Microstructure and Mechanical Properties of TiB-Containing Al–Zn Binary Alloys

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The microstructure and mechanical properties of newly developed Al–35Zn cast alloys with TiB refiner addition were evaluated by X-ray diffractometry, optical microscopy, and scanning electron microscopy coupled with energy dispersive spectrometry. The microstructure of these alloys featured α-Al dendrites surrounded by Al–Zn (α + η) eutectic structures. After the addition of TiB refiner, the alloy grain sizes decreased, and its morphology abruptly changed from dendritic to equiaxed grains. Such an improved microstructure of the modified alloys was accompanied by a significant increase in the tensile strength and elongation percentage compared to those of the Al–Zn or Zn–Al-based alloys. The results showed that with the increase of TiB content up to 0.05%, the morphology of α-Al dendrites and α + η phases changed from coarse dendrite and lamellar structures into independent and fine ones. Based on these results, the effect of TiB refiner addition on the microstructure and mechanical properties of the Al–35Zn binary alloys was investigated.

1. Introduction

Al–Si cast alloys are common casting alloys that exhibit excellent specific strength, good castability, and high corrosion resistance[1–3]. Thus, they are widely utilized in manufacturing lightweight Al alloys. Despite these advantages, Al–Si cast alloys are characterized by poor mechanical properties because of the brittleness of the Si phase. An additional T6 heat treatment of the alloys after casting does not raise their strength to the required level of 320 MPa, while extra post-treatment procedures only increase unit costs[4]. Therefore, the Al–Si alloys cannot be used for producing high-strength structural materials with good toughness. However, castings with excellent mechanical properties obtained by modifications of wrought aluminum alloys have recently attracted significant interest[5,6]. Compared to other cast alloys, the Al wrought alloys characterized by high melting temperatures, low fluidity, and extensive solidification ranges, which easily produce various defects, such as hot tears, and result in shrinkage or the presence of intermixed gases. However, the Al–Zn-based alloys recently developed by Shin et al. not only exhibited very good mechanical properties and fluidity, but was also characterized by a low melting point. Thus, the addition of large amounts of Zn can effectively lower the melting point of

the alloys and improve their fluidity[7]. When a small amount of Cu was added to an Al–Zn alloy, superior mechanical properties were achieved. This result may enable high strength Al–35Zn and Al–Zn–Cu alloys[8], which have been developed as substitutes for cast iron, to be produced for use as bearing caps in the crankcases of internal combustion engines.

According to the Al–Zn phase diagram[9], the solubility of Zn in Al is very high, and a lamellar structure is formed after the α-Al and η-Zn phases are solidified at the grain boundary regions between the α-Al grains. These structures are obtained from a monotectic reaction that is similar to the eutectic reaction ($L_1 = α + L_2$ designates the reaction that generates liquid and solid solution phases from a single liquid phase). This solidification type makes such alloys suitable for producing special bearing and abrasive materials. In addition, the Al–Zn alloys possess excellent castability, high fluidity, and good wear resistance, while their formation requires relatively low energy. Because of these properties, Al–Zn alloys have been utilized for manufacturing various engineering components and certain friction materials[10,11]. For instance, Alemdag and Savaskankan added a maximum amount of 40% Al to Zn, making an alloy that exhibited excellent mechanical properties and high wear resistance[12]. The results indicate that large amounts of Zn mixed with Al produce particularly fine structures because of the monotectic reaction, improving the mechanical properties of the material because of the refinement of the Al phase. In general, the formation of fine grains through heterogeneous nucleation has been

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considered as the two main grain refinement mechanisms[13–15]. A rapid quenching technique is a relatively easy method to obtain the grain refinement, but it is difficult to control the cooling rate. In some previous studies, Zr[16] and Ti[17] were used as main refiners to reduce the Al grain sizes, with Ti being more effective than Zr for this purpose[18,19].

In this work, Al–35Zn alloys containing small amounts of 0.01%–0.1% TiB were prepared. The primary α-Al phase and α + η lamellar structure of the Zn-rich grain boundary regions were simultaneously refined by the addition of TiB, changing the mechanical properties of the alloy. The Al–35Zn alloys exhibited excellent mechanical properties characterized by elongations greater than 13.8% and a tensile strength of 380 MPa without additional heat treatment after casting. Based on these results, the effects of TiB addition on the microstructure and mechanical properties of the Al–35Zn binary alloys were investigated.

2. Experimental

A binary alloy containing Al 65% and Zn 35% was used in this study. It was produced by melting a mixture of 99.8% pure Al with 99.95% pure Zn at 750 °C, while gases were removed from the melt by nitrogen bubbling at 720 °C. Next, the molten metal was stabilized by holding at 700 °C for 10 min and refined by adding different amounts of TiB (Al–5%Ti–1%B) to give a final content ranging from 0.01% to 0.10% at the same temperature. The resulting alloys were poured into pre-heated (at 150 °C) permanent molds with dimensions of W 39 mm × L 33 mm × H 190 mm. We conducted chemical composition analysis of the prepared Al–35Zn alloy as a function of TiB refiner content by using inductively coupled plasma–atomic emission spectroscopy (ICP-AES, SP51550, Seiko), as shown in Table 1.

