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PRIMARY SILICON SEGREGATION DURING ISOTHERMAL HOLDING OF HYPEREUTECTIC Al-18.3 wt%Si ALLOY IN THE FREEZING RANGE

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1. Introduction

Some recent experimental studies have shown that there is a tendency for primary silicon to segregate in Bridgman solidification [1] and laser surface treatment [2] of hypereutectic Al-Si alloys. Significant such segregation was also observed earlier in slowly solidified castings with more than 15 wt%Si [3]. Buoyancy driven convection [3-6] and nucleation preferentially at the side walls and bottoms of moulds [4,6,7] were generally considered to be the major causes of this primary silicon segregation in castings. Natural convection driven by thermal and solutal gradients in the melt is a further possibility explored, for example, for Pb-Au [8], Sn-Pb [9], Al-Cu [10] and Pb-Sn [11] alloys. Isothermal holding experiments in the freezing range have been carried out by us in an attempt to quantify the kinetics of this silicon segregation.

2. Experimental

An Al-18.3 wt%Si alloy was melted in a resistance furnace where it was held first for 10 minutes at some 150 to 200K above the alloy liquidus in graphite or alumina cylindrical crucibles 30 mm in internal diameter and 30 mm in height. The temperature of the melt was then reduced to 600±2°C, between the liquidus (657°C [12]) and eutectic temperature (577°C [12]), at a cooling rate of 0.2 to 0.4K/s by steadily reducing the power, and held at this second holding temperature for 0 to 40 minutes. During the cooling and second holding periods, thermocouples placed in the melt showed that the temperature difference between the core and periphery of the sample was less than 2K. The second holding treatment was terminated by transferring the crucible and contents onto a copper block which cooled its contents to room temperature at a cooling rate of 1.7 to 2.2K/s measured in the sample 15 mm from the bottom of the crucible.

Longitudinal sections of resulting samples were micrographed on an optical microscope without etching after grinding and polishing. Atomic adsorption spectrophotometry was used to analyse the composition of samples from specific positions on the longitudinal section.

3. Results

Figs 1a to c are optical micrographs of the longitudinal section of Al-18.3 wt%Si specimens after the treatment described. They show that coarse primary silicon was concentrated at the top surface and near the bottom and side walls of the crucible. The effect at the top surface was most severe when there was no holding treatment at 600°C (Fig 1a), almost disappearing when the holding time was 15 minutes (Fig 1b) then returning after a further hold (Fig 1c). Most of the coarse primary silicon, however, was concentrated near the bottom and side walls of the crucible, for which the measured thickness, X, of the bottom layer is given as a function of holding time in Table 1. Table 1 indicates that the main thickening of the coarse silicon layer occurred in the first 10 minutes (X increased by 0.9 mm during this period), thickening being much less subsequently (X increased by 0.3 mm only in the second 10 minutes). Chemical analyses on a sample held for 20 minutes at 600°C gave the Si-content of the coarse silicon layer as 25.0±0.2 wt%, giving the volume fraction of primary silicon particles as 0.24 assuming that the matrix in the layer has the eutectic composition 12.6 wt%Si [12].

The primary silicon particles at the top surface were partly branched plate-like and partly polyhedral in morphology when there was no holding treatment at 600°C (Fig 2) becoming polyhedral only on holding (Fig 3a). The primary silicon near the bottom and side walls was branched plate-like always (Fig 3b). This branched plate-like primary silicon was typically 8 to 10 times larger in size than the polyhedral primary silicon particles near the top surface (Figs 3b). Each sample showed a core region that was fully eutectic (Fig 3c), apart from a small number of isolated silicon particles. This core of typical composition 14.6±0.2 wt%Si according to chemical analysis was separated from the silicon-enriched periphery by an intermediate region showing αAl dendrites in the eutectic (Fig 3d). This intermediate region typically contained 13.9±0.2 wt%Si according to chemical analysis.

4. Discussion

4.1 Segregation at the top surface and near the bottom and side walls

Since the effect of silicon concentration on the density of liquid aluminium is small (it increases by less than 0.03 Mg m^{-3} at 700°C between the eutectic composition, 12.6 wt%Si, and the alloy composition, 18.3 wt%Si, [13]) and the temperature within the sample was almost uniform, there should not be significant thermal nor solutal convection during holding at 600°C or during the cooling that preceded it. Localized growth of the primary silicon (involving diffusive transport of silicon atoms in the melt) as well as flotation of primary silicon particles (buoyancy driven convection) were operative, however, because time was available for both processes and so the effects of nucleation and growth as well as flotation of the primary silicon were to be expected in the experiments.

