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Effect of solute content on the grain refinement of binary alloys

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Data are presented for the grain refining of Al–Si and Pb–Sb alloy systems. These show a minimum grain size near the maximum solubility limit. An explanation in terms of the solidification interval is presented. In general, the optimum grain refining is predicted to occur at the solubility limit since it is at this concentration that the solidification times are longest.

1. Introduction

Grain refinement of cast and wrought alloys is very important in improving the casting behaviour and metallurgical properties of the product. Previous studies [1–5] dealt with the correlation between the grain refining process and the nucleation agent, the morphology of the master alloy, the casting parameters and the impurities contained in the alloy. Nevertheless, the effect of solute content on grain refining efficiency has not been fully explained. In the present work, the relationship between grain refining efficiency and solute concentration in the binary alloys Pb–Sb and Al–Si has been investigated using different nucleation agents.

2. Experimental details

2.1. Material

Commercially pure lead (99.98%) and pure antimony (99.999%) were used to prepare the Pb–Sb alloy. Pb–Sb alloy was grain refined by using either 0.03 wt % Ag_2Se or a combination of 0.02 wt % beryllium, 0.02 wt % tin and 0.05 wt % arsenic. The grain refining effect of this combination on Pb–Sb alloys was reported in an earlier study [1].

Commercially pure AlSi13 was diluted with 99.7 aluminium to prepare Al–Si alloys having different silicon contents. For the grain refinement of the Al–Si alloys, 0.2 wt % additions of AlTi5B1 (5/1 TiBAl) master alloy were used.

2.2. Procedure

2.2.1. Grain refining tests

2.2.1.1. Pb–Sb alloys. About 100 g of each alloy composition was melted in an iron crucible and superheated to 500° C. After adding the grain refiner the melt was held at this temperature for 20 min and then poured into an iron mould preheated to 150° C. Before pouring, the melt was stirred with an iron rod. The cast samples were sectioned longitudinally and these sections were metallographically prepared and etched to reveal the grain boundaries. The grain size was determined using the line intercept method.

2.2.1.2. Al–Si alloys. About 100 g of each alloy composition was melted in an alumina crucible and superheated to 720° C. After adding the grain refiner the melt was held for about 10 min at 720° C and poured either into a water-cooled iron mould or, in order to obtain a slower cooling rate, into a graphite mould. Before pouring, the melt was stirred with a coated iron rod.

To compare the grain refining results at different holding times, a set of experiments was carried out by LSM using 0.1 wt % 5/1 TiBAl master alloy. Aluminium was melted in a refractory-washed cast iron pot and AlSi added to adjust the charge to the required silicon content. Total charge weight was 10 kg. The charge was heated to 720° C and the 5/1 TiBAl master alloy was added. The melt was stirred for 30 sec, after which no further stirring took place. Samples were taken in preheated conical steel moulds and quenched: sampling times were between 1 and 60 min. The sample was sectioned and polished parallel to the base at about 35 mm from the apex. Grain sizes were measured by an intercept count method at the centre of the prepared sample. A full description of the test procedure has been published [6].

3. Observations

3.1. Effect of antimony content on the grain size of Pb–Sb alloy

Fig. 1 shows that, when using Ag_2Se as a grain refiner, the grain size of the alloy was reduced as the antimony content increased up to 1.5 wt %. From 1.5 wt % to 4 wt % Sb there was no significant change in the grain size of the alloy. On increasing the antimony content above 4 wt % there was a rapid linear increase in the grain size.

In all cases, the microstructure shows primary lead dendrites enveloped by lead antimony eutectic on the grain and cell boundaries (Fig. 2).

