JOURNAL OF MATERIALS SCIENCE 31 (1996) 3731–3737

Quench modification of aluminium–silicon eutectic alloys

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Directional solidification of aluminium–silicon eutectic alloys were carried out in order to investigate the mechanism by which the quench modification takes place. For this purpose a new type of Bridgman furnace was designed which can attain a high temperature gradient and a high interfacial growth velocity up to 1000 $\mu m\,s^{-1}$. It is established that the fibrous structure is the result of faceted–non-faceted growth of the coarse silicon particle at high solidification rate. It is observed that refining of the flake structure closely follows the characteristics of normal eutectic.

1. Introduction

The term modification has been used for many years to indicate an alteration in the microstructure that is produced by eutectic freezing from the commonly observed form to another. In an eutectic system, one phase solidifies in a faceted and the other in a non-faceted manner. It is well established that the eutectic microstructure may change significantly with solidification conditions. Al–Si is one of the most widely used alloys in which the structure can be modified by changing the freezing rate or by changing the composition of the alloy [1–4].

Modification of Al–Si eutectic promotes a change from coarse flake eutectic silicon to a fine fibrous form and can be achieved either by impurity addition, such as sodium or strontium or by fast cooling exceeding above 400 $\mu m\,s^{-1}$ [5].

Earlier modification studies [5, 6] concluded that flake–fibre transition is related to a massive increase in the density of twins in the silicon phase with progressive refinement of the eutectic. Other studies [7–10] have revealed that this is not the case when Al–Si eutectic is quenched modified. The information obtained from transmission electron microscopy (TEM) observations indicates that the density of twins in quench-modified fibres is very low, and even that some fibres appeared to be twin free.

Jackson [11] has suggested that in quench modification the transition in shape seems to correspond to a change from somewhat anisotropic growth by an intrinsic mechanism at higher undercooling. This is probably due to transition from faceted to non-faceted behaviour.

Recent investigation [12] has proposed that quench-modified fibres are considered to retain the characteristics of flakes refined by a large undercooling. However, the twin density is slightly higher than for flakes. All these clearly indicates that the impurity and quench modifications are entirely different in character.

This work attempted to examine the features obtained when the Al–Si eutectic is quench modified.

2. Experimental procedure

A detailed description of the experimental procedure is given elsewhere [13–15]. Briefly, aluminium and silicon of high purity were melted in a graphite crucible under an argon atmosphere. The alloy was also treated with 0.18 wt % Sr in order to establish a microstructural difference between the impurity and the quenched modifications. After homogenization, the molten alloy was sucked into a pre-heated alumina tube of 200 mm length and 2.5 mm inner diameter. A rotary pump was used to cause the molten alloy to rise in the specimen tube. The flow of the alloy was regulated with the valve attached to the pump. Excessive filling of the tube was prevented by circulating cold water in a holder which holds the specimen from the top. A successful filling of the tube can be achieved by adjusting the rotary pump valve, control of melt temperature and pre-heating time and temperature of the alumina tube.

Thermocouples used to measure the interface temperature during solidification were prepared by butt welding. T_1 and T_2 types of chromel–alumel thermocouple wires, 0.17 mm diameter, were welded together to produce a bead size of less than 0.4 mm diameter. A fine hole, of approximately 0.4 mm diameter, was drilled through the alumina tube and the specimen. The thermocouple wire was passed through this hole until the bead was fixed exactly in the centre of the hole. This specimen assembly was then

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positioned in a vertical Bridgman type of directional solidification apparatus. A sectional view of the Bridgman furnace and details of the experimental apparatus are given elsewhere [13, 14]. A period of 2 h was allowed for thermal equilibrium to be established in the specimen before it was grown at a chosen velocity. The quenched sample was then sectioned both longitudinally and transversely to examine the structural features. The mean diffusion distances of the silicon phase were measured on a micrograph of known magnification, M, counting the number of fibres, N, within a known area, A. The average spacing is given by

$$\lambda = 1/M \quad (A/N)^{1/2} \tag{1}$$

3. Results and discussion

The practical attraction of the modification process is that the resultant morphology consists of a fibre-reinforced composite with improved mechanical properties. The structure of the directionally solidified Al–Si eutectic becomes finer as the solidification rate increases. It is observed that quench modification starts at a rate of 505 $\mu m\,s^{-1}$ and is completed at 807 $\mu m\,s^{-1}$. This is evident in Fig. 1 which shows the gradual change in the Al–Si eutectic structure.

