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Coarsening during stircasting

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A difference in coarsening of Al–6Cu alloy and the organic substance neopentylalcohol (NPA) was observed during stircasting. It was found that the coarsening of Al–6Cu is independent of the applied stirring speed, whereas the coarsening of NPA was found to increase with increasing stirring speed. It appears that this difference can be explained by the influence of convection around the suspended primary particles, which have a different morphology in Al–6Cu and NPA in the early stages of the solidification during stircasting.

1. Introduction

Recently, batch-type stircasting experiments have been performed using the binary Al–6Cu alloy [1] and the organic substance neopentylalcohol (NPA) [2, 3]. The latter was used as a model substance to study the morphological changes in structure of the primary solid phase during stircasting [3, 4]. It was assumed that NPA is a suitable model substance for binary metal alloys as its Jackson α-factor, defined as the nondimensional ratio of the entropy of fusion and the gas constant, is approximately 1.4. Transparent organic substances with an α-factor smaller than 2 are commonly considered as model substances for alloys, because the solidification morphology is normally similar [5–12].

The aim of the experiments with NPA was to observe the formation of primary crystals *in situ* during stirred solidification, and to establish how the typical non-dendritic structure of stircast alloys is formed. In these experiments important differences with respect to stircast Al–6Cu were observed. Firstly, the dendritic structure observed during stirred solidification of NPA has not been found in stircast Al–6Cu [1, 4]. Secondly, a difference in coarsening of NPA and Al–6Cu was observed. In this paper this difference will be explained by considering the influence of the convection on the coarsening of the primary phase.

2. Experimental procedure

The experimental procedure followed in the batch-type stircasting experiments is described elsewhere [1–3]. A number of important differences in the experimental conditions are summarized here.

The experiments with Al–6Cu as well as those with NPA were performed in an annular space between two concentric cylinders, the inner cylinder rotating, and the outer cooled. However, the sizes and the materials of the apparatus were different. Different stirring speeds and cooling rates were applied. The microstructure of Al–6Cu was studied after quenching when the volume fraction solidified was roughly 50%. In contrast, the microstructure of NPA was observed *in situ*, and in most of the experiments the volume fraction solidified remained small (<0.01). Other important experimental differences are summarized in Table I.

3. Results

3.1. Microstructure

The changes in microstructure as a function of the solidification time were discussed in previous publications [1, 4], but are summarized briefly for convenience.

With long solidification times (long stirring times), the particle morphology in Al–6Cu and NPA is similar: the primary particles consist of agglomerated cells. With short solidification times, a difference in the solidification of Al–6Cu and NPA is observed: the primary particles observed in NPA are equiaxed dendrites, whereas the rosette-type particles found in Al–6Cu have a cellular appearance [1, 4]. To explain why the rosettes are not observed after long stirring times, it was suggested [13, 14] that these particles do not survive high shear rates at long stirring times.

In non-dendritic structures such as those of stircast metals, the secondary dendrite arm spacing (DAS) used to describe the structure of conventional (unstirred) alloys, cannot be determined. In order to describe stircast microstructures and make quantitative comparisons with structures of unstirred substances, a parameter is required similar to the secondary DAS. For this purpose the cell tip diameter and the dendrite tip diameter have been defined previously [1–3]. Figs 1a and b show how the cell tip diameter in Al–6Cu is defined for a rosette and for a particle consisting of agglomerated cells, respectively. Fig. 1c shows how the dendrite tip diameter of an equiaxed dendrite in

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TABLE I Experimental conditions in stirring experiments with NPA and Al–6Cu

	NPA	Al–6Cu
Radius of stirrer (mm)	30	13
Annular gap (mm)	2	3
Rotational speeds (r.p.m.)	10, 100, 1000	250, 750, 1500
Liquidus temperature (K)	325*	917
Solidus temperature (K)	286*	821
Solidification time (sec)		8–2700
Cooling rate ($\mathrm{K\,sec^{-1}}$)	0.001–0.04	0.03–12
Stirred fraction solid	< 0.01	~ 0.5

*See [20].

TABLE II Constants in Equation 1 for different stirring experiments

Substance	Stirring speed (r.p.m.)	Slope *A*	Constant *B*
Al–6Cu	250, 750, 1500	0.42	1.01
NPA	10	0.30	1.10
NPA	100	0.34	1.09
NPA	1000	0.40	1.04

NPA is defined. Fig. 1d illustrates the cell tip diameter of a particle in NPA consisting of agglomerated cells. Fig. 1e, for comparison, shows how the secondary dendrite arm spacing in a conventional dendritic structure is defined. The dendrite tip diameter (Fig. 1c) was measured in the early stage of the stirred solidification of NPA. After some time in which coarsening takes place, the dendrites change to agglomerates resembling those observed in Al–6Cu after quenching (Fig. 1d). In these particles the cell tip diameter was measured, in the same manner as in the metal.