The simultaneous addition of beryllium, tin and arsenic as a grain refiner brought about similar behaviour to that described above, although the grains were much finer than those found when adding Ag_2Se

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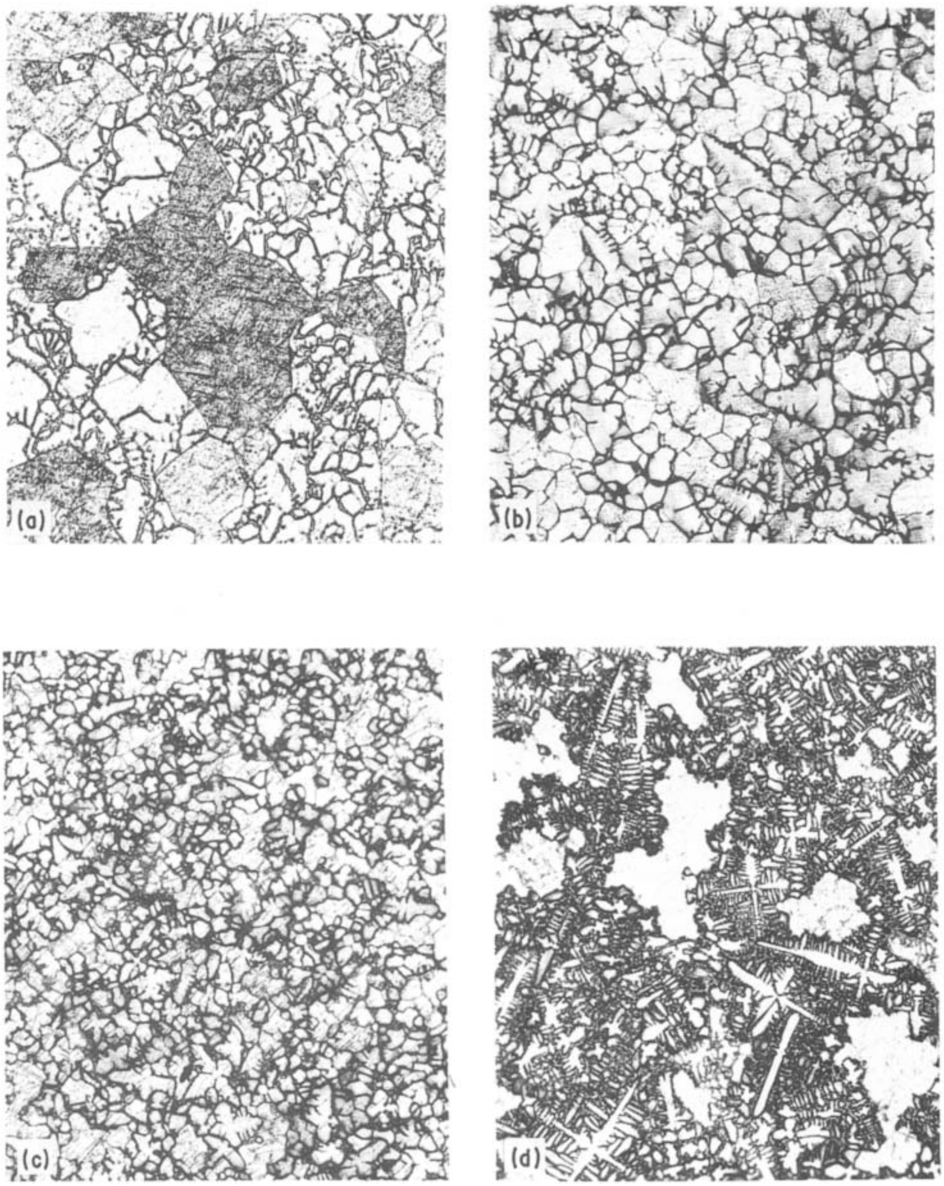

Figure 1 Microstructure of the alloy PbSbx, grain refined with 0.03 wt % Ag_2Se (× 50 : 1) (a) x = 0.15 wt %, (b) x = 1 wt %, (c) x = 4 wt %, (d) x = 6 wt %.

Figure 2 Microstructure of the alloy PbSb5 (× 1000 : 1).

(Fig. 3). The results presented in Figs 1 and 3 are shown graphically in Fig. 4.

3.2. Effect of silicon content on the grain size of Al–Si alloy

A master alloy addition of 0.2 wt % 5/1 TiBAl was made to the melt which was then poured into a water-cooled mould. The grain size decreased when up to 0.4 wt % silicon was present. At 0.5 wt % silicon content a sudden increase in the grain size was observed (Fig. 5). From 0.5 wt % up to about 3 wt % silicon the grain size remained constant. The addition of more than 3 wt % silicon caused a further rapid increase in the grain size.

