A New Extruded Mg-6Bi-3Al-1Zn Alloy with Excellent Tensile Properties

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Abstract: Aiming to develop low-cost Mg alloys with good mechanical properties, a new Mg-6Bi-3Al-1Zn (wt.%, BAZ631) alloy having a high ultimate tensile strength of ~402 MPa and an elongation of ~15% was fabricated by single pass extrusion. The as-extruded BAZ631 alloy demonstrates an almost fully dynamic recrystallized microstructure with an average grain size of ~2.9 \( \mu \)m. Moreover, both nano-scale Mg \(_3\)Bi\(_2\) and Mg\(_{17}\)Al\(_{12}\) precipitates were found dispersed in the matrix. These excellent mechanical properties are attributed to the combined effects of grain boundary strengthening, dispersion and precipitation strengthening induced by both micro and nanoscale second phase particles, and solid-solution strengthening. This high strength and good ductile Mg-Bi based alloy without rare-earth elements addition is expected to inspire a new alloy design strategy for fabricating high performance Mg products for larger-scale industrial applications.

Keywords: Mg alloy; extrusion; microstructure; dynamic recrystallization; mechanical properties

1. Introduction

Application magnesium (Mg) alloys in the transportation industry is attracting increasing attention these years due to their high specific strength [1,2]. However, the mechanical properties of commercial high-strength Mg alloys such as AZ80 and ZK60 are still much lower than that of aluminum (Al) alloys such as 2024 and 7075 [3]. Therefore, further improving the mechanical properties of Mg alloys is of great significance in becoming a commercially viable alternative to Al alloys.

In this respect, Mg-Bi-based alloys, based on a typical precipitation-type phase equilibrium, are desirable candidates in developing low-cost high-strength extrudable materials without rare-earth elements (RE) [2,4]. In addition, the Bi element is non-toxic and is called “green metal” [5], the price of which is much lower than that of RE. Therefore, alloying Mg with Bi also has great potential in biomedical applications [6]. Recently, several Mg-Bi-based alloys exhibiting attractive mechanical properties have been fabricated. It is reported that alloying Mg with 3–8 wt.% Bi can greatly enhance the strength of the extruded Mg alloys due to the grain refinement and precipitation strengthening by micro and nanoscale Mg\(_3\)Bi\(_2\) phases [7,8]. Compared with pure Mg, the as-extruded Mg–6Bi(wt.%), B6 all compositions quoted in this work are in wt.%) alloy demonstrates greatly improved strength and ductility with ultimate tensile strength (UTS) of 228 MPa and an elongation (EL) of 170% [9]. H. Somekawa et al. [9] reported that Mg-3Bi alloy can be extruded at the temperature less than 210 \( ^\circ \)C and demonstrates an EL of 170%. Additionally, Ca [10–14], Si [10], Mn [15], Al [16], Zn [16], and Sn [17] have been used as alloying elements to improve
the mechanical properties of Mg-Bi based alloys. For example, biomedical Mg-5Bi-1Ca/Si alloys having an EL of over 40% were successfully fabricated by the rapid solidification and extrusion process [10]. Based on this study, our former studies [11,12] further found that dilute Ca addition in as-extruded Mg-1.5Bi alloy will introduce weakened <2–1–12>⁄∥ED texture and greatly increase its ductility. Additionally, medium strength Mg-8Bi-1Al-1Zn (BAZ811) alloy with UTS of 331 MPa and an EL of 14.6% were fabricated by extrusion in our former research [16]. By combining extrusion and 3-pass caliber rolling processing, a high strength Mg-1.32Bi-0.72Ca (BX11) alloy with a UTS of 381 MPa and an EL of 13.2% was fabricated [14]. More recently, alloying the Mg-Bi alloy with Sn was also used to further increase its mechanical properties, but the UTS of as-extruded Mg-5Bi-6Sn alloy having a typical basic fiber texture and partial dynamic recrystallization (DRX) microstructure is only 301 MPa [17]. Until now, the UTS of all the Mg-Bi based alloys processed by extrusion is still less than 390 MPa, which is much lower than that of Al alloys and steel, and thus the strength of Mg-Bi based alloys needs to be improved urgently.

In order to explore the strengthening and toughening potential of low-cost Mg-Bi based extrusion alloys, we designed a new RE-free Mg-6Bi-3Al-1Zn alloy based on the good combination of strength and ductility of as-extruded Mg–6Bi alloy [7]. The addition of Zn and Al is usually known to improve the mechanical properties of Mg-Bi alloys by enhancing the precipitation response and the solution hardening effect [16]. Therefore, in this study, an experimental RE-free Mg-6Bi-3Al-1Zn alloy was fabricated by single pass extrusion, and its microstructure evolution and mechanical properties were analyzed in detail.

