Formation of Primary Silicon during Cooling and Solidification of Al–20%Si Alloy

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The relationship between the cooling curve and formation of primary silicon from the melt has been investigated for Al–20%Si alloy in the uninoculated state and when prior-treated with a phosphorus-bearing inoculant. The results suggest that coarse branched silicon forms from an uninoculated melt at sub-liquidus temperatures well above the primary silicon arrest temperature and that increasingly effective inoculation both reduces intensity of the arrest and shifts it to higher temperature eventually eliminating it completely in favour of a sharp reduction in slope of the cooling curve at or just below the liquidus temperature. It is proposed that this could be used as a simple diagnostic test for efficiency of refinement of primary silicon by inoculant additions under specified conditions.

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1. Introduction

Hypereutectic Al–Si base alloys are of continuing interest for applications as engineering castings for automotive, aircraft and consumer applications where their wear resistance, low thermal expansion coefficient, high thermal conductivity, corrosion resistance, low density and very good casting characteristics are attractive.1,2 A key requirement is to refine the primary silicon from a coarse branched morphology, which degrades properties, into a fine, uniform equiaxed distribution which enhances properties and performance. This can be achieved by making a phosphorus-bearing addition to the melt prior to casting, either as a master alloy, such as Cu–P, Al–Cu–P or Al–Fe–P or via compounds or fluxes. This is considered to operate by generating a uniform fine distribution of AIP particles in the melt or addition, which act as nuclei for primary silicon before the sparsely distributed impurity inoculants that are already present can nucleate the coarse branched primary silicon. AIP has the same crystal symmetry and similar lattice parameter to silicon so should provide an excellent substrate for nucleation. Indeed, evidence has been reported of faceted pips at the centre of primary silicon particles only when P-inoculation had been carried out.2–8 Such ‘pips’ have been shown to be rich in Al and P4.5,7,9 and evidence of growth of silicon crystals on large AIP crystals has also been published.10 The present contribution reports on the evolution of primary silicon following sand shell casting of Al–20 wt%Si alloy, with and without a prior inoculant addition. Samples were taken at decreasing temperature down the cooling curve in an attempt to identify the form and scale of the primary silicon at representative temperatures and times, during its formation. A similar approach was used earlier by Weiss and Loper11 and by Sigworth12 but neither attempt was made to relate the results to the sampling temperature11 or the results were found not to be related to the recorded cooling curve, at least not in any simple way.12 Furthermore, neither study applied the technique to phosphorous-inoculation of primary silicon: Weiss and Loper confined their report to the effect of cerium addition which did not refine their primary silicon, while Sigworth reported the effects of small additions of strontium and tungsten.

2. Experimental

The Al–Si alloy was supplied as ingot by the industrial collaborator of the project and had composition Al–20Si–0.3Fe–0.08Mn–0.06Mg with < 0.02Cu, Zn, Ti and Cr (mass%). The collaborator also supplied the P-containing

\[\text{Direction of metal flow on sampling} \]

\[\text{Alumina crucible} \]

\[\text{Thermocouple bead} \]

\[\text{To datalogger} \]

\[\text{Airtight refractory cement} \]

\[\text{Entrance} \]

\[\text{Temperature, } ^\circ\text{C} \]

\[\text{Distance, } \text{mm} \]

Fig. 1 (a) Schematic of preheated tube used to sample melt bottom cast into Quik-Cup® sand moulds. (b) Temperature profile along sampling tube prior to insertion into the melt.
inoculant as billet 30 mm in diameter with composition Al–11.6Fe–4.14P–0.66Mn–0.38Si–0.13Ti (mass%). Melting, addition of inoculant and casting was carried out with the system described in Ref. 13). This comprised a melting chamber containing a bottom stoppered crucible, the contents of which could be transferred into a square section bonded sand mould situated below it, by withdrawing the stopper, which contained a thermocouple for monitoring the temperature of the melt. The melt size was 150 g, the crucible discharge nozzle bore was 7 mm and the commercially-supplied square-section mould had cavity dimensions 35 mm × 35 mm and wall thickness 8 mm with a built-in silica sheathed thermocouple midway up the cavity (20 mm above its base). Resulting cooling curves were logged by a personal computer with the aid of an analogue to digital signal convertor. Sampling of the melt in the mould was achieved by suction casting into preheated alumina tubes (bore 3 mm, wall thickness 0.5 mm, length 100 mm). Diagonically opposite flats were ground on each tube to perforate the wall 20 mm from its entrance. This allowed a thermocouple to be located with its bead on the axis of the crucible for temperature recording purposes, and the thermocouple exit leads to be cemented to the tube at the two perforations (Fig. 1(a)). The resulting assembly was preheated in a furnace such that the first 50 mm from the entrance was isothermal at 950°C with the remaining 50 mm exhibiting a temperature gradient down to 300°C (Fig. 1(b)). Sampling was carried out at predetermined temperatures of the melt in the mould by reference to its cooling curve, with contact times between 1.2 and 1.7 s registered by the sampling tube thermocouple. Each sample was water quenched immediately after sampling, and sectioned longitudinally for metallographic characterization. Outputs from the thermocouples recording cooling of the melt in the mould and the temperature of the melt entering the sampling tube were fed simultaneously to the computer so that the point on the cooling curve at which the sample was taken could be determined precisely, along with the bulk melt/sampling tube contact time.