By pouring the melt into a graphite mould to obtain a lower cooling rate similar behaviour to that described above was observed (Fig. 6). In all cases the microstructure showed a primary phase of aluminium solid

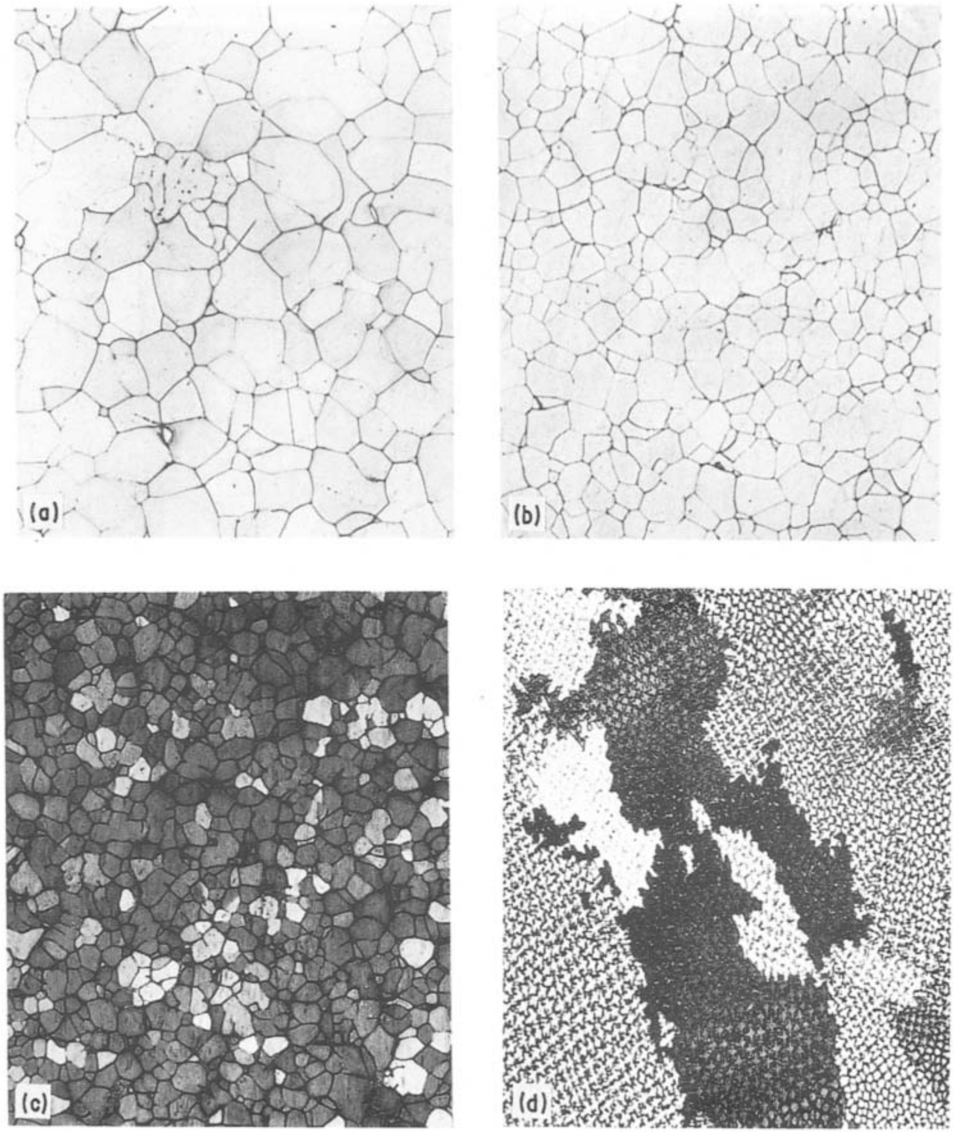

Figure 3 Microstructure of the alloy PbSbx, grain refined with 0.02 wt % Be + 0.05 wt % As + 0.02 wt % Sn (× 100 : 1) (a) x = 0.3 wt %, (b) x = 0.5 wt %, (c) x = 4.0 wt %, (d) x = 6.0 wt %.

solution enveloped by an aluminium–silicon eutectic phase on the grain and cell boundaries. Fig. 7 presents the data in Fig. 6 in graphical form.

