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Microstructural Characterization of Rapidly Solidified Al–Si Alloys*

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Abstract

Al–Si alloys of composition varying from 9% Si to 30% Si have been rapidly solidified by melt spinning. Alloys up to 25% Si showed either fine or coarse microstructure depending on the thickness of the ribbon. Primary silicon phase was not observed in either case. The structure consisted of primary α-Al phase, outlined by a very fine duplex structure in thin ribbons, whereas discrete silicon crystals decorated the α-Al phase in thick ribbons. At 30% Si composition primary silicon phase formed abundantly in the form of idiomorphic crystals. In this alloy, eutectic grains, exhibiting an almost regular morphology, were also observed.

The decomposition process of the alloys was followed using differential scanning calorimetry and a correlation was observed between the thermal response and the microstructure of the samples as a function of their thickness and composition.

1. Introduction

Various rapid solidification techniques have been applied to Al–Si alloys of a wide range of compositions. Among them splat quenching [1, 2] melt spinning [3, 4] and atomization [5] resulted in an increase in the solid solubility of silicon in α-Al without forming either intermetallic compounds or amorphous phases. However, the presence of an amorphous phase has been reported in Al–12%Si, produced by the planar flow casting technique [6]. Since the cooling rate varies from one technique to another and also with the distance solidified within the sample, different microstructures may be obtained.

In the present study, the microstructural characteristics of melt-spun Al–Si alloys have been revealed by examining the overall and local solidification morphology of the ribbons and following the thermal response of the samples by differential scanning calorimetry (DSC).

2. Experiments

Alloys of various silicon concentrations from 9% to 30% Si (9, 12, 16, 20, 25 and 30% Si) were melt spun by ejecting the melt at 0.07 MPa argon pressure through an orifice of 0.8 mm diameter onto a copper drum rotating at a linear speed of about 20 m s^{-1}. The ejected liquid alloys were formed into continuous ribbons with more or less uniform thickness. However, the thickness of the ribbons varied from about 25 μm for thin ribbons to about 50 μm for thick ribbons.

The overall solidification pattern of the ribbons was examined across their longitudinal sections in light and scanning electron microscope after etching with Keller's reagent. For transmission electron microscopy (TEM), samples were prepared by ion-beam thinning. Some fragments of ribbons with perforated areas were observed directly by TEM in the as-received condition. Some of the samples run in the DSC were also examined in the TEM. TEM work was carried out in Philips EM 300 and 400 microscopes operated at 100 kV and 120 kV respectively. EM 400 was also used for the STEM analysis at 100 kV for the determination of silicon concentration.

In order to observe the decomposition of the metastable α-Al, samples weighing about 6 mg were run in a Perkin Elmer DSC-2 differential scanning calorimeter at 20 K min^{-1} scanning rate.

3. Results and discussion

Microstructural examination of the ribbons did not show primary silicon phase up to 30% Si. A fine microstructure consisting of a columnar zone at the substrate side and an equiaxed zone at the top was observed in thin ribbons. In relatively thick ribbons, however, the microstructure was too coarse to see a dendritic pattern, and primary α-Al was outlined by large silicon crystals. At 30% Si, a copious precipitation of primary silicon occurred throughout the section. While the SEM study gave an overall picture of the solidification pattern of the alloys, more information about the microstructure was obtained by examining the ribbons in the TEM either after thinning or

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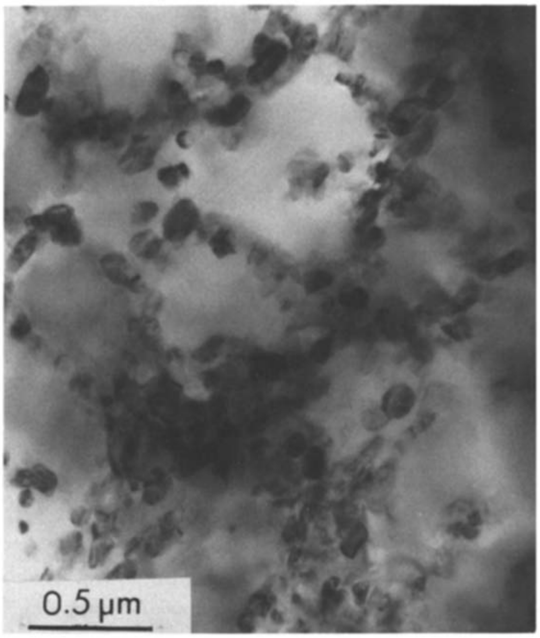

Fig. 1. TEM micrograph showing free silicon crystals outlining the α-Al in a ribbon of Al–12%Si 50 µm thick.

in the as-received condition. Depending upon the thickness of the ribbon, the intercellular region was either decorated by a network of individual silicon crystals, or did not reveal any free silicon precipitates (see Figs. 1 and 2). The average cell size was found to be less than 0.5 µm, suggesting a cooling rate of approximately 10^6 K s^{-1} [7]. In the electron-transparent areas of the as-received ribbons the cells were elongated and were all lying in the same orientation according the diffraction pattern shown in Fig. 3.