The most favourable solidification condition for detecting the cooling arrest is a very low temperature gradient in the liquid. However, the present conditions are not conducive to the significant arrest, in aiming to understand the influence of a temperature gradient on this particular Al–Si system. An alternative means of locating the interface temperature was adopted [14]. In this context, a cooling curve for a growth velocity of 875 $\mu m\,s^{-1}$ is shown in Fig. 2, which also demonstrates the calculation of interface temperature. The change in slope of the cooling curve as the interface passes the thermocouple bead depends on the latent heat evolved, the change in conductivity on passing from liquid to solid, any modification to the heat flow caused by the thermocouple sheets, and solidification conditions.

The experimentally measured undercooling and interparticle spacings are given in Table I and are plotted as a function of growth velocity (V) in Fig. 3. The most important information obtained from these results is that the transition from flake to quench-modified fibrous structure is accompanied by a drop in undercooling. Also it can be seen that there are discontinuities in the λ–V relationship at a certain growth velocity after which a fibrous structure starts to form. There is more scatter in the experimental relationship for quench-modified samples than for flake. This fact is associated with the calculation of the interfacial growth temperature. From Fig. 2, it appears that the accurate location of the growth temperature depends on the accurate calculation of the displacement of the time scale, which is very small. This distance could have been increased if a higher chart speed had been available. Possibly it would be possible to draw a line through the points fitting a relationship of the form

