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Structure refinement of Pb–6Sb alloy

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Structure refinement of Pb–6Sb alloy was investigated experimentally using two techniques: first by adding a grain refiner of 0.02% Ag_2Se to the liquid alloy, and second by introducing mechanical stirring of the molten alloy during its cooling from above the melting point to a temperature in the mushy zone. Four different stirring speeds of 400, 700, 900 and 1100 r.p.m. were used. The alloy was allowed to cool to room temperature at different cooling rates. Cooling rate, solidification rate, grain size and primary particle size were measured.

1. Introduction

Grain refinement of most alloys is important in improving the properties of the cast metal. Fewer hot tears can be obtained, and the mechanical properties can be considerably improved by grain refinement [1–3]. Previous work [2–5], dealing with a lead–antimony binary alloy, showed a correlation between the grain refinement process and solute content, the nucleation agent, the casting parameters and the morphology of the master alloy. Earlier work [6] showed the effect of solute content (Sb) on the grain refinement of Pb–Sb alloys through the addition of two types of grain refiner. The alloy which had 6 wt % Sb showed the same grain size of primary phase as the pure lead. In the present work, the structure refinement of Pb–6Sb alloy is achieved by introducing mechanical stirring during its solidification.

2. Experimental procedure

2.1. Grain refinement of Pb–6 wt % Sb alloy using Ag_2Se

Pb–6Sb alloy was prepared from 99.99 wt % Pb and 99.999 wt % Sb in a steel crucible. 1250 g of the alloy was melted and superheated to 440 °C using an electrical resistance furnace. Two sets of experiments were carried out in order to investigate the structure of the cast alloy and measure the temperature history during its solidification. In the first set of experiments the melt was poured into steel moulds preheated to 220 °C without any addition. In the second set 0.02 wt % Ag_2Se was added to the melt, which was then stirred manually by a steel rod for 10 s, isothermally held for 10 min and then poured into the same steel mould, which were preheated to 220 °C. Four steel moulds having different diameters of 18, 25, 32 and 40 mm with the same height and wall thickness of 36 and 4 mm, respectively, were used in the two sets of experiments in order to vary the solidification rate of the alloy ingot. In each experiment a Chromel–Alumel thermocouple was located before pouring in the centre of each mould at a certain level as shown in Fig. 1, and the temperature–time curve was plotted using a chart recorder. A sample slice was taken from each ingot at the same level of the thermocouple.

2.2. Stirring of the alloy in its mushy zone

The alloy was melted and superheated to 440 °C in a 50 mm inner diameter steel crucible using an electrical resistance furnace, then transported to its place in the stir-cast equipment shown in Fig. 2. Stirring was introduced in the alloy melt using a steel stirrer with three wings of 30 mm outer diameter. The stirrer was fixed in the spindle of a variable-speed d.c. motor, and the stirring speeds used in the experiments were 400, 700, 900 and 1100 r.p.m. The crucible was fixed between refractory blocks at the equipment base. Stirring of the melt was started while the alloy was left to cool with a primary cooling rate of 37 °C min^{-1}. When a predetermined temperature within the liquid–solid range was reached (265 °C), stirring was

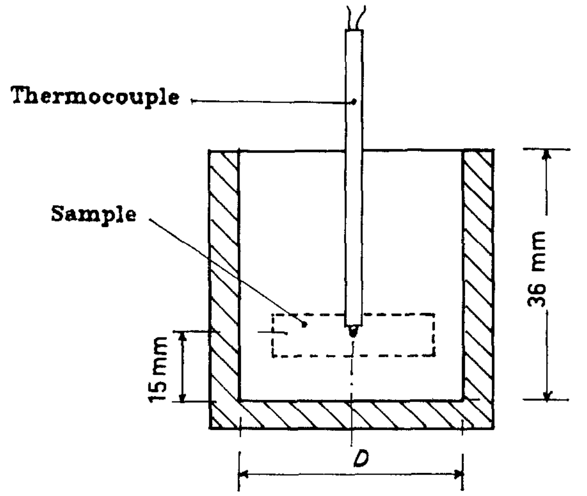

Figure 1 Level of thermocouple and microstructure sample in the steel mould of four different diameters (*D*) of 18, 25, 32 and 40 mm.

