

Evolution of Particle Morphology in Semisolid Processing

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Experimental results are summarized of the formation of spheroidal grain structures in an Al-4.5 wt pct Cu alloy by (1) isothermally holding very fine equiaxed dendrites in the liquid-solid region and (2) direct spheroidal solidification from the melt. The fine-grained dendritic structure was obtained by very rapid solidification in a thin-section (0.8 mm) permanent-mold plate casting under conditions such that solidification took place during the filling process and, hence, during rapid fluid flow. Grains of approximately 30 μm in diameter (representing a grain density of about $3 \times 10^4 \text{ mm}^{-3}$) were obtained; these ripened to a spheroidal morphology in the liquid-solid region in less than 5 seconds. A similarly high grain count was then obtained in the bulk melt by vigorous agitation and rapid cooling near the liquidus temperature; the melt was thereafter cooled more slowly. Under these conditions, a spherical morphology formed early in solidification and grew in that form. The evolution of particle size with time in the liquid-solid region is shown to be essentially identical in the initially dendritic and spherical-growth experiments.

I. INTRODUCTION

SEMISOLID metal forming of nondendritic structures has been studied and practiced commercially for some decades. Much of the progress in semisolid forming has been summarized in a series of biennial conferences^[1-8] and review articles.^[9,10,11] The wide variety of different semisolid forming techniques all aim to achieve as nearly as possible a spheroidal semisolid structure with minimum entrapped second phase and to do so in an economic manner. Relatively little work has been devoted to understanding the fundamentals of the critically important initial solidification of the semisolid structure. Experiments reported here are aimed at studying structure evolution during those initial stages (at times as short as 5 seconds); experiments comprise the ripening of fine dendritic structures and the formation of spheroids directly from the melt.

II. EXPERIMENTAL PROCEDURES

A. Ripening of Equiaxed Dendrites

Typically, a very-well-grain-refined aluminum alloy casting will have a grain size of about 100 μm .^[12,13] Grain sizes in actual castings are often much larger. In this work, a grain size of 30 μm was obtained, employing a technique developed earlier of drawing a molten alloy rapidly into a thin-plate mold in such a way that some solidification takes place while flow is still occurring.^[14]

The plate mold employed is shown schematically in Figure 1. The mold consisted of two 12.7-mm-thick copper plates separated by 1-mm-thick "graphite felt" spacers. The thin channel created between the copper plates was 0.8-mm thick, 30-mm wide, and 125-mm long. The top end of the mold was connected to a vacuum reservoir which could be set to

a variety of vacuum levels. The bottom end of the mold was covered with a small piece of thin plastic Saran wrap (15- μm -thick polyvinylidene chloride film), which adequately sealed the vacuum within the mold. The mold was attached to a pneumatic piston which, when extended, would lower the mold into a furnace holding the melt, as shown in Figure 2. In the lowered position, the bottom 10 mm of the quench mold was immersed into the melt and the small piece of plastic wrap melted almost instantly, drawing metal upward into the evacuated channel. The quench mold used was initially at room temperature, between 22 °C and 30 °C. The melt comprised $745 \pm 5 \text{ g}$ of the Al-4.5 wt pct Cu alloy, held in a thin-walled steel crucible coated in boron nitride spray. The melt temperature was held at 654 °C (roughly 5 °C above the measured liquidus temperature). The bulk melt temperature was measured by at least one K-type thermocouple contained in a 2-mm-i.d., 3-mm-o.d. quartz tube. Bulk melt temperatures were recorded with a datalogger, which acquired readings at 1 Hz.

For ripening experiments, samples with dimensions of $10 \times 10 \times 0.8 \text{ mm}$ were cut from the quenched thin plate of metal. Each sample was wrapped in a steel foil along with the tip of a thin K-type thermocouple that had a 0.25-second response time. The tip of the thermocouple was held in contact with the surface of the samples by steel alligator clips located on the outside of the steel foil. Each assembly was plunged into a tin bath at a temperature at $620 \text{ °C} \pm 5 \text{ °C}$, well above the Al-Cu eutectic temperature (550 °C), and the temperature was recorded. From the Scheil equation, the fraction of solid at this isothermal holding temperature was approximately 0.80. Five experiments were performed in which the measured temperature of each sample was above the eutectic temperature for 5, 15, 60, 120, and 480 seconds, respectively. Each sample was water quenched immediately after being removed from the tin bath, polished using standard metallographic techniques, and etched with Keller's reagent.

