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The role of melt superheat in splat-quenching

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The influence of experimental parameters in the gun splat-quenching technique is briefly discussed. The effect of initial melt temperature on cooling rate as manifested by lamellar spacing measurements in eutectic aluminium-copper alloy is small. Foils quenched from just above the melting point are generally thicker than those quenched from higher temperatures and thus there is a slight decrease in cooling rate with decrease in melt superheat. Increase in the temperature of quenching increases the proportion of degenerate eutectic microstructure obtained.

1. Introduction

In the past decade a large number of devices have been developed to rapidly solidify small quantities of metal alloys (splat-quenching). The most popular techniques are the "gun" [1] in which the molten alloy is sprayed against a cold metal substrate and the "piston and anvil" [2] in which the molten droplet is sandwiched between two rapidly moving metal plates. At the high cooling rates obtainable ($> 10^5$ K sec^{-1}) it is possible to prepare metastable phases in a large number of binary systems. The formation of these phases, their structures and their properties have been the subject of several recent reviews [3, 4]. However, there have been few investigations of the splat-quenching technique itself, even though the literature contains many examples of discrepancies between the results obtained in different laboratories and on different pieces of equipment. To a large extent the possible effects of the many experimental variables on attainable cooling rate and consequent metastable phase formation have been ignored. This paper, therefore, discusses briefly the role of some of the major variables in the gun technique and describes the measurement of the effect of initial melt temperature on the cooling rate in splat-quenched eutectic aluminium-copper alloy.

In a theoretical study Ruhl [5] deduced that the cooling efficiency was determined primarily by the thermal contact between the splat and the substrate and by the foil thickness. Good contact is usually achieved by using a roughened substrate of high conductivity material, although the author [6] has recently shown that the improved contact achieved with a glass substrate may compensate for the decreased conductivity. Evidence has also accrued that better contact may be obtained when the entire quenching process occurs in an inert atmosphere [7, 8]. Assuming all other factors constant the dependence of average cooling rate on foil thickness should vary between a proportionality to $1/d^2$ (ideal) and $1/d$ (Newtonian). The thickness of the splat may be influenced by a number of factors, for example the mass and size distribution of the molten droplets, their speed of impact with the substrate and their rate of solidification [9, 10].

Theoretically, the initial temperature of the molten alloy should have only secondary influence on the cooling rate. Under conditions approaching ideality a higher initial melt temperature might be expected to give slightly lower cooling rates because of the increased local heating of the substrate. This effect should only be minor and disappear at intermediate temperatures, i.e. those at which the liquid-solid transformation occurs and which are consequently of most significance. Empirical observations [11], however, have suggested that whilst a certain amount of superheat is necessary to counteract in-flight cooling of the molten

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droplets any increase above this minimum value gives thinner and therefore more rapidly cooled splats.

It is worth noting that in a number of cases [12, 13] variations in metastable intermediate phases have been reported on quenching the same alloy from different initial melt temperatures. It has been argued [13] that these phases may be due to the existence of nuclei of metastable phases in the melt which may be "quenched-in" if the cooling rate is high enough. Evidence for the existence of clusters in metallic melts has been presented in several cases. Correlations have been shown between both the physical [14, 15] and thermodynamic [16] properties of liquid alloys and the compositions at which stable and metastable phases form on solidification. Unfortunately no controlled splat-quenching experiments have been performed on an alloy for which the dependence of liquid properties on temperature is well known.

2. Experimental

The eutectic aluminium-copper alloy was made by induction melting the required weights of 5N purity aluminium and copper in alumina crucibles under a pure argon atmosphere. The alloy was cast into 5 mm diameter rods which were subsequently homogenized under vacuum. Chemical analysis showed the rods to be within 0.1% of the eutectic composition. In addition, optical metallographic specimens were taken from various points to check for the absence of any primary phase.