To observe the changes in the α-Al phase caused by the addition of various TiB amounts, a cross-section of the tensile test specimen was processed by cutting, followed by polishing to a mirror finish, and then etching in Keller's solution (175 mL distilled water + 20 mL NHO$_3$ + 3 mL HCl + 2 mL HF). The microstructures were then studied with an optical microscope (Nikon, ECLIPSE MA200) and a scanning electron microscope (SEM, Carl Zeiss Supra 40). Energy-dispersive spectrometry (EDS) and field emission scanning electron microscopy (FE-SEM) were used to analyze the composition and phases of the alloys. The average α-Al phase size (grain size) was determined by electron backscattering diffraction (EBSD; S-4300, Hitachi) at a scanning step size of 0.7 μm. The EBSD results were processed using orientation imaging microscopy analysis software (TSL-OIM, EDAX); the data points with a confidence index below 0.1 were removed from the EBSD data. To observe the phase distribution and formation of intermetallic compounds, an XRD analysis (CuK$_\alpha$, Rigaku-D/MAX 2500-V/PC) was performed.

Tensile tests were conducted to evaluate the mechanical properties of the alloys. The tensile test specimens were produced in accordance with the ASTM 370-05 test requirements. The tensile tests were performed at room temperature (about 15 °C) using an Instron-5989 tester at a constant cross-head speed of 1 mm/min. Non-contacting advanced video extensometers (AVE) of the tester

were utilized to measure specimen elongations. The hardness of the Al–35Zn alloys as a function of TiB refiner was determined using a Vickers hardness tester (HM-122, Akashi, Japan) with a diamond indenter at a load of 50 gf.

3. Results and Discussion

Fig. 1 shows the XRD patterns of the Al–35Zn alloys containing 0–0.1% of TiB, which consist of the α-Al phase, η-Zn phase, TiB$_2$ and Al$_3$Ti intermetallic compounds. The XRD results reveal that diffraction patterns of the alloys without and with TiB resemble, but different peak intensities are found at 2θ values of about 45°, 65° and 78°. Thus, the TiB refiner addition to the Al–Zn alloy generates heterogeneous nucleation sites. Meanwhile, an Al–Ti–B master alloy is widely used as a grain refiner for Al alloys, and most of the B phase exists in the form of TiB$_2$[20] or (Al$_{1-x}$Ti$_x$)B$_2$[21], and the excess Ti exists as TiB$_2$, but Ti presents as a single form in the molten metal because of its dissociation at elevated temperatures. When the Al–Ti–B master alloy was added to Al molten alloy, the excess Ti created the Al$_3$Ti layers, which environ the TiB$_2$ particles in the alloy, resulting in the refinement of α-Al grain. Because of the excess Ti in the molten alloy, TiB$_2$ and TiAl$_3$ core-shell structures are formed[22–25], which are most likely related to the grain refinement. As indicated by the XRD patterns, the main crystal phase includes the α-Al-rich phase and the η-Zn-rich phase, which co-exist as a single phase, while no diffraction peaks corresponding to the Ti single phase were observed. However, both the TiB$_2$ and Al$_3$Ti were detected by XRD technique. According to these results, the TiB$_2$ and Al$_3$Ti phases heterogeneously nucleated in the Al–Zn binary alloy and refined the primary α-Al phase.

The XRD analysis reveals that the consequence of adding TiB refiner to the Al–35Zn binary alloy was the formation of TiB$_2$ and Al$_3$Ti phase. XRD, optical microscopy, EBSD, SEM, and EDS techniques investigated the morphology and distribution of each phase as functions of TiB content. The optical micrographs depicted in Fig. 2(a)–(d) and the EBSD micrographs in Fig. 2(e)–(h) display the size and distribution of grains for the gravity cast Al–35Zn alloys containing 0–0.1% of the TiB refiners. Fig. 2(a) shows the typically big scale dendrite morphology of the α-Al grain in the Al–35Zn alloy. In contrast, the grain boundary region is composed of the non-equilibrium solidification phases or Zn-rich phase, which is
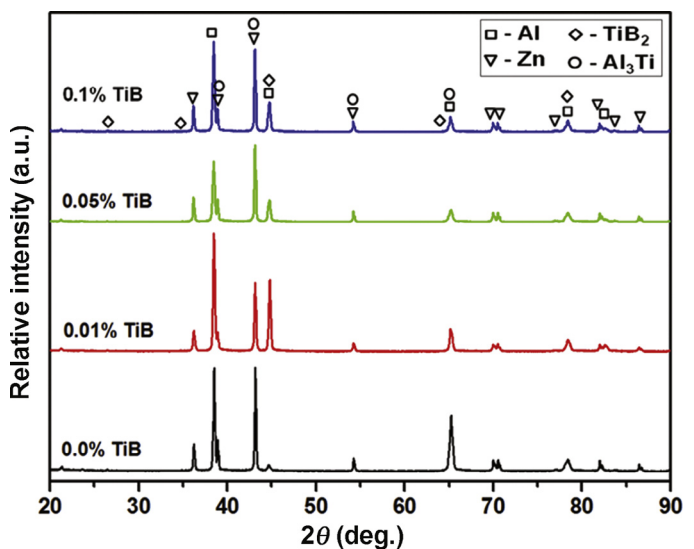
Table 1
Chemical composition (wt%) of the Al–35Zn alloys with 0–0.1% TiB refiner contents as determined by ICP-AES

TiB content (%)	Zn	Ti	Al
0.0	35.107	0.000	Balance
0.01	35.179	0.012	Balance
0.05	35.245	0.054	Balance
0.1	35.263	0.107	Balance

Fig. 1. XRD patterns of the Al–35Zn binary alloys with 0–0.1% TiB refiner content.