The major observed effect of a layer of coarse primary silicon near the crucible bottom and wall was not present for castings [3-7]. It appears to have resulted from preferred heteronucleation at the wall and bottom, followed by continued growth characterised by a branched plate-like morphology of primary silicon. The fact that the thickness of this primary silicon layer increased with increase in holding time at 600°C and that silicon particles were few in other parts of the sample (Fig 3c) indicates that growth of these wall-nucleated particles rather than nucleation of new particles away from the wall consumed the excess silicon in the bulk of melt. This also explains why the size of the particles near the bottom and side walls of the crucible were much larger than elsewhere.

When there was no holding treatment at 600°C, primary silicon near the top surface evidently resulted from preferred nucleation of silicon particles on the cooled top surface to form branched plate-like particles together with flotation of polyhedral silicon particles which had nucleated in the bulk of the melt, which is consistent with previous work [3-6] for castings. The fact that the top accumulation of primary silicon was most evident when there was no hold at 600°C is attributable to the continued nucleation of silicon throughout the melt followed by flotation to the top surface and the availability of nucleation sites on the cooler top surface during continuous cooling of the sample. When there was holding at 600°C, growth of silicon particles near the side walls and bottom of crucibles consumed silicon from all of the melt during which the isothermality ensured that further nucleation in the bulk of the melt was limited. The particles that did nucleate in the melt then floated to its top surface which was no longer cooler than the bulk while isothermal holding continued.

4.2 Simulation of silicon layer growth from bottom and side walls

The Flow 3-D package (Flow Science Inc), which is based on a finite volume method and general diffusion equations, was used to simulate the silicon diffusion process associated with the growth of silicon particles from the bottom and side walls during isothermal holding at 600°C. There was assumed to be no artificial convection in the solidification process, and for purpose of two-dimensioned modelling, the sample was assumed to be cylindrical with constant radius 15mm and height 30mm (Fig 4). The assumed boundary and initial conditions were: at R=0 and t≥0, melt concentration C=12.6wt%Si; at R=15mm and t≥0, dC/dR=0; at Y=0 and t≥0, C=12.6wt%Si; at Y=30mm and t≥0, dC/dY=0; and at t=0, C=18.3wt%Si except at R=0 and Y=0. The operative diffusion coefficient of silicon within the melt was taken to be $6.0x10^{-9}$ m^2s^{-1} at 600°C [14].

The result of this simulation is shown in Fig 5, which shows silicon concentration vs time at 600°C in the positions marked A, B, C, D, E, F and G in Fig 4. The corresponding distances (Y) from the bottom of the crucible are 3, 5, 7, 9, 11, 13 and 15 mm, respectively. The concentration of the melt next to the primary silicon layer (at A position 3mm from the crucible) is reduced to close to the eutectic concentration in the first 10 to 15 minutes. This implies that the layer of the primary silicon near the bottom could be established within 10 to 15 minutes. This is in reasonable agreement with the measurements for the thickness of the primary silicon layer at the bottom (Table 1), which reveals that the silicon layer was established in about 10 minutes.

Assuming that all the silicon taken from the melt deposits on the bottom and side walls of the crucible, a thickness of this silicon deposited at a volume fraction of 1 can be predicted (Table 1). With the actual volume fraction of primary silicon in the silicon layer as 0.24, the equivalent thickness of that silicon deposit can then be estimated (Table 1) and compared with measured values. This comparison shows measured values 1.1 to 1.8 larger than predicted, indicating reasonable agreement so supporting the idea that local growth of primary silicon particles in the silicon layer consumed most of the silicon in the melt. However, the simulation predicts that the silicon concentration of the melt at the core of sample remains close to 18.3 wt%Si even after 40 minutes at 600°C compared with the measured core concentration of 14.6 wt%Si. This difference arises from the formation of primary silicon in the core of the melt and its flotation to the top surface of the sample, which become more evident with increase in time of hold (Figs 1b and c).

The simulation predicts that the areas between the centre and edge should have the lowest concentration as confirmed by chemical analysis. The simulation also predicts that the centre of the sample has the highest Si concentration in the remaining melt. This result is consistent with the observation that floated primary Si particles were positioned towards the centre of the top surface (Fig 1), rather than at its edge, implying that they come mainly from the excess silicon in the melt near the centre of the sample.

5. Conclusions

1. Isothermal holding of samples in the freezing range is a useful experimental technique to study the nucleation and growth kinetics of segregating primary silicon particles in hypereutectic Al-Si alloys.

2. Localized growth of primary silicon particles after initial heteronucleation near the crucible wall consumes most of the excess silicon in the remaining melt.

3. The effect of flotation of primary silicon particles in the melt on primary silicon segregation is insignificant when there is an appreciable time of isothermal holding in the freezing range.