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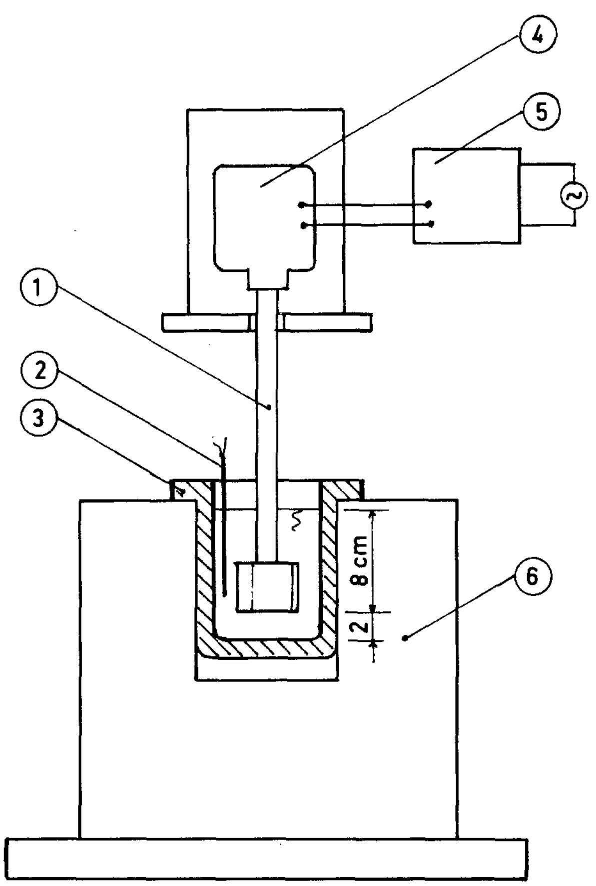

Figure 2 Schematic drawing of the stirring apparatus: (1) steel stirrer, (2) thermocouple, (3) steel crucible, (4) variable-speed motor, (5) speed control unit, (6) refractory material.

stopped and the alloy slurry was poured into the four different diameter steel moulds, leaving them to cool in air. The four different diameter moulds were also preheated to 220 °C. A sample slice was taken from the longitudinal section of each ingot for microstructural examination.

Both the conventional and stirred samples were prepared for the optical microscope. Sample preparation was made in the following manner: cutting of the slice, microgrinding, electrolytic polishing and etching using Mao Rao etching solution. The preparation was done very carefully so that any deformation of the sample surface could be avoided. The grain size was determined using the line intercept method.

3. Results and discussion

3.1. Structure of Pb–6Sb alloy

The cooling history of the alloy ingots was measured in the two cases of no additions (conventional casting, CC) and with the addition of 0.02% of Ag_2Se grain refiner (grain refinement, GR). The cooling curves are represented in Figs 3 to 6, and a few degrees of undercooling are observed. The solidification time, duration of thermal arrest and the cooling rate were determined for each ingot. The solidification time was defined as the time elapsed during cooling the alloy from the melting temperature to the eutectic temperature at the end of the thermal arrest. The thermal arrest was defined as the period of constant temperature during the solidification of the eutectic phase. A few degrees of undercooling were observed in the cooling curves of CC and GR ingots; in this case the thermal arrest was measured as the sum of undercooling and recalescence time plus the time of constant temperature. The cooling rate was determined as the difference between the melting temperature and the eutectic temperature divided by the solidification time. The results are shown in Figs 7 to 9. Fig. 7 shows that the solidification time increases with increasing mould diameter either with added grain refiner (GR) or without addition (CC). Increasing the mould diameter at the same height leads to an increasing amount of heat capacity contained in it; consequently it needs more time to transfer heat to the environment until complete solidification of the ingot.

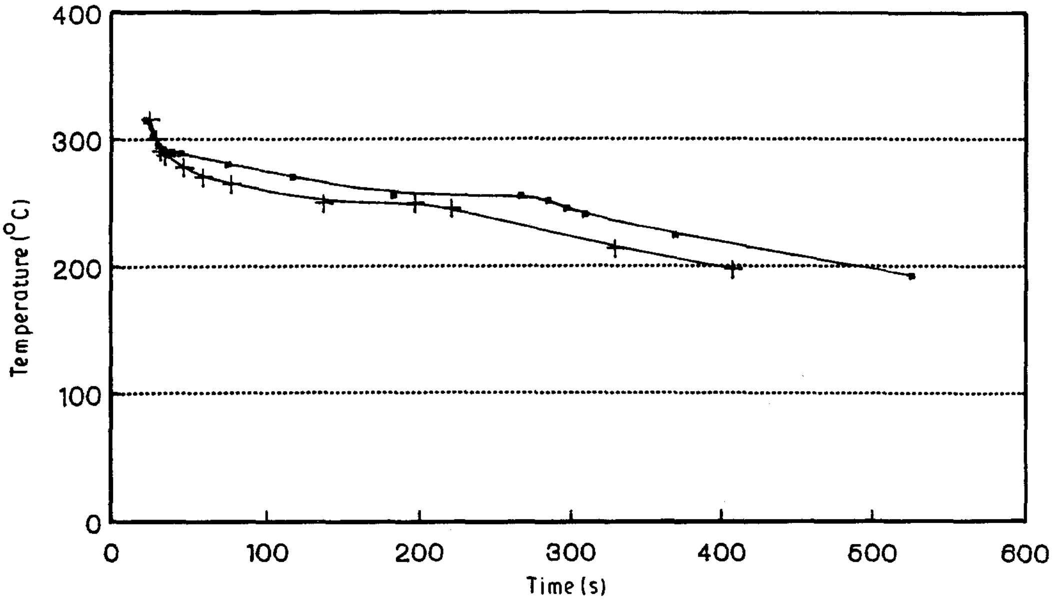

Figure 3 Cooling curves of Pb–6Sb alloy conventionally cast in an 18 mm inner diameter steel mould, (+) with addition of 0.02% Ag_2Se grain refiner (Gr) and (■) without addition (CC).

