Available online at www.sciencedirect.com
SciVerse ScienceDirect
Acta Materialia 61 (2013) 360–370
Acta MATERIALIA
www.elsevier.com/locate/actamat

Revisiting the role of peritectics in grain refinement of Al alloys

Feng Wang [a], Zhilin Liu [a], Dong Qiu [a], John A. Taylor [a,b], Mark A. Easton [b,c], Ming-Xing Zhang [a,*]

[a] *School of Mechanical and Mining Engineering, The University of Queensland, St. Lucia, QLD 4072, Australia*
[b] *CAST Cooperative Research Centre, Australia*
[c] *School of Materials Science and Engineering, Monash University, Clayton, VIC 3800, Australia*

Received 5 September 2012; received in revised form 29 September 2012; accepted 29 September 2012

Abstract

The grain refining effect of four peritectic-forming solutes (Ti, V, Zr and Nb) as well as three eutectic-forming solutes (Cu, Mg and Si) on pure Al was investigated. Significant grain refinement is observed by the addition of peritectic-forming solutes, whereas the addition of eutectic-forming solutes only slightly decreases the grain size. The mechanisms underlying the grain refinement of these alloys were then studied by a new analytical methodology for assessing grain refinement that incorporates the effects of both alloy chemistry and nucleant potency. It is found that the low degree of grain refinement by the addition of eutectic-forming solutes is mainly attributed to the segregating power of solutes, i.e. the constitutional undercooling contribution. However, peritectic-forming solutes do not only cause grain refinement by their segregation power but, more importantly, they introduce copious potent nuclei into the melt and promote significant grain refinement via heterogeneous nucleation.

Keywords: Al alloys; Grain refinement mechanism; Peritectics; Growth restriction factor; Nucleant particles

---

1. Introduction

Grain refinement of Al and its alloys has been an important process in commercial production for over half a century because fine grains not only deliver enhanced casting soundness and mechanical properties of cast metals, but also facilitate the subsequent mechanical working and forming processing [1,2]. In spite of over a half-century of scientific study, the details of the mechanisms of grain refinement are still a matter of some controversy. Many theories have been proposed to explain the phenomena observed in both practice and experiment [3–14]. However, none of them can fully account all the observations. Currently, it is generally accepted that both the potency of the nucleant particles and the segregating power of the solute are critical to effective grain refinement [12–16]. These two factors are essentially based on two fundamental contributions, i.e. heterogeneous nucleation and solute segregation.

Heterogeneous nucleation primarily focuses on the role of potent nucleant particles in promoting nucleation of grains. It suggests that an increase in either nucleant potency or number density of the nucleant particles considerably increases the nucleation rate, leading to effective grain refinement [3–11]. In contrast, the contribution of solute is related to the role of solute segregation in front of the liquid–solid interface in restricting growth of grains and developing constitutional undercooling providing a driving-force to activate further nucleation on the substrates present [12–16]. Although most observations of grain refinement have been successfully explained from these two aspects, there is still some confusion and issues that remain unsolved. One of the major problems is that a number of newly developed grain refiners based on these two approaches do not work as effectively as expected,

---

* Corresponding author.
E-mail address: mingixng.zhang@uq.edu.au (M.-X. Zhang).

1359-6454/$36.00 © 2012 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.actamat.2012.09.075

particularly for Mg–Al-based alloys [17–19] and Ti alloys [20,21]. Hence something further may be required for effective grain refinement to be achieved.

It has long been realized that peritectics often effectively refine the grains of a metal [22], e.g. Ti and Zr with Al [23], Zr with Mg [24], etc. Furthermore, the most successful grain refiners to date are Ti-based compounds (TiB_2, $TiAl_3$ and TiC) in Al alloys and Zr in Al/Mn/Si-free Mg alloys. Although many investigators [5,6,23] have studied the effect of peritectics on the grain refinement of Al and attributed the consequent grain refinement to the peritectic reaction, it has been difficult to understand why peritectic elements can refine the grains of alloys at concentrations below which the peritectic reaction occurs [25,26]. Even at hyperperitectic concentrations, it has been suggested that the formation of the peritectic phase is the result of direct crystallization from the melt on the properitectic phase rather than a peritectic reaction [27,28] under normal solidification conditions. However, using different experiment techniques, many investigators [10,11,29–31] have recently obtained evidence that the properitectic $TiAl_3$ phase is formed on TiB_2 prior to the nucleation of α-Al, indicating that a $TiAl_3$ phase may be responsible for the enhanced grain refinement in this system.