$$\Delta T = K_1 V^{0.5} \tag{1}$$

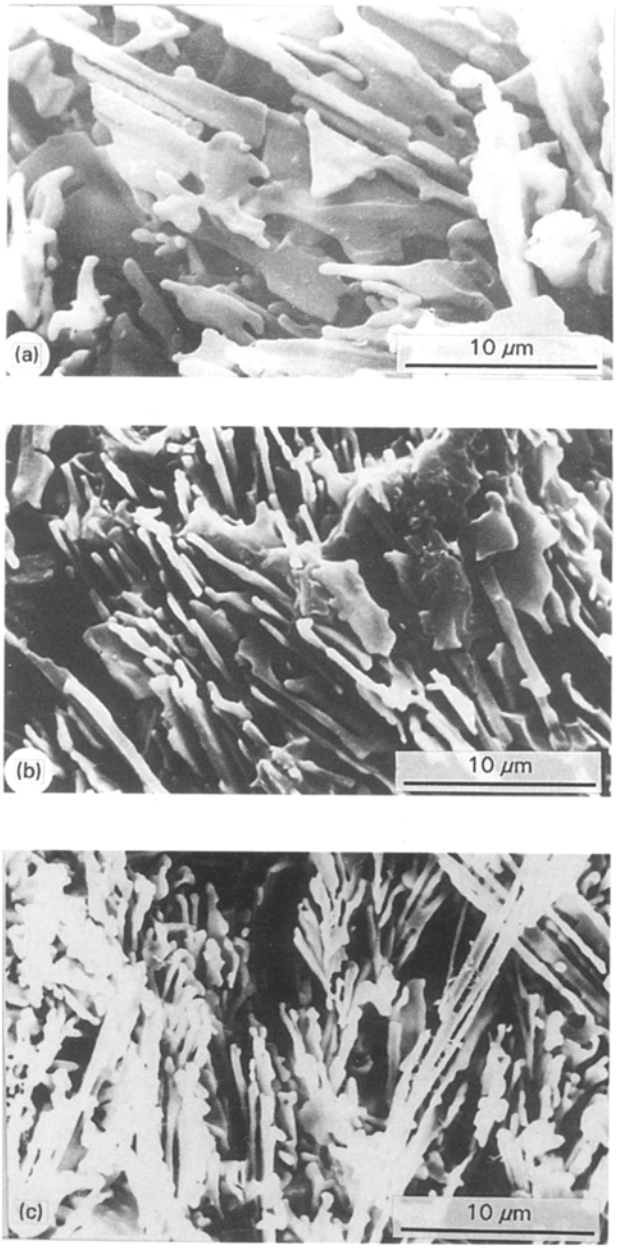


Figure 1 The change in the silicon phase morphology with growth velocity. (a) Completely flake, grown at 308 $\mu m\,s^{-1}$, (b) mixed form of flake and fibrous structure grown at 505 $\mu m\,s^{-1}$, (c) completely fibrous structure grown at 807 $\mu m\,s^{-1}$.

Likewise, the interfibre spacings were found to vary with growth velocity, according to an equation of the form

$$\lambda = K_2 V^{-0.54} \tag{2}$$

or

$$\lambda^{1.85} V = 2.17 \times 10^{-3}\,(\mu m\,s) \tag{3}$$

as shown in Fig. 3b. In addition, the undercooling and interparticle spacing results do not show any clear dependence on temperature gradient, as exhibited by the measurements for the flake structure [14, 15].

Modification of the Al–Si eutectic may be approached by considering that the factor which influences the growth behaviour tends to produce a fine microstructure. This problem must be resolved: why

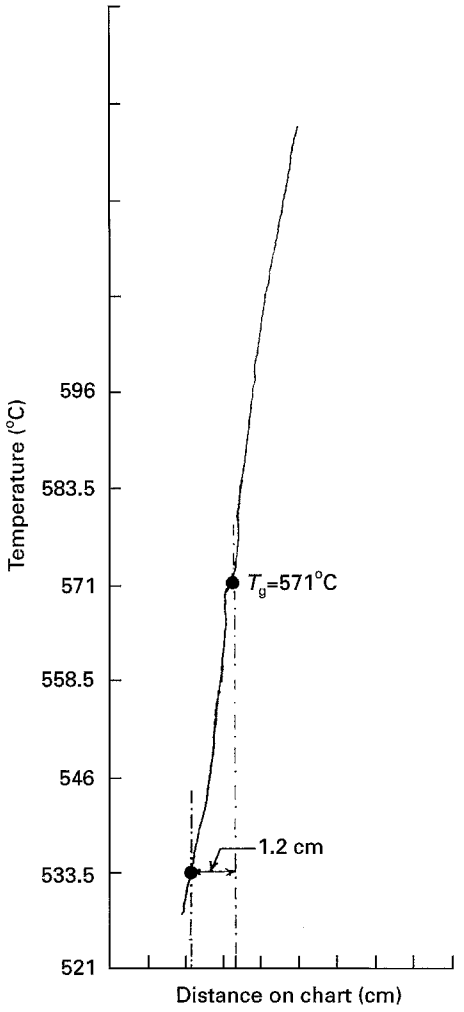


Figure 2 The actual cooling curve for the sample solidified at a growth velocity of 875 μm s^{-1} and calculation of growth temperature.

and how does the silicon phase change its morphology from flake to fibre as the growth velocity increases.

There is considerable experimental evidence to show that flake growth is dominated by the {111} internal twins habit with a low and variable density of {111} internal twins parallel to their flat surface. These twins intersect the interface, creating re-entrant edges and grooves on the growing edge of the flakes. TEM studies have confirmed these and showed that the spacing of twins is greater than the estimated spacing of the intrinsic steps on the {111} surfaces [16]. Consequently, although twining occurs it may not be essential for growth, because growth can occur with less kinetic undercooling by atomic attachment at intrinsic steps. It is concluded that flake growth occurs by intrinsic steps and/or by TPRE growth. Multiple undercooling relationships shown in Fig. 4 probably hold for TPRE growth, because there is likely to be dynamic equilibrium between kinetic undercooling, growth velocity and twin density. As the growth velocity increases the kinetic undercooling for growth of the silicon phase will increase. If this increase is greater than that for the non-faceted aluminium phase, the silicon phase lead will be lost, and growth will occur at a near isothermal interface in a coupled manner with the aluminium phase covering the sides of the silicon phase. If this occurs, the shape of the silicon phase may no longer be controlled by the faceted growth of the silicon Si phase but by over growth by the aluminium phase which can result in an apparent shift to non-faceted growth. This concept has been given by Major and Rutter [17] from observations made on a quench-modified eutectic sample