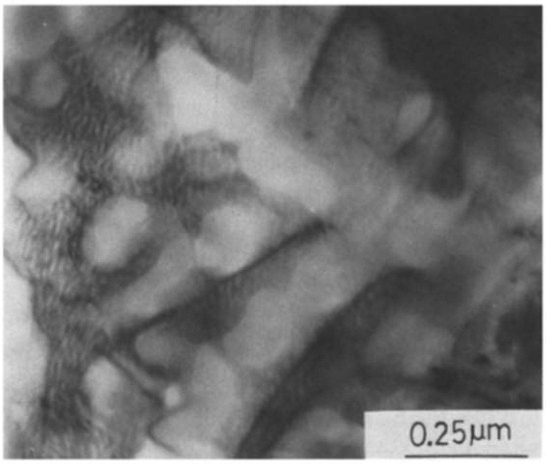

Fig. 2. TEM micrograph showing the duplex structure within the intercellular region in a ribbon of Al–25%Si 25 µm thick.

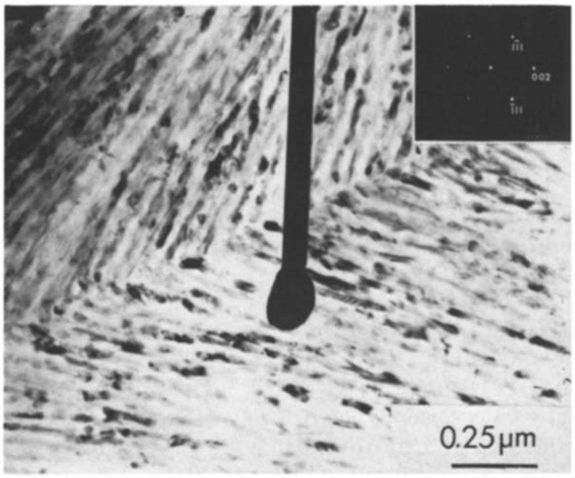

Fig. 3. Elongated aluminum cells and the corresponding diffraction pattern from the area indicated with the beam stop (not thinned).

In thick ribbons, the silicon precipitates were coarse enough to see well defined facets as well as twins inside the precipitates. The intercellular region is the last part of the alloy to solidify following a eutectic reaction. However, the polyhedral shape of the crystals was not a typical eutectic silicon morphology expected at such a high cooling rate. In thinner samples, however, the duplex structure of the intercellular region suggests that silicon and aluminum grew in a coupled manner. A possible explanation of this result, consistent with the quench modification of silicon in Al–Si alloys frozen less rapidly by conventional chill casting, would be that the duplex structure arose directly from the melt by rapid cooling, whereas the discrete faceted silicon precipitates lying in the cell boundaries in thick samples resulted from post solidification annealing. In fact, the microstructure of the thin ribbons run in the DSC appeared similar to that of the thick samples. In the electron transparent region of the as-received samples a featureless zone has been observed, from which α-Al cells seem to originate, as evidence of the potential nucleation from this zone. The diffraction pattern indicated the amorphous nature of this zone. The featureless zone with radiating α-Al cells and the diffraction pattern are given in Fig. 4. After heating the sample in the DSC up to 770 K, no transformation was seen to have occurred in this amorphous phase. It is quite likely that the stream of molten alloy formed an oxide layer before or during hitting the drum. This oxide layer eventually acted as a nucleation agent for α-Al primaries.

Although a copious precipitation of idiomorphic silicon was observed across the entire section of 30% Si containing ribbon, in the TEM study silicon crystals were also seen occasionally in the 25% Si alloy. Silicon crystals with a "star-shaped" morphology contained twins and appeared to nucleate the α-Al

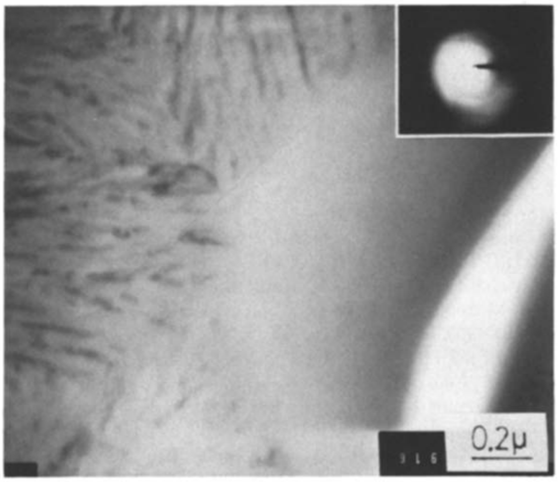

Fig. 4. Featureless zone and the radiating aluminum cells in the electron-transparent region of the ribbon. The diffraction pattern indicates the zone to be an amorphous phase (not thinned).

