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ARTICLE

Age Hardening and Microstructure of ZA84 Magnesium Alloy with the Combined Addition ofCr and Bi

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Abstract: The age hardening and microstructure of ZA84 magnesium alloy with the combined addition of Cr and Bi was studied by SEM and HRTEM. The results show that a trace amount of Cr and Bi has a significant enhancement effect on the hardness of aging. When the ZA84-0.2Cr-0.5Bi alloy was aged at 160 °C, during the early aging period, the matrix has serious lattice distortion and a large number of crystal defects. The microstructure at the peak aging consists of a large number of rod-like or blocky β_1'-$MgZn_2$ phases and granular Bi_2Mg_3 phases, and the peak hardness HV value is 924.8 MPa. When ageing proceed, the precipitates coarsening results in the hardness value reduction.

Key words: ZA84-0.2Cr-0.5Bi alloy; crystal defect; age hardening; strengthening phase

Strengthening and toughening is an important research problem in magnesium alloy, which restricts the application of magnesium alloy to a great extent [1-4]. Mg-Zn solid solution has the metastable solubility gap and age hardening characteristics, which has become a hot research topic in the present study. During aging heat treatments, the aging sequences of Mg-Zn alloy are as follows: SSSS → G. P. zone/β_1' (rods or blocky $MgZn_2$ or Mg_4Zn_7, $\perp[0001]_{Mg}$) → β_2' (laths $MgZn_2 \perp [0001]_{Mg}$ or coarse plates $MgZn_2 // [0001]_{Mg}$) → β (Mg_2Zn_3)[5,6]. It is generally believed that the G.P. zone and β_1'-$MgZn_2$ is the most effective strengthening phase in Mg-Zn alloy. However, the aging hardening effect of Mg-Zn binary alloy is not satisfying. This is due to the low precipitation density and poor thermal stability of the β_1' phase, so it is easy to grow up into laths or coarse plates β_2' phase. The β_2' phase can significantly reduce the strength of Mg-Zn based alloy. Therefore, how to strengthen the aging hardening effect of Mg-Zn-based alloys has become a research hotspot. It is well known that adding some alloy elements to improve the nucleation rate and precipitate density is an effective method to improve the aging strength of Mg-Zn-based alloys. Buha et al have studied the effect of Cr[7], Ba[8] and Ti[9] on the microstructure and age hardening of Mg-Zn alloy. The results revealed that a trace amount of Cr, Ba or Ti are exceptionally effective in enhancing the age hardening processes of Mg-Zn alloy by stimulating the nucleation of the precipitates. Mendis et al [10] have studied effect of Li addition on the age hardening response and precipitate microstructures of Mg-2.4Zn-0.16Zr alloy. The results showed that Li improved the kinetics of precipitation hardening and the number density of the precipitates in the Mg-2.4Zn-0.16Zr alloy. Although the Mg-Zn alloy containing Cr, Ba, Ti or Li has a higher precipitation density and aging hardness than Mg-Zn binary alloy, the size of effective strengthening phase β_1' remains relatively coarse. Therefore, the aging hardening response of the Mg-Zn-based alloys needs to be further enhanced. In the recent years, many research groups believe that combined addition of above 2 or 3 trace element is the future development of the aged Mg-Zn-based alloys. Zhang et al [11] have studied the effect of artificial aging on microstructure of the Mg-4.5Zn-4.5Sn-2Al alloy. The results indicated that there are some types of precipitates in the microstructure of the alloy and the peak hardness HV can increase to more than 900 MPa.

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Bhattacharjee et al [12] have studied the effect of Ag and Ca additions on the age hardening response of Mg-Zn alloys. Their research showed that the peak hardness of the alloy with the combined addition of Ag and Ca is much higher than that of the binary and ternary alloys. In addition, Oh-ishi's [13] and our previous [14] research indicated that the Mg-Zn-Al alloy has more variations of the morphology and finer distribution of precipitates than Mg-Zn alloy. Thus, we studied the age hardening and microstructure of Mg-8Zn-4Al alloy (ZA84 magnesium alloy) with the combined addition of Cr and Bi. Depending on the role of Cr [7] in promoting nucleation of the precipitates and Bi [15,16] in inhibiting the growth of the β_1' -$MgZn_2$ phase, the ZA84 magnesium alloy containing Cr-Bi element has a better effect on age hardening response than the ternary ZA84 magnesium alloy.

