

Effect of B_2O_3 on microstructures and mechanical properties of cast Mg–Al–Ti–B alloys

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Abstract: The Mg–Al–Ti–B alloy prepared by mechanical alloying is poor in microstructural uniformity and compactness. In order to improve the microstructural uniformity and compactness of Mg–Al–Ti–B alloy and thus to improve the mechanical properties, effect of B_2O_3 on microstructure and mechanical properties of cast Mg–9Al–6Ti alloy was studied by optical microscopy, scanning electron microscopy, X-ray diffraction and mechanical property testing. The results show that due to the addition of B_2O_3 , the average grain size of Mg–Al–Ti–B alloys is refined to 12 μm , dispersed Ti phases completely disappear, the amount of precipitation phase $Mg_{17}Al_{12}$ is reduced and $TiAl_3$ is increased, and new phases MgB_6 and Ti_3B_4 are precipitated. The average hardness, average tensile strength, yield strength and elongation of the alloy are HV 77.1, 171.2 MPa, 113.5 MPa and 5.2%, respectively.

Key words: magnesium alloy; boron trioxide; microstructure; mechanical properties

1 Introduction

Magnesium and magnesium alloys are the lightest structural materials in engineering so far [1]. Magnesium alloys with high strength, good thermal conductivity, damping capacity, and electromagnetic shielding, easy mechanical processing and recoverability are known as green engineering metals in the 21st century [2,3]. More and more magnesium alloys, such as AM50, AZ31 and AZ91, have been increasingly applied to automotive industry [4].

Four series of magnesium alloys have been developed: Mg–Al–Zn–Mn (AZ series), Mg–Al–Mn (AM series), Mg–Al–Si (AS series), Mg–Al–RE (AE series), but they still cannot satisfy the requirements of some important high-strength structural components. Generally, the strength and heat resistance of magnesium alloys are significantly improved [5,6] through adding rare earth elements. Magnesium alloys are strengthened by the dispersion strengthening of rare earth compounds and their effect on grain boundary sliding [7]. Mechanical alloying has been applied to Mg–Al–Ti–B alloys, and their structure and performance have been analyzed and studied [8], but their microstructure and

mechanical properties are not ideal yet.

For Mg–Al–Ti–B alloy by mechanical alloying, its microstructure uniformity is poor, and the compactness is not good. In order to improve the microstructure uniformity and compactness of Mg–Al–Ti–B alloy, thus to improve the mechanical properties, in this work, Mg–9Al–6Ti alloys were fabricated by casting, and the effects of B_2O_3 on microstructure and mechanical properties of Mg–9Al–6Ti alloy were studied.

2 Experimental

The chemical compositions of raw materials are listed in Tables 1–4. In order to fabricate Mg–Al–Ti–B alloys, pre-alloys Mg–9Al–6Ti were prepared by stirring casting processing. Magnesium and aluminum metals were firstly melted in an electric heating crucible furnace at 720 °C, and then titanium powders were added. The mixture was stirred for 10 min with stirring speed of 500 r/min. After that, the melt was heated to 800 °C and cast in a metal mold. The melting was under the protection of argon.

B_2O_3 was used as the precursor of B to prepare Mg–Al–Ti–B alloys. The pre-alloys Mg–9Al–6Ti were melted at 720 °C, and then 3% or 6% B_2O_3 in mass

Table 1 Chemical composition of magnesium (mass fraction, %)

Al	Si	Fe	Mn	Mg
0.02	0.01	0.04	0.03	Bal.

Table 2 Chemical composition of aluminum (mass fraction, %)

Mg	Si	Fe	Ti	V	Ga	Al
0.001	0.03	0.09	0.01	0.01	0.01	Bal.

Table 3 Chemical composition of titanium powder (mass fraction, %)

C	H	Cl	O	N	Si	Fe	Ti
0.1	0.05	0.15	0.65	0.06	0.01	0.35	Bal.