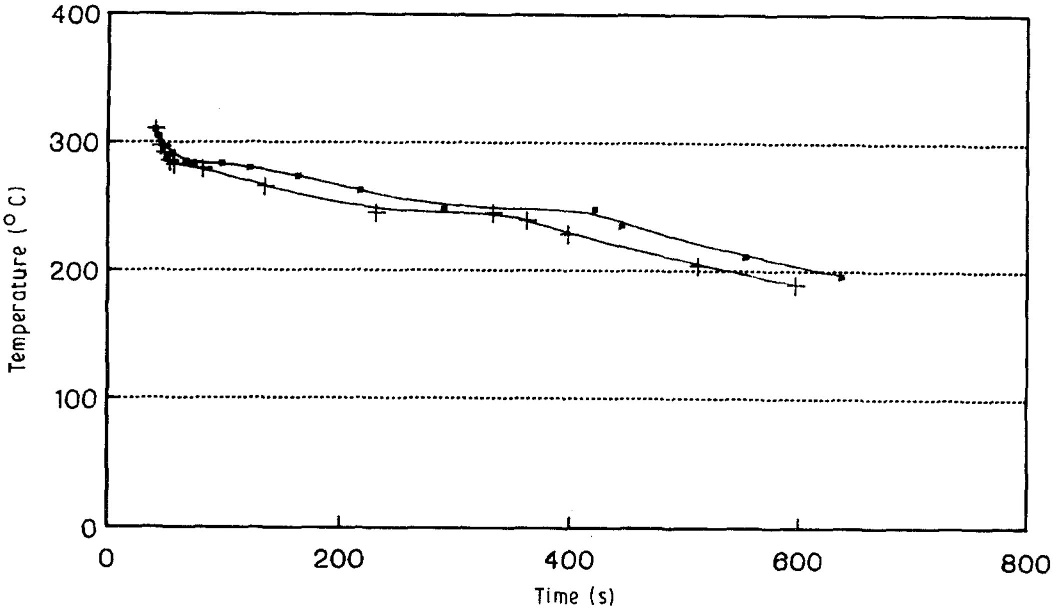

Figure 4 Cooling curves of Pb–6Sb alloy conventionally cast in a 25 mm inner diameter steel mould, (+) with addition of 0.02% Ag_2Se grain refiner (GR) and (■) without addition (CC).

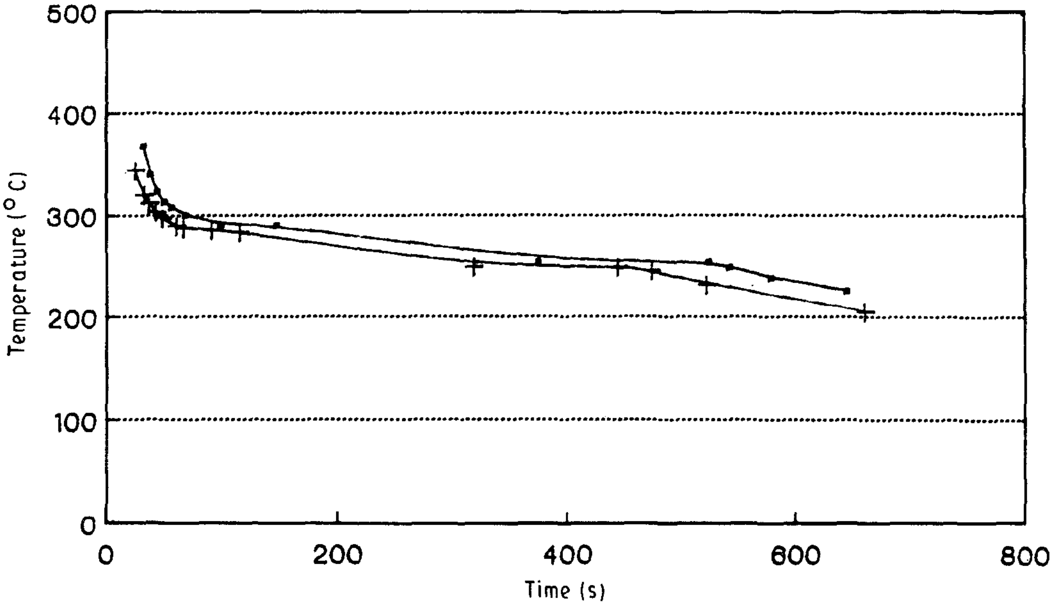

Figure 5 Cooling curves of Pb–6Sb alloy conventionally cast in a 32 mm inner diameter steel mould, (+) with addition of 0.02% Ag_2Se grain refiner (Gr) and (■) without addition (CC).