TABLE I Experimental results of the directionally solidified Al–Si eutectic alloys

G (°C cm^{-1})	Alloy comp. (wt % Si)	Growth velocity (μm s^{-1})	Lead distance (cm)	Growth temp. (°C)	Under cooling (°C)	Interparticle spacing (μm)
122	12.7	28	0.22	575.9	1.3	6.3
		54	0.19	575.4	1.8	4.99
		104	0.155	574.8	2.4	3.83
		152	0.22	573.5	3.7	3.24
		205	0.19	572.5	4.7	2.38
	14.6	308	0.17	572.0	5.2	2.1
		408	0.16	570.0	7.2	–
		505	0.18	566.0	11.2	1.79
		641.8	0.14	575.0	2.2[a]	1.62[b]
		807	0.12	573.87	3.3[a]	1.45[b]
		833	0.4	571.75	5.45[a]	1.35[b]
		875	0.105	571.0	6.2[a]	1.15[b]
76	12.7	28	0.47	575.5	1.7	6.84
		54	0.37	575.0	2.2	5.25
		104	0.31	574.1	3.1	4.2
		152	0.26	572.5	4.7	3.3
	14.7	308	0.22	570.0	7.2	2.56
		505	0.42	563.0	14.2	1.89
		641.8	0.18	573.8	3.4[a]	1.87[b]
		807	0.14	573.0	4.2[a]	1.69[b]
		833	0.13	571.0	6.2[a]	1.6[b]
		875	0.09	570.75	6.45[a]	1.5[b]

[a] Undercooling for quench-modified samples.
[b] Interparticle spacing for quench-modified samples.

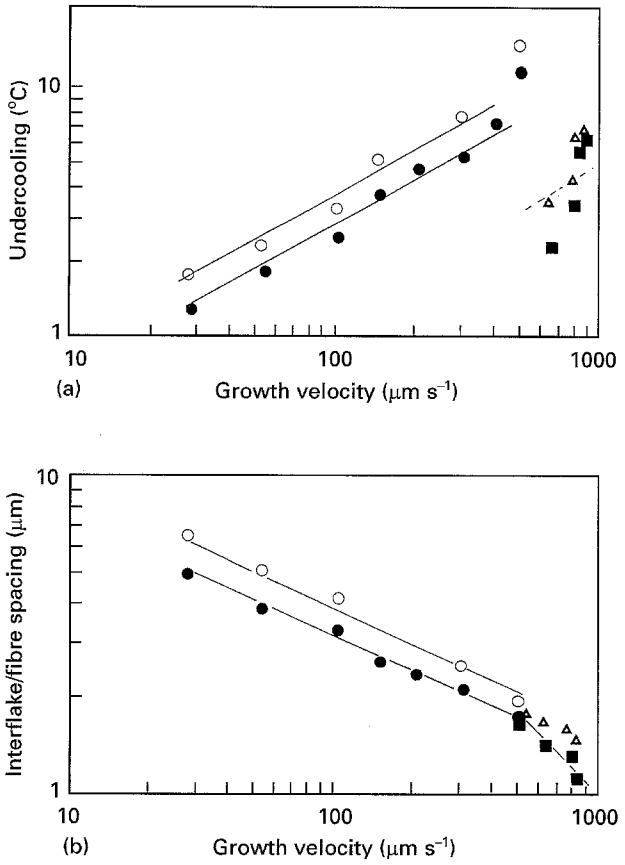


Figure 3 (a) Undercoolings and (b) interparticle spacings, for (●, ○) unmodified and (■, △) quench-modified Al–Si eutectic plotted as function of growth velocity for different temperature gradients: (●, ■) 122°C cm^{-1}, (○, △) 76°C cm^{-1}.