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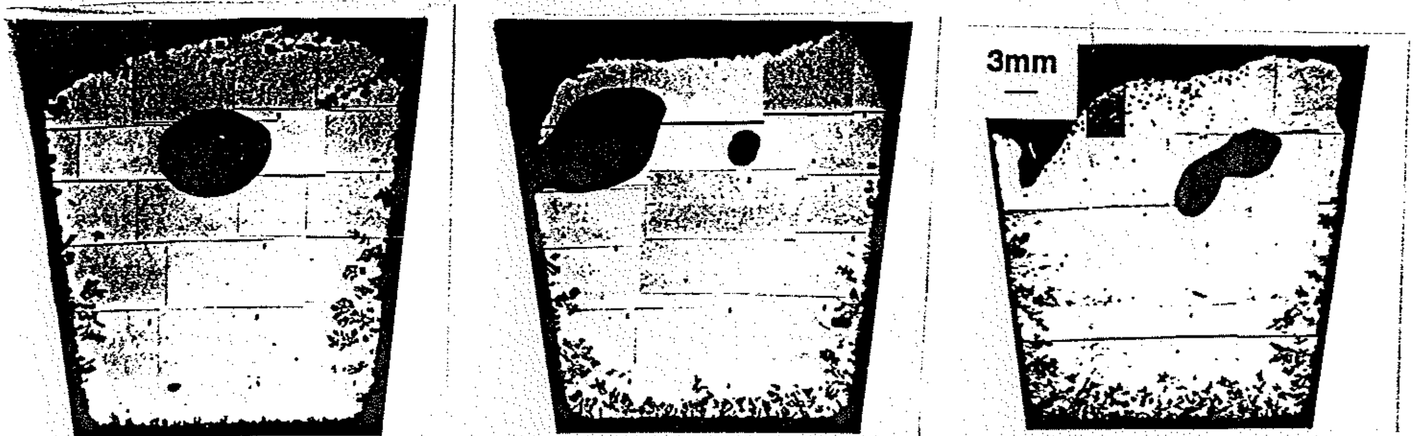
TABLE 1

Measured overall thickness, X (mm), and simulated thickness, $X - X_0$ (mm), of the primary silicon layer formed near the bottom of samples versus duration of hold at 600°C for Al-18.3 wt%Si. Measurements are for an assumed volume fraction, f, of primary silicon of 0.24 in the layer (25.0 wt%Si).

Duration of hold (minutes)	**0**	**5**	**10**	**15**	**20**	**40**
Measured X at f=0.24	X_0=0.8±0.3	1.2±0.5	1.7±0.6	1.9±0.9	2.0±0.8	2.2±0.9
Measured $X - X_0$ at f=0.24	0	0.4	0.9	1.1	1.2	1.4
Simulated $X - X_0$ at f=1	0	0.12	0.18	0.22	0.25	0.33
Simulated $X - X_0$ at f=0.24	0	0.36	0.54	0.66	0.75	1.00
Ratio of measured to simulated $X - X_0$ at f=0.24	-	1.1	1.8	1.7	1.7	1.4



(a) (b) (c)

Fig 1: Optical micrographs of longitudinal section of Al-18.3 wt%Si samples held (a) 0, (b) 15 and (c) 40 minutes at 600°C before transfer to a copper chill block.

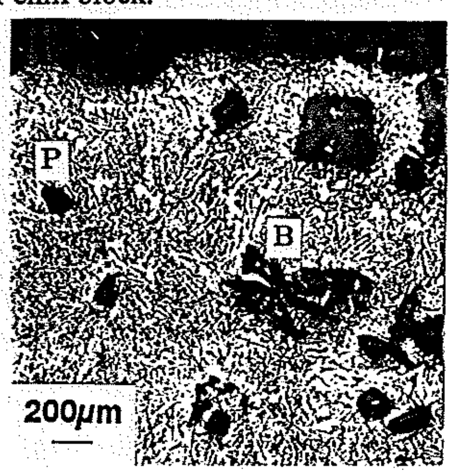


Fig 2: Optical micrograph showing primary silicon near the top surface in the longitudinal section shown in Fig 1a. B = branched plates; P = polyhedral.

