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# Improvement of mechanical properties of Al-Si alloy with effective grain refinement by in-situ integrated Al2.2Ti1B-Mg refiner

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## ABSTRACT

In order to improve the effectiveness and stability AlTiB grain refiners for cast Al-Si alloys, the present study investigated the grain refinement of cast Al-Si alloys using an in-situ integrated Al2.2Ti1B-Mg master alloy, which was synthesized through two-step chemical reaction to create $TiB_2$ particles and magnesium aluminate ($MgAl_2O_4$) phase in the master alloy. Experimental results showed that the fine equiaxed grains were obtained for A356 alloy treated with Al2.2Ti1B-Mg master alloy. In comparison with the α-Al grain size at a level of 950 ± 135 μm and 620 ± 95 μm for A356 alloy without refinement and refined by conventional Al5Ti1B master alloy, the fine grain size of about 320 ± 50 μm could be obtained for A356 alloy refined by Al2.2Ti1B-Mg master alloy. The yield strength, ultimate tensile strength and elongation of the A356 alloy refined by Al2.2Ti1B-Mg was 257±5 MPa, 313±5 MPa and 7.8 ± 0.5% respectively, which was increased by 6% (14 MPa), 3% (8 MPa), and 13% (1.0%) in comparison with that obtained by Al5Ti1B. The improvement of mechanical properties of A356 alloy after treated by Al2.2Ti1B-Mg was attributed to the effective nucleation of α-Al phases. The formation of $MgAl_2O_4$ layer on the $TiB_2$ surface was expected to reduce the misfits between $TiB_2$ and Al and promote the nucleation of α-Al, and therefore improve the effectiveness of grain refinement.

## 1. Introduction

Grain refinement by adding master alloy containing inoculant particles had been a common manufacturing practice over decades for most commercial aluminium alloys because the refined microstructure would reduce casting defects, increase castability and thus improve the mechanical properties of as-cast components [1,2]. The most popular grain refiners were based on Al-Ti-B master alloys [3–5], which can be generally divided into two groups: $TiB_2$ with excessive Ti and $TiB_2$ with excessive B.

The representative system of $TiB_2$ with excessive Ti was Al5Ti1B [6], which usually containing 3.2 wt.% $TiB_2$, 7.5 wt.% $Al_3Ti$ and balanced Al. Al5Ti1B had been the dominant grain refiner for aluminium alloys since its first application in 1960's [4,7,8]. It had been identified that the addition of Al5Ti1B master alloy at a level of 0.2 wt.% of total weight of melt can achieve the best refinement, and extra addition was not necessary and cannot improve the refinement any more [9,10]. However, $TiB_2$ particles are still not recognized as the most effective nuclei for α-Al due to the large misfit between $TiB_2$ and Al [11]. It was generally agreed that the $Al_3Ti$ in Al5Ti1B master alloy would instantly melt in aluminium melt and exist in the form of free Ti to supply constitutional undercooling during grain growth [12], and a mono-layer of $Al_3Ti$ was formed on the $TiB_2$ surface to decrease the $TiB_2$/Al misfit and to activate $TiB_2$ particles as effective nuclei for α-Al phases [13–16]. However, Al5Ti1B master alloy was not very effective in the aluminium alloys containing specific elements. For example, the excessive Si could deteriorate the grain refinement of Al5Ti1B in cast Al-Si alloys [15,17]. The grain size increased with increasing the Si content at a level of higher than 3 wt.%. Therefore, the application of Al5Ti1B could not obtain significant grain refinement in cast Al-Si alloys, although it was still popular in industry as a common grain refiner. Other master alloys in this group included Al5Ti0.2B [18], Al3Ti1B [19,20] and Al3Ti0.2B [21], which were all designed by controlling the amount of excessive Ti in the master alloys.

On the other hand, the alternative master alloys containing $TiB_2$ with extra B included Al1Ti3B, Al1Ti5B, Al3Ti3B [22,23], and Al2.5Ti2.5B [24]. It was reported that the excessive B in AlTiB grain refiner was able to offer better grain refinement than Al5Ti1B for

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cast Al-Si alloys. This was indicated that AlTiB refiner with B-rich was more effective than Al5Ti1B as grain refiners for cast Al-Si alloys. The refinement mechanism had been identified that the excessive boron was segregated at the $TiB_2$/Al interface and would form a boron-rich layer to undergo an eutectic reaction and subsequently nucleate α-Al phase at a temperature above the liquidus of aluminum alloys [10]. However, one of the major problems associated with these grain refiners was their stability due to the unavoidable transformation of $AlB_2$ to $TiB_2$ during refinement process [25,26].

In fact, AlTiB master alloys contain $TiB_2$ only (weight ratio Ti:B = 2.2:1) without excessive Ti and/or B could not be used as grain refiner. The main reason was that the misfit between $TiB_2$ and Al was too large to nucleate α-Al on the surface of $TiB_2$ particles. In order to improve the refinement effectiveness and stability of AlTiB based refiners for cast Al-Si alloys, several attempts had been carried out in recent years. One progress was that $MgAl_2O_4$ (spinel) phase had a small misfit with Al, which could possibly nucleate Al under appropriate conditions [27,28]. Although the spinel was expected to be able to increase the stability of grain refinement, the generation of spinel was not easily controlled. More importantly, it was not easy to distribute spinel throughout the melt as the oxidation was always formed near the melt surface and there was lack of carriers to disperse spinel in the melt. It was anticipated that these problems can be overcome if foreign carriers were introduced to enhance the distribution of spinel phases and promote the grain refinement. $TiB_2$ particles were the first option for these purposes.

