Available online at www.sciencedirect.com

ScienceDirect

Acta Materialia 59 (2011) 6133–6144

Acta MATERIALIA

www.elsevier.com/locate/actamat

Thermodynamic aspects of grain growth restriction in multicomponent alloy solidification

R. Schmid-Fetzer *, A. Kozlov

Institute of Metallurgy, Clausthal University of Technology, Robert-Koch-Strasse 42, D-38678 Clausthal-Zellerfeld, Germany

Received 14 March 2011; received in revised form 17 June 2011; accepted 17 June 2011
Available online 19 July 2011

Abstract

The growth restriction factor Q is the key quantity in current descriptions of the solutal effect on grain growth and grain refinement during solidification of alloys. A rigorous treatment for the evaluation of Q in multicomponent alloys based on consistent thermodynamic descriptions of the alloy phase equilibria is presented. On closer inspection the conventional approach to calculate Q in multicomponent alloys from liquidus gradient m_i and partition coefficient k_i must fail for a wide range of common alloys exhibiting minute amounts of primary crystallizing intermetallic phase, exemplified for Mg–Al–Mn and Al–Si–Ti alloys. The rigorous approach provides an extension of the applicability range of the concept of Q. The qualitative similarity of inoculant particles and primary intermetallic phases is verified by calculations for Al–Si–Ti–B alloys.

Keywords: Growth restriction; Multicomponent alloys; Thermodynamics; Casting; Grain refinement

1. Introduction

The concept of the growth restriction factor Q [1,2] has proved of value in analyzing grain refinement during solidification of alloys and, thus, in controlling an important quality aspect of both cast and wrought alloys. The combination $m \cdot (k-1) \cdot c_0$, detailed below, was first included in the classical criterion for constitutional undercooling by Tiller et al. [3], and Maxwell and Hellawell [4] were the first to treat it as an independent alloy parameter relevant to the grain refinement of binary Al alloys. It emerged from the simple model of Maxwell and Hellawell [4] for the growth of a spherical crystal restricted by the partitioning of a single solute in a binary alloy. The final grain size results from competition between nucleation and growth, and the key parameter describing the development of constitutional supercooling is the growth restriction factor Q (denoted $1/X$ in Maxwell and Hellawell [4])

$$Q = m \cdot (k-1) \cdot c_0 \quad (1)$$

where m is the liquidus slope, k is the equilibrium partition coefficient, and c_0 is the solute content in the alloy. For consistency all three quantities must be evaluated on the same basis of mass%, although this does not show explicitly in the unit of Q (K). Significantly different values of Q may be obtained if the evaluation is done on the basis of at.%, which will not be used in this work. The unit of mass% is abbreviated to wt.% in the following.

The simple model had been significantly advanced in order to evaluate the relative or actual as-cast average grain size, including aspects such as the potency, size and shape of the nucleants [1,2,5–9]. It was also shown that of the four contributions to the total solidification undercooling (kinetic, curvature, thermal, and solutal) the solutal or constitutional supercooling (ΔT_{cs}) is the controlling term under typical aluminum alloy casting conditions [10]. The most recent analytical model for constitutional supercooling driven grain formation and grain size prediction was given by Qian et al. [11]. It overcomes the main limitation of a semi-empirical equation [7], namely the

---

* Corresponding author. Tel.: +49 5323 72 2150; fax: +49 5323 72 3120.
E-mail address: schmid-fetzer@tu-clausthal.de (R. Schmid-Fetzer).

1359-6454/$36.00 © 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2011.06.026

assumption of a constant liquid composition during grain growth and development of the solid fraction, as in the Scheil–Gulliver equation. Even with these improvements the same previously known semi-empirical linear relationship of average grain size d and $1/Q$ is derived for both spherical and planar growth [11]. A comprehensive and detailed literature review on the development of that subject has also been given [11]. Agreement has been established [10,11] that the solutal effect is of the utmost importance for grain growth restriction in alloy solidification and that Q, expressing the phase diagram properties of the alloy, possesses the best correlation with grain size. This has been demonstrated for magnesium [12] and aluminum [13] alloys, with numerous additional examples given in the references cited above [1,2,5–7]. The growth restriction factor Q is also a key quantity in the modeling of grain refinement using a cellular automaton finite control volume method [14].

