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Effects of solute content on grain refinement in an isothermal melt

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Abstract

It is well accepted in the literature that for effective grain refinement some solute is required in the melt to restrict the growth of the solid even if potent nucleating particles with a favourable physical nature are present. In this paper we investigate the effect of the solute on grain initiation in an isothermal melt, and an analytical model is developed to account for the effect of solute elements on grain size. This study revealed that the solute elements in the liquid ahead of the growing crystals reduce the growth velocity of the nucleated crystals and increase the maximum undercooling achievable before recalescence. This allows more particles to be active in nucleation and, consequently, increases the number density of active particles, giving rise to a finer grain size. The analytical model shows that the final grain size can be related to the maximum undercooling, average growth velocity and solid fraction at the moment of recalescence. Further analysis using the free growth model and experimental data in the literature revealed that for a given alloy system solidified under similar conditions the grain size can be empirically related to $1/Q$ (Q is the growth restriction factor) to a power of 1/3, which is considerably different from the empirical linear relationship in the literature. It is demonstrated that the 1/3 power law can describe the experimental data more accurately than a linear relationship.

Keywords: Solidification; Grain refinement; Undercooling; Isothermal melt; Solute elements

1. Introduction

The solute content has significant effects on grain refinement of engineering alloys [1–4]. For effective refinement, not only do the grain refining particles themselves need to be potent for heterogeneous nucleation, but some solute elements are also required to enhance the efficiency of the particles by restricting growth of the solid, either at a columnar growth front competing with equiaxed solidification or from particles where nucleation has already occurred [5–7]. The degree of growth restriction for a particular solute was initially described by the constitutional supercooling parameter P [8]:

$$P = \frac{m(k-1)C_0}{k}, \tag{1}$$

where m is the liquidus slope, k the equilibrium partition coefficient and C_0 the solute content in the alloy melt. Maxwell and Hellawell [9] suggested that, for spherical growth restricted by the partitioning of a single solute the crystal growth rate for a given undercooling is, to a good approximation, inversely proportional to the parameter Q:

$$Q = C_0 m(k-1). \tag{2}$$

The parameter Q is usually referred to as the growth restriction factor, and is used as a measure of the effects of a solute on grain refinement in the absence of solute interactions [10–16]. It was found that the experimental data were better interpreted in terms of Q [17]. Empirically, the average grain size $\bar{l}$ can be described as a linear function of $1/Q$ for various Al [4,10–14,18,19], Mg [1,20] and Ti alloys [21]:

$$\bar{l} = a + b/Q, \tag{3}$$

where a and b are empirical constants. From further analysis of the experimental data it is believed that a is related

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to the number density of active nucleating particles and b is related to the efficiency of the nucleating particles [22].

To characterize and quantify the effect of nucleating particles on grain refinement the contribution made by solute elements needs to be established. Maxwell and Hellawell [9] analysed heterogeneous nucleation in a spatially isothermal melt using classical heterogeneous nucleation theory by assuming spherical diffusion-controlled growth. They demonstrated that the latent heat evolved by growth of the solid raises the melt temperature above the heterogeneous nucleation temperature (recalescence) and thus suppresses further nucleation events. The role of the solute is to restrict the growth rate of the growing interface, which in turn allows time for further nucleation events to occur, and the final grain size is the result of competition between heterogeneous nucleation and growth.

Winegard and Chalmers [23] proposed a constitutional supercooling driven nucleation model and suggested that the constitutional supercooling arising from solute enrichment in the liquid ahead of an advancing solid front could trigger nucleation on available nucleating particles. Following this nucleation mechanism, St. John and co-workers [14,24] considered grain nucleation in the liquid ahead of a growing crystal with a small temperature gradient. They suggested that nucleation occurs when the amount of constitutional supercooling generated (ΔT_{cs}) reaches the undercooling required for nucleation (ΔT_n) and that the constitutional supercooling driven nucleation mechanism is responsible for the development of the solidified grain structure. Such semi-empirical models [14,24] were represented by a linear relationship between $\bar{l}$ and $1/Q$. On the other hand, Quested and Greer [25] analysed the efficiency of grain refiners during directional solidification and found that the diffusional composition profile from the growing grains actually reduced the undercooling available for grain initiation.