2. Materials and Methods

The alloy ingot with a designed composition of Mg-6Bi-3Al-1Zn (denoted as BAZ631) was fabricated by melting high purity Mg, Bi, Al, and Zn in a crucible resistance furnace (Tongda Furnace, Tianjin, China) and gravity casting. The analyzed composition was confirmed as Mg-6.3Bi-3.1Al-1.1 Zn by inductively coupled plasma (ICP), which is consistent with the nominal composition. Based on the homogenization and extrusion parameters of Mg-Bi binary alloys [7,8], BAZ811 alloy, and AZ31 alloy [15] in our previous studies, the as-cast BAZ631 alloy with a dimension of Ø60 mm × 150 mm was homogenized at 450 °C for 5 h, and then directly extruded at 300 °C with an extrusion ratio of 36:1 at a ram speed of 1.1 mm/s using a horizontal extrusion press with a capacity of 300T (HJY-300T, Wuxi, China). Microstructure characterization was conducted by the Olympus BX51M optical microscope (OM, OLYMPUS, Shanghai, China), scanning electron microscopy (SEM, JEOL JSM-7000F, JEOL, Tokyo, Japan) and energy dispersive spectrometer (EDS). The specimens for the OM and SEM microscopy were polished and etched using a solution of 10 mL acetic acid + 4.2 g picric acid + 70 mL ethanol + 10 mL distilled water. The average grain size (AGS) of the as-homogenized and as-extruded BAZ631 samples was determined using the linear intercept method in homogenized OM pictures and as-extruded SEM images, respectively. Moreover, the volume fraction of undissolved micro-scale second phase (Vµ) in homogenized OM pictures was measured using Image-Pro Plus 6.0 software. The Bruker D8 Focus (Karlsruhe, Germany) was used to conduct X-ray diffraction (XRD) analysis in order to figure out the phase in the as-homogenized specimen. The precipitation behavior of as-extruded BAZ631 alloy was revealed by a transmission electron microscope (TEM, JEM 2100F, JEOL, Tokyo, Japan) equipped with energy-dispersive X-ray spectroscopy (EDX). Finally, the gauge dimension of the specimens for tensile tests had a diameter of 6 mm and a length of 25 mm. The tensile tests along the extrusion direction (ED) were carried out using the SUNS-UTM5105X mechanical testing machine (Shenzhen Suns Technology Stock Co., Ltd., Shenzhen, China) at room temperature with a strain rate of 1 × 10^{-3} s^{-1}.

3. Results and Discussion

Figure 1 shows the OM and SEM microstructures of the as-homogenized BAZ631 alloys. The AGS of the as-homogenized BAZ631 sample is 55 ± 5 µm, which is finer than
that of homogenized BAZ811 (AGS, ~70 μm) [16]. Moreover, there are some sphere-like and rod-like second phases ranging in size from 1 μm to 20 μm still maintained in the grain interior or along the grain boundaries, as shown in Figure 1b–d. In order to clarify these intermetallic compounds, EDS analyses were carried out, as presented in Figure 1e,f. The typical EDS spectrum taken from the particles and α-Mg matrix of homogenized BAZ631 indicates that the second phase consists of Mg and Bi and that the α-Mg matrix consists of Mg, Bi, Al, and Zn, respectively. As shown in Figure 2, the peaks arising from α-Mg and MgBi2 phases (hcp, a = 0.4666 nm, c = 0.7401 nm) are clearly identified in the diffraction patterns of homogenized BAZ631 alloy. Therefore, it can be concluded that the major micro-scale phase remaining in the homogenized BAZ631 alloy is MgBi2, demonstrating its relatively good thermal stability at the homogenization temperature of 450 °C. However, there are no peaks from phases containing Al and Zn in the X-ray diffraction spectra of the as-homogenized BAZ631 sample. This is because 3% Al and 1% Zn were all dissolved into the α-Mg matrix when homogenized at 450 °C for 5 h considering their large solid solubility in Mg at a homogenization temperature of 450 °C, which is consistent with our former research [16]. Moreover, the total volume fraction of second phases in homogenized BAZ631 is ~5.3%, a little lower than that of the homogenized BAZ811 sample due to the lower Bi addition in BAZ631.

Figure 1. OM (a,b), SEM (c,d) micrographs, and EDS results (e,f) of as-homogenized BAZ631 alloy.

