Fig. 3 $(1\bar{2}10)$ projection of atomic stacking sequence in {0001} basal plane for $\{10\bar{1}2\}$ twin

The twinning process cannot be energetically favored unless there is a low-energy twin boundary equivalent to a low-energy stacking fault (hereafter referred to as SFE) of the material [9]. Here Cu is of the lowest SFE among all the alloying elements used in the Mg−Zn−Cu−Zr alloys, as reported by MURR and STAUDHAMMER [17]. It can be speculated that the addition of Cu probably reduces SFE in the Cu-bearing Mg alloys, thus facilitating the twin formation. More importantly, the substitutional atoms can facilitate twinning by decreasing the SFE, while the interstitial impurities are adverse to twinning by controlling the stress concentrations reached in dislocation pileups [11]. It is well known that the substitutional solid solution tends to form if the relative difference (δ) in atomic radius between solvent and solute is less than 15%. Here $\delta=(r_{solute}-r_{solvent})/r_{solvent}$, is calculated to be 8.7% for Cu in Mg matrix. This suggests that the alloying element Cu is a crucial factor to contribute to the twinning formation in the present study. Based on the aforementioned analysis, a possible mechanism illustrating the twinning behavior in the aged Mg−Zn−Cu−Zr alloys is proposed, as shown in Fig. 4.

3.4 Twinning behavior of Mg−Zn−Cu−Zr alloys

The twinning behavior is significantly affected by two main factors, namely the chemical composition of the Mg alloys and the heat treatment procedures applied to them. The property, content and the binding energy with vacancies of the alloying element have a remarkable influence on the vacancy concentration, although different amounts of vacancies are needed to maintain

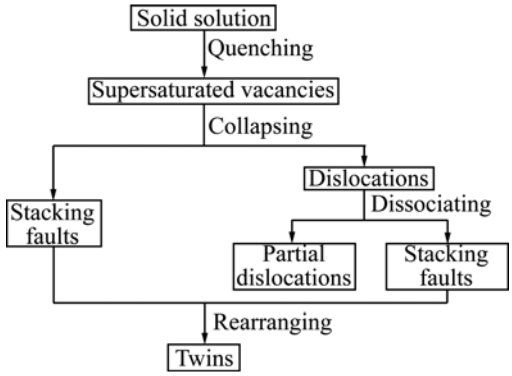

Fig. 4 Schematic diagram of twinning process in aged Mg−Zn−Cu−Zr alloys

the balance of the alloy system.

According to result by BUHA and OHKUBO [12], vacancies play a role in relieving the lattice strains induced by accommodation of substitutioal atoms into the Mg matrix, thus more vacancies are available to do the job by accommodating Cu with a small size of ~256 pm than Zn with a larger size of ~268 pm into the Mg matrix with a size of ~320 pm. Meanwhile, Cu atoms possess a significantly higher binding energy with vacancies (0.2 eV for Cu-vacancy [18]) than Zn atoms (0.06 eV for Zn-vacancy [19]). Therefore, the presence of the substitutional solute atom Cu could effectively impede a large vacancy flow into the sinks and hence stabilize the dispersion of vacancy clusters for forming twins. The composition ratio of Zn to Cu is estimated to be 12:1 and 6:1 for ZC61 alloy and ZC31 alloy, respectively. Thus, a greater twinnability is obtained for the ZC31 alloy than the ZC61 alloy, with the aid of strong Mg−Cu-vacancy complexes [20]. This explains much more twins occurring in the ZC31 alloy than in the ZC61 alloy.

With respect to the heat treatment procedure, the twinning phenomenon also occurs in T5 treated Mg−Zn−Cu−Zr alloys (as-cast alloys followed by direct aging) through our investigation. Hence, twins are invisible in the as-cast or the solutionized condition because some unstable vacancies are prone to migrate or even disappear in the positions of stacking faults, and the growth/collapse of vacancy clusters is restrained without the subsequent aging. The results presented herein can also account for the fact that twins is observed in the AZ series Mg alloys in aged condition, but not in their as-cast or solutionized condition [8]. In addition, it is worth noting that the stress or strain induced by the sample preparation method used in Ref. [7], and the unique character of the non-hexagonal CaMgSi phases observed in Ref. [9] may have led to the occurrence of twins.

4 Conclusions

1) The growth twinning behavior of cast Mg−Zn−Cu−Zr alloys is significantly affected by the characteristics of alloying elements and the heat treatment procedure. No twins are visible in the as-cast or solutionized alloys while $\{10\bar{1}2\}$ twins are exclusively formed in the aged alloys, and much more twins occur in the ZC31 alloy than in the ZC61 alloy.

2) The rearrangement of stacking faults derived from vacancies in solid solution during subsequent ageing probably leads to the heterogeneous nucleation of twins. Further TEM observations on the crystallographic features of such growth twins are still needed to understand the twin formation mechanism better.

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铸造 Mg−Zn−Cu−Zr 合金的生长孪晶行为

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摘　要：在铸造 Mg−Zn−Cu−Zr 合金 100 °C 时效过程中观察到生长孪晶，采用光学显微镜和透射电子显微镜表征生长孪晶的形貌和位向。结果表明：在铸态和固溶态的 Mg−Zn−Cu−Zr 合金中未发现生长孪晶，仅在时效态合金中出现 $\{10\bar{1}2\}$ 型生长孪晶。Zn 含量和热处理工艺显著影响其孪生行为。最后，从空位角度讨论此类生长孪晶可能的生长机制。

关键词：Mg−Zn−Cu−Zr 合金；镁合金；孪生；热处理；空位

(Edited by Chao WANG)