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Mechanisms of enhanced heterogeneous nucleation during solidification in binary Al–Mg alloys

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Abstract

The mechanisms involved in the grain refinement of Al–Mg alloys through varying the Mg content and applying intensive melt shearing were investigated. It was found that the oxide formed in Al–Mg alloys under normal melting conditions is $MgAl_2O_4$, which displays an equiaxed and faceted morphology with {1 1 1} planes exposed as its natural surfaces. Depending on the Mg content, $MgAl_2O_4$ particles exist either as oxide films in dilute Al–Mg alloys (Mg < 1 wt.%) or as naturally dispersed discrete particles in more concentrated Al–Mg alloys (Mg > 1 wt.%). Such $MgAl_2O_4$ particles can act as potent sites for nucleation of α-Al grains, which is evidenced by the well-defined cube-on-cube orientation relationship between $MgAl_2O_4$ and α-Al. Enhanced heterogeneous nucleation in Al–Mg alloys can be attributed to the high potency of $MgAl_2O_4$ particles with a lattice misfit of 1.4% and the increased number density of $MgAl_2O_4$ particles due to either natural dispersion by the increased Mg content or forced dispersion through intensive melt shearing. It was also found that intensive melt shearing leads to significant grain refinement of dilute Al–Mg alloys by effective dispersion of the $MgAl_2O_4$ particles entrapped in oxide films, but it has marginal effect on the grain refinement of concentrated Al–Mg alloys, where $MgAl_2O_4$ particles have been naturally dispersed into individual particles by the increased Mg content.

Keywords: Aluminium alloys; Grain refinement; Heterogeneous nucleation; Solidification microstructure; Oxide particles

1. Introduction

In direct chill (DC) casting of Al alloys, a grain-refined as-cast microstructure is generally desirable. Grain refinement has an influence on the mechanical properties of solidified materials, the kinetics of homogenisation treatment, the formability and defect formation during downstream thermo-mechanical processing, and anodizing quality [1–3]. During casting, grain refinement directly affects the formation of porosity, the tendency of hot tearing, the pattern of macro-segregation and the scale of micro-segregation. In industrial practice, Al–Ti–B master alloys are commonly used as grain refiners during DC casting of wrought Al alloys. However, only less than 1% of the added TiB_2 particles are active for nucleation of α-Al grains [2]. This low efficiency is undesirable not only due to its immediate cost implications, but also because refiner particles may themselves be detrimental in the final microstructures, particularly for products intended for extrusion, rolling, deep drawing, or high performance structural applications [2].

So far there is no consensus on the detailed mechanisms of grain refinement [4,5]. Greer and co-workers developed the free growth model to describe the physical mechanism behind the low efficiency of commercial grain refiners based on the Al–Ti–B system [6,7]. This model suggests that the undercooling for free growth is inversely proportional to the particle diameter. This means that larger particles will nucleate first and this will be followed by progressively smaller ones until the occurrence of recalescence, which prevents further nucleation by the smaller particles. This model clearly demonstrated theoretically that the size distribution of inoculant particles plays an important role

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in determining the efficiency of a given grain refiner [6,7]. On the other hand, the theoretical basis of the growth restriction theory is that restriction of the growth of already nucleated grains permits further nucleation in the undercooled melt ahead of the solidification front, until the total latent heat release is sufficient to cause recalescence [8]. The growth restriction factor Q is often used as a measure of the solute effect on grain refinement in the absence of solute interactions [8–14]. Empirically, it was found that grain size can be described as a linear function of $1/Q$ [9]. More recently, an analytical model was developed by Men and Fan [15] to account for the effect of solute elements on grain size and it was shown that, for a given alloy system solidified under similar conditions, a 1/3 power law can describe the solute effect on grain refinement more accurately than a linear relationship: $D = KQ^{-1/3}$, where D is the grain size and K is a constant which is independent of alloy composition but strongly dependent on the alloy system, solidification conditions and physical nature of the nucleating particles, such as number density, size and size distribution [15].