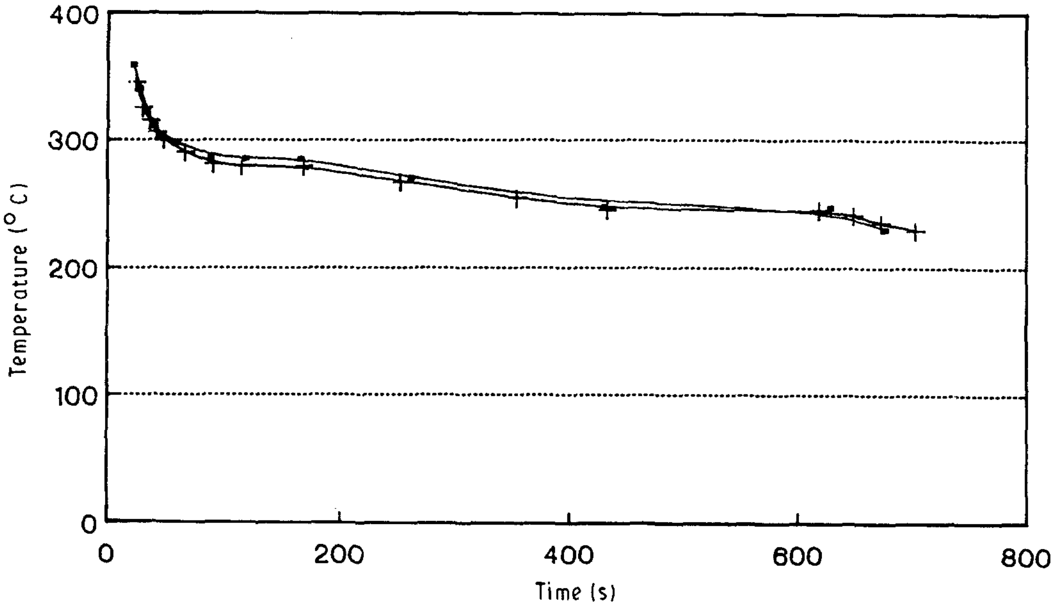

Figure 6 Cooling curves of Pb–6Sb alloy conventionally cast in a 40 mm inner diameter steel mould, (+) with addition of 0.02% Ag_2Se grain refiner (GR) and (■) without addition (CC).

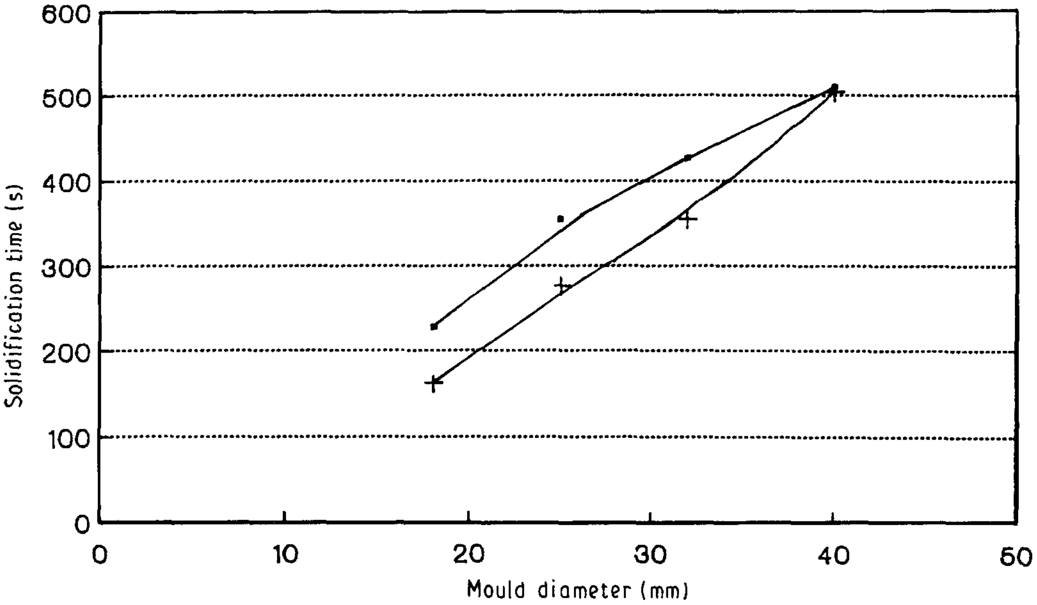

Figure 7 Influence of mould diameter on the solidification time of (■) conventionally cast (CC) and (+) grain-refined (GR) alloy.