Three micrographs were taken from random locations in each reheated dendritic sample. The average linear grain size in each sample was measured using the line-intercept method. Between 170 and 380 grains were analyzed for each reheated sample.

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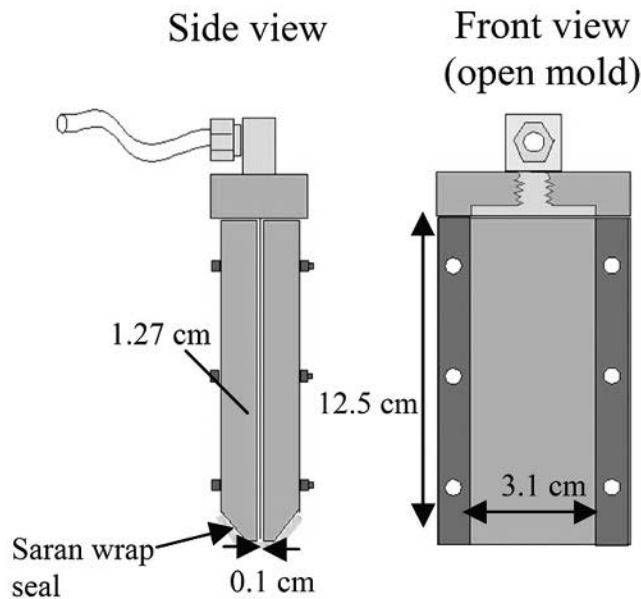


Fig. 1—Schematic of the geometry and dimensions of the thin-plate mold used to produce a fine equiaxed dendritic structure in the Al-4.5 wt pct Cu alloy.

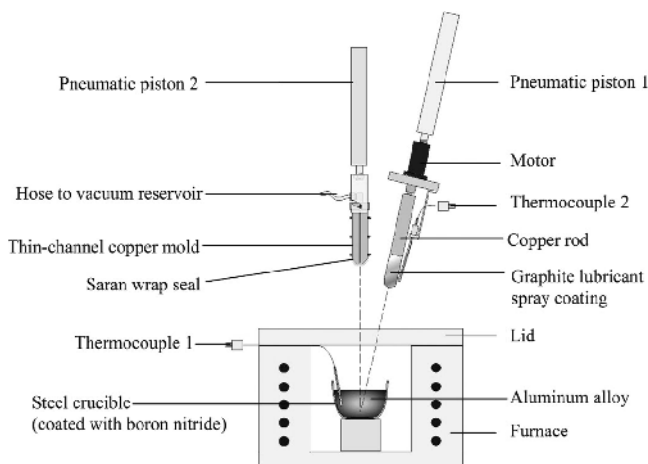


Fig. 2—Schematic of equipment designed and built for this study.

B. Direct Formation of the Spheroidal Structure

To achieve a high grain density in the bulk melt, the Al-4.5 wt pct Cu melt was rapidly cooled and vigorously agitated during initial solidification (*i.e.*, “rheocast”). The process is shown schematically in Figure 3: a cold rotating copper rod was immersed into the melt, which was held slightly above the liquidus temperature; the rod was rotated vigorously, cooling and stirring the melt to just below the liquidus.^[15] The rod remained in the melt just long enough for the first few percentages of solid phase to form; a high solid-grain density was obtained as a result of grain fragmentation. The melt was then rapidly quenched, thus “trapping” the structure which first formed.