3. Results

Figure 2(a) shows the heating/cooling curves for an uninoc-

\[ \text{Fig. 2} \] Heating/cooling curves for Al–20 mass%Si cast from 800°C into a Quik-Cup® sand mould (a) showing primary silicon arrests for an uninoculated melt (b) comparing curves down to the first arrest for uninoculated (i) and inoculated (100 ppm P, contact time 10 min) (ii) melts with sampling temperatures indicated (c) same comparison for the eutectic arrest (d) showing superimposed cooling curve from thermocouple in sampling tube for highest sampling temperature from the uninoculated melt. Key: (i) uninoculated melt (ii) inoculated melt.
Fig. 3  Microstructure of Al-20 mass %Si quenched from different temperatures $T$ while cooling in the sand mould (a) uninoculated, $T = 717^\circ C$; (b) uninoculated, $T = 656^\circ C$; (c) inoculated, $T = 720^\circ C$; (d) inoculated, $T = 670^\circ C$.

...ulated sample cast at 800°C into the sand mould. An arrest is evident at $\sim 635^\circ C$ associated with primary silicon followed by slower cooling to a second arrest at $\sim 575^\circ C$ associated with solidification of the residual eutectic liquid. Figures 2(b) and (c) compare the heating/cooling curves down to the first arrest and at the eutectic arrest respectively for uninoculated and inoculated (100 ppm of phosphorus) melts. The primary silicon arrest for the uninoculated sample is replaced for the inoculated sample by a change in slope at $\sim 680^\circ C$. Figure 2(b) indicates the temperatures at which samples were taken from the uninoculated and inoculated melts and Fig. 2(d) superimposes on the cooling curve for the uninoculated sample the temperature history given by the sampling tube thermocouple for the highest sampling temperature used.

Figures 3(a)–(d) compare the quenched microstructures in the near-entrance part of the sampling tube for the highest and lowest sampling temperatures for both inoculated and uninoculated melts. Figure 3(a) shows the uniform fine distribution of primary silicon produced by quenching the sample of uninoculated melt from 717°C, well above the liqudus ($\sim 680^\circ C$). Figure 3(b), in contrast, shows in addition coarse branched primary silicon obtained by quenching uninoculated melt from 656°C, well below the liqudus. Figures 3(c) and (d) show the effect of quenching from similar temperatures (720 and 656°C) for the inoculated melt. Both show uniform fine primary silicon attributable for Fig. 3(c) to operation of inoculation during quenching and in Fig. 3(d) primarily to inoculation prior to quenching. While the sampling-tube formed primary silicon in Fig. 3(c) and prior-to-sampling formed silicon in Fig. 3(d) for the inoculated melt are not immediately distinguishable, any coarse-branched primary silicon such as in Fig. 3(b) in quenched samples of uninoculated melt must evidently have been present in the melt prior to sampling. Measurements of the number, $N$, of such branched silicon particles in axial longitudinal sections of the first (pre-heated) 50 mm length of the quenched sample are plotted versus sampling temperature in Fig. 4. The systematic increase with decreasing sampling temperature of $N$ (which thus represents the number in an area of dimensions 50 mm $\times$ 2.8 mm) is evident.
4. Discussion

4.1 Cooling curves

The forms of cooling curve shown in Figs. 1(a)–(d) are comparable with those reported in earlier work for hypereutectic Al–Si alloys. In particular the primary silicon arrest at 633 to 637°C for the uninoculated melt in Figs. 1(a), (b) has also been observed by Crosley and Mondolfo, by Sigworth, and by Park et al. For an alloy composition identical with ours, Park et al. obtained a primary silicon arrest at ~645°C but for a cooling rate ~1°C/s compared with ours of ~8°C/s down to 650°C. Park et al. also showed that the arrest temperature increased to ~670°C at 1°C/s when the melt was pre-inoculated with phosphorus. This is in line with the upward shift of the entire cooling curve in Fig. 2(b) for the inoculated melt indicating a significant change in slope at or below ~680°C (the assessed liquidus temperature for Al–20 mass%Si), compared to the more gradual change for the uninoculated melt from 680°C downwards to the arrest temperature. The presence of coarse primary silicon in samples of the uninoculated melt quenched from 680 down to 656°C (Figs. 2(b) and (4)) suggests that some nucleation of primary silicon had occurred in the temperature range 680°C down to the arrest temperature so that the massive heat evolution at 633 to 637°C must represent a much more substantial primary silicon nucleation and/or growth event. The relative continuity of the cooling curve for the inoculated melt over the same temperature range 680 to 535°C indicates a process of nucleation and growth starting at or just below the liquidus temperature 680°C, fully consistent with effective nucleation on a population of pre-formed AIP particles derived from the inoculant addition.

Trials with a series of P-containing inoculant additions indicated a gradual increase in the temperature of the primary silicon arrest as the efficiency of the inoculant increased until it disappeared completely, as for curve (ii) in Fig. 2(b) for the most effective inoculant, which was used for the present study. Finally, the reduction in number of coarse branched primary silicon particles in quenched samples with increase in sampling temperature (Fig. 4) is in accord with the comparable observation of Pekguleryuz and Pedneau for uninoculated Al–16 mass%Si cooling at 0.03°C/s. For the lower liquidus temperature (630°C), applicable they observed just a few branched primary silicon particles in an area of 0.16 mm² on quenching from 613°C and many more on quenching from 660°C.

5. Conclusions

(1) Sampling experiments have been carried out at different temperatures during cooling of uninoculated and phosphorus-inoculated Al–20%Si melts to investigate the evolution of primary silicon during cooling and solidification.

(2) Samples of uninoculated melts show a continuous increase in the number of pre-formed coarse branched primary silicon particles with decrease in sampling temperature from 718 to 660°C.

(3) The effect of added phosphorus in progressively reducing or eliminating the primary silicon arrest and in shifting it to higher and higher temperature could be used as an indicator of effectiveness of a phosphorus inoculation treatment for a defined set of cooling and solidification conditions.

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REFERENCES