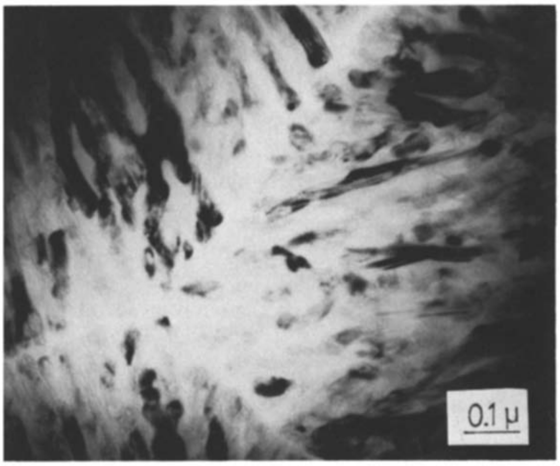

Fig. 5. Eutectic grains in Al–35%Si ribbon (not thinned).

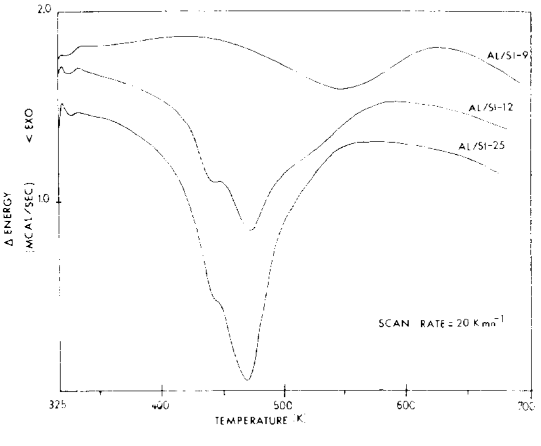

Fig. 6. Thermal behavior of thin ribbons of various composition in DSC.

phase. In the as-received ribbon of the 30% Si alloy, a large area of eutectic was found. The eutectic microstructure was almost regular and silicon phase showed branching and frequent twinning as seen in Fig. 5. This indicates that the eutectic in Al–Si can be extended by rapid solidification from the equilibrium 12% Si up to 30% Si. The STEM analysis results obtained in the 20% Si alloy is in good agreement with this observation as the silicon concentration was found to be about 7% and 30% inside cells and at cell walls respectively.

The decomposition of the samples in the DSC was accompanied by an exothermic reaction. Thin samples at and above 12% Si showed a shoulder prior to their peak which appeared at about 470 K at a scan rate of 20 K $\min^{-1}$ (see Fig. 6). The presence of a shoulder in the DSC trace apparently resulted from the two overlapping peaks indicating that the decomposition proceeded in two steps. Since in Al–Si alloys the supersaturated α-Al phase decomposes into two equilibrium phases (α-Al and silicon) without giving rise to an intermediate metastable phase, the first step should not be attributed to the precipitation of a non-equilibrium phase. In passing it should be pointed out that earlier workers [4, 5] did not observe a shoulder in their alloys. However, they reported the existence of a small peak appearing at 650 K. No indication of such a peak was found in any of the samples examined in this study. However, the DSC curves of the thick ribbons (regardless of their composition) as well as those of thin ribbons of hypoeutectic composition showed up at higher temperatures as a shallow peak without forming a shoulder as shown in Fig. 6.

The results presented so far permit us to correlate the thermal response of the ribbons with their microstructures. In thin ribbons, the α-Al phase of the eutectic decomposed first because the diffusion distance was much shorter than the cell size, and this was manifested by the appearance of a shoulder in the DSC trace.

4. Conclusions

Al–Si melt-spun ribbons up to 25% Si with 25–30 µm thickness displayed a fine solidification pattern with a distinct transition from cellular to equiaxed dendritic structure. A fine duplex structure outlined the primary α-Al phase. Thicker ribbons of about 50 µm showed a rather coarse structure with free idiomorphic silicon crystals precipitated along the grain boundaries of the α-Al phase. Those observations are correlated with the thermal response of the ribbons by DSC. According to the shape of the DSC traces, in thick samples decomposition took place by coarsening of the pre-existent silicon crystals which are believed to be formed by a post-solidification annealing mechanism.

Primary silicon formation was first observed at 25% Si and at 30% Si copious primary silicon precipitation took place.

Rapid solidification shifted the eutectic point toward 30% Si composition. The eutectic grains showed more or less regular morphology, with the silicon phase forming some branching and frequent twinning.

During ejection the melt was oxidized and the oxide layer eventually acted as a nucleation site for α-Al phase.

Acknowledgments

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