To confirm that the spheroidal morphology of particles resulted from the combination of cooling and vigorous convection provided by the stirring rod, an experiment was conducted where the copper rod was immersed in the metal

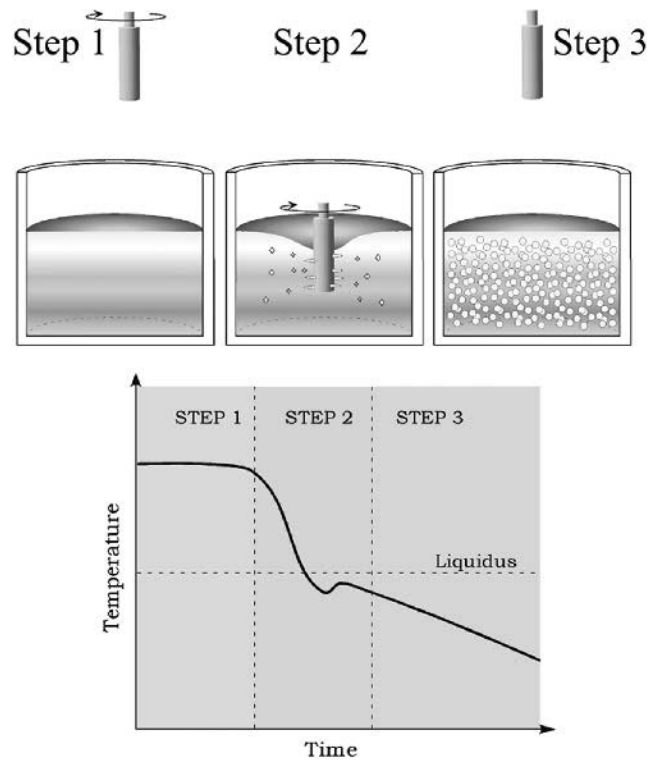


Fig. 3—Three basic steps of efficient rheocasting of an aluminum alloy: combining vigorous convection with a region of localized rapid cooling during the early stages of solidification.

without rotating. When the rod was removed, a solid metal skin had formed around the rod. The microstructure of this metal had a fine columnar-dendritic structure, reaching radially outward away from the rod/metal interface. The alloy remaining in the crucible was also found to be dendritic.

The experimental arrangement employed for rheocasting and quenching is shown in Figure 2, comprising a rotating copper stirring rod attached to a pneumatic piston that could be rapidly immersed and extracted from the melt, as well as the copper quench mold and piston described earlier. By operating the pneumatic pistons with a set of switches, both the copper stirring rod and the quench mold could be immersed into the melt, which was held in the furnace at various times and at various melt temperatures. The copper stirring rod was 286 mm in diameter and 255-mm long, with a rounded end, and coated with a graphite dry-film lubricant spray. It was at room temperature before being immersed in the metal.

The Al-4.5 wt pct Cu alloy was held in the furnace at 653 °C, approximately 4 °C above the measured liquidus temperature (stage 1 of Figure 3). The copper stirring rod, rotating at 409 rpm, was then immersed into the melt, removing the 4 °C of superheat almost instantly (stage 2 of Figure 3). Once the liquidus temperature was reached, the measured cooling rate was approximately 0.28 °C s⁻¹. After very short immersion times, the rod was removed (stage 3 of Figure 3). Using the measured cooling rate and the physical properties of the melt and copper rod, the heat-transfer coefficient for the rod/melt interface was estimated to be roughly 2500 W m⁻² K⁻¹.

Two experiments were conducted in which the rotating copper rod was immersed in the melt for 5 and 20 seconds,

respectively, and then the metal was drawn immediately into the quench mold. Two additional experiments were conducted in which the immersion time was 20 seconds, and the metal was allowed to slowly, and quiescently, cool for 60 seconds and 9 minutes, respectively, before being quenched. Using the Scheil relation, the fraction of solid in the rheocast slurries at the time of the quench was estimated to be 0.05 for the 5-second sample, 0.18 for the 20-second sample, 0.30 for the 80-second sample, and 1.0 for the 9-minute sample.