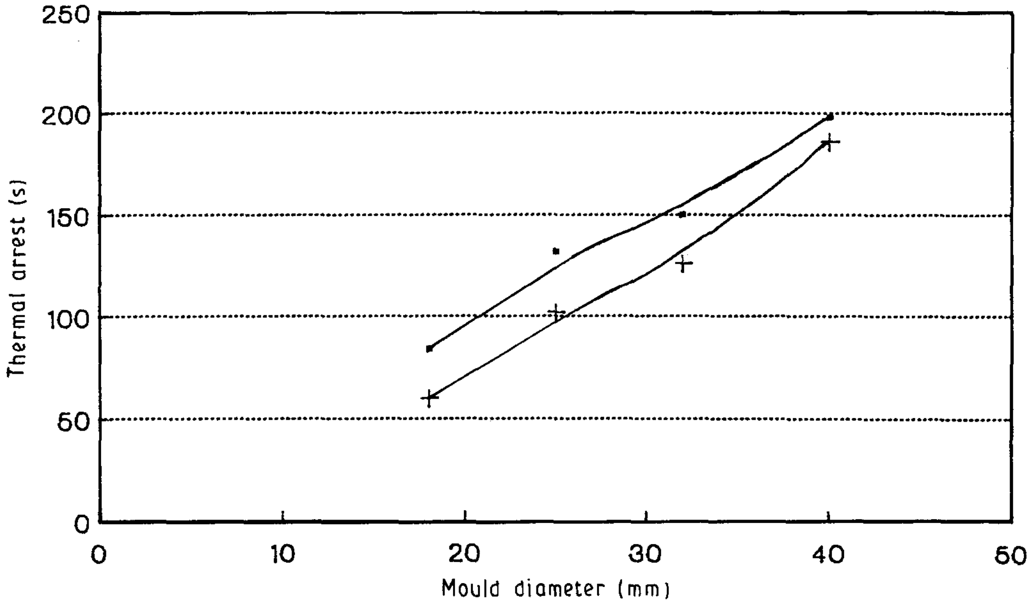

Figure 8 Influence of mould diameter on the thermal arrest of (■) conventionally cast (CC) and (+) grain-refined (GR) alloy.

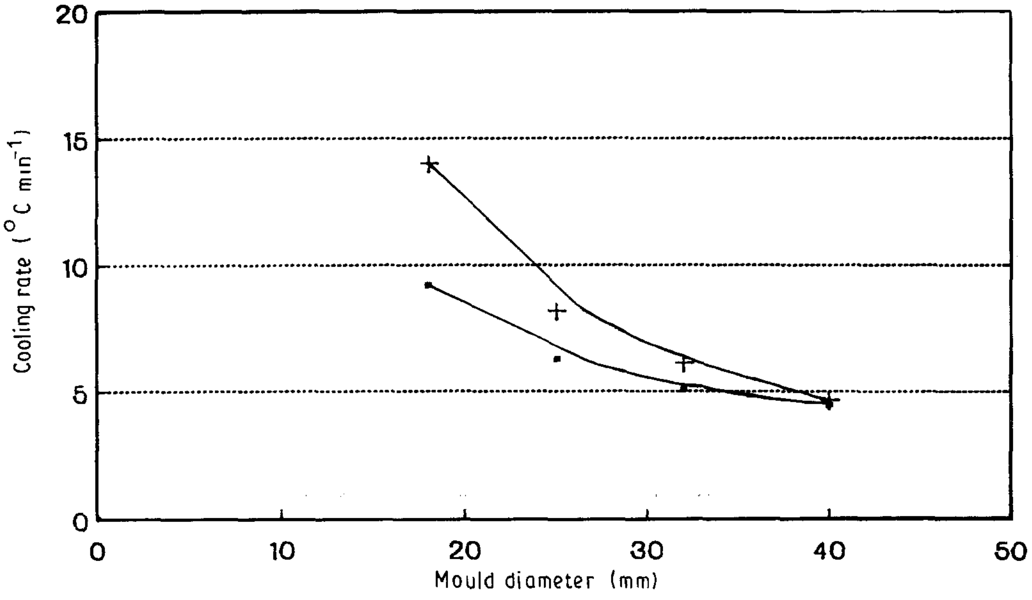

Figure 9 Average cooling rate of (■) conventionally cast (CC) and (+) grain-refined (GR) alloy as function of mould diameter.

At the same mould diameter the solidification time is always larger in the case of CC than in the case of GR, but the difference between the two cases is most pronounced at the smallest ingot diameter. The solidification time is shorter in the case of GR than for CC, due to the introduction of the grain refining agent which leads to an increased rate of nucleation and then an increased cooling rate [6]. In the same liquidus–solidus temperature range, with increasing cooling rate there will be a decrease in solidification time.

Fig. 8 shows that the duration of thermal arrest during the solidification of the eutectic phase increases with increasing mould diameter, in the case of both GR and CC. Also at the same mould diameter the thermal arrest in the case of CC is larger than in the case of GR. Plotting the values of cooling rate *E* versus the mould diameter as shown in Fig. 9, it is clear that at the same mould temperature the value of *E* decreases with increasing mould diameter at the same mould height, in the case of both GR and CC. The difference in the cooling rate is significant at the smaller mould diameters.

Fig. 10 shows the resultant average grain size in the case of both GR and CC as a function of mould diameter. The average grain size increases with increasing mould diameter in both cases. At the same mould diameter the average grain size is smaller in the case of GR than in the case of CC. Fig. 11 shows a comparison between the microstructure obtained under both GR and CC conditions; it shows completely equiaxed dendrites but the tertiary arm spacing is finer in the case of GR.

