

# Refinement effect of two rare earth borides in an Al-7Si-4Cu alloy: A comparative study

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## ABSTRACT

In this paper, refinement performance of Al-La-B and Al-Ce-B refiners in Al-7Si-4Cu alloy and their effects on alloy defects and tensile properties were investigated. Due to the orientation relationships between rare earth borides and Al,  $\text{CeB}_6$  and  $\text{LaB}_6$  can act as the nucleation substrate of  $\alpha$ -Al and refine Al-Si-Cu casting alloy effectively. Al-Ce-B refiner showed better refining efficacy than Al-La-B refiner because of the lower lattice mismatch and less angle difference of the certain orientation relationship between  $\text{CeB}_6$  and Al, demonstrated by TEM analysis. Tensile properties of Al-7Si-4Cu alloy were prominently improved from  $204.4 \pm 5.9$  MPa to  $250.6 \pm 6.7$  MPa in as-cast state and  $335.7 \pm 6.5$  MPa to  $386.0 \pm 7.0$  MPa in heat treatment state owing to the better refined microstructures and much fewer shrinkage defects. However, when the addition level of the refiners was higher than 1.0 wt%, the amount of gas pores in the alloy significantly increased. Hence, the best refiner addition level in this alloy is considered to be 1.0 wt%.

## 1. Introduction

Refining grain structures with inoculation was usually expected to enhance the mechanical properties of casting alloy [1–4]. Except enhancement in strength and toughness, grain refinement can improve the inner quality of aluminum alloys as well [5,6]. For example, Al-Si-Cu alloy, a kind of Al-Si casting alloys, possesses good mechanical properties and heat-resistant ability [2,7,8]. However, because of dendrite impingement resulting from coarse grain structures, shrinkage porosity forms for insufficient feeding of liquid during casting solidification [9,10], which generates adverse effects on the tensile properties. Refined grain structures enabled improvement of feeding ability during solidification and then eliminated shrinkage defects [9].

The ternary Al-Ti-B refiners, e.g. Al-5Ti-1B refiner, have been extensively utilized to refine grain size in the wrought aluminum alloys [11–13]. However, it shows unfavorable refining efficiency in Al-Si casting alloys due to the interaction of Ti with Si, forming titanium silicides, which depletes the effective quantity of Ti elements in the melt of alloys [14–16]. Previous study demonstrated that some rare earth borides, such as  $\text{CeB}_6$  and  $\text{LaB}_6$ , show observable refinement efficiency in Al-Si casting alloys for low lattice mismatch with Al and high chemical stability [17–19]. However, how  $\text{CeB}_6$  or  $\text{LaB}_6$  refine Al-Si-Cu casting alloy effectively is still unclear. It also deserves investigation on the effect of the addition of  $\text{CeB}_6$  or  $\text{LaB}_6$  on the

shrinkage defects in Al-Si-Cu alloy.

The refinement efficacy of refiner is closely related to the nucleation capacity of refinement particle. A large number of studies compared the nucleation potency between  $\text{Al}_3\text{Ti}$ ,  $\text{TiB}_2$  and  $\text{AlB}_2$  in Al-Ti-B refiners [20–22], from a theoretical or experimental point of view. Nevertheless, there was few research on the comparison of nucleation potency between  $\text{CeB}_6$  and  $\text{LaB}_6$  in Al-Si-Cu alloy. It is worth unveiling the refinement mechanism of  $\text{CeB}_6$  and  $\text{LaB}_6$  to which understanding the higher nucleating potency.

In present work, two kinds of refiners, Al-2Ce-1B and Al-2La-1B were prepared. The grain refining efficacy of Al-2Ce-B and Al-2La-B was investigated in Al-7Si-4Cu alloy, respectively. The nucleation potency of  $\text{CeB}_6$  and  $\text{LaB}_6$  was compared through TEM analysis and lattice mismatch calculation. The influence of the refiners on alloy defects and mechanical properties of tensile samples was also studied.

## 2. Experimental procedure

### 2.1. Synthesis of alloys

The master alloy and Al-7Si-4Cu alloy used in present work were both prepared with a graphite crucible in a 5Kw resistance furnace. Commercial pure aluminum (99.7 wt% Al), Al-10La and Al-3B master alloys were used to prepare the Al-2La-B refiner. Firstly, the pure

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**Table 1**  
Chemical composition (wt%) of Al-7Si-4Cu alloy in the present work.

Samples	Si	Cu	Fe	La	Ce	B	Al
S0	7.13	3.85	0.0865	0.0005	0.0013	0.0006	Balance
S1	7.06	3.88	0.0765	0.0005	0.0120	0.0041	Balance
S2	7.01	3.91	0.0821	0.0008	0.0230	0.0087	Balance
S3	7.22	3.99	0.0663	0.0005	0.0301	0.0180	Balance
S4	6.86	3.81	0.0733	0.0006	0.0386	0.0205	Balance
S5	6.97	3.79	0.0739	0.0105	0.0012	0.0052	Balance
S6	7.09	3.87	0.0773	0.0218	0.0011	0.0095	Balance
S7	7.31	3.96	0.0768	0.0315	0.0013	0.0162	Balance
S8	7.23	3.95	0.0875	0.0416	0.0010	0.0238	Balance

aluminum was melted at  $760 \pm 5^\circ\text{C}$ , and then the Al-10La and Al-3B master alloys were separately added into the melts at the temperature of  $800 \pm 5^\circ\text{C}$ . After holding the melts at  $900 \pm 20^\circ\text{C}$  for 30 min, the melts were poured into a permanent waffle mold to obtain the Al-2La-1B refiner ingots. The fabricating method of Al-2Ce-1B master alloy is similar to Al-2La-1B master alloy, introduced in prior study [23].