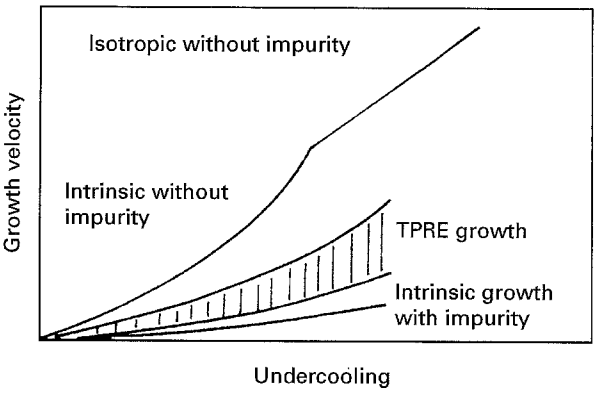


Figure 4 Kinetic undercooling relationships for different silicon phase growth modes.

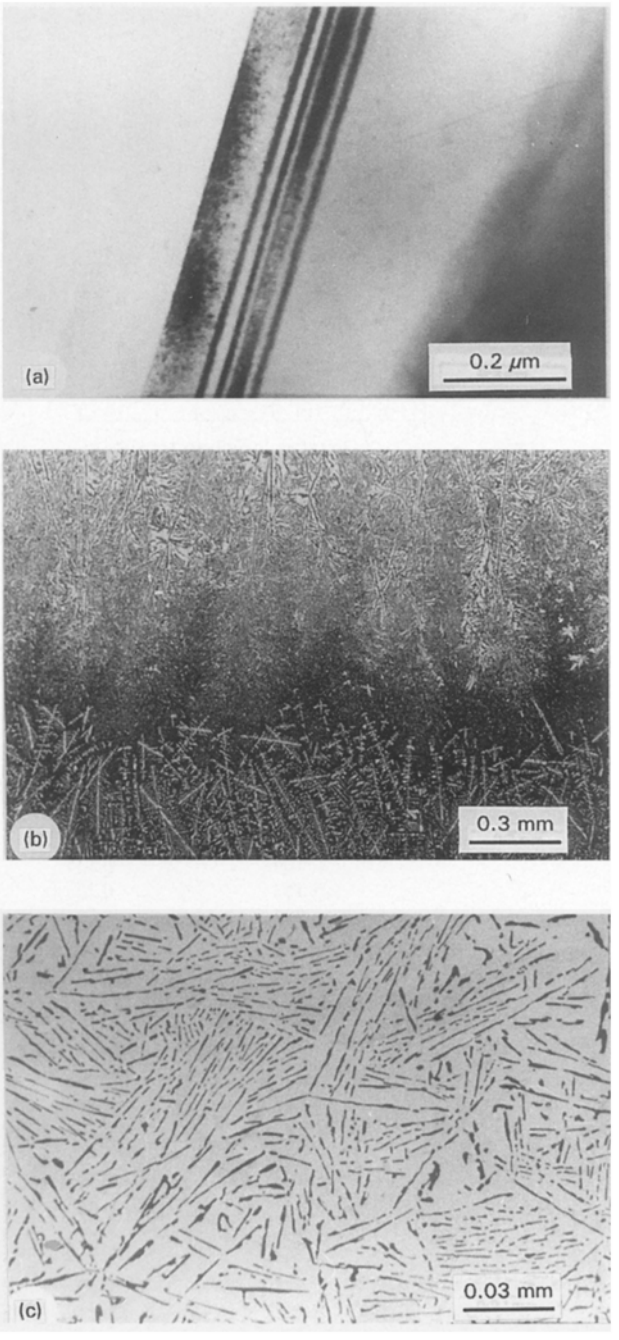
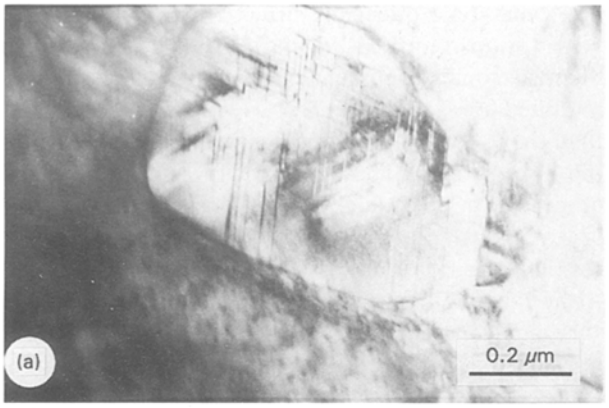
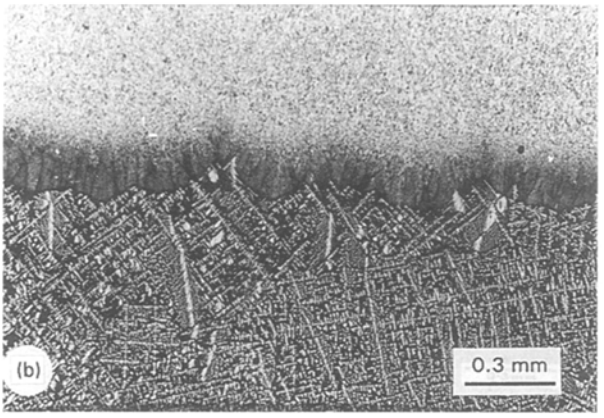