1 Experiment

An alloy having a composition ZA84-0.2Cr-0.5Bi (wt%) was prepared from pure magnesium, pure chromium, pure bismuth and Mg-Zn-Al pre-alloys, which was prepared from pure components in the same manner, with an electrical resistance furnace under protective 0.1 SF_6-99.9CO_2 (wt%) atmosphere. About 500 g melts were heated to 720 °C, held for 20 min and then poured into a 15 mm (dia.) × 200 mm pre-heated permanent mould (the preheating temperature 500 °C) made of steel. The as-cast alloys were solid solution treated at 350 °C for 12 h prior to quenching in cold water. Artificial aging (T6) was performed at 160 °C in an oil bath. The age hardening value was obtained with a Vickers hardness tester (HXD-1000) under a load of 500 g. The final value reported here was averaged from at least 10 measurements. The scanning electron microscope (SEM) images were obtained by ZEISS Supra 55. The specimens for high resolution transmission electron microscope (HRTEM) were obtained from aged material using a Precision Ion Polishing System (Gatan 691). The HRTEM images were obtained by JEOL JEM-2010FEF at 300 kV.

2 Results and Discussion

2.1 Age hardening

The age hardening curves of ZA84 magnesium alloy and ZA84-0.2Cr-0.5Bi alloy aged at 160 °C are shown in Fig.1. The two curves indicate that the age hardening process of the ZA84 magnesium alloy and the ZA84-0.2Cr- 0.5Bi alloy follow a similar pattern: the hardness rises in the earlier stage and then declines with prolonging age time. For the ZA84 alloy, the hardness HV value in the as-quenched samples is ~670 MPa. When this alloy is aged at 160 °C, the kinetics of precipitates in the early aging period (0~20 h) is much lower than that of ZA84-0.2Cr-0.5Bi alloy. When aging time is 64 h, a peak hardness HV value of 861.2 MPa is obtained. The ZA84 alloy only shows a small amount of age hardening (△HV≈90 MPa). For the ZA84-0.2Cr-0.5Bi alloy, a hardness

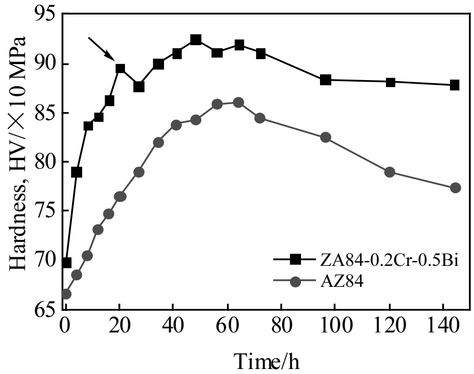

Fig.1 Age hardening curves of ZA84 alloy and ZA84-0.2Cr-0.5Bi alloy aged at 160 °C

HV value of ~700 MPa is obtained in the as-quenched samples. When the alloy is subjected to aging at 160 °C, the kinetics of precipitates at initial stage (0~20 h) is considerably accelerated and the alloy reaches 96.86% of its maximal hardness level after 20 h (arrowed). The hardness HV reaches the peak (924.8 MPa) after 48 h of ageing, and then decreases slightly with the prolonging of aging time. Therefore, although the content of Cr and Bi is at a trace level, they have a significant enhancement effect on the hardness of aging.

2.2 Microstructures

The HRTEM images of the microstructure of ZA84-0.2Cr-0.5Bi alloy aged at 160 °C for 8 h are shown in Fig.2. There is no precipitates found in the microstructures of alloy, but the matrix has severe moiré fringes and lattice distortion. Some moiré fringes (arrows) with different sizes are visible in Fig.2a. These moiré fringes indicate that some precipitates were generated in the early aging period. The lattice distortion Frank loops and stacking faults around the dislocation in the matrix can be clearly observed (Fig.2b). This may be that Cr has an extremely low solubility, and it is very likely that in the initial stage of ageing or possibly even during quenching, Cr dissociated from the magnesium solid solution, thereby providing suitable (heterogeneous) nucleation sites for the aggregation of Zn or Bi atoms (and vacancies)[7]. It is well known that solute atoms are easier to aggregate at the crystal defects; therefore, the number of crystal defects in the matrix is increased, and the nucleation rate of the subsequent precipitates is promoted obviously. In addition, numerous lattice contractions shown in the rectangular regions A and lattice expansions shown in the rectangular regions B can also be observed in Fig.2b.