3.2. Coarsening of Al–6Cu

In Fig. 2, the average cell-tip diameter measured in stircast microstructures of Al–6Cu is plotted as a function of the total solidification time. It was assumed [1], in correlation with work by Bower *et al.* [15] and Kattamis *et al.* [16, 17] that the points in this graph are on a straight line of the form

$$\log\langle d\rangle = A\log t_s + B \qquad (1)$$

where $\langle d\rangle$ is the cell-tip diameter (μm), and t_s the solidification time (sec). The constants A and B were determined using the least squares method, and are given in Table II. The triangles in Fig. 2 represent the results for unstirred samples, which are in agreement with the result obtained by Bower for conventional Al–4.5Cu (dashed line). Fig. 2 shows that the cell-tip diameter of the primary solidified phase in the stirred samples is greater than the secondary dendrite arm spacing in unstirred samples, at equal solidification times. The slope of the solid line is somewhat greater (0.42) than that of Bower's (0.39). The difference in slope is small and might well be within experimental error. However, the difference with respect to the theoretically predicted slope of 0.33 [16] is significant. The stirring speeds applied were 250, 750 and 1500 r.p.m. Within this range, the cell-tip diameter was found to be independent of the stirring speed [1].

3.3. Coarsening of NPA

In Fig. 3, the tip diameter of the primary stems of equiaxed dendrites observed in stirred NPA is plotted as a function of the total solidification time. Three different stirring speeds were applied: 10, 100 and 1000 r.p.m. Assuming that for each stirring speed the points obtained are on a straight line of the form of Equation 1, and using the least squares method, the values of the constants A and B obtained are given in Table II. From this table it is seen that the tip diameters observed for Al–6Cu are practically identical to those obtained for NPA at the highest stirring speed. However, we consider this result as accidental.

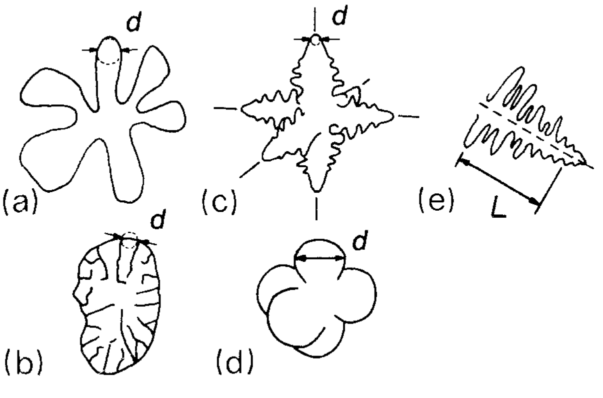

Figure 1 (a) Cell tip diameter in a rosette in stircast Al–6Cu. (b) Cell tip diameter in a particle consisting of agglomerated cells in Al–6Cu. (c) Dendrite tip diameter of an equiaxed dendrite in neopentylalcohol. (d) Cell tip diameter in a particle consisting of agglomerated cells in neopentylalcohol. (e) Secondary dendrite arm spacing $d = L/(n-1)$ in a dendritic structure; L is the distance across $n-1$ secondary dendrite arms.

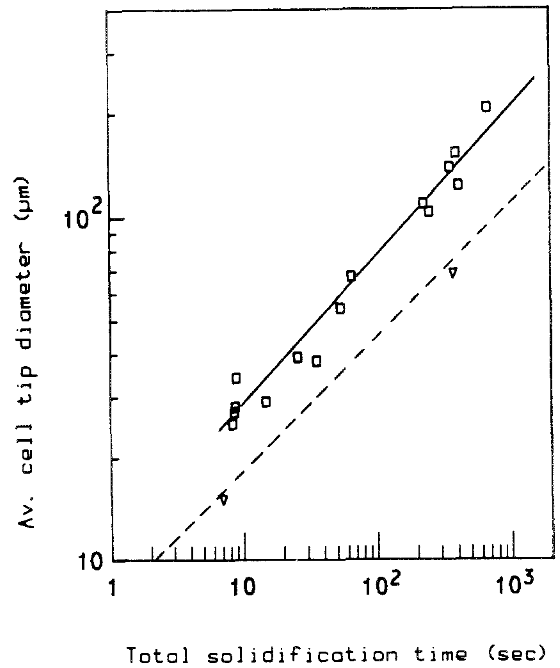

Figure 2 Average cell spacing in stircast structures of Al–6Cu plotted as a function of the total solidification time. Squares indicate average cell-spacings obtained in stirring experiments, for which the solid line was obtained as the best fit using the least squares method. Triangles represent results of reference experiments (unstirred samples). Bower's result (dashed line) is shown for comparison.