Fig. 8 shows that at different holding times a minimum grain size was still observed at 0.4 wt % Si. The grain size became coarser with higher silicon contents at increased holding times.

4. Discussion

The binary Pb–Sb system shows a maximum solubility limit of 3.5 wt % antimony at a eutectic temperature of 251° C. The solubility of lead in antimony has not been determined [7]. The binary Al–Si system shows a maximum solubility limit of 1.65 wt % silicon in aluminium at an eutectic temperature of 577° C.

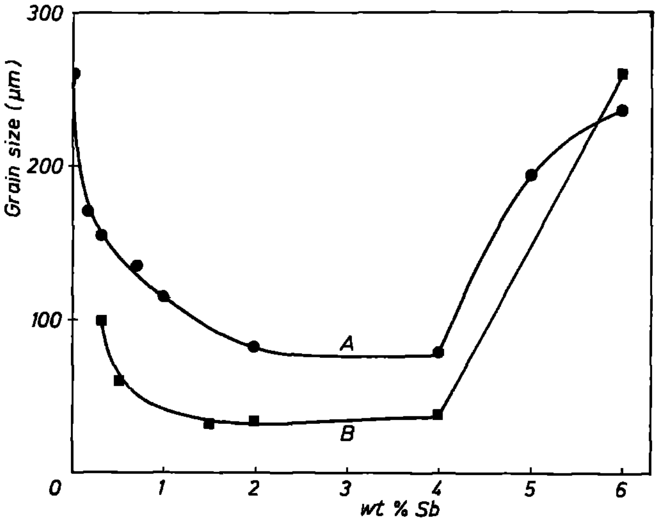

Figure 4 Effect of antimony on the grain size of the grain refined alloy PbSbx. (a) Grain refined with Ag_2Se. (b) Grain refined with Be + As + Sn.

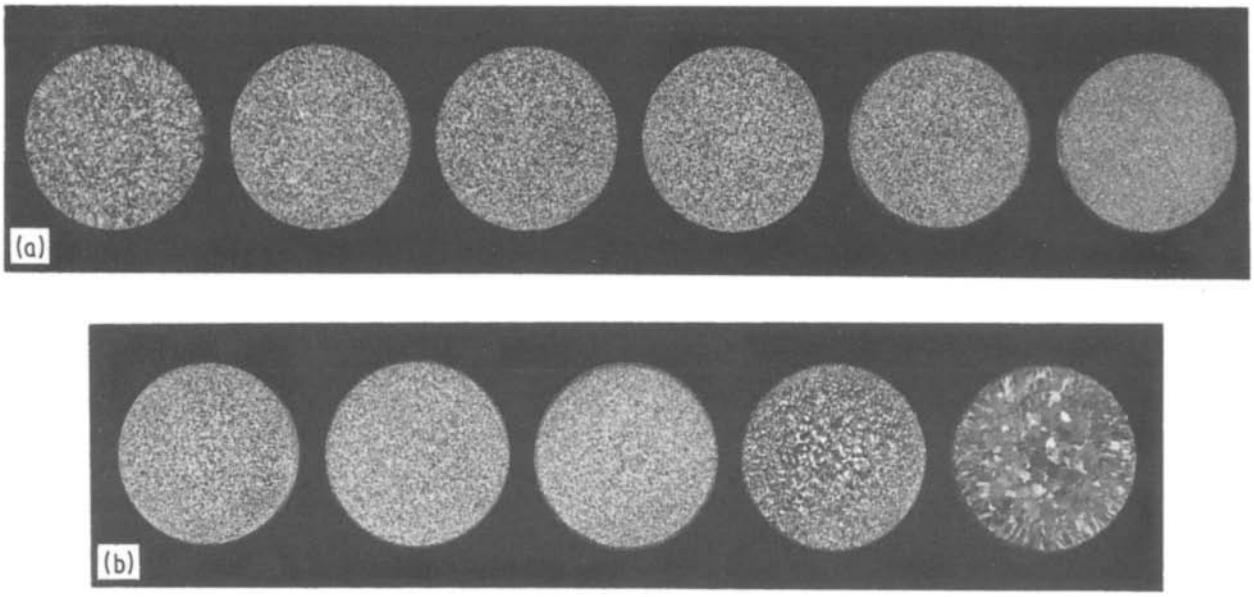

Figure 5 Macrostructure of the alloy AlSix, grain refined with 0.2 wt % AlTi5B1 master alloy, water-cooled mould (× 0.57 : 1). From left to right (a) x = 0.1, 0.2, 0.3, 0.4, 0.5 and 1 wt %, (b) x = 1.6, 2.0, 3.0, 5.0 and 7 wt %.

