Development of new oxide based master alloys and their grain refinement potency in aluminium alloys

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Abstract

In this study, grain refinement efficiency of a new oxide master alloy based on $MgAl_2O_4$ was demonstrated in Al alloys. The grain size of the reference alloy was reduced by 50-60% with the addition of the master alloy and introduction of ultrasonic cavitation. While cooling rate has an influence on the grain size reduction, more addition of master alloy was found to be not effective in further reducing the grain size.

Introduction

Grain refinement has been an important technique for improving the quality of aluminium products for many decades. Addition of grain refiners in the form of master alloys containing potent nucleants suppresses the formation of columnar grains and promotes equiaxed structure [1-3]. Finer grain size reduces the casting defects and eventually improves the mechanical properties of the material. For foundry alloys, grain refiners increase the casting properties as well. The grain refinement technique has become a well-established practice in aluminium based wrought and foundry alloys [4]. In industrial practice, Al–Ti–B master alloys are the most commonly used grain refiners in cast and wrought Al alloys.

There have been numerous studies conducted till date on the development of new grain refiners and their grain refinement characteristics in aluminium [1-4]. Also mechanism of grain refinement by Al-Ti-B grain refiners has been explained by various analytical models and theories and verified experimentally [1-7]. It has been realized that peritectic reactions can play siginificant role in refining the grains of Al, e.g. solidification reactions of Ti, V, Nb, Zr with Al [5]. In line with several theories suggested earlier, investigators have obtained experimental evidence that the pro-peritectic $TiAl_3$ phase is formed on TiB_2 or AlB_2 prior to the nucleation of α-Al, indicating that a $TiAl_3$ phase may be responsible for the enhanced grain refinement in Al-Ti-B system [5, 6]. The most successful grain refiners to date are Ti-based compounds (TiB_2, $TiAl_3$ and TiC) [8, 9] in Al alloys and Zr in Al/Mn/Si-free Mg alloys [5]. Titanium boride-containing master alloys are much less efficient in Al-Si alloys due to the formation of titanium silicide [1, 2]. Therefore, the search for an efficient grain refiner for Al-Si foundry alloys is an ongoing research topic. In regard to the efficiency of grain refiner, free growth model theoretically demonstrated that undercooling for free growth is inversely proportional to the inoculant particle diameter, and the size distribution of the particles plays an important role in determining the efficiency of a given grain refiner [10].

Oxides are naturally occurring phases on Al surface. These oxides are found to be thermodynamically and crystallographically stable with Al in different conditions. Possibility of utilizing these naturally formed oxide particles as nucleating substrates for grain refining Al alloys, especially under condition of external physical field applied, has been reported [11-14]. Atamanenko et al. showed the grain refining effect of Al_2O_3 film in pure Al by ultrasonic cavitation-induced heterogeneous nucleation through the activation of oxides [12]. Further, Li et al.

demonstrated grain refinement of Al-Mg alloys via dispersing naturally occurring oxides such as $MgAl_2O_4$ (200-500 nm) in Al alloys using an intensive melt shearing technique [13].

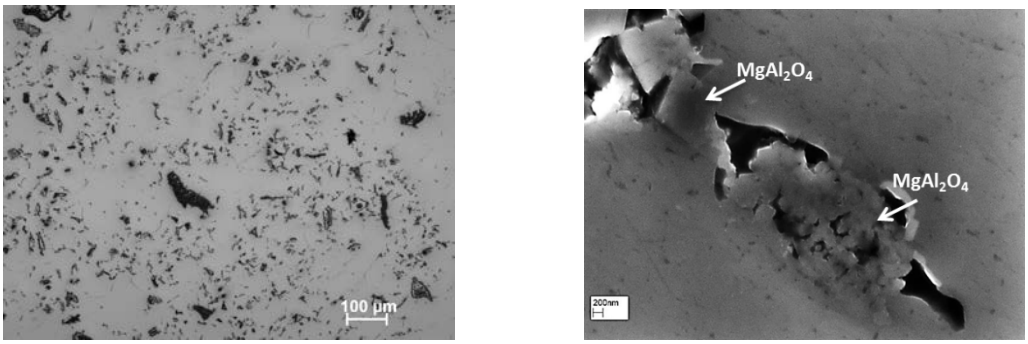
This paper outlines the synthesis of Al-MgAl2O4 master alloy and its grain refinement potency in binary Al alloys and commercially important alloy A357. Detailed microstructure characterization demonstrates the extent of grain refinement in the alloy with different additions of the master alloy and introduction of ultrasonic cavitation.