3.2. Effect of stirring on the structure of Pb–6Sb alloy

The effect of stirring in the mushy zone on the structure of Pb–6Sb alloy is shown in Fig. 12 and represented in Fig. 13. Fig. 12 shows the structure morphology of the stirred samples which consists of a primary solid phase, the solidified remanent liquid and a eutectic matrix. The primary solid phase is composed of spheroidal particles which solidified during the stirring, and these can be found individually at high stirring speed or agglomerated together at low stirring speed. These results are in agreement with previous work using different alloy systems [7]. The solidified remaining liquid shows small particles with a fine dendritic morphology which we call secondary particles. The dendritic structure obtained by conventional casting of the alloy is thus replaced by primary solid particles obtained during the stirring of the melt in the mushy zone and secondary particles obtained from the solidified remaining liquid.

The effect of stirring on the structure refinement is then clear, that it not only breaks down the dendrites and transfers the material to spherical particles [7–9], but also gives a chance to the remaining liquid to solidify in the form of semi-spherical or irregular particles in the alloy under consideration.

Fig. 13 shows the effect of stirring speed on the average primary particle size λ at different mould diameters, i.e. different secondary cooling rates. It is clear that λ decreases with increasing stirring speed at the same mould diameter. Also it increases with increasing mould diameter at the same stirring speed. Increasing the mould diameter means decreasing the secondary cooling rate, which gives a chance to the primary solid particles to grow.

4. Conclusions

1. The solidification time and the duration of thermal arrest are longer in the case of cast ingots without addition of grain refiner than in the case of addition.
2. Ag_2Se has a small effect on the structure refinement of the Pb–6Sb alloy.

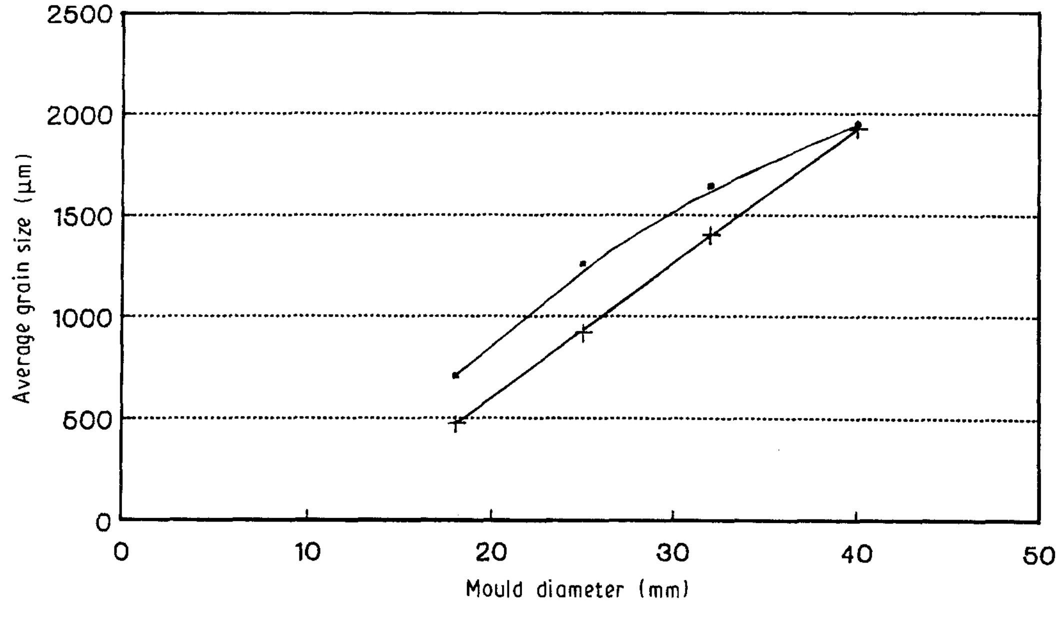

Figure 10 Average grain size of the alloy solidified (■) without addition (CC) and (+) with addition of the grain refiner (GR).