The cross sections of the thin-plate samples of the rheocast alloy were polished and etched with Keller's reagent. About ten micrographs were taken from random locations in samples formed by rheocasting and quenching the alloy after being below the liquidus temperature for 5, 20, and 60 seconds and 9 minutes. Average-sized particles in which the etching revealed the lightly shaded central region were identified in each of the micrographs. The diameter of the lightly shaded central region, referred to as the initial particle diameter, was considered to be the particle size just before the quench. It is believed that additional spheroidal growth occurred during the quench, marked by the darker-shaded spheroidal ring surrounding the lighter center. Using the micrographs, measurements of the initial particle diameter (lightly shaded particle centers) were made on about 30 particles from each sample. For each particle, two measurements were taken in roughly orthogonal directions and then averaged. The average particle size for a given rheocast sample was taken to be the average over the number of particles measured.

A microprobe was used to measure the solute concentration within two spheroidal particles in the rheocast sample quenched after 20 seconds of rheocasting. For each spheroid, the copper concentration was measured at eight or more locations along the particle diameter.

III. RESULTS AND DISCUSSION

A. Ripening of Equiaxed Dendrites

Correlations of dendrite-arm spacing with solidification time (or isothermal holding time in the liquid-solid region) have been made repeatedly. Figure 4 summarizes data for solidification gathered by a number of investigators (Bower *et al.*^[16] Bardes and Flemings,^[17] and Annavarapu and Doherty^[18]); data are for Al-Cu alloys of roughly 4 to 7 wt pct Cu. Data for isothermal holding of dendritic structures in the liquid-solid region are also shown in Figure 4, from experiments by Kattamis *et al.*^[19] for the Al-4.5 wt pct Cu alloy and by Poirier *et al.*^[20] for Al-15.6 wt pct Cu. In spite of the range of alloy compositions and solid fractions tested (0.3 to 0.5), all the previous data fall within the upper and lower bounds drawn in Figure 4. The midpoint of the scatter band drawn is given by

$$d = 10t_f^{1/3} \quad [1]$$

where d is the average diameter of the grain in micrometers, and t_f is the local solidification time in seconds.

In experiments conducted in this work on ripening of equiaxed dendrites, the initial dendrite-arm spacing and grain size were approximately 30 and 5 μm , respectively (Fig-

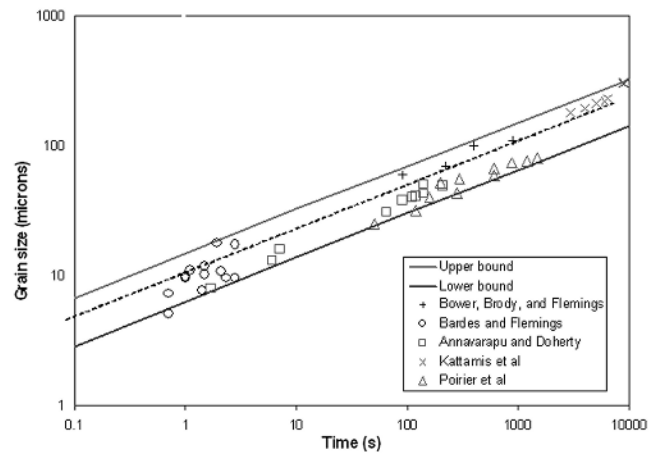


Fig. 4—Dendrite-arm spacing vs local solidification time or isothermal holding time. Dendrite-arm spacings measured in solidified castings are shown by the triangles: data from a number of investigators as assembled by Bower *et al.*,^[16] Bardes and Flemings,^[17] and Annavarapu and Doherty.^[18] Dendrite-arm spacings measured in castings reheated and held isothermally in the liquid-solid region are shown for experiments by Kattamis *et al.*^[19] for an Al-4.5 pct Cu alloy and by Poirier *et al.*^[20] for Al-15.6 pct Cu.

ure 5(a)). From Eq. [1], the 5- μm dendrite-arm spacing indicates that the structure solidified in approximately 0.2 seconds, or, from the scatter band of Figure 4, the solidification time was within a range of about 0.1 to 0.5 seconds, in agreement with that estimated in an earlier study using a similar mold setup.^[14]

As is evident from Figure 4, very short reheating times are sufficient to ripen the small dendrites to the point that the initial dendrite-arm spacing of 5 μm approaches the grain size of 30 μm . In these experiments, after reheating above the eutectic for only 5 seconds, the equiaxed dendrites of Figure 5(a) evolved into nondendritic grains (Figure 5(b)). The nondendritic grains then grew larger in samples ripened for longer times (Figures 5(c) through (f)). Data for this ripening, the square points in Figure 6, follow approximately the 1/3-power growth law along the upper bound of the dendrite-arm spacing plot of Figure 4. In all of the reheated dendritic microstructures, there is entrapped eutectic within the nondendritic grains.