Table 4 Chemical composition of B₂O₃ (mass fraction, %)

B ₂ O ₃	SO ₄ ²⁻	Heavy metals (as Pb)	Fe
99.4	0.02	0.005	0.005

fraction was added. The mixture was stirred for 5 min with stirring speed of 500 r/min. After holding the mixture for 10 min, the melts without molten slags were cast into the metal mold ($d30\text{ mm}\times 150\text{ mm}$).

The microstructures and phase composition of Mg–Al–Ti–B alloys were studied by optical microscopy (Nikon LWD200–4xC), scanning electron microscopy (JEOL JSM-6510), X-ray diffraction (Lab XRD-6000). Their hardness was measured (075020 SHANGHAI HX-1000TM), and the tensile properties were evaluated with a tensile instrument (AUTDGRAPH IS-2000).

3 Results and discussion

3.1 Micro-hardness

Figures 1 and 2 show the schematic diagram of point distribution for hardness testing and hardness values of alloys, respectively. The hardness values of Mg–9Al–6Ti alloy are dispersed (Fig. 2(a)), those of Mg–9Al–6Ti–3B₂O₃ are more concentrated (Fig. 2(b)), and those of Mg–9Al–6Ti–6B₂O₃ are middle (Fig. 2(c)). There are three reasons for the dispersion and centralization of the hardness. Firstly, in the crystallization process from the pouring to the solidification, due to different degrees of undercooling, the hardness value of point 1 is lower than that of point 4 or 7. Secondly, the degrees of uniformity of the microstructure of the alloys are different. Finally, the degree of densification of the alloys after the crystallization is also an important influencing factor. The later two are the main reasons of the dispersion and concentration of hardness values.

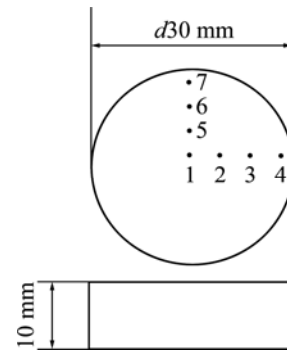
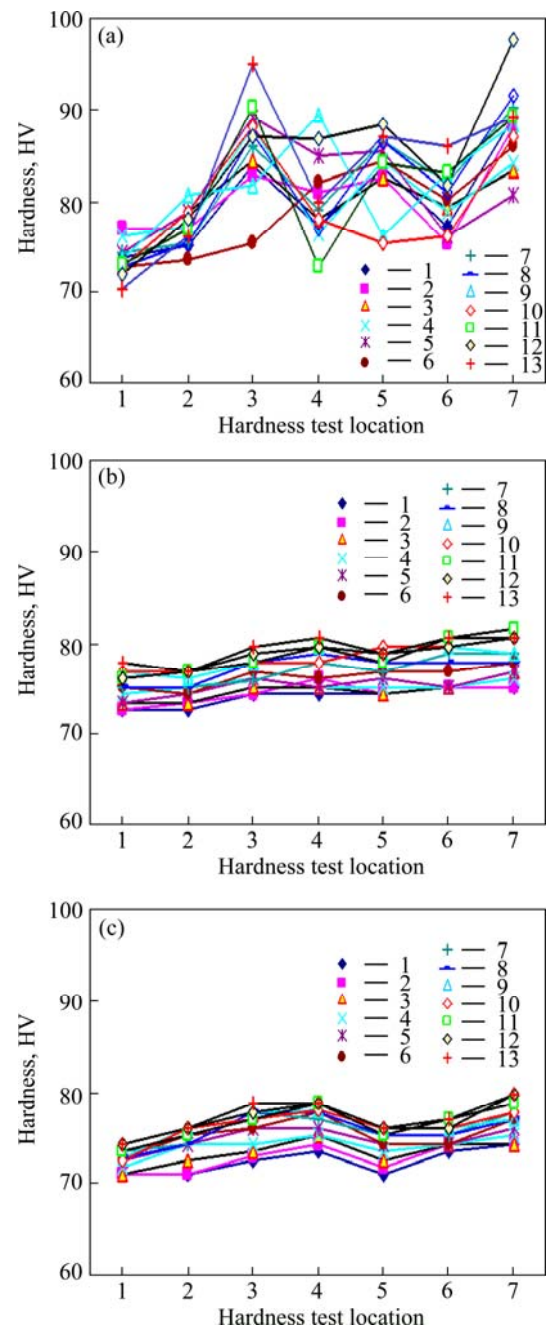

