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The formation of AlB_2 in an Al–B master alloy

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Abstract

The formation of borides in an Al–3 wt.%B master alloy, produced via chemical reactions of KBF_4 and aluminium has been investigated. The chemical reactions produce boron, which dissolves into molten aluminium and subsequently forms aluminium borides. Backscattered electron imaging (BEI) of the Al–3 wt.%B master alloy under a scanning electron microscope (SEM) revealed the presence of two types of phases that contain different levels of boron. Combined with X-ray diffraction (XRD) results, the two types of phases are identified as AlB_2 on AlB_{12}. This gives a direct evidence for a peritectic reaction of AlB_{12} and aluminium, which produces AlB_2. The thermodynamic properties of the reactions that may be involved are examined, and the presence of AlB_{12} phase in the master alloy explained. The observed microstructure is explained according to the peritectic reaction in an Al–B phase diagram. The stability of AlB_2 and AlB_{12} at lower temperature than 975 °C is clarified.

Keywords: AlB_2; AlB_{12}; Al–B master alloy; Al–B system

1. Introduction

Al–B master alloys are widely used in the production of electrical conductive grade aluminium to remove transition metal impurities, such as titanium, vanadium, chromium and zirconium [1,2]. These elements are brought into aluminium as impurities with bauxite or from scraps. The contents of these elements are merely higher than several tens ppm. However, as solutes, the transition elements reduce the electrical conductivity of aluminium dramatically [3]. To overcome this problem, boron is used to precipitate these impurities by forming borides because the borides of transition metals in aluminium do not contribute to a major reduction in the electrical conductivity. Furthermore, the borides can be removed from aluminium melt by gravity settling. Due to the high stabilities of the transition metal borides compared to aluminium borides, Al–B master alloys are selected to precipitate the transition metal impurities [2]. Details on how to use the master alloys and their performance were described elsewhere [2]. Al–B master alloys are also used in the in situ fabrication of aluminium matrix composites. One example is the in situ fabrication of AlB_2 fibre reinforced aluminium metal matrix composites using an Al–B master alloy [4]. By using an Al–5 wt.%B master alloy, an Al–AlB_2 composite reinforced with AlB_2 fibres was produced, which shows increased mechanical properties.

Commercial Al–B alloys are produced via chemical reactions of KBF_4 with molten aluminium. Boron is reduced from the fluoride salt by aluminium and disperses into the aluminium melt in the forms of aluminium borides, AlB_2 and AlB_{12}. AlB_{12} is a high temperature phase, whereas AlB_2 is stable at room temperature when the boron content is less than 44.5 wt.%, according to the Al–B phase diagram, shown in Fig. 1 [5–7]. According to the phase diagram, a peritectic reaction, $L + AlB_{12} \rightarrow AlB_2$, takes place at 975 °C. There is a discrepancy about the peritectic temperature, which has been given in different numbers by different investigators ranging from 956 °C to 1350 °C [5–8]. During cooling AlB_{12} reacts with liquid aluminium to form AlB_2. However, AlB_{12} is always detected in Al–B master alloys that have been produced via molten salt reactions at temperatures lower than

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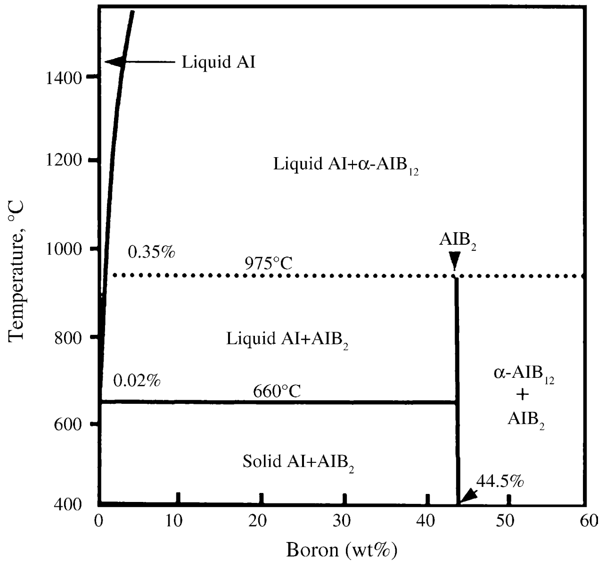

Fig. 1. Al-rich side of Al–B phase diagram [5–8].

the peritectic reaction temperature. The presence of AlB_{12} was also reported in Al–Ti–B master alloys that have been produced via arc melting of aluminium and boron at 800 °C [9]. The presence of AlB_{12} at temperatures lower than 975 °C causes confusion regarding the stabilities of the boride phases in aluminium.