For comparison, other investigator's data for spheroidal grain-size evolution as a function of ripening time are included in Figure 6: that of Annavarapu and Doherty (triangles)^[18] and of Manson-Whitton *et al.*^[21] (crosses). The discrepancy between our results and those of the aforementioned investigators is quite large, being about an order of magnitude for the time required to reach a given grain size. The reason for this discrepancy is not clear to us, but may be related to the much finer initial dendrite-arm spacing in our samples.

B. Direct Formation of the Spheroidal Structure

Figures 7(a) through (d) show the typical rheocast microstructure obtained by stirring the liquid alloy with the copper rod (rheocasting), then drawing metal into the quench mold after being below the liquidus temperature for 5, 20, and 60 seconds and 9 minutes, respectively. Approximately

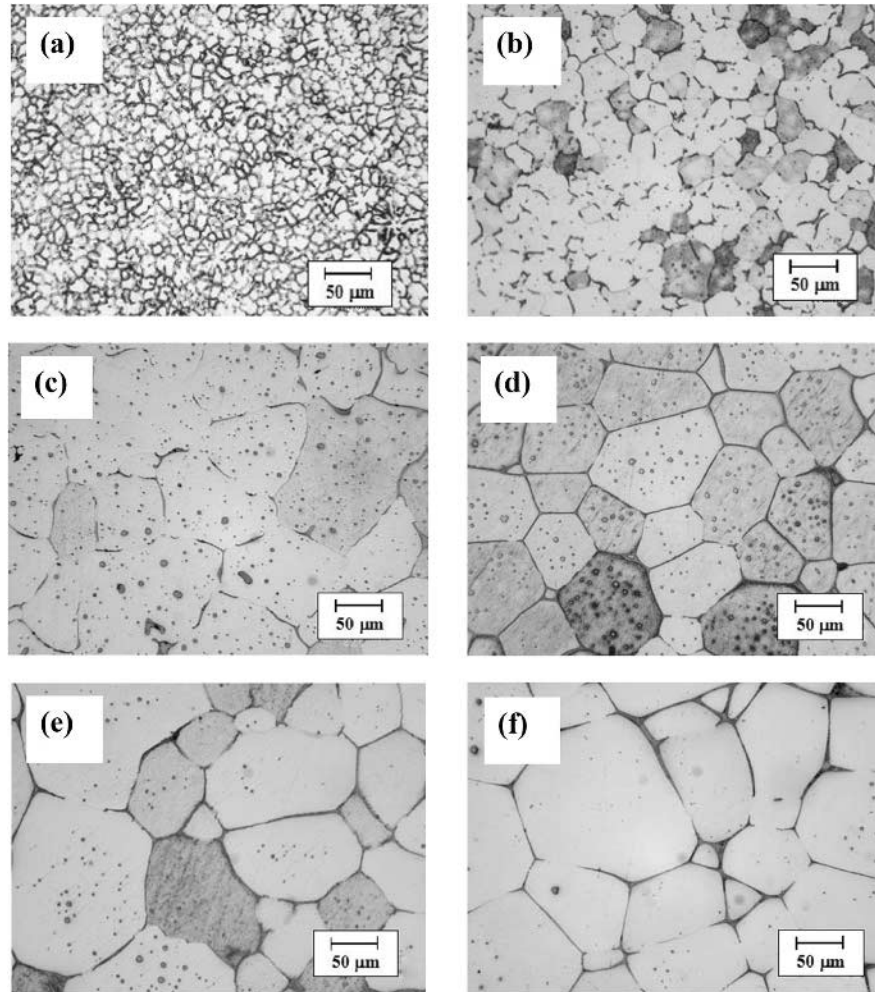


Fig. 5—Microstructure of (a) a sample cast by drawing a slightly superheated liquid alloy in the quench mold with a pressure drop of 50 torr. The same microstructure is shown after reheating it above the eutectic temperature for (b) 5 s, (c) 15 s, (d) 60 s, (e) 120 s, and (f) 480 s.