The Al-7Si-4Cu alloy is melted with commercial pure aluminum, Al-50 wt% Cu and A413.0 alloy. When studying the microstructure evolution and tensile properties transformation of Al-7Si-4Cu alloy, grain refiners were added into the melt when the temperature was increased to  $720 \pm 5^\circ\text{C}$  and the holding time was 15 min. The melts ( $720 \pm 5^\circ\text{C}$ ) were poured into ASTM: B-108 type permanent mold preheated to  $250 \pm 5^\circ\text{C}$  to produce tensile test bars.

The samples were heat treated in a muffle furnace. Firstly, all tension bars were kept at  $510^\circ\text{C}$  for 8 h, then were taken out and quenched instantly in  $60^\circ\text{C}$  water. Secondly, all quenched samples were ageing treated at  $170^\circ\text{C}$  for 6 h and then cooled in the air.

## 2.2. Characterizations

### 2.2.1. Observation of microstructure

The grain refining performance of grain refiners was evaluated with the cylindrical graphite mold ( $\phi 25\text{ mm} \times 100\text{ mm}$ , the thickness of the mold is 5 mm) surrounded by fire clay brick. The cooling rate of melt was approximately 0.4 K/s–0.7 K/s. The as-cast samples were sectioned 25 mm from the bottom surface. The samples were anodized in Barker's solution and then examined with an optical microscope under polarized

light. The grain sizes were measured with the linear intercept method. The grain sizes were measured with the linear intercept method (ten pictures for each specimen, three lines for each picture).

The chemical compositions of the samples were analyzed with Optical Emission Spectroscopy (OES) (Table 1). The original alloy (Al-7Si-4Cu without inoculation) was labeled S0, after adding 0.5 wt%, 1.0 wt%, 1.5 wt% and 2.0 wt% Al-2Ce-B, 0.5 wt%, 1.0 wt%, 1.5 wt%, 2.0 wt% Al-2La-B, the experimental alloys were labeled from S1 to S8, respectively. For more obvious contrast, when analyzing the nucleation potency and fractographs, only S2, S4, S6 and S8 alloys were compared. The phase composition was characterized by means of X-ray diffraction (D8-Discover, Bruker, Germany). The morphology of the particles in the prepared sample was observed by scanning electron microscope (SEM, Sirion, FEI) equipped with Energy Dispersive X-Ray Spectrometer (EDX). Transmission Electron Microscopy (TEM) analysis was utilized to investigate the crystalline orientation relationship between  $\text{LaB}_6$  and  $\alpha\text{-Al}$ , which was performed on a JEM-2100F instrument. The samples for TEM analysis were fabricated by Focused Ion Beam (FIB, Helios nanolab 600, FEI) machine.

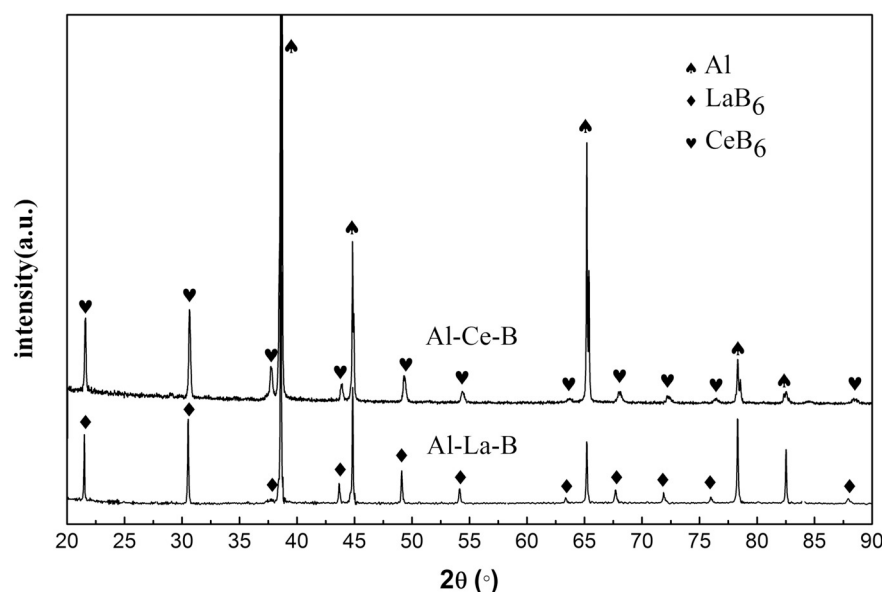
### 2.2.2. Testing of mechanical properties

The tensile properties test of each alloy under as-cast and heat treatment condition was conducted on a mechanical testing machine (CMT5105, SANS). Tension testing and preparation of test bar were based on ASTM: B557-2010 standard. Each composition was test at least 5 tensile bars at both as-cast and heat treated condition. The microhardness was measured on an automatic microhardness measurement system (FM-700, FUTURE-TECH) with the load of 0.3 Kgf.

## 3. Result and discussion

### 3.1. Refiner characterization

Fig. 1 shows the XRD pattern of as-synthesized Al-2La-1B and Al-2Ce-1B refiner. Except a group of diffraction peaks referring to the Al matrix (JSPDF No. 65-2869), only  $\text{LaB}_6$  phase (JSPDF No. 65-1831), with adding Al-2La-1B, and  $\text{CeB}_6$  phase (JSPDF No. 79-2163), with adding Al-2Ce-1B, can be detected. This result suggests that a sufficient reaction between La, Ce and B elements to produce  $\text{LaB}_6$  and  $\text{CeB}_6$  phase under current experimental condition.



**Fig. 1.** The XRD spectrum of Al-2Ce-1B and Al-2La-1B refiners.

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