Figure 5 The structural features of unmodified Al–Si eutectic, solidified at 104 μm s^{-1}. (a) Co-zonal twining in the silicon flake. (b) Longitudinal section showing the quenched interface. (c) Transverse section of the above sample.

directionally solidified at low velocities. It was demonstrated that if the aluminium phase covered the adjacent silicon facet plane, right up to the edge of the flake, growth will result in the formation of smoothly covered non-faceted-appearing solid–liquid interphase boundaries, irrespective of how strongly faceted the silicon solid–liquid interface may be. Shu-Zu-Lu and Hellawell [7] have demonstrated that strontium-modified fibres display a faceted surface while the surface of the quench-modified fibres is smooth. All TEM studies reveal that the twin density in the quench-modified eutectic fibres is much less than that in the strontium-modified eutectic fibres. Atasoy [18] has observed that flake silicon exhibits co-zonal twining and strontium-modified fibre has multiple twining, suggesting the importance of the TPRE growth mechanism in these structures. The action of strontium is attributed to the poisoning of the growth sites rather than the prevention of nucleation. TPRE growth of the silicon particle is readily poisoned, whereas the effect on layer growth sites is more gradual, producing holes, branching and dispersed equixed structure as the strontium concentration increases [18]. However, it is reported that the number of twins in the flake decreases as the growth approaches the transition from flake to quenched fibre. As the growth velocity exceeds the transition range, twinning is reduced to a single twin which gradually disappears as the





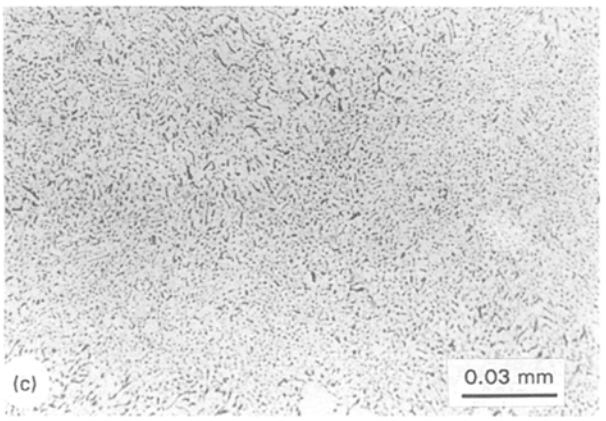
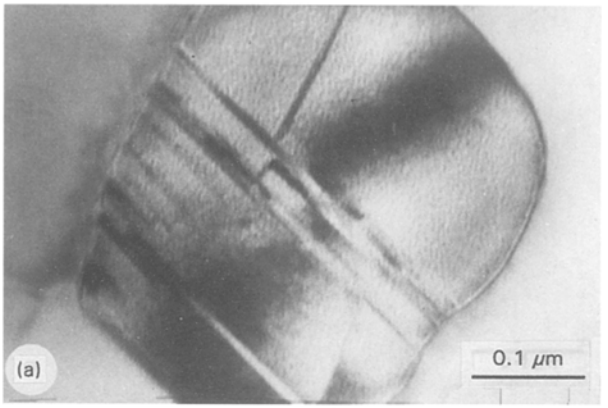
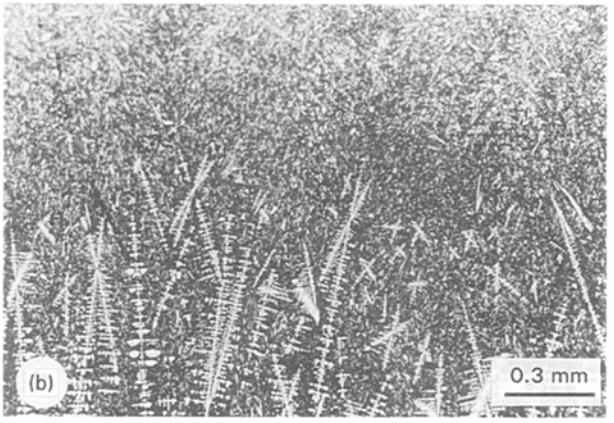