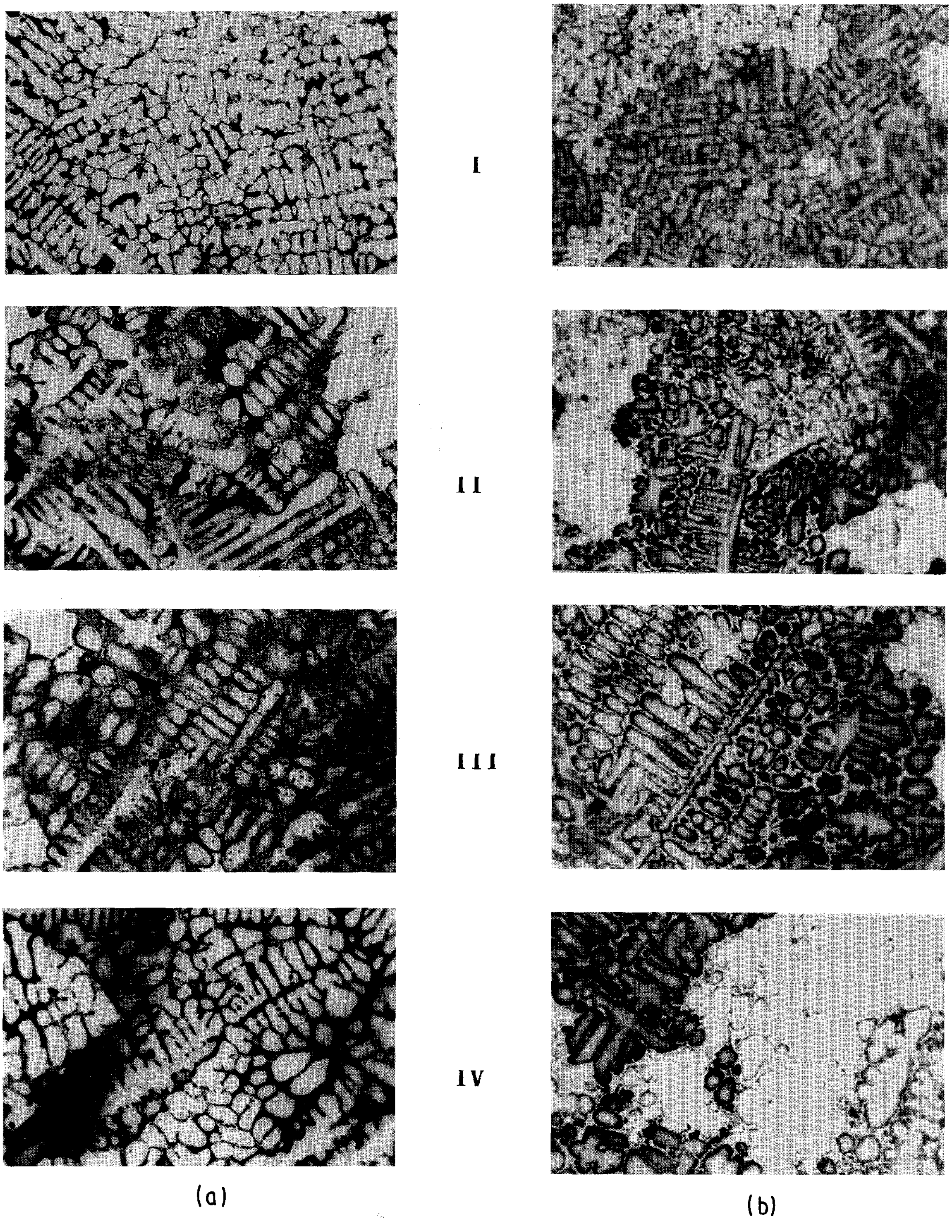

Figure 11 Typical microstructure of Pb–6Sb alloy casted in four different diameters of steel mould: (I) 18 mm, (II) 25 mm, (III) 32 mm and (IV) 40 mm, at a melt temperature of 440 °C, (a) without addition of Ag_2Se and (b) with addition of Ag_2Se (50 ×).