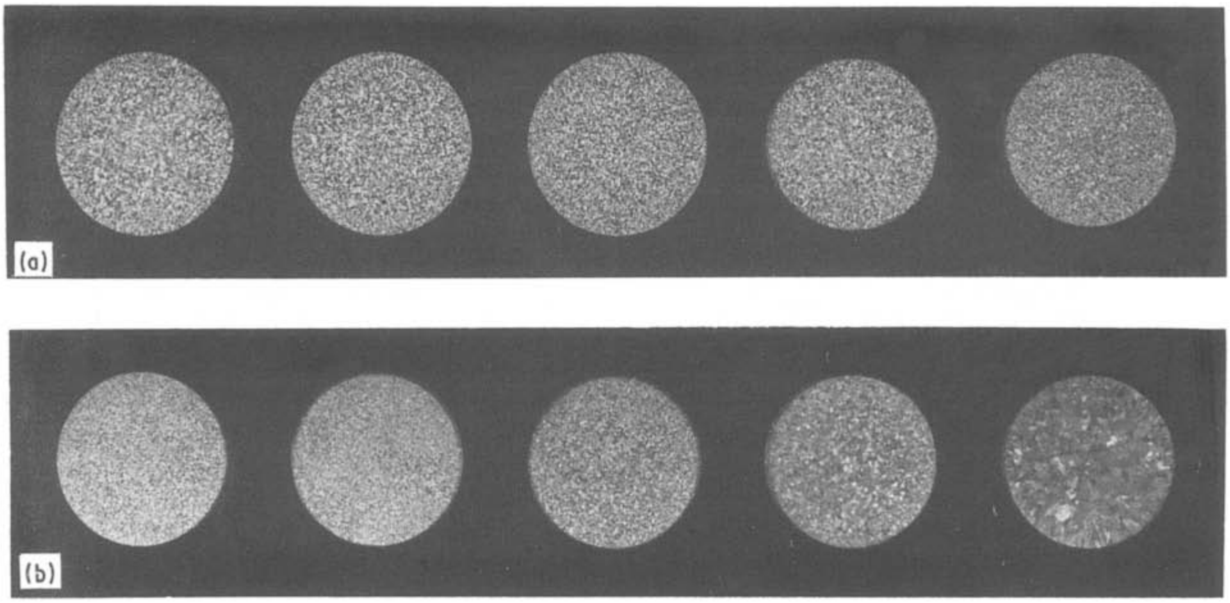

Figure 6 As Fig. 5, but cast into a graphite mould (× 0.7 : 1). From left to right (a) 0.1, 0.2, 0.4, 0.5 and 1 wt %, (b) 1.6, 2.0, 3.0, 5.0 and 7.0 wt %.

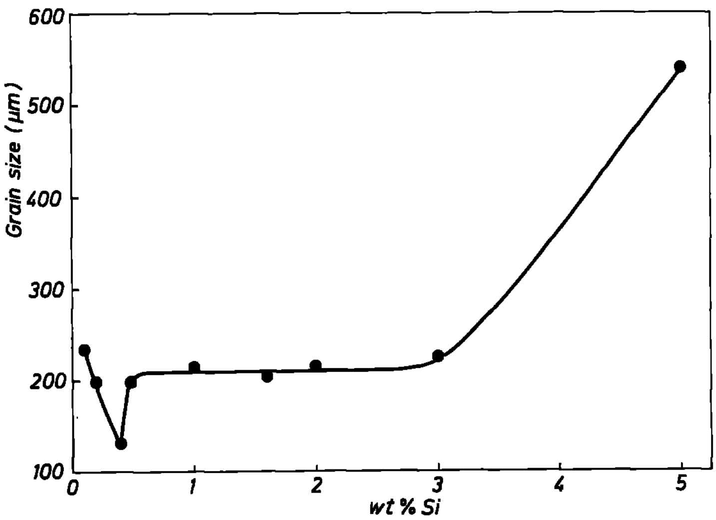

Figure 7 Effect of silicon content on the grain size of the grain-refined alloy AlSix–0.2 wt % AlTi5B1, holding time = 10 min.