Figure 6 The structural features developed during strontium modification, solidified at 104 μm s^{-1}. (a) Increased twin density in strontium-modified fibres. (b) Longitudinal section showing the quenched interface. (c) Transverse section of the above sample.





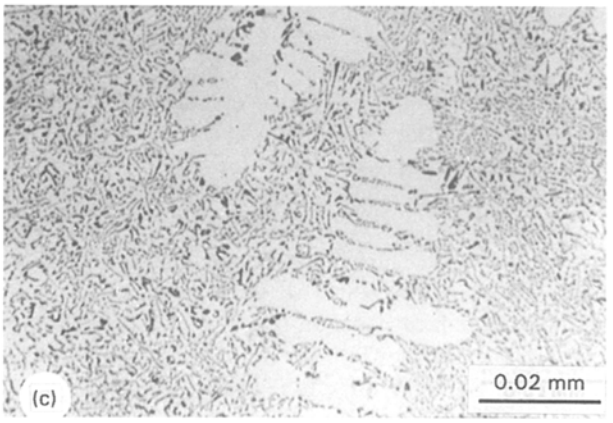


Figure 7 The structural features developed during quench modification, solidified at 807 μm s^{-1}. (a) Decreased twin density in quench-modified fibres. (b) Longitudinal section showing the quenched interface. (c) Transverse section of the above sample.

velocity increases. At high growth velocity, twins were rarely observed.

Investigation by Abdi [19] concluded that even in the strontium-modified alloy, twins can only be seen up to 400 μm s^{-1}. The twining disappears gradually as the velocity increases and twin-free fibres were observed at higher growth velocities. Although detailed TEM studies were not performed in this work, Figs 5–7, obtained for pure, strontium- and quenched-modified alloys, respectively, confirm the findings of Atasoy and Abdi. These observations are consistent with the silicon phase growth mechanism. It is suggested that the silicon phase has undergone a faceted to non-faceted transition associated with the higher growth velocity. Recently, Liu et al [20, 21] have presented a growth model that incorporates a kinetic undercooling term. This is given by

$$\Delta T_k = 0.67\, V^{0.5} G^{-0.2}$$

$$(V = \mu m\, s^{-1},\quad G = {}^{\circ}C\, cm^{-1}) \qquad (4)$$

The value of undercooling for the silicon phase given by this equation is 5.8 °C when growth occurs at a velocity of 505 μm s^{-1} with a temperature gradient of 122 °C cm^{-1} in the liquid. This undercooling is of the order of that associated with a transition to non-faceted growth. The drop in undercooling and the