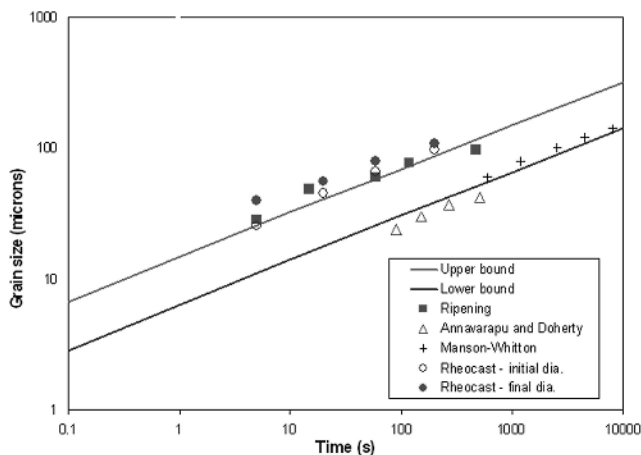


Fig. 6—Diameter of nondendritic grains vs time in the liquid-solid region. Ripening experiments performed in this study are represented by the squares. Data from isothermally holding initially dendritic structures, as obtained by Annavarapu and Doherty, are represented by the triangles;^[18] that of Manson-Whitton *et al.*^[21] is represented by the crosses. The rheocasting experiment performed in this study is represented by the circles. Also shown are the midpoint of the scatter band (dashed line) and upper and lower bounds for the dendrite-arm spacing from Figure 4.

spherical grains formed and grew in the bulk melt prior to quenching. During the quench, the spheres continued to grow for a period of time, and the remaining liquid then rapidly solidified as the fine dendritic structure seen in Figures 7(a) through (c). The dendrite-arm spacing in this residual liquid is approximately 5 μm .

The circles in Figure 6 represent the average final diameter of the rheocast particles measured on the polished surface after the quench. These points also lie along the upper-bound line. The amount of growth of the spheres that took place during the quench was estimated from the thickness of the darkened periphery of the etched grains (as may be seen, for example, in several grains in Figure 7(b)). Figures 8(a) through (c) confirm that the darkened periphery represented a high-copper region. These figures show the backscattered electron images of two particles and the measured copper content along the particle diameters. In both particles, the central region of $\pm 20 \mu\text{m}$ has about 1.0 wt pct Cu. Closer to the center of the particles, the copper content is slightly higher, about 1.1 wt pct Cu. At radial distances greater than 20 μm away from the particle centers, the copper content in both particles increases abruptly. Thus, in these cases, the particles grew to roughly 40 μm in diameter during