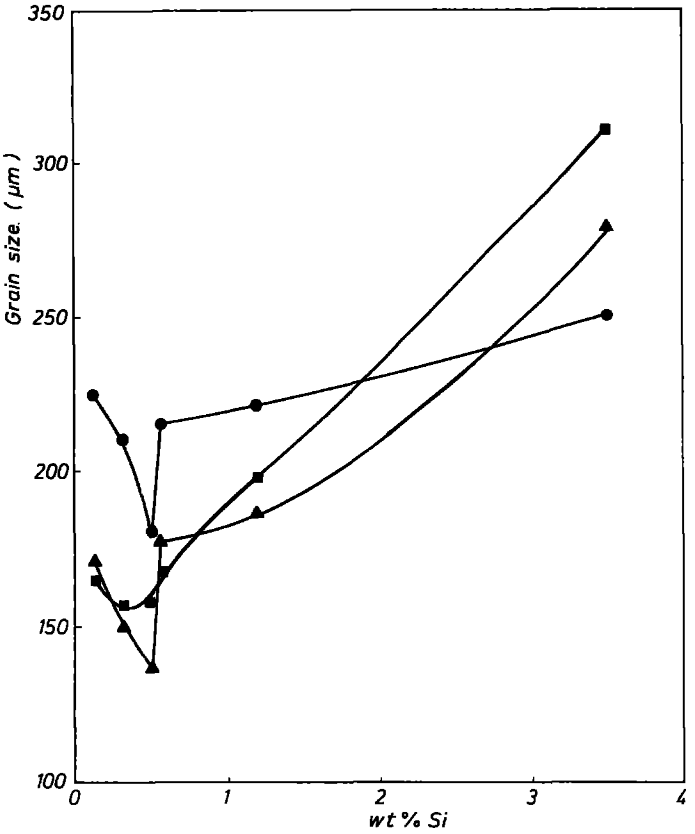

Figure 8 Effects of silicon content on the grain size of the grain refined alloy AlSi*x*–0.1 wt % AlTi5B1, at different holding times: (●) 1 min, (▲) 10 min, (■) 60 min.

There is no information about the solubility of aluminium in silicon [7]. The shapes of the two equilibrium phase diagrams are similar.

Fig. 4 shows that 2 to 4 wt % Sb produced an optimum grain refining efficiency in the Pb–Sb system, whichever grain refiner was used. Ag_2Se was less efficient than other grain refiners. In the case of the Al–Si system, optimum grain refining was achieved at about 0.4 wt % silicon regardless of the cooling rate and holding time. In both systems optimum grain refining was observed at a concentration close to the maximum solubility limit of the solute element.

Under the conditions used in the experiments, there will be deviations from equilibrium conditions. This is expected to lead, among other things, to the maximum solubility limit occurring at lower concentrations of the alloying element. This shift may be due to:

(i) non-equilibrium cooling conditions;

(ii) impurities introduced by the use of commercially pure materials;

(iii) the introduction of solute impurities with the grain refiner: titanium to the Al–Si alloy, Ag_2Se or beryllium, arsenic and tin to the Pb–Sb alloys.

Experiments have shown that the cast structure of both Pb–Sb and Al–Si alloys without grain refiner has a minimum grain size near the maximum solubility limit (Fig. 9). Furthermore, the grain refined specimens show a minimum grain size near the maximum solubility limit. This minimum grain size is substantially reduced by the introduction of the grain refining agent.

As commercial purity materials were used, we can be confident that heterogeneous nucleation occurs, and ignore any possibility that homogenous nucleation takes place. Heterogeneous nucleation takes place on impurities functioning as nucleation centres, or on grain refiners forming nucleation centres.