Fig. 1 Seven-point distribution of hardness test location

Fig. 2 Hardness of alloy at different points: (a) Mg–9Al–6Ti; (b) Mg–9Al–6Ti–3B₂O₃; (c) Mg–9Al–6Ti–6B₂O₃

Figure 3 shows the average hardness values of these alloys. The average hardness value of Mg–9Al–6Ti is higher than that of Mg–9Al–6Ti–3B₂O₃, and the value of Mg–9Al–6Ti–6B₂O₃ is lower than that of Mg–9Al–6Ti–3B₂O₃. By comprehensive considering numerical dispersion in Fig. 2, it suggests that the average hardness value of Mg–9Al–6Ti is HV 81.1, which is relatively high, but the difference of the hardness values for 7 points is large. The reason is that the relative density of the material is low and the uniformity is bad due to the existing pore in this alloy. The average hardness of Mg–9Al–6Ti–3B₂O₃ is HV 77.1, but the difference of hardness values for 7 points is small due to the densification and uniformity of the material. The average hardness value of Mg–9Al–6Ti–6B₂O₃ is HV 75.5, which is relatively low, but the hardness value is very discrete. It is probably because the oxide impurity exacerbates the microstructures of the alloy.

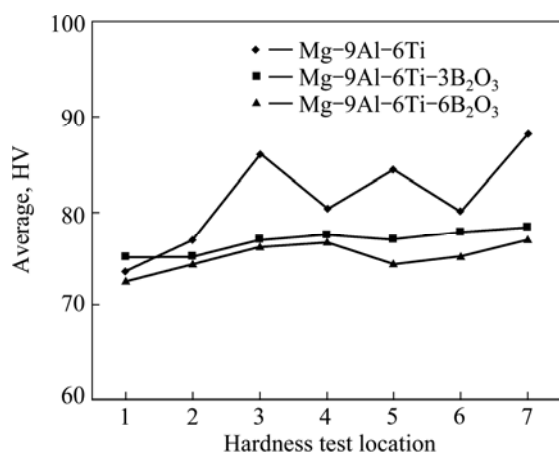


Fig. 3 Average value of three alloys

3.2 Microstructure

Figure 4 shows the optical microstructures of the three alloys. The densification and uniformity of the alloys have been improved by adding 3%–6% B₂O₃ into Mg–9Al–6Ti alloy. Specially, the microstructure of Mg–9Al–6Ti–3B₂O₃ is more homogeneous and denser than that of Mg–Al–Ti–B alloy prepared by mechanical alloying.

According to the phase diagrams of binary alloys Mg–Al, Mg–Ti and Al–Ti [9], the calculated mixing free energy suggests that magnesium is rarely combined with titanium, and the binding force between titanium and aluminum is strong. Therefore, α -Mg, β -Mg₁₇Al₁₂, TiAl and TiAl₃ might be found in the alloys. However, Fig. 4(a) shows that the titanium powders of 10–30 μ m in diameter are not dissolved. Figures 4(b) and (c) also show that the titanium powders in the two alloys disappear after adding B₂O₃. B₂O₃ can remove the TiO₂ film on the surface of the titanium powders, and the