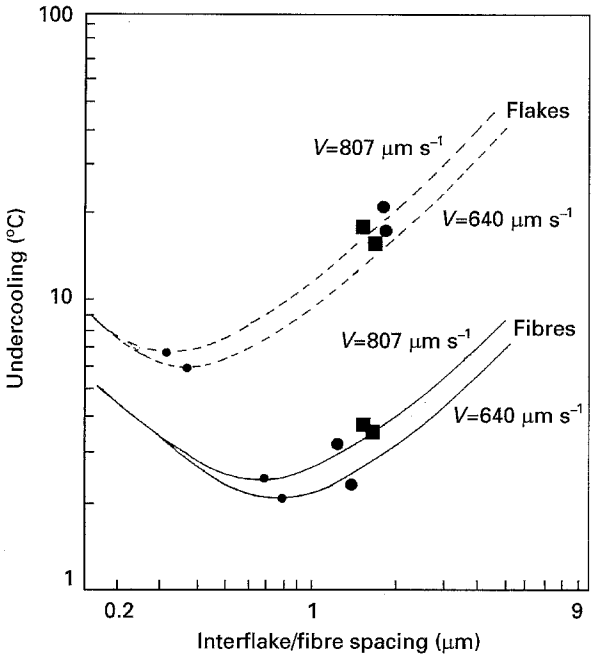


Figure 8 Growth curves for (– – –) flake and (——) fibrous silicon morphology for the two growth velocities showing the displacement of the operative growth points from the extremum points for unmodified and quench-modified alloys. (●) $G = 122\,°C\,cm^{-1}$, (■) $G = 76\,°C\,cm^{-1}$.

change in the λ–V relationship coincides with the transition from flake to fibrous growth. Atasoy has reported that quench-modified eutectic grows at a lower undercooling than impurity-modified eutectic. If a value 5.8° is accepted for the silicon phase kinetic undercooling, as the total interface undercooling is less than this value, it is likely that the silicon phase has undergone a faceted–non-faceted transition.

The kinetic measurements may be analysed to show that they are consistent with those expected from an NF–NF system rather than those of an NF–F system. Fig. 8 shows growth curves for flake growth at velocities of 640 and 807 $\mu m\,s^{-1}$ calculated using the constant defined by Grugel and Kurz [22]. The expected operative growth points are indicated in the curves. The growth curves for fibrous structure also included in the same figure calculated using a constant due to Hogan and Song [23] namely $K_1 = 2.17 \times 10^{-3}\,°C\,s\,\mu m^{-2}$ and $K_2 = 0.214\,°C\,\mu m^{-1}$. The operative growth points for quench-modified fibres bears little relationship to the growth curve for flake. The fibre kinetics conform with the established criterion for normal eutectic growth, that is just to the right of the extremum point.

Shamsuzzoha and Hogan [12] have argued that quench-modified eutectic silicon consists of a mixture of short flakes and retains the original features of unmodified flake eutectic structure. In contrast to the arguments, it is shown in this work that there is a sudden change in ΔT–V and λ–V relationship. In addition, the operative points are approaching the extremum condition of the curves. It is also evident that quench-modified fibres are non-faceted. The TEM study reveals that the twin density decreases and even some quenched fibres are twin free. These observations required the clarification of Hogan and Shamsuzzoha's arguments. If, however, the quench-modified fibres retain the features of unmodified flake, then they should follow the characteristics defined for the flake growth. The high growth rate in quenched modification retards the growth anisotropy of the fastest growing face of the silicon crystals. This induces the transition from irregular to normal behaviour. Although impurity- and quench–modified fibres are very similar with regard to the morphology and λ–V relationship, however, the two have entirely different growth modes.

4. Conclusions

1. The structural transition from flake to quench-modified fibrous structure is accompanied by a drop in undercooling. This is associated with transition of faceted silicon phase to non-faceted behaviour.

2. The λ–V relationship obtained for quench-modified fibrous growth ($\lambda^{1.85} V$ = constant) is very close to that anticipated for a normal eutectic. The operative growth points for quench-modified structure follow the established criterion for normal eutectic growth lying just to the right of the extremum points. These observations suggest that the structural transition from flake to fibrous growth closely follows the features of a normal eutectic, rather than the flake structure.

Acknowledgement

This work was performed at the Material Science Centre, University of Manchester. The authors thank Professor F. R. Sale for the provision of laboratory facilities and the Government of Pakistan for financial assistance. The authors also thank Dr Anwar-ul-Haq and Dr A.Q. Khan for their keen interest in the publication of this paper.

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Received 12 May
and accepted 1 December 1995