Earlier studies [8, 9] have suggested that a certain time delay is needed for nuclei to become effective before the melt can crystallize on them. After this delay the growth process can proceed unhindered. The time delay t is given as follows:

$$t = K_0 \frac{kTS^3V^2}{\Delta\mu^4 D_k}$$

where K_0 is a constant, T the absolute temperature, k the Boltzmann constant, D_k the diffusion flux of all atom species in the melt to the nucleus surface, S the

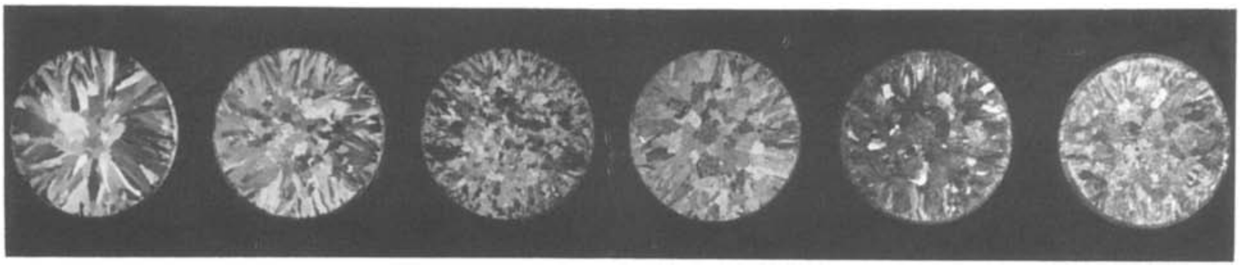

Figure 9 Macrostructure of the alloys AlSi*x* without grain refiner (× 0.66 : 1). From left to right, x = 0.5, 1.0, 1.6, 2.0, 5.0 and 7.0 wt %.

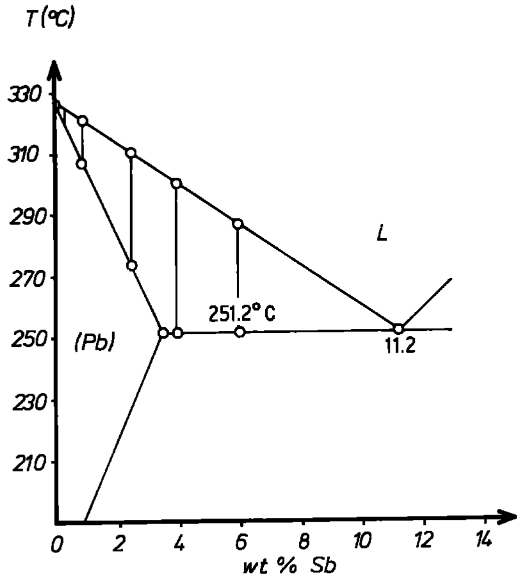

Figure 10 Part of Pb–Sb equilibrium diagram.

specific surface energy, $\Delta\mu$ the difference between chemical potential of the melt and the nucleus, and V the molecular volume of the nucleus.

At a given cooling rate, with increasing temperature difference between liquidus and solidus, there will be increased solidification time. The larger the time delay (t) available, the greater will be the proportion of potential nuclei which can function as crystallization centres in the melt. Those nuclei which do not have the opportunity to function as crystallization centres may well be pushed ahead of the growth front and remain in the grain and cell boundaries.

In both the systems under consideration the largest solidification interval exists around the maximum solubility limit as shown in Fig. 10 for Pb–Sb alloy. Furthermore, it is known that by adding grain refiner less undercooling is required for the solidification process to start. Similar data for Al–Si alloys is readily available [7].

The growth in the grain size with increasing solute content beyond the solubility limit can be explained as follows:

(a) With increasing solute content the solidification time (solidification interval) decreases. Consequently, there is a smaller proportion of potential nuclei which can function as crystallization centres.

(b) In both the systems investigated (Al–Si and Pb–Sb) the material to be refined is the α primary phase. With increasing solute content beyond the maximum solubility limit, the volume fraction of α phase decreases by eutectic precipitation. As a result the entire microstucture becomes coarser.

This analysis suggests that where other conditions are constant, the longest solidification time, associated with the maximum solubility limit, will lead to optimum grain refining.

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