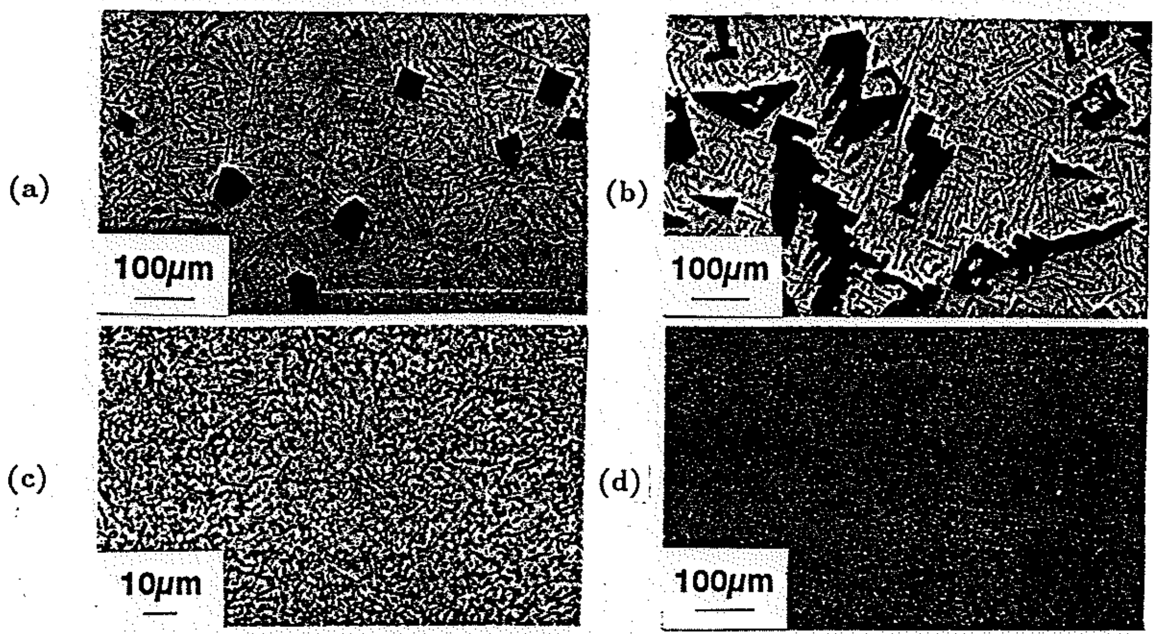


Fig 3: Optical micrographs at specific positions in the longitudinal section shown in Fig 1c. (a) near top surface; (b) near bottom; (c) centre; and (d) between centre and periphery.

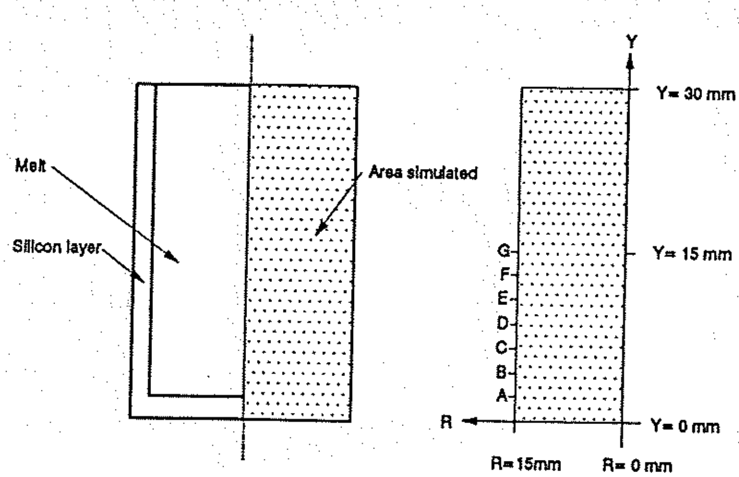


Fig 4: Schematic of the geometry for simulation of silicon diffusion in isothermal holding of Al-18.3 wt%Si at 600°C.

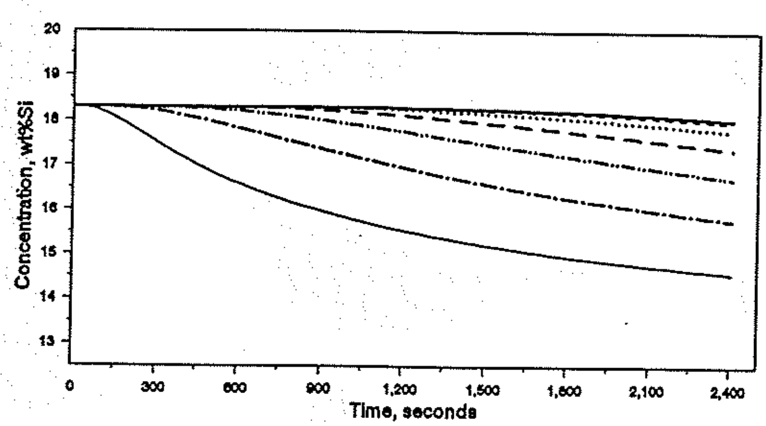


Fig 5: Predicted silicon concentration in Al-18.3 wt%Si versus time of hold at 600°C for different distances, Y, from the crucible bottom. Y: —— 15 ------ 13 ······· 11 – – – 9 –··– 7 –·–· 5 —— 3 (mm)