Figure 2. X-ray diffraction spectra of as-homogenized BAZ631 alloy at 450 °C for 5 h.
Figure 3 indicates OM and SEM images taken of longitudinal sections of the as-extruded BAZ631 alloy. The as-extruded BAZ631 sample exhibits a homogeneous microstructure which is almost fully dynamic recrystallized (DRXed), as presented in Figure 3a,b. Compared with the homogenized sample, the DRXed microstructure of the extruded sample has been greatly refined with an AGS of 2.9 ± 0.4 µm, clearly presented in Figure 3c,d. Moreover, the micron Mg₃Bi₂ strips and broken particles (Figure 3b,c) distributed along the ED, which is original from insoluble Mg₃Bi₂ phase particles in homogenized microstructure (Figure 1). In particular, as shown in Figure 3d, high magnification SEM image of the as-extruded BAZ631 specimen suggests numerous fine intermetallic particles, which were not detected in the as-homogenized sample, demonstrating that dynamic precipitation happened during extrusion.

In order to elucidate the precipitation behavior of BAZ631 alloy during extrusion, TEM characterization was conducted, and the corresponding results are presented in Figure 4. Both micro-scale second phase and ultra-fine precipitates dispersed in the fine DRXed matrix, which well agreed with the OM and SEM observations. The most distinctive feature of the TEM microstructures is that abundant nano-scale globular particles with a size varying from 50–200 nm are distributed both at grain boundaries (GBs) and within grain interiors. Most of the nano-scale particles were further identified as Mg₃Bi₂ by the selected area diffraction pattern (SADP) (Figure 4d). In addition, some fine Mg₁₇Al₁₂ precipitates were also identified according to the results of SADP in Figure 4e, which is quite different with the as-extruded BAZ811 alloy only containing Mg₃Bi₂ precipitates. The distribution of these fine Mg₃Bi₂ particles both at GBs and within grain interiors indicates that dynamic precipitation occurred during high-speed extrusion at 300 °C, which is well agreed with recent research on low-speed extruded Mg-Bi binary alloys [7,8] and high-speed extruded Mg-Bi-Al alloy [18,19]. As a typical precipitation-hardenable Mg alloy system, the solubility of Bi in Mg at the homogenization treatment temperature (450 °C) in this study is
about 5 wt.%, which decreases nearly to 0 wt.% at extrusion temperature (300 °C) [4,7]. The plastic deformation during high-speed extrusion can introduce dislocation tangles, providing nucleation sites for the Mg$_3$Bi$_2$ precipitation in Mg-Bi binary alloys. In particular, there are also ultra-fine DRXed grains with a size of ~300 nm in the as-extruded BAZ631 alloy together with globular particles at its GBs, as presented in Figure 4b,c. In addition, some micro-scale Mg$_3$Bi$_2$ particles were also observed in the BAZ631 alloy (Figure 4a), consistent with the above OM and SEM observations. Furthermore, the AGS of the BAZ631 alloy is only 0.3–3 µm, which is smaller than that of Mg-6Bi (B6) extruded under similar conditions [7], demonstrating that 3 wt.% Al and 1 wt.% Zn addition can further refine the microstructure.

Generally, the size, spacing, and fraction of second particles in the BAZ631 alloy can either promote or hinder DRX in various circumstances during extrusion [20–22]. There are both ultra-fine Mg$_3$Bi$_2$ precipitates and micro-scale Mg$_3$Bi$_2$ particles in the BAZ631 sample. It is believed that the undissolved particles having a size larger than 1 µm can act as nucleation sites for DRX by generating local inhomogeneity in strain energy during hot extrusion, which is well-known as Particle-Stimulated Nucleation (PSN) [23]. Moreover, the smaller initial grain size of the BAZ631 alloy is also likely to increase the DRX fraction compared with the BAZ811 alloy due to the higher density of grain boundary nucleation sites [16]. This may be the two reasons why almost fully DRXed microstructure was obtained in the as-extruded BAZ631 alloy. The ultra-fine Mg$_3$Bi$_2$ precipitates (<1 µm)

![Figure 4. TEM images of as-extruded BAZ631 alloy at low (a) and high (b,c) magnification, selected area diffraction patterns of (d) Mg$_3$Bi$_2$ and (e) Mg$_{17}$Al$_{12}$ precipitates and (f) EDX analysis of matrix.](image-url)
are well known to substantially retard DRX by greatly reducing the mobility of grain boundaries and inhibiting boundary bulging required for the nucleation of new DRXed grains during hot extrusion, which is referred to as the Zener pinning effect [24]. The ultra-fine Mg$_3$Bi$_2$ and Mg$_{17}$Al$_{12}$ precipitates in the BAZ631 alloy will inhibit the growth of DRXed grains through the grain-boundary pinning effect, thereby resulting in considerable grain refinement of the DRXed grains, causing the formation of ultra-fine grains in as-extruded BAZ631 (Figure 4b,c).