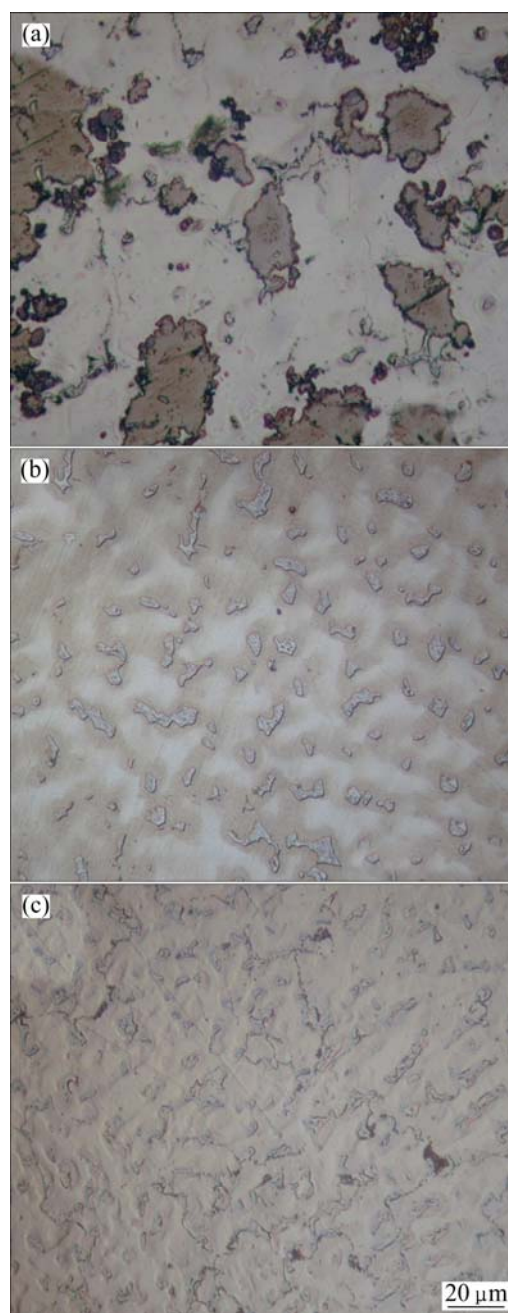


Fig. 4 Optical microstructures of alloys: (a) Mg–9Al–6Ti; (b) Mg–9Al–6Ti–3B₂O₃; (c) Mg–9Al–6Ti–6B₂O₃

aluminum, titanium and boron in magnesium alloy cause atomic state contact. Due to the strong binding force between titanium and boron, the titanium and boron preferentially bind and generate TiB or Ti₃B₄. Besides, TiAl or TiAl₃ is generated.

The grains of the Mg–9Al–6Ti alloys are obviously refined through adding B₂O₃. 3% is the threshold value of B₂O₃ for grain refinement of the Mg–9Al–6Ti alloy, which makes the average grain size reduced from 54.8 to 12 μ m. When the added amount of B₂O₃ deviates from this value, the grain size of alloy is coarse. SEM image of Mg–9Al–6Ti–3B₂O₃ alloy is shown in Fig. 5.

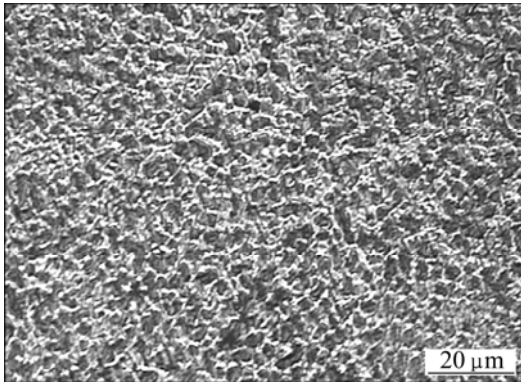


Fig. 5 SEM image of Mg-9Al-6Ti-3B₂O₃ alloy

SEM photograph and EDS spectrum of Mg-9Al-6Ti-3B₂O₃ are shown in Fig. 6. The white phase at this position is composed of Al, Ti, Mg, B and O. Real-time multi-element surface scanning and line scanning distribution measurements are shown in Fig. 7. The results show that the magnesium is matrix, the distribution of aluminum is more concentrated and it is

gradually outward dispersed around the concentration, but the Ti, O and B are dispersed.

XRD patterns of alloys are shown in Fig. 8, which further confirms the phase composition. The Mg-9Al-6Ti alloy is composed of α -Mg, β -Mg₁₇Al₁₂, TiAl₃ and α -Ti. However, due to the reaction of B₂O₃ with Mg and Ti, in the alloy with 3% B₂O₃ (Fig. 8(b)), Ti phase disappears completely, new phases MgB₆ and Ti₃B₄ appear, precipitate Mg₁₇Al₁₂ phases reduce, and TiAl₃ phases increase. In the alloy with 6% B₂O₃ (Fig. 8(c)), MgO appears due to the reaction of excess B₂O₃ with Mg.