In the models mentioned previously, single sized nucleating particles were explicitly or implicitly assumed. Greer et al. [17] found that the efficiency of a grain refiner could be better explained using the free growth criterion to describe grain initiation in the isothermal melt, in which a distribution of particle sizes was assumed. The undercooling required for grain initiation (ΔT_{fg}) on an individual particle with size d is given by [17]:

$$\Delta T_{fg} = \frac{4\sigma}{\Delta S_v d}, \tag{4}$$

where σ is the solid–liquid interfacial energy and ΔS_v the entropy of fusion per unit volume. The free growth model revealed that the larger particles become active at a smaller undercooling and most of the smaller particles remain inactive due to the occurrence of recalescence. For small castings the assumption of an isothermal melt and the application of the free growth criterion give a quantitatively correct prediction of the grain size by numerical calculation [17,26–28].

In this paper we analyse the effect of solute content on grain refinement in an isothermal melt and the effect of constitutional undercooling on grain initiation. An analytical model will be presented to predict grain size as a function of solute content in an isothermal melt. The analytical model will be validated against experimental results available in the literature.

2. Effect of constitutional undercooling on grain initiation

It is well known that a solidification structure depends strongly on the solidification conditions. For simplicity we will confine our discussion in this paper to solidification under isothermal conditions. Isothermal solidification is not only a hypothetical condition, but is also found in many practical cases as a good approximation. Due to the large thermal diffusion coefficient in the liquid state, the thermal diffusion length is usually two to three orders of magnitude greater than the solute diffusion length [9]. This makes it possible to achieve isothermal or near isothermal solidification through the interplay between external heat extraction and latent heat release from the growing solid phase [17,26]. Such cases can be found in the solidification of small castings with a low cooling rate, solidification of alloys with a low superheat and formation of the equiaxed zoon in direct chill casting.

Fig. 1 shows a typical cooling curve during solidification under isothermal conditions. According to the free growth model [17], nucleation starts on the largest particle at a temperature just below the alloy liquidus temperature (T_l) and progressively on the smaller particles. Nucleation ceases when recalescence occurs at temperature T_f, at which external heat extraction balances latent heat release due to the growth of already nucleated crystals. T_f corresponds to the temperature at which the smallest active particle nucleates. The thermal plateau after recalescence corresponds to the growth temperature (T_g) of the nucle-

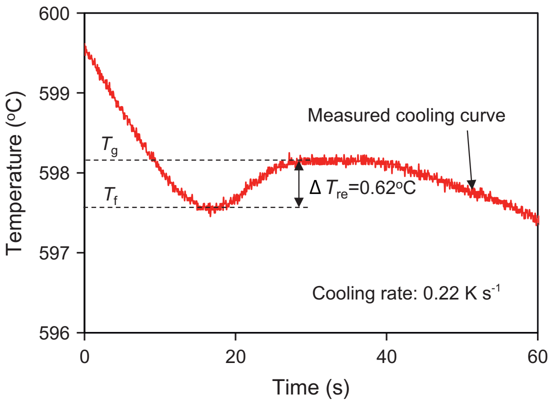

Fig. 1. Measured cooling curve for the AZ91 alloy melt with intensive melt shearing. The cooling curve exhibits pronounced recalescence, with T_f corresponding to the temperature at the moment of recalescence and T_g the thermal plateau after recalescence. The maximum undercooling ΔT_{re} at recalescence is estimated by the value of $T_g - T_f$. The measured cooling rate near the liquidus T_l is 0.22 K s^{-1}, and ΔT_{re} is 0.62 K.