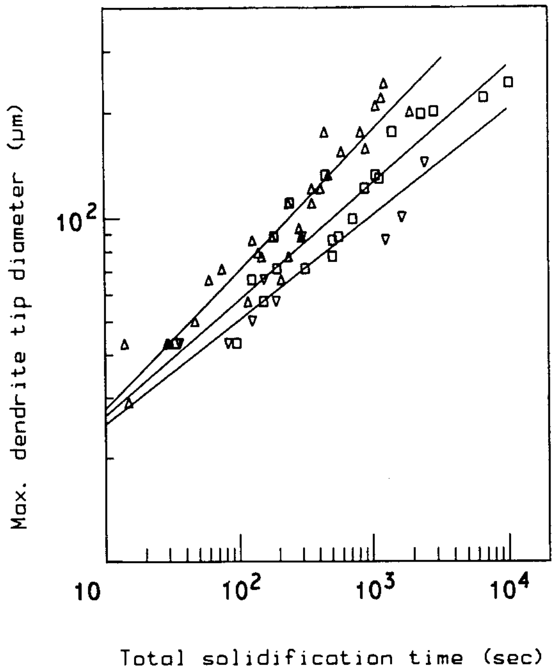

Figure 3 Maximum dendrite tip diameter in stirred neopentylalcohol (1.5 wt % H_2O) plotted as a function of the total solidification time, for three different stirring speeds: ▽: 10 r.p.m., □: 100 r.p.m., △: 1000 r.p.m.

4. Discussion

Transparent organic substances are commonly used as model substances for alloys to study the growth of solid during solidification. Provided the Jackson α-factor is smaller than two, the growth morphology is known to be the same as that of alloys [5–12]. Use of these substances has made it possible to study the different growth morphologies which can be observed with metals, and has contributed to the quantitative confirmation of the theory of constitutional supercooling. In general however, the properties of the organic substances are very different compared to those of alloys. For example, the thermal conductivity is only about one-thousandth and the latent heat of fusion and the solid–liquid interfacial energy are of the order of a tenth of the values of alloys. It seems unlikely that the solidification of these substances is invariably similar when the conditions vary. This is in fact reflected in the results presented above.

4.1. Effects of convection

The regimes in which convection or diffusion are predominant are determined by the value of the Peclet's number, which is defined by

$$Pe = \frac{v \cdot L}{a} \tag{2}$$

where v represents the flow velocity, L is a characteristic length, and a is either the thermal diffusivity or the diffusion coefficient, depending on whether heat or mass-transport is considered.

If $Pe > 1$, convective heat or mass-transport is predominant. If on the other hand $Pe < 1$, diffusion is predominant. In both regimes the convection may influence the solidification. If $Pe > 1$, the condition of the growing solid is influenced directly by changes in the thermal field or the solute distribution in the liquid. Independent of the value of the Peclet's number, the convection may also have a mechanical effect. For example, the thermal condition of a particle changes when it is fragmented from a dendrite at the chilled wall of the annular gap and transported into the bulk liquid, where it acts as a nucleus for further growth.

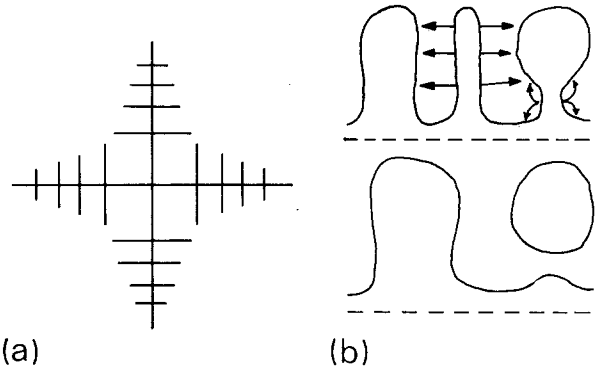

Figure 4 (a) Schematic representation of equiaxed dendrite with secondary arms growing on primary stems. (b) Coarsening of secondary arms due to solute transport from regions with high curvature to regions of low curvature.