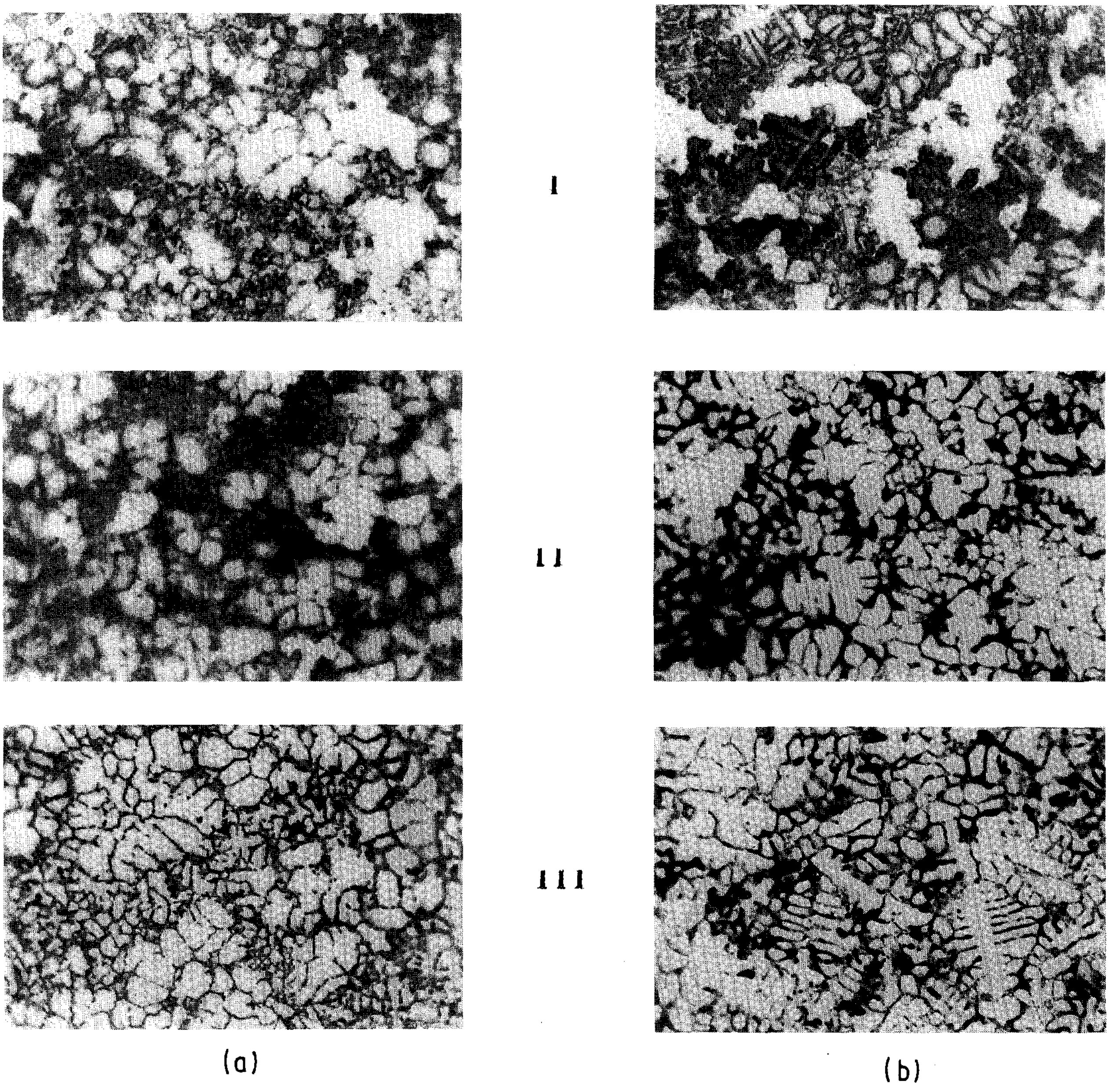

Figure 12 Typical microstructure obtained in stir-cast Pb–6Sb alloy cast at a temperature in the mushy zone (265 °C) in three different steel moulds: (I) 18 mm, (II) 25 mm and (III) 32 mm diameter for speeds of (a) 1100 and (b) 400 r.p.m. (50 ×).

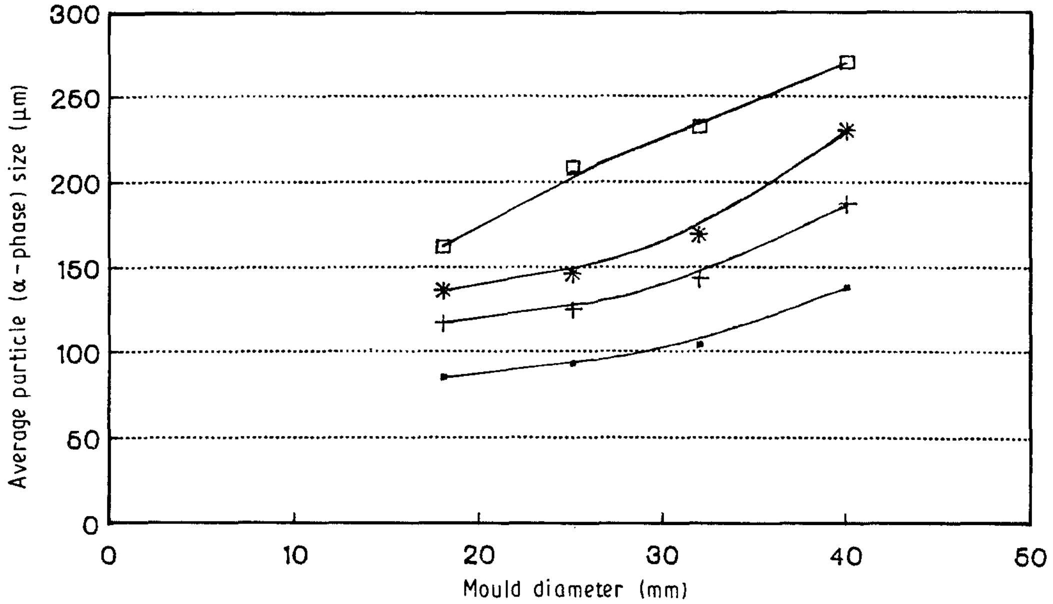

Figure 13 Effect of mould diameter on the average particle (α-phase) size of Pb–6Sb alloy stirred at four different stirring speeds: (□) 400, (*) 700, (+) 900 and (■) 1100 r.p.m.

3. The structure refinement of Pb–6Sb alloy depends greatly on the stirring speed. At low speed agglomerations of primary particles form, while at high speed individual primary particles form which are nearly spherical, relatively smaller and homogeneously distributed.

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