The extension to multicomponent systems was first given by Desnain et al. [15]. They suggested an additive contribution of the binary values of the individual solutes (i) to a total value $Q_{\Sigma\text{bin}}$,

$$Q_{\Sigma\text{bin}} = \Sigma Q_{\text{bin,i}} = \Sigma m_{\text{bin,i}}(k_{\text{bin,i}} - 1) \cdot c_{0,\text{i}} \tag{2}$$

The summation is taken over all the solutes (i) in the alloy. Any multicomponent interaction between the solutes is disregarded. This is a crude approximation for higher compositions or strong interactions, as demonstrated by proper calculations based on the multicomponent phase diagram [5,10], which, in practice, require the use of thermodynamic software and a reliable thermodynamic database of the alloy system. The total value of Q in the multicomponent system Q_{multi} is calculated from

$$Q_{\text{multi}} = \Sigma m_{\text{i}} \cdot (k_{\text{i}} - 1) \cdot c_{0,\text{i}} \tag{3}$$

The actual slope of the liquidus surface T_{L} is evaluated at the multicomponent composition point vector $\vec{c}_0$ from partial derivatives with respect to each solute (i), at the expense of the solvent composition, keeping the other solutes (j) constant:

$$m_{\text{i}} = \left(\frac{\partial T_{\text{L}}}{\partial c_{0,\text{i}}}\right)_{(\text{j}\neq\text{i})\text{const}} \tag{4}$$

The equilibrium partition coefficient at the multicomponent liquidus point $(T_{\text{L}}, \vec{c}_0)$ is calculated for each solute (i) from the tie line joining the solid ($c^*_{\text{S,i}}$) and the liquid ($c^*_{\text{L,i}}$) composition at the interface:

$$k_{\text{i}} = c^*_{\text{S,i}}/c^*_{\text{L,i}} \tag{5}$$

Since the composition gradient in the liquid phase near the interface is generally not known, or assumed to be small, this evaluation was made by setting $c^*_{\text{L,i}} \approx c_{0,\text{i}}$ in Eqs. (4) and (5) [5,10].

Quested et al. [10] gave a detailed thermodynamic analysis of these aspects of composition dependence. The basic quantity $m \cdot (k-1)$ is found to vary strongly with composition even in binary aluminum alloys. From dilute solutions ($c_0 \approx 0$) to the maximum at the primary α liquidus ($c_0 \approx c_{0,\text{max}}$) the relative deviation from linearity in the resulting Q ranges from −46% for Mn to +22% for Si. They also investigated the error in additivity between Q_{multi} (Q_{real} in their notation) and $Q_{\Sigma\text{bin}}$ for a number of actual ternary aluminum alloys. Even for moderate solute contents of $c_{0,\text{i}} = 0.5$ wt.% for each of the two solutes the relative error in additivity ranges from −2.5% (AlFe0.5Si0.5) to +4.5% (AlFe0.5Mg0.5) [10]. Throughout this work alloy compositions will be denoted in this abbreviation, e.g. AlFe0.5Mg0.5 for 99%Al-0.5%Fe-0.5%Mg, wt.%. Easton and StJohn noted that Eq. (2) grossly overestimates the actual growth restriction factor for an $\text{AlSi}_7\text{Mg}_{0.3}\text{Ti}_{0.2}$ alloy, where Q_{multi} (Eq. (3)) was calculated to be smaller by a factor of 0.58 compared with $Q_{\Sigma\text{bin}}$ (Eq. (2)) [5].

Quested et al. [10] also provided a detailed and enlightening analysis of underlying thermodynamic parameters and the shape of the ternary phase diagram in the (Liquid + α) region for some hypothetical Al–X1–X2 systems in relation to the impact on Q. They briefly noted that the best way of calculating Q from thermodynamic models is given by the initial slope in the development of constitutional supercooling ΔT_{cs}, with fraction of solid f_{S}, however, in the remaining body of their paper and for the definition of the additivity error they used Eq. (3) above. The idea of using the initial rate of development of constitutional supercooling was also been briefly mentioned in Easton and StJohn [5]. This quantity will be denoted Q_{true} in the present work:

$$Q_{\text{true}} = \left(\frac{\partial(\Delta T_{\text{cs}})}{\partial f_{\text{S}}}\right)_{f_{\text{S}}\to 0} \tag{6}$$

For simplicity for this partial derivative the alloy composition $\vec{c}_0$ is taken to be constant. It is generally assumed that the thermal gradient in the narrow liquid diffusion layer ahead of the interface is negligible compared with solutal undercooling. It follows that in a binary alloy the maximum value of the constitutional supercooling ΔT_{cs}, always taken as the positive temperature difference to the liquidus point at c_0, is directly given by the corresponding liquid interface composition in the phase diagram c^*_{L} as

$$\Delta T_{\text{cs}} = m \cdot (c_0 - c^*_{\text{L}}) \tag{7}$$

This linearization with the liquidus slope is reasonable for not too large undercooling or composition differences. The liquid interface composition may be eliminated in Eq. (7) and expressed by the developing fraction of solid using either the lever rule (equilibrium) or Scheil–Gulliver solidification equations. In the limit $f_{\text{S}} \to 0$ these two models become identical and, therefore, the following relation with Q is obtained [5]:

$$\left(\frac{\partial(\Delta T_{\text{cs}})}{\partial f_{\text{S}}}\right)_{f_{\text{S}}\to 0} = m \cdot (k-1) \cdot c_0 = Q \tag{8}$$

It is the purpose of this work to demonstrate that the definition of the growth restriction factor should be solely based on Eq. (6). Evaluation of Q_{true} using intermediate