Experimental method

Commercially pure Al (0.08 wt% Si-0.1 wt% Fe-remaining Al) and commercially pure Mg (99.97 wt%) were taken as initial metals. SiO_2 was chosen as a solid oxygen source for $MgAl_2O_4$ formation. The particle size of the oxide supplied by Sigma-Aldrich was varied from 0.5 to 10 µm (more than 80% between 1 and 5 µm). 2 wt% of SiO_2 particles was stirred in the molten Al-2 wt%Mg alloy at temperatures between 650 and 700 °C using a mechanical impeller made up of a Ti alloy coated with a high temperature ceramic glue to minimize Ti pickup in Al during processing. The stirred metal was heated up and held at 900 °C for 30 min to facilitate the reaction between SiO_2 particles and Al. Later, the molten metal was ultrasonicated (17.5 kHz, 3.5 kW, 40 micron amplitude, Nb sonotrode) while mixing with the impeller for 5 min at 680-710 °C to ensure the dispersion of $MgAl_2O_4$ particles and complete the reaction of SiO_2 particles. The holding and mixing processes were repeated several times and cast. Grain refinement study was conducted on CPAl, two binary Al alloys: Al-0.8 wt% Mg and Al-4 wt% Cu and a commercial alloy: A357 (Al-7% Si-0.3% Mg-0.1% Ti). In all the alloys, master alloy was added at 730 °C and cast at 750 °C in a steel mould (cooling rate ~2 °C/sec) and copper mould (~20 °C/sec) preheated at 250 °C before casting. Some of the samples were treated with ultrasonication for 3 min at 730-750 °C before casting. The cast sample was ground using SiC paper (400-2500 grid size) and polished using OPS. For identification of grain size, polished samples were anodized using 0.5% HBF_4 solution for approximately 1 min at 20 VDC and analysed in polarized light by pptical microscopy (Zeiss Axioscope). Microstructure of the master alloy was examined in an optical microscope (Zeiss Axioscope) and scanning electron microscope (SEM) (Zeiss Supra 35VP) and phase identification was done using X-Ray Diffraction (Bruker D8 Advance).

Results

Al-$MgAl_2O_4$ Master alloy: The microstructures of the master alloy are given in Figure 1. The $MgAl_2O_4$ particles are found to be dispersed well in the matrix (Fig. 1 (a)). SEM analysis identified $MgAl_2O_4$ crystals within the matrix (Fig. 1 (b)). The $MgAl_2O_4$ particles were found to be varied in size from 200 nm to 2 µm at different places. The XRD analysis further confirmed the predominant presence of $MgAl_2O_4$ phase in the master alloy (Fig. 2).



(a) (b)

Figure 1. (a) Optical microstructure of Al-$MgAl_2O_4$ master alloy (b) $MgAl_2O_4$ crystals embedded in Al alloy.

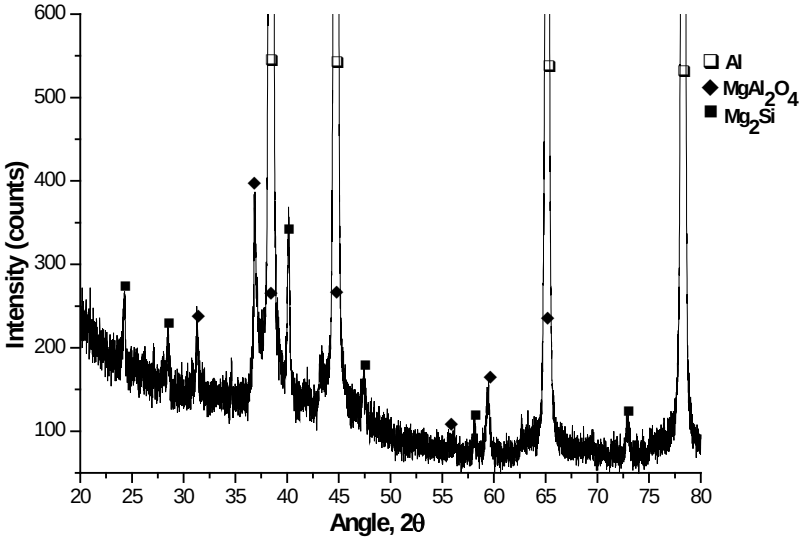


Figure 2. X-ray diffraction of Al-$MgAl_2O_4$ master alloy.

Grain refinement in Al alloys: Following figures (Fig. 3) show the etched samples of CPAl added with master alloy and treated with mechanical stirring (b, e) and ultrasonication (c, f) before casting. Except (f), others do not show grain refinement. This demonstrates the fact that simultaneous presence of ultrasonication and $MgAl_2O_4$ particles refines Al. Also reveals that only addition (with hand stirring) or addition with mechanical stirring is not capable of dispersing the nucleants particles. It is to be noted that columnar grains are still present in the grain refined sample. From the understanding of the above observation, ultrasonication was carried out after the master alloy addition for other experiments.