3.3 Tensile properties

Cast AZ91 magnesium alloy has been used in the automotive and industrial applications [10–12]. The comparison of the tensile properties between the AZ91 alloy and the three alloys is shown in Fig. 9. The average tensile strength, yield strength and elongation of cast AZ91 are 123.5 MPa, 82.4 MPa and 3.4%, which are lower than those of Mg-9Al-6Ti-3B₂O₃ alloy, 171.2 MPa, 113.5 MPa and 5.2%, respectively.

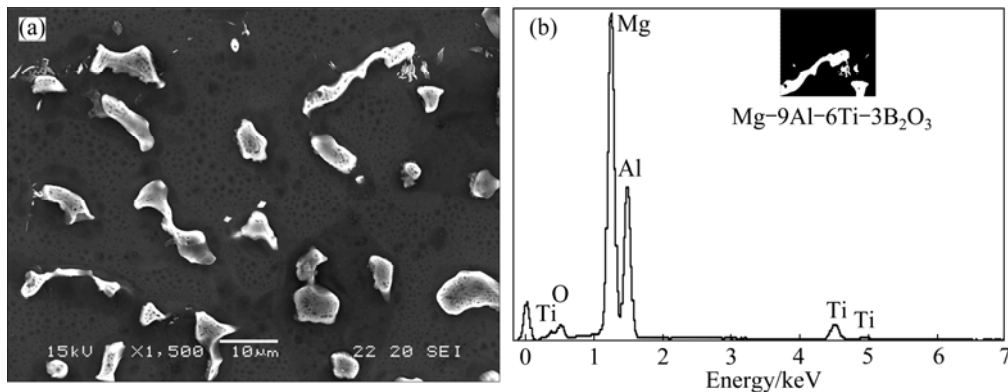


Fig. 6 SEM image (a) and EDS spectrum (b) of Mg-9Al-6Ti-3B₂O₃ alloy

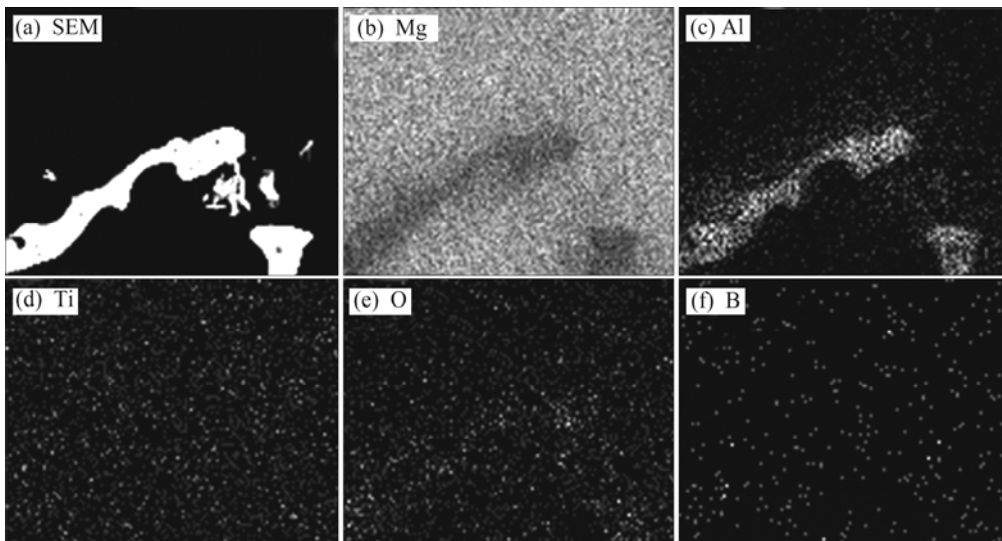


Fig. 7 Elemental surface distribution of Mg-9Al-6Ti-3B₂O₃ alloy

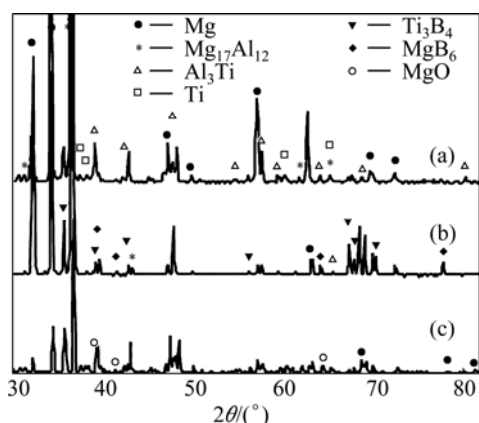


Fig. 8 XRD patterns of alloys: (a) Mg-9Al-6Ti; (b) Mg-9Al-6Ti-3B₂O₃; (c) Mg-9Al-6Ti-6B₂O₃

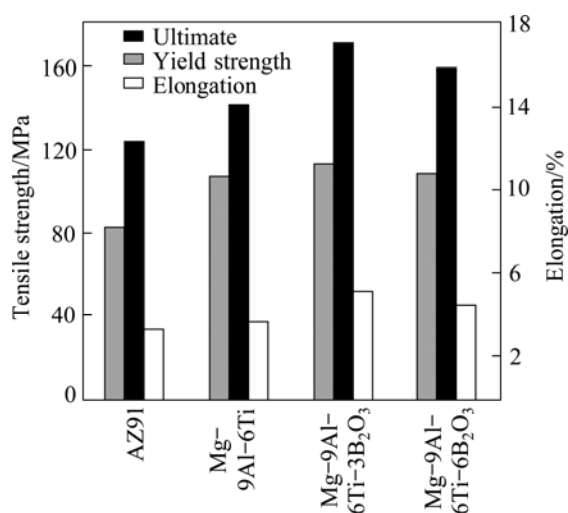


Fig. 9 Tensile properties of cast alloys at ambient temperature

4 Conclusions

1) During the casting processing of Mg-9Al-6Ti alloy, titanium powder is completely melted due to the addition of B₂O₃. The hardness of the alloy reduces, and its densification and uniformity can be improved.