The peak aged microstructure of ZA84-0.2Cr-0.5Bi alloy aged at 160 °C for 48 h are shown in Fig.3. These images are taken with the electron beam parallel to the $[2\bar{1}\bar{1}0]_\alpha$ direction. Fig. 3a shows the microstructure consisting of numerous rod-like precipitates that are 150~300 nm in length and growing along the $[0001]_\alpha$ direction, blocky precipitates that are growing along the $[0\bar{1}10]_\alpha$ direction, and a small amount

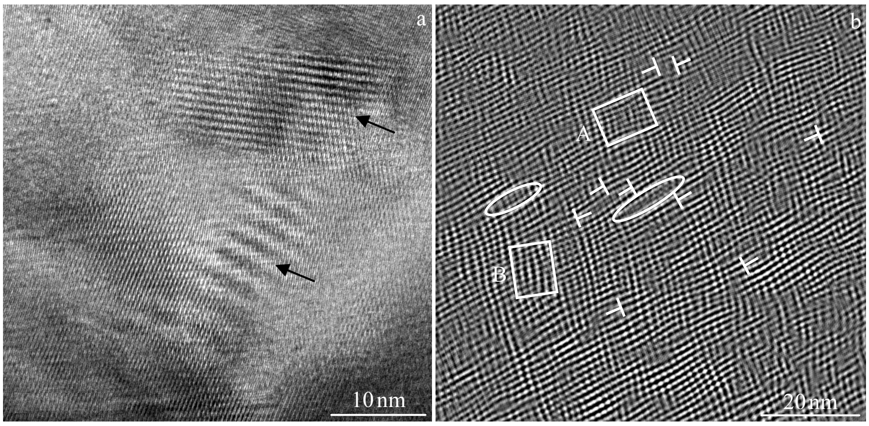

Fig.2 HRTEM images of the microstructure of ZA84-0.2Cr-0.5Bi alloy aged at 160 °C for 8 h

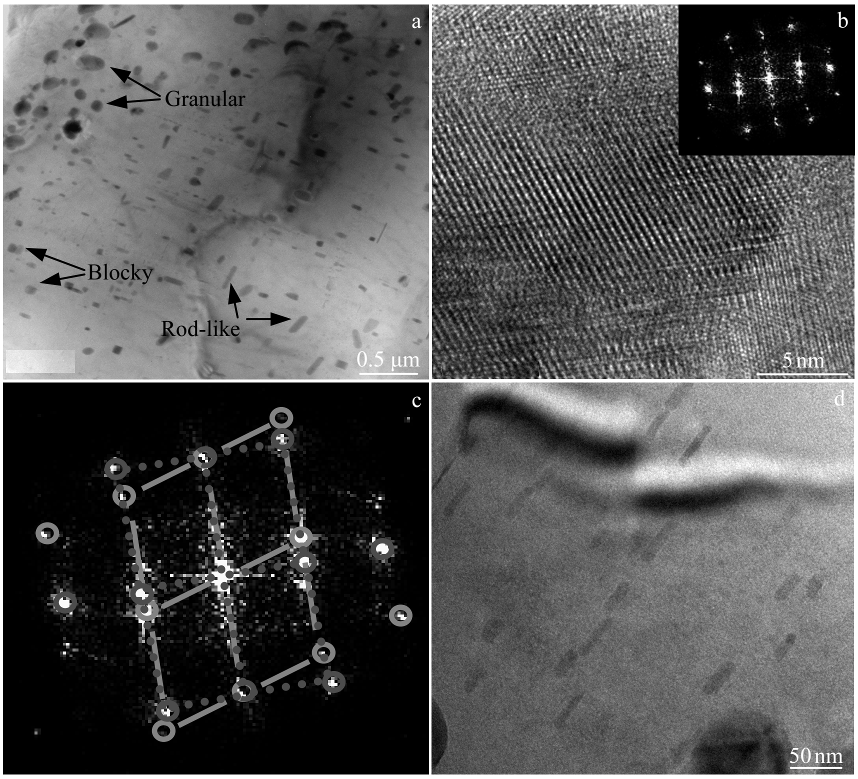

Fig.3 HRTEM images of ZA84-0.2Cr-0.5Bi alloy aged at 160 °C for 48 h: (a) rod-like precipitates of 150~300 nm in length, (b) HRTEM image of the granular precipitate, (c) $(01\bar{1}\bar{2})_{Bi_2Mg_3}$//$(0\bar{1}10)_\alpha$ and $[\bar{2}4\bar{2}3]_{Bi_2Mg_3}$//$[2\bar{1}\bar{1}0]_\alpha$, and (d) β_1'-$MgZn_2$ phases of 30~50 nm in length