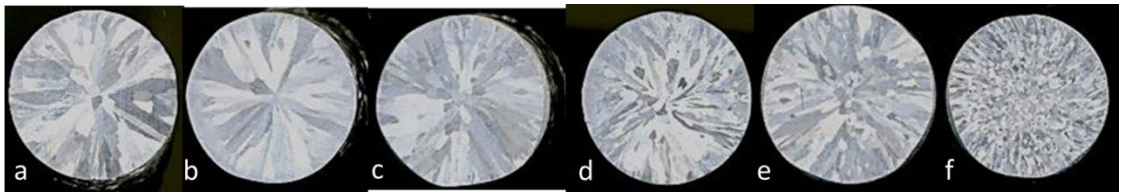
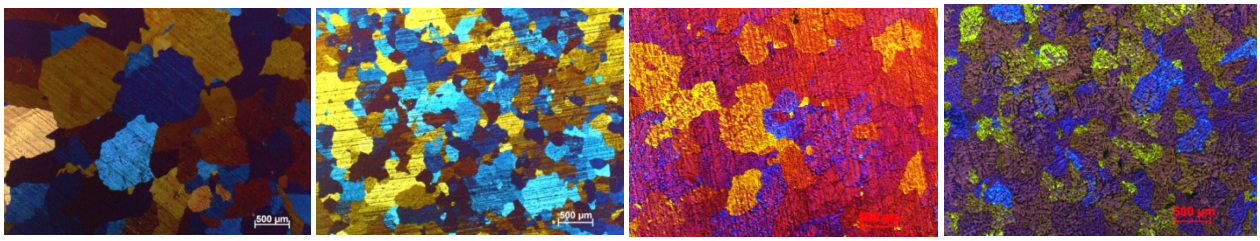


Figure 3. Macro etched CPAl samples cast at 750^0C (a) no addition and no treatment (b) no addition and mechanical stirring (c) no addition and ultrasonication (d) addition of 4 wt% MA (e) addition of 4 wt% MA and mechanical stirring (f) addition of 4 wt% MA and ultrasonication.

The following microstructures (Fig. 4) show the grain size of alloys added with master alloy in comparison with reference alloy. The alloys were cast in steel mould (~2 °C/sec). There is a clear difference of grain size change with the addition of master alloy. The grain size of non-grain refined alloys (Al-0.8% Mg and Al-4% Cu) was calculated to be 800-900 µm (Fig. 4 (a and b)), whereas grain refined alloys have grains 300-400 µm in size (Fig. 4 (c and d)). Master alloy was added at different levels in A357 alloy (Fig 5). The initial grain size was noticed to be ~900 µm. The grain size was reduced appreciably with the addition of master alloys. However, there was no more grain size reduction observed after 1.7 wt%. The grain size reduction was further confirmed from the microstructures given in Figure 5.



(a) (b) (c) (d)

Figure 4. Microstructures of (a) Al-0.8% Mg (900±25 µm) (b) Al-0.8% Mg with 4 wt% MA (300±10 µm) (c) Al-4% Cu (800±21 µm) (d) Al-4% Cu with 4 wt% MA (400±13 µm) (all are at the same magnification).

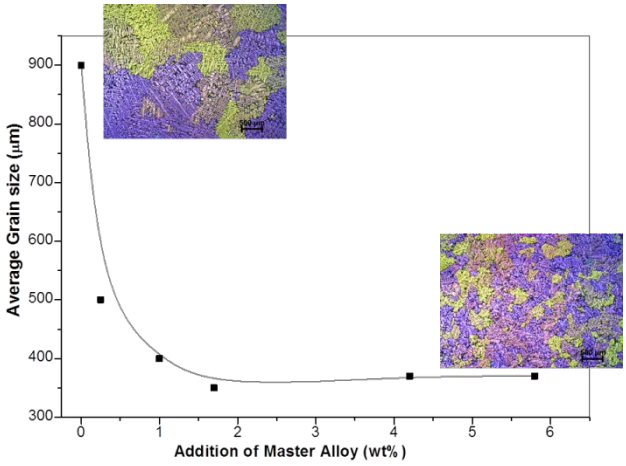
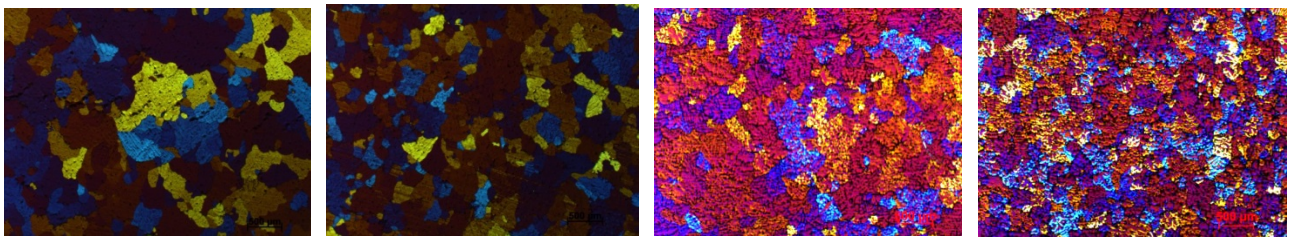


Figure 5. The average grain size vs addition of the master alloy in an A357 alloy (microstructures are at the same magnification).