Splat-quenching was carried out in a modified gun-type apparatus constructed so that the entire quenching operation could be performed in an inert atmosphere. Before each quench the chamber containing the gun was evacuated, flushed with argon, re-evacuated to 10 N m^{-2} (0.1 Torr) and filled with high purity argon to a pressure of 60 kN m^{-2} (600 Torr). 250 $\pm$ 20 mg specimens of the alloy were quenched from 600, 800, 1000 and 1200°C (corresponding to superheats of 50, 250, 450 and 650°C) onto a water cooled copper substrate which had been roughened with grade 400 emery paper. The temperature of the specimens before quenching was measured by a small Pt-Pt/Rh thermocouple fixed inside the crucible. The shock wave was created by rupturing melinex diaphragms with pure argon gas at 3 MN m^{-2} (450 p.s.i.).

The resulting foils were mounted transversely in Araldite and their thicknesses measured at 0.5 mm intervals along their lengths using a calibrated eye piece in an optical microscope. After polishing these specimens to a $\frac{1}{4}$ µm surface finish and etching in 10% NaOH solution plastic-carbon replicas of the foil cross-sections were made for electron microscopic observation. These replicas allowed not only examination of the microstructure of the foils but measurement of the local foil cross-section at areas of interest. An AEI 6G microscope operating at 80 kV was used.

3. Estimation of cooling rates

Burden and Jones [17] have shown that for the Al–$CuAl_2$ eutectic the growth rate (R) and lamellar spacing (λ) are related by the expression:

$$\lambda^2 R = 108\ \mu m^3\ sec^{-1} \tag{1}$$

If it is assumed that essentially Newtonian conditions apply the heat transfer coefficient (h) and growth rate are related by [18]:

$$h = \frac{\rho L R}{\theta_F - \theta_A} \tag{2}$$

where ρ is the density (3.84 $\times$ 10^6 g m^{-3}), L is the latent heat of solidification (340 J g^{-1}), θ_F and θ_A are respectively the freezing and substrate temperatures (548 and 20°C).

The cooling rate (C) is given by:

$$C = \frac{108 L}{c d \lambda^2} \tag{3}$$

where c is the specific heat (0.71 J g^{-1}), d is the foil thickness.

There has been some controversy [19-21] over this and other methods of measuring cooling rates in splat-quenching. Whilst there may be some doubt as to the accuracy of the absolute values obtained, the technique is perfectly adequate for comparative studies of variations in cooling rate with different experimental conditions. It is for this purpose that it is used in the current work.

4. Results and discussion

Optical examination of the metallographically mounted foils revealed that they were very irregular in thickness e.g. Fig. 1 which shows the frequency of measurement of various widths in a typical foil. For each foil the mean thickness and the standard deviation from the mean were calculated (Table I). That these values are larger than those quoted by previous investigators of the gun technique [17, 18] was probably a consequence of the larger amount of material used (250 mg) in the present case. Although insufficient samples were studied for a detailed statistical analysis there appeared to be a significant decrease in average foil thickness with increasing initial melt temperature. Overall, increasing the melt superheat from 50 to 650° C gave an almost 50% decrease in average foil thickness.

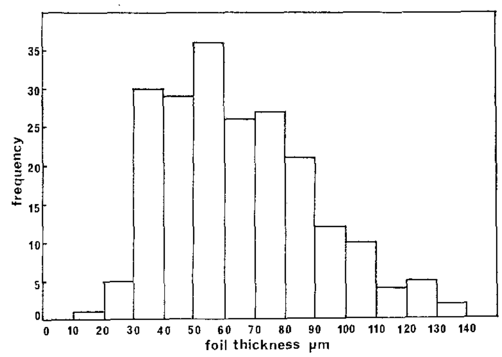

Figure 1 Histogram to show distribution of thicknesses in a typical foil.

TABLE I Mean thicknesses of splat-quenched foils. (Values are in μm.)