For convenience, the process of direct crystallization from a melt onto a properitectic phase is termed peritectic nucleation. In fact, how the peritectic phase forms, through peritectic nucleation or peritectic reaction, would not significantly affect the grain refining efficiency. The only difference between these two processes is that the peritectic reaction involves consumption of the properitectic phase at slow cooling rate close to equilibrium, and in the peritectic nucleation process, the growth of the peritectic phase only occurs in the melt once it nucleates on the properitectic phase under faster cooling conditions. Both are heterogeneous nucleation processes. However, the question still remaining is: which factor, the heterogeneous nucleation or solute segregation contribution, governs the grain refinement efficiency? Therefore, it is intriguing to reinvestigate the underlying grain refinement mechanisms operating in peritectic alloys, and the outcome may shed new light on the factors affecting grain refinement.

One of the most important considerations is how to separate the effects of nucleant particles and solute. Most recently, a new analytical model of grain refinement (i.e. the Q-model) has been developed by Easton and StJohn [32–34]. It has been found that the grain size, d, can be expressed as [14,32,35,36]:

$$d = \frac{1}{\sqrt[3]{f \cdot \rho_V}} + \frac{D \cdot \Delta T_n}{v \cdot Q}, \tag{1}$$

where ρ_V is the volumetric number density of nucleant particles; f is the fraction of these particles that are activated; D is the diffusion coefficient; v is the growth velocity; ΔT_n is the undercooling required to active nucleation, and Q is the growth restriction factor, defined by $Q = m(k-1) \cdot c_0$, in which m is the slope of the liquidus; k is the partition coefficient; and c_0 is the concentration of the solute. One of the major advantages of this model lies in the simple representation of the relationship between grain size and the reciprocal of growth restriction factor, Q, a measurable and reliable parameter based on factors that can be obtained from the phase diagram. To investigate and compare the grain refinement efficacy of alloys and master alloys [37], Eq. (1) is usually simplified by:

$$d = a + \frac{b}{Q}, \tag{2}$$

where the slope, b, is related to the potency of the nucleant particles, and the intercept, a, corresponds to the maximum number of activated nuclei [24,32,37]. As the potency of the nucleant particles increases, the slope, b, of the line decreases; while as more nuclei are introduced, the term, a, decreases. It has been shown that this new analytical model gives a reasonable description of the grain refinement phenomena observed across a range of Al alloys [32–34] and is also applicable to studies of grain refinement of Mg alloys [24,37,38] and Ti alloys [20,39–41] over a wide range of solidification rates [34] and conditions [42].

As a result, this paper first focuses on studying the effect of a range of elements, including four peritectic-forming solutes (Ti, V, Zr, Nb) and three eutectic-forming solutes (Cu, Mg, Si), on the grain size of Al. Using the new grain refinement assessment approach (i.e. the Q-model), the grain refinement due to the addition of these solutes is then evaluated.

2. Experimental

High-purity commercial Al ingots (99.96% Al, 0.016% Si, 0.017% Fe, 0.0001% B and 0.0001% C; all the compositions hereinafter are in wt.% unless otherwise specified) were used as the base material in the present work. Commercial-purity Ti, V and Nb powders and Zr particles were selected as peritectic-forming alloying elements. To compare the effect of peritectic-forming elements on grain refinement with the eutectic-forming solutes in Al alloys, Cu, Si and Mg powders were also chosen as another test group of alloying elements. All the peritectic and eutectic solute additions were added in the form of compacted pellets, which were made by mixing the metal powders with freshly cut Al chips followed by compaction of the mixture in a die. Details of the solute addition levels and their corresponding growth restriction factors are listed in Table 1. The levels of additions were determined by the value of the growth restriction factor, Q. To compare the influence of Q, the actual addition levels of both peritectic-forming and eutectic-forming solutes were deliberately selected so that the same values of Q are achieved. In the present work, four different Q levels, $Q = 1$, 2, 5 and 12, were used.

It should be noted that the Q values of various solutes in Al were calculated using the $m(k-1)$ values listed in the paper of Easton and StJohn [12]. Furthermore, the Q val-