Following microstructures (Fig. 6) detail the grain size of Al-0.8% Mg and Al-4% Cu alloys cast in a copper mould (~20 °C/sec). Grain size of reference and grain refined alloys were reduced significantly. The grain size was reduced for reference alloys from 900 µm (Fig. 4 (a)) to 400 µm (Fig. 6 (a)) and from 800 µm (Fig. 5 (c)) to 400 µm (Fig. 6 (c)) by increasing in cooling rate. However, the reduction was not significant in the case of MA added alloys from 300 µm (Fig. 5 (b)) to 230 µm (Fig. 6 (b)) and from 400 µm (Fig. 5 (d)) to 200 µm (Fig. 6 (d)).



(a) (b) (c) (d)

Figure 6. Microstructures of (a) Al-0.8% Mg (400±15 µm) (b) Al-0.8% Mg with 4 wt% MA (230±10 µm) (c) Al-4% Cu (400±17 µm) (d) Al-4% Cu with 4 wt% MA (200±11 µm) (all are at the same magnification).

Discussion

The interfacial free energy at the nucleating interface is one of the controlling factors in heterogeneous nucleation. The importance of low interfacial energy for a potent substrate was demonstrated long ago by the classical nucleation theory. However, the issues related to wetting of exogenous inoculants with molten Al often fail to reduce the interfacial energy to a lower level. Once particles are wetted by reactions (i.e., reactive wetting) as typically found in in-situ composites, nucleation potency can be related to the lattice matching at the solid-substrate interface during heterogeneous nucleation. Better the lattice matching, higher the nucleation potency. Few studies reported a cube on cube parallel orientation relation (OR) [15], or a mismatch of 2.5° along the [110] direction on the (111) plane between Al and $MgAl_2O_4$ [16]. Also, the lattice misfit between $MgAl_2O_4$ and Al (1.4%) was found to be smaller than that of the Al/TiB_2 system (–4.2%) [13]. All these satisfy the conditions for $MgAl_2O_4$ as a potent substrate. Nucleation efficiency refers to the effectiveness of a given type of inoculant with specific physical characteristics and solidification conditions, such as number density, size distribution and cooling rate. The TiB_2 particle population in Al-5 wt% Ti-1 wt% B master alloy was estimated to be 10^8 particles/cc [17]. Similarly for the $MgAl_2O_4$ between 200 nm and 2 μm in size, number density was approximated to be between 10^8 and 10^{10} particles/cc. The undercooling required for large particles of TiB_2 in Al-5 wt% Ti-1 wt% B master alloy was calculated to be quite small (i.e., 1 K for 500 nm and 0.2 K for 3 μm) [17], which may be true for $MgAl_2O_4$ crystals as well.

In the present study, ultrasonication was used above the liquidus in the completely liquid metal. The influence of ultrasonication on the grain refinement was extensively studied by several researchers [11, 12, 18]. However, much of the studies carried out during solidification of the alloys. A recent study in Al-2% Cu alloy made clear that ultrasonication in the liquid state has negligible effect on grain refinement [18]. Hence, cavitation and associated acoustic streaming are seemed to be solely contributing to the distribution of the particles within the metal ensuring more particles for the nucleation event. Additionally, hand stirring or mechanical stirring often fails to distribute fine particles in liquid metal. Effect of grain size with respect to change in cooling rate is related to undercooling and heterogeneous nucleation on the particles. At low cooling rate, the less undercooling results a few nucleation sites in alloys, whereas heterogeneous nucleation dominates in grain refiner added alloys, resulting in a signidicant difference in the grain size between the alloys with and without grain refiner addition. Larger undercooling at higher cooling rate results in more nuclei and appreciable reduction in the grain size in the alloys without grain refiner. In grain refiner added alloys more particles are activated for heterogeneous nucleation, however reduction in the grain size is not proportionately high.

Summary

(1) New Al-$MgAl_2O_4$ master alloy was successfully synthesized using SiO_2 aided by ultrasonication.
(2) New master alloy based on $MgAl_2O_4$ is capable of grain refining all the Al alloys studied.
(3) Introduction of ultrasonic cavitation along with master alloy addition improves the grain refinement of the alloy by 50-60%.
(4) Addition levels of master alloy higher than 1.7 wt% do not show additional effect in grain size reduction in A357 alloy.
(5) Cooling rate has additional effect on the grain size reduction in the alloys studied.

Acknowledgement

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