600°C	800°C	1000°C	1200°C
95 ± 40	80 ± 40	55 ± 25	55 ± 25
75 ± 30	85 ± 40	55 ± 25	55 ± 25
100 ± 35	70 ± 30	110 ± 30	45 ± 20
90 ± 30	60 ± 30	80 ± 30	50 ± 15
90 ± 35	70 ± 30	60 ± 25	60 ± 20

The thickness of a foil is determined by the spreading of the molten alloy on the substrate. This spreading may terminate either when all the initial kinetic energy of the droplets is exhausted or when solidification occurs [10]. However, Jones [9] has calculated that for aluminium quenched from 50° superheat the rate of solidification should be several orders of magnitude less than the rate of spreading. Thus it seems probable that the decrease in foil thickness with increasing melt superheat arose from the decrease in viscosity and surface tension of the molten alloy with increasing temperature. The viscosity of molten aluminium falls by a factor of 2 between 600 and 1200° C [22] whilst the surface tension decreases by about 15% in the same temperature range [23].

The microstructure of the foils was similar to that shown earlier for aluminium-copper eutectic alloy quenched onto a polished copper substrate [17]. Three distinct morphologies were observed: parallel lamellae, a degenerate structure and a few radial lamellar arrangements apparently nucleated at primary particles (Figs. 2 to 5). In general the region adjacent to the substrate was degenerate but otherwise there appeared to be no correlation between type of morphology and position within the foil. Moreover there was no predominance of any type of morphology in particularly thick or particularly thin sections.

Spacing measurements were made only on well defined lamellar regions and always well away from any primary particles. No corrections were made for sectioning effects and it was assumed that in any area the minimum observed spacing approximated to the true spacing. (Even if the lamellae with the smallest apparent spacing were inclined at 20° to the foil normal the error in estimating the true spacing by this assumption would be only 6%.) Values ranged from 600 Å to in excess of 2000 Å. Since the variations in local foil thickness were large comparisons between lamellar spacings were of little use. Consequently values of the heat transfer coefficient (h), Nusselt number (N) and cooling rate were evaluated for each spacing measurement. The Nusselt number ranged between 0.002 and 0.020 with no startling dependence on the initial melt temperature. In most cases, therefore, the cooling was Newtonian and the assumptions made in the derivations of Equations 2 and 3 were justified. The magnitude of h lay between about 4×10^3 and 3×10^4 J m^{-2} K^{-1} sec^{-1}. This is consistent with previous values for the same alloy quenched onto a copper substrate [17].

To facilitate comparison between the different groups of specimens the calculated cooling rates are presented in Fig. 6. There appeared to be little variation with melt superheat. The maximum cooling rate at all four temperatures was about 2×10^5 K sec^{-1} and the spread of the values the same in each case. If anything there was a slight increase in the average cooling rate with increase in melt superheat, the value rising from about 2×10^4 K sec^{-1} at 600° C to 5×10^4 K sec^{-1} at 1200° C. This effect almost certainly arose from the decrease in foil thickness with increasing superheat. Certainly such variations would be too small to explain any anomalies in metastable phase formation which have been reported to occur on quenching various alloys from different temperatures [12, 13].

Whilst quantitative estimates of the cooling rate could be made only from the lamellar regions it was felt that some significance could be

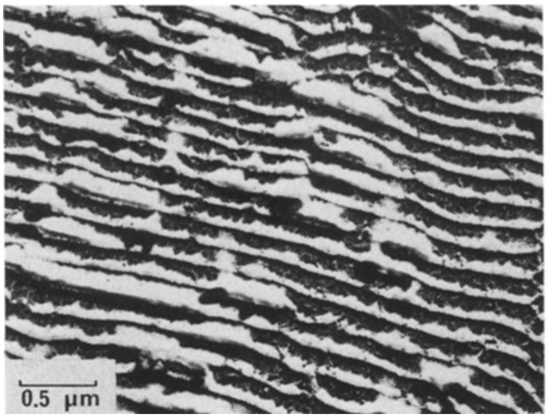

Figure 2 Replica showing lamellar morphology.