2) Adding 3% B₂O₃ (mass fraction) makes the average grain size of Mg-9Al-6Ti alloy reduce from 54.8 to 12 μm.

3) The amount of precipitation phase Mg₁₇Al₁₂ is reduced and TiAl₃ is increased, and new phases MgB₆ and Ti₃B₄ are precipitated due to the addition of B₂O₃.

4) The average hardness, average tensile strength, yield strength and elongation rate of Mg-9Al-6Ti-3B₂O₃ alloy are HV 77.1, 171.2 MPa, 113.5 MPa and 5.2%, respectively.

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B₂O₃ 对铸态 Mg-Al-Ti-B 合金的显微组织与力学性能的影响

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摘 要: 采用机械合金化制备的 Mg-Al-Ti-B 合金, 其微观组织的均匀性较差, 而且致密性也不好。为了提高 Mg-Al-Ti-B 合金微观组织的均匀性和致密性, 使其力学性能得到改善, 制备了铸态 Mg-9Al-6Ti 合金。采用金相显微镜、扫描电镜、X 射线衍射与力学性能测试等手段, 研究 B₂O₃ 对 Mg-9Al-6Ti (质量分数, %)合金的显微组织与力学性能的影响。结果表明: 添加 3% 的 B₂O₃ 使 Mg-Al-Ti-B 合金的晶粒尺寸减小到 12 μm, Ti 颗粒完全消失, 沉淀相 Mg₁₇Al₁₂ 减少, 而 TiAl₃ 相增多。由于新沉淀相 MgB₆ 和 Ti₃B₄ 的析出, Mg-9Al-6Ti-3B₂O₃ 合金的结构变得均匀, 平均硬度为 HV77.1, 平均抗拉强度、屈服强度和伸长率分别是 171.2 MPa、113.5 MPa 和 5.2%。

关键词: 镁合金; 三氧化二硼; 显微组织; 力学性能

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