AlB_2 has a hexagonal close packed (HCP) crystal structure with lattice parameters: $a = 0.3006$ nm and $c = 0.3252$ nm, whereas AlB_{12} has a tetragonal crystal structure with $a = 1.0161$ nm and $b = 1.4238$ nm. Boron and aluminium occupy alternative layers in the HCP AlB_2 crystals [10]. The melting points of AlB_2 and AlB_{12} were reported as 1655 ± 50 °C and 2163 ± 50 °C, respectively [11]. Other Al–B compounds, such as β-AlB_{12} and AlB_{10}, were also reported. These compounds were later proved to be metastable or ternary compounds that are stabilized by small amount of impurities [12].

An understanding of the stability of borides in the Al–B system is also important for the in situ fabrication of Al–TiB_2 composites, which involves chemical reactions of aluminium with KBF_4 and K_2TiF_6 [13,14]. However, the phase relationship at the Al-rich corner for the Al–Ti–B system is still not clear. To tailor the microstructure of the Al–TiB_2 composites, a thorough understanding of the Al–B system becomes imminent.

The present paper reports the results of SEM analysis of an Al–3 wt.%B master alloy. By using BEI techniques in SEM, AlB_2 and AlB_{12} phases were distinguished in the master alloy. The microstructure is explained on the basis of the thermodynamic phase equilibria for the peritiectic and molten salt reactions leading to the formation of borides. The analysis therefore aims to provide a new insight in the region of B-rich side of the Al–B phase equilibria, which will complement the phase relationships in the Al–Ti–B system, essential for grain refinement of aluminium.

2. Experimental procedures

The Al–3 wt.%B master alloy was produced via chemical reactions of KBF_4 and aluminium at 850 °C. KBF_4 powder was incorporated into molten aluminium at a manually controlled feeding speed, and mixed with aluminium by mechanical stirring. $KAlF_4$ was produced as a by-product and removed from the surface of the melt. After a certain period of holding time for 5 min at 850 °C, the melt was cast into a steel mould.

The cast ingot was sectioned into small pieces for microstructural analysis by SEM and phase analysis by XRD. The samples were ground by using SiC papers up to a 1000 mesh grade, followed by polishing to a 1 μm finish using diamond pastes. A Camscan Series 4 SEM was used for the analysis. The SEM was operated in a BEI mode at a 20 kV accelerating voltage. XRD analysis was performed on a Philips APD 1700 Automatic Diffraction System.

3. Results and discussions

A typical BEI image of the Al–3 wt.%B master alloy is shown in Fig. 2. Under a BEI mode borides appear as dark particles in a bright aluminium matrix because boron has a lower atomic number than aluminium, therefore less backscattered electrons being generated by boron-rich particles than those by aluminium matrix. A majority of the boride particles show a plate-like morphology. The boride particles form clusters within the aluminium matrix. It is evident from the sizes and shapes of the clusters that a majority of the boride particles are dispersed inside aluminium grains, despite no aluminium grains can be distinguished from the image.

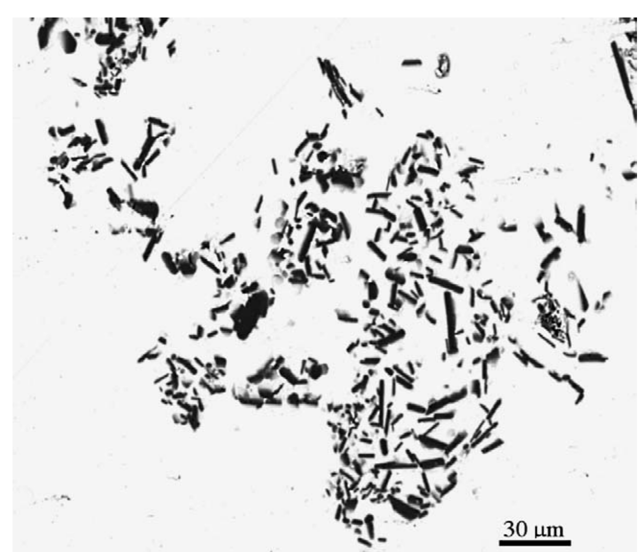

Fig. 2. SEM BEI image of Al–3 wt.%B master alloy showing clusters of boron-rich particles in an aluminium matrix.