The mechanical properties including tensile yield strength (TYS), UTS and EL of extruded BAZ631 alloy are summarized in Table 1 and their typical tensile stress-strain curves were represented in Figure 5, compared with B6 and BAZ811 alloys extruded under the similar conditions. The as-extruded BAZ631 alloy shows a UTS of 402 ± 4 MPa and an acceptable elongation of 15.2 ± 0.4%. The UTS of the BAZ631 sample is much higher than that of B6 [7], and even higher than that of the more Bi concentrated BAZ811 sample [16]. The RE-free BAZ631 alloy by simple one-step extrusion in this study shows much higher UTS than that of Mg-Bi-Ca alloy processed by combining extrusion and caliber rolling [14], which ranks first among all the previously reported Mg-Bi-based alloys until now. It is widely accepted that the microstructure characteristics, such as AGS, second phase particles, and solute atoms in the Mg alloys, significantly affect their mechanical properties. Based on the above microstructure characterization results, the fine and ultra-fine DRXed grains in the BAZ631 alloy can significantly contribute to the high strength according to the Hall–Petch relationship [7,25]. The abundant ultra-fine Mg$_3$Bi$_2$ and Mg$_{17}$Al$_{12}$ precipitates, micro-sized Mg$_3$Bi$_2$ particles, and dissolved solute atoms (about 3 wt.% Al and 1 wt.% Zn) should also contribute to the resultant high strength. Furthermore, extruded BAZ631 alloys also have good ductility with an EL of more than 15% compared with the newly developed ultra-high-strength Mg-2Sn-2Ca alloy [26], the BAZ631 alloy shows much longer elongation and comparable ultra-high strength. The RE-free alloying method, and the simple one-step extrusion, are expected to inspire a new alloy design strategy for fabricating high performance Mg products for larger-scale industrial applications.

Table 1. Microstructural characteristics and tensile properties of extruded BAZ631 alloy, compared with B6 and BAZ811.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Microstructural Characteristics $^1$</th>
<th>Tensile Properties $^2$</th>
<th>Remark</th>
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<tr>
<td>BAZ631</td>
<td>$d_{DRX}$ (μm) Mg$_3$Bi$_2$ + few</td>
<td>TYS (MPa) 282 ± 3.2 UTS (MPa) 402 ± 4.3 EL (%) 15.2 ± 0.4</td>
<td>This study</td>
</tr>
<tr>
<td>B6</td>
<td>~3.9 Mg$<em>{17}$Al$</em>{12}$</td>
<td>TYS (MPa) 189 ± 3.0 UTS (MPa) 228 ± 3.2 EL (%) 19 ± 2.0</td>
<td>Ref. [7]</td>
</tr>
<tr>
<td>BAZ811</td>
<td>~2.3 Mg$_3$Bi$_2$</td>
<td>TYS (MPa) 291 ± 1.2 UTS (MPa) 331 ± 1.4 EL (%) 14.6 ± 0.5</td>
<td>Ref. [16]</td>
</tr>
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</table>

$^1$ $d_{DRX}$ and $V_{f_p}$ denote the average size of DRXed grains and volume fraction of undissolved Mg$_3$Bi$_2$ particles, respectively. $^2$ TYS, UTS, and EL denote the tensile yield strength, ultimate tensile strength, and elongation, respectively.

![Figure 5. Typical tensile stress-strain curves of as-extruded BAZ631 alloy, compared with B6 and BAZ811 [7,16].](image-url)
4. Conclusions

In summary, aiming to develop low-cost Mg alloys with good mechanical properties, an extraordinary high-strength RE-free BAZ631 alloy with a UTS of ~402 MPa and an EL of ~15% was successfully fabricated by one-step extrusion. The RE-free alloying strategy will inspire a new alloy design strategy for fabricating high-performance Mg products. Moreover, the ultra-fine Mg$_3$Bi$_2$ and Mg$_{12}$Al$_{12}$ precipitates were identified dispersed on the DRXed α-Mg matrix with an average grain size of 2.9 ± 0.4 μm. The good tensile property originated from the combined effects of grain boundary strengthening, dispersion, and precipitation and solid-solution strengthening. Furthermore, the effects of Mg$_3$Bi$_2$ and Mg$_{12}$Al$_{12}$ particles on DRX behavior were also revealed, which provide inspiration for microstructure control of extruded Mg-Bi based alloys.

**Author Contributions:** Methodology, S.M., H.X. and Z.L.; data curation, S.M., H.X. and M.Z.; writing—original draft preparation, S.M.; writing—review and editing, S.M., H.X., Z.L., R.J., X.C. and H.Y.; supervision, S.M. and H.Y.; project administration, S.M.; funding acquisition, S.M. All authors have read and agreed to the published version of the manuscript.

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**References**