Therefore, the present research aimed to investigate the combined effect of Al2.2Ti1B and $MgAl_2O_4$ on the grain refinement of an A356 Al-Si alloy, in which the $TiB_2$ particles were used as the carriers for $MgAl_2O_4$ and the spinel was used to minimize the misfit between $TiB_2$ and Al. The effectiveness of Al2.2Ti1B with $MgAl_2O_4$ grain refiner was comparably evaluated in association with Al5Ti1B, Al3Ti3B refiner. The discussion was focused on the possible mechanisms of grain refinement.

## 2. Synthesis and analysis of Al2.2Ti1B-Mg master alloy

The new grain refiner of Al2.2Ti1B-Mg was synthesized by a two-step chemical reaction: the synthesis of $TiB_2$ particles and the creation of magnesium aluminate phase. The synthesis of $TiB_2$ particles was achieved by salt reactions among molten Al, $K_2TiF_6$ and $KBF_4$ at the stoichiometry ratio of Ti and B at 850 °C for 30 min, in which the amount of $TiB_2$ particles was controlled at a level of 3.2 wt.% in aluminium melt [29,30]. The creation of magnesium aluminate phases was obtained by adding pure Mg into the melt made in the previous step to react with oxygen and aluminium by holding the mixture at 700±5 °C for 4 h to form $MgAl_2O_4$ (spinel) phase in the aluminium melt [27]. The flux and by products in the first step reaction were removed from the crucible before adding pure magnesium into the melt for the second step reaction. Once finishing the synthesis, the melt was subjected for a degassing and slag removal process. The ingots of master alloy were subsequently made at a size at 130 mm long with a square cross section of 15 × 15 mm. The master alloy was analyzed by ICP-AES and the composition was 2.2 wt%Ti, 1 wt.%B, 0.4 wt.%Mg, and balanced by Al and unavoidable impurity elements at trace levels. The amount of $TiB_2$ particles in the master alloy was thus to be 3.2 wt.% according to the mole calculation. This master alloy was defined as Al2.2Ti1B-S hereafter.

In order to confirm the phase formation of new grain refiner, X-ray Diffraction (XRD) analysis was carried out for Al2.2Ti1B-S master alloy. The results were shown in Fig. 1, in which only $TiB_2$ and Al were clearly shown in the XRD pattern, but the $MgAl_2O_4$ phase was not detected in the Al2.2Ti1B-S master alloy possibly because the limited content was below the tolerance of diffractor instrument. In order to further confirm the formation of spinel phase, the master alloy was examined by scanning electron microscopy (SEM). The morphology, size and distribution of $TiB_2$ particles were shown in Fig. 2. It was confirmed that the size of $TiB_2$ particles was in a range of 500 nm to 1.6 μm and the average value was 1 μm. The previous results [29] had confirmed that this type of distribution of $TiB_2$ particles was able of ensuring the particles as the potency substrates of α-Al nucleation [3]. However, the results in Fig. 2 confirmed that no $Al_3Ti$ was detected in the Al2.2Ti1B-S master alloy. The analysis of the $TiB_2$ particle composition was shown in insert table in Fig. 2. It was confirmed the existence of Mg and O in association with $TiB_2$ particles in the Al2.2Ti1B-S master alloy, whereas no Mg was added into commercial Al5Ti1B and Al3Ti3B master alloy according to the compositions of refiners shown in Table 1. Although $MgAl_2O_4$ phases were not observed obviously in Al2.2Ti1B-S master alloy, the previous study had

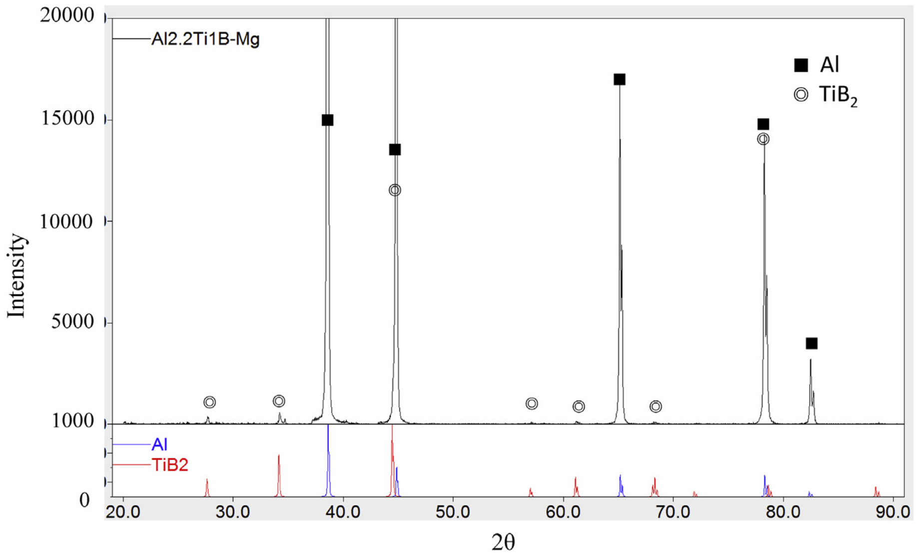

**Fig. 1.** XRD pattern of the Al2.2Ti1B-S master alloy.