4.2. Coarsening of NPA

To demonstrate the influence of convection on the coarsening of an equiaxed dendrite, we recall a result from a previous paper [4]. In this paper the heat and mass flows around a suspended spherical particle in a flow field of constant shear were considered. A function h (R) was derived, representing the distance h where $Pe = 1$, to the surface of the sphere as a function of its radius R. This function is defined as follows:

$$\begin{aligned} R \ll (a/\dot{\gamma})^{1/2}&: \quad h(R) = a/\dot{\gamma}R \\ R \gg (a/\dot{\gamma})^{1/2}&: \quad h(R) = h^{\infty} = \left(\frac{2}{15}\frac{a}{\dot{\gamma}}\right)^{1/2} \end{aligned} \tag{3}$$

where $\dot{\gamma}$ is the shear rate, and h^{∞} the value of h if the radius of the sphere approaches infinity. It was shown that convection is predominant in mass-transport at only a few microns from the surface of the sphere, and that this distance decreases with increasing radius R. Now let us consider an equiaxed dendrite as observed in the stircasting experiments with NPA, and as sketched in Fig. 4a. The dendrite rotates in a field of constant shear around one of its axes. Note that the period of revolution is determined by the shear rate only, and not by the size of the dendrite. We will consider the coarsening of the secondary dendrite arms growing on the primary stems. The liquid slips past the secondary arms. The flow velocity increases in the direction of the tips of the primary stems. Coarsening of the secondary arms growing on the primary stems will take place, as shown schematically in Fig. 4b [16]. The smaller arms remelt due to solute transport through the liquid to the greater arms. It is evident that convection contributes to this transport and therefore will enhance arm coarsening. A given increase of the secondary dendrite tip diameter is achieved in a shorter time period due to convection.

Equation 3 shows that the effect of convection is stronger at the coarser arms. The same coarsening mechanism causes an increase in primary tip diameter. The observed transition of equiaxed dendrites which exist in the early stage of the solidification, to agglomerates [3, 4] is explained by simultaneous dendrite fragmentation, coarsening and agglomeration of fragmented parts in a build-up and break-down process. Due to fragmentation of equiaxed dendrites, observed experimentally [3, 4], new particles will form and the individual growth rates will decrease in time. The extent of crystal multiplication increases strongly at the higher stirring speeds [3]. Therefore the coarsening of the primary dendrite tip diameter is enhanced accordingly. We conclude that both before and after the transition of equiaxed dendrites to agglomerates the rate of coarsening increases with increasing flow intensity, which explains that the slope of the lines in Fig. 3 increases with increasing stirring speed.

4.3. Coarsening of Al–6Cu

As already noted, equiaxed dendrites have not been observed with the Al–6Cu alloy, and the slope of the line in Fig. 1 was found to be independent of the applied stirring speed [1].

This result is consistent with the fact that the primary particles in stirred semisolid metal slurries consist of agglomerated cells, or are of the rosette-type. The intercellular liquid in these particles is immobilized [18]. Flow of intercellular liquid can only be due to volume contraction of the solid, and to solute and density gradients in the liquid. This natural convection is much less compared to the flow past the secondary arms of rotating equiaxed dendrites, and will be independent of the external shear rate. This explains that the slope of the solid line in Fig. 2 is independent of the stirring speed, and within experimental error is equal to the slope of Bower's line.

Based on the conclusions in the previous section, we suggest that the difference between the slope of Bower's line (0.39) [15] and the theoretically predicted slope (0.33) [16] is due to natural convective intercellular solute transport.

The greater cell-spacing in the stircast alloy, with respect to the secondary DAS in the unstirred alloy (Fig. 2), is attributed to a more stable type of solid growth during stircasting. It is assumed that growth of suspended particles in the bulk liquid is cellular. Based on the interface stability theory of Mullins and Sekerka [19], a difference in morphological stability of the solid–liquid interface of suspended particles in organic substances and metals may be due to a difference in thermal gradient at the interface.

5. Conclusions

1. The coarsening of Al–6Cu alloy and of neopentylalcohol (NPA) is enhanced by stirring. However, the result of coarsening is achieved in different ways.

2. In Al–6Cu, the coarsening is a result of a more stable type of growth of the primary solidified phase. The coarsening is independent of the stirring speed.

3. In neopentylalcohol, convection contributes to the solute transport in the liquid phase, which enhances secondary dendrite arm coarsening. Dendrite fragmentation and agglomeration cause a transition of equiaxed dendrites to particles consisting of rounded cells. The rate of coarsening is dependent on the stirring speed.

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