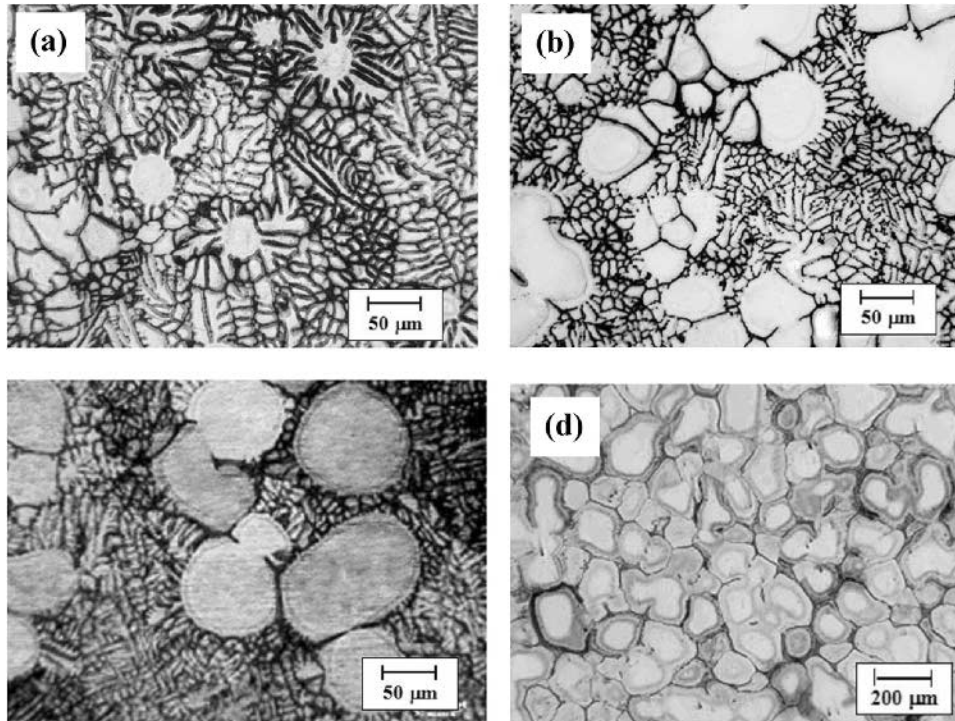


Fig. 7—Microstructure of the rheocast Al-4.5 wt pct Cu alloy quenched after being stirred and cooled below the liquidus temperature for (a) 5 s, (b) 20 s, (c) 60 s, and (d) 9 min.

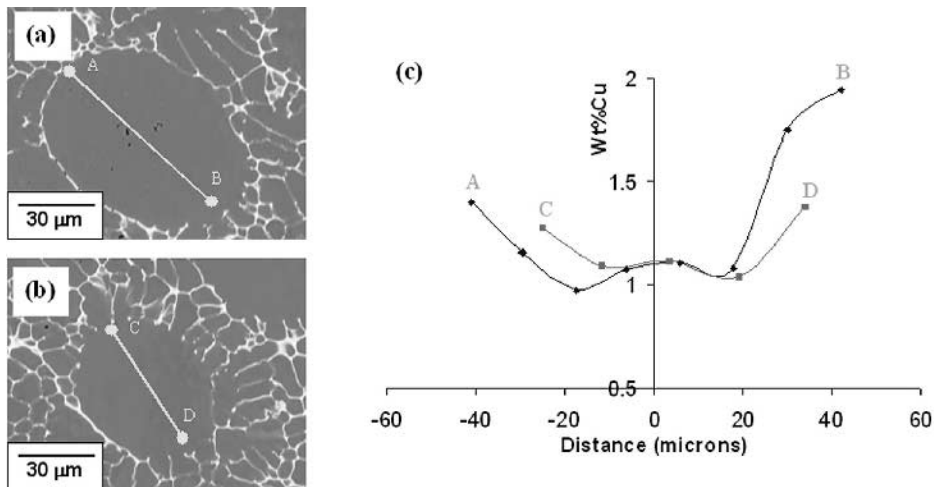


Fig. 8—(a) and (b) Backscattered electron images of rheocast particles in an Al-4.5 wt pct Cu sample quenched after being rheocast for 20 s. (c) The copper content within the particles, obtained by a microprobe line scan.

the 20-second period of slow cooling and then another $40\ \mu\text{m}$ or so during the quench. Based on measurements of the thickness of the darkened periphery of the grains, the open circles in Figure 6 represent the estimated particle diameter just before the quench.

While these experiments provide little information on growth morphology for times less than about 5 seconds, it is clear that from 5 seconds on (*i.e.*, at fractions of solid greater than about 0.05), growth was fully nondendritic. Moreover, no evidence of a previous dendritic structure was seen in the etched structures or from microprobe results. It

is, therefore, clear that dendritic growth can be circumvented in solidification if the grain number per unit volume is sufficiently high for a given cooling rate. The grain density in the rheocast alloy after 5 seconds of rheocasting (calculated as the reciprocal of the cube of the average grain diameter) was about $6.4 \times 10^4\ \text{grains} \cdot \text{mm}^3$ and $3.6 \times 10^3\ \text{grains} \cdot \text{mm}^3$ after 60 seconds of rheocasting. The high initial grain densities resulted from dendrite multiplication (separation of a dendrite from a “mother” dendrite). It is promoted by vigorous agitation combined with rapid heat extraction during the earliest stages of solidification.