of granular precipitates. These rod-like and blocky precipitates correspond well to the β_1'-$MgZn_2$ phases, which are typical for the artificially aged condition of Mg-Zn based alloys[17]. The HRTEM image of the granular precipitate is shown in Fig.3b. The FFT pattern inserted in Fig.3b obtained from the granular precipitates could be indexed consistently according to a hexagonal structure, with lattice parameters a=0.468 nm, c=0.742 nm. This structure of the granular precipitates is similar to that of the Bi_2Mg_3. Fig.3c shows that the granular Bi_2Mg_3 precipitate has the orientation relationship with the magnesium matrix such that $(01\bar{1}\bar{2})_{Bi_2Mg_3}$//$(0\bar{1}10)_\alpha$ and $[\bar{2}4\bar{2}3]_{Bi_2Mg_3}$//$[2\bar{1}\bar{1}0]_\alpha$. It is worth noting that there are some fine and rod-like β_1'-$MgZn_2$ phases in the microstructure of the alloy at a high magnification. These β_1'-$MgZn_2$ phases are 30~50 nm in length and grow along the $[0001]_\alpha$ direction, and they can effectively improve the aging hardness of the ZA84-0.2Cr-0.5Bi alloy (Fig.3d).

Fig.4 shows the microstructure of ZA84-0.2Cr-0.5-Bi alloy aged at 160 °C for 144 h. As the aging time increases, the size of precipitates increases, and the precipitate free zone (PFZ)

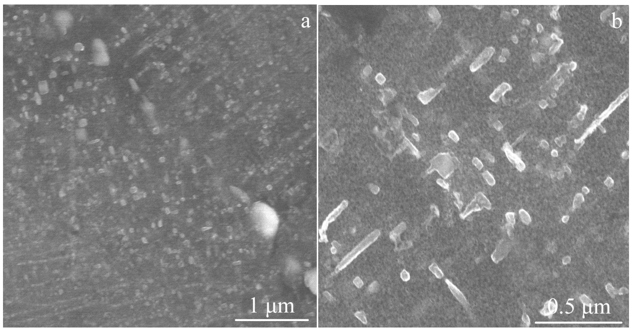

Fig.4 SEM microstructure of ZA84-0.2Cr-0.5Bi alloy aged at 160 °C for 144 h

is observed along grain boundaries (Fig.4a). The rod-like precipitates are about 500 nm in length, which is much longer than that of the peak aged microstructure (48 h). The precipitate coarsening results in the hardness value reduction.

3 Conclusions

1) The ZA84-0.2Cr-0.5Bi alloy exhibits rather high hardening rate at initial stage of aging, the hardness HV reaches the peak (924.80 MPa) after 48 h of ageing, and then decreases slightly with the prolonging of aging time.

2) For ZA84-0.2Cr-0.5Bi alloy aged at 160 °C, during the early aging period, the matrix has serious lattice distortion and a large number of crystal defects. The microstructure at the peak aging consists of a large number of rod-like or blocky β_1' -$MgZn_2$ phases and granular Bi_2Mg_3 phases. Then precipitate coarsening results in the hardness value reduction when the ageing proceeds.

3) Although the content of Cr and Bi is at a trace level, they had a significant enhancement effect on the hardness of aging.

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复合添加 Cr、Bi 元素的 ZA84 镁合金时效硬化及微观组织研究

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摘　要：利用扫描电镜及高分辨透射电镜对复合添加 Cr、Bi 元素的 ZA84 镁合金的时效硬化及微观组织进行了研究。结果表明：在 ZA84 合金中复合添加微量的 Cr、Bi 元素能显著增强合金时效硬化效果。ZA84-0.2Cr-0.5Bi 合金经 160 ℃时效，在时效初期基体存在严重的晶格畸变并含有数量较多的晶体缺陷。峰时效阶段合金微观组织中析出大量呈棒状或块状的 $MgZn_2$ 相以及粒状的 Bi_2Mg_3 相，此时合计峰时效硬度 HV 达到 924.8 MPa。随着时效时间的延长，沉淀相继续长大并粗化，其硬度也略有下降。

关键词：ZA84-0.2Cr-0.5Bi 镁合金；晶体缺陷；时效硬化；强化相

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