In practice, oxides are inevitably present in liquid Al alloys. Several studies have been performed to investigate the possibility of using oxide particles as nucleating substrates for grain refining Al alloys. Nucleation of the α-Al grains on externally added oxide particles in Al–Si–Fe alloys was investigated by Khalifa et al. [16]. Their results showed that in dilute Al alloys containing less than 1.5 wt.% (Si + Fe) (all compositions given hereafter in wt.%), nucleation of the α-Al phase could be promoted by the addition of oxide particles, although the grain size evolution associated with the oxide addition was not reported. Cao and Campbell [17] investigated the formation of Fe-bearing intermetallics on oxides in Al–Si cast alloys. Their results indicated that the wetted side of an oxide film can act as nucleation sites for the Fe-bearing intermetallics. More recently, Atamanenko et al. [18] investigated the grain refining effect of exogenous oxides combined with ultrasonic treatment in pure Al (99.95% Al), and attributed the grain refinement to cavitation-induced heterogeneous nucleation through the activation of oxides. In addition, it has been demonstrated that, via the introduction of intensive melt shearing using the MCAST process, naturally occurring oxides in liquid Mg and Al alloys can be harnessed to enhance heterogeneous nucleation for microstructural refinement in Mg and Al alloys [19–21]. The enhanced heterogeneous nucleation was explained through the significantly increased number density of individual oxide particles by the strong dispersive power of intensive melt shearing [20].

This study aims to investigate experimentally the mechanisms of enhanced heterogeneous nucleation in binary Al–Mg alloys. Intensive melt shearing was used as an effective tool to modify the particle distribution in the alloy melt. The grain structures of a wide range of Al–Mg alloys either with or without intensive melt shearing were quantified. The oxides formed naturally in the Al–Mg alloy melts were concentrated by a pressure filtration technique. The morphological variation of oxides and crystallographic match between oxides and the α-Al phase were characterised to understand the enhanced heterogeneous nucleation of α-Al on the oxides. The discussion will be focused on the formation of oxide in Al–Mg alloys, and the potency and efficiency of oxide particles as effective sites for heterogeneous nucleation.

2. Experimental

To investigate the effect of Mg content on grain refinement of Al–Mg alloys, a set of Al–Mg alloys with varying Mg contents (0%, 0.2%, 0.7%, 1.0%, 3.0%, 5.0% and 7% Mg) were melted and cast into TP-1 samples, either with or without melt shearing. The TP-1 test [22] was operated in conditions to provide a consistent cooling rate of 3.5 K s^{-1} at the central region of a cross-section, 38 mm from the base of the TP-1 sample. The starting materials used were commercial purity Al (>99.86% Al) and commercial purity Mg (>99.95% Mg). The compositions of the commercial purity Al are listed in Table 1. Titanium is usually considered as the most effective solute element for growth restriction. To examine the effect of titanium addition on the grain refinement of high Mg containing Al–Mg alloys, various Ti content from 0.05, 0.1, and 0.15 wt.% was added to Al–5 Mg alloys. An Al–10 Ti master alloy was used. In all cases, the temperature of the electric resistance furnace was set at 750 °C for melt preparation. After the alloys were completely melted, the temperature of the melting furnace was changed to 700 °C for the use of isothermal holding. The pouring temperature for either the TP-1 mould or the MCAST unit [23,24] was always at 700 °C. For the sheared samples, the alloy melts were sheared in the MCAST unit for 60 s, which was set at 700 °C and the screw rotation speed at 500 rpm. In view of the fact that magnesium has high affinity with oxygen and the low value of PBR for MgO with a value of 0.73, there should be less protective oxide scale formed on the surface of liquid Al–Mg melts. In the present study, to ensure that the oxidation products were naturally occurring oxides such as $MgAl_2O_4$ or MgO or Al_2O_3, rather than other oxides introduced by element additions, no other oxidation inhibitor elements, such as beryllium (Be), were added; during the handling of the melting process, special care was taken to avoid the occurrence of burning of magnesium or excessive oxidation on the surface of liquid aluminium when the magnesium was added. After aluminium was melted, weighed pure magnesium was submerged into the liquid aluminium under the protection of Ar gas. After the magnesium was dissolved, Ar protection gas was stopped. The isothermal holding time has a significant influence on the formation of oxides on the surface of liquid Al–Mg alloys. For a given alloy with specified Mg content, more oxides can be produced on the surface of alloy melt with an increase in isothermal holding time. In all the cases investigated, alloy melts were isothermally held