IV. CONCLUSIONS

1. A semisolid structure of an Al-4.5 wt pct Cu alloy comprising nondendritic grains can be obtained by reheating equiaxed dendritic material of sufficiently fine grain size. The time is short for a very-fine-grain-sized material, being less than 5 seconds for a 30- μm grain size.
2. Rapid cooling, combined with vigorous agitation during the initial stage of solidification, can result in a sufficiently high grain density that growth is spheroidal from very early on in the solidification process. In this work, spheroidal grains were observed to grow in an alloy quenched after 5 seconds of solidification, at only about a 0.05 fraction of solid. These grains showed no sign of entrapped eutectic or of microsegregation with isoconcentrates that would indicate an earlier dendritic structure.
3. Spheroidal grains in semisolid alloys grow according to a 1/3-power relationship during isothermal ripening and also during solidification.

REFERENCES

1. *Proc. 1st Int. Conf. on Semisolid Processing*, Sophia-Antipolis, France, Apr. 4–6, 1990.
2. *Proc. 2nd Int. Conf. on Processing of Semisolid Alloys and Composites*, Cambridge, Massachusetts, June 10–12, 1992.
3. *Proc. 3rd Int. Conf. on Processing of Semisolid Alloys and Composites*, Tokyo, June 13–15, 1994.
4. *Proc. 4th Int. Conf. on Semisolid Processing of Alloys and Composites*, Sheffield, United Kingdom, June 19–21, 1996.
5. *Proc. 5th Int. Conf. on Semisolid Processing of Alloys and Composites*, Golden, CO, June 23–25, 1998.
6. *Proc. 6th Int. Conf. on Semisolid Processing of Alloys and Composites*, Turin, Italy, Sept. 27–29, 2000.
7. *Proc. 7th Int. Conf. on Semisolid Processing of Alloys and Composites*, Tsukuba, Japan, Sept. 25–27, 2002.
8. *Proc. 8th Int. Conf. on Semisolid Processing of Alloys and Composites*, Limassol, Cyprus, Sept. 21–23, 2004.
9. M.C. Flemings: *Metall. Trans. B*, 1991, vol. 22B, pp. 269-93.
10. D.H. Kirkwood: *Int. Mater. Rev.*, 1994, vol. 39 (5), pp. 173-89.
11. Z. Fan: *Int. Mater. Rev.*, 2002, vol. 47 (2), pp. 49-85.
12. A.A. Greer: *Proc. Solidification of Aluminum Alloys Symp.*, TMS Annual Meeting 2004, Charlotte, NC, March 14–18, 2004, pp. 131-45.
13. M. Easton and D. St. John: *Proc. Solidification of Aluminum Alloys Symp.*, TMS Annual Meeting 2004, Charlotte, NC, Mar. 14–18, 2004, pp. 147-56.
14. T.F. Bower and M.C. Flemings: *Trans. TMS-AIME*, 1967, vol. 239, pp. 216-19.
15. R. A. Martinez: Ph.D. Thesis, Massachusetts Institute of Technology, 2004.
16. T.F. Bower, H.D. Brody, and M.C. Flemings: *Metall. Trans.*, 1966, vol. 236, p. 624.
17. B.P. Bardes and M.C. Flemings: *Trans. AFS*, 1974, vol. 66, p. 406.
18. S. Annavarapu and R.D. Doherty: *Acta Metall. Mater.*, 1995, vol. 43, p. 3207.
19. T.Z. Kattamis, J.C. Coughlin, and M.C. Flemings: *Metall. Trans.*, 1967, vol. 239, p. 1504.
20. D.R. Poirier, S. Ganesan, M. Andrews, and P. Ocansey: *Mater. Sci. Eng. A*, 1991, vol. 148, p. 289.
21. E.D. Manson-Whitton, I.C. Stone, J.R. Jones, P.S. Grant, and B. Cantor: *Acta Mater.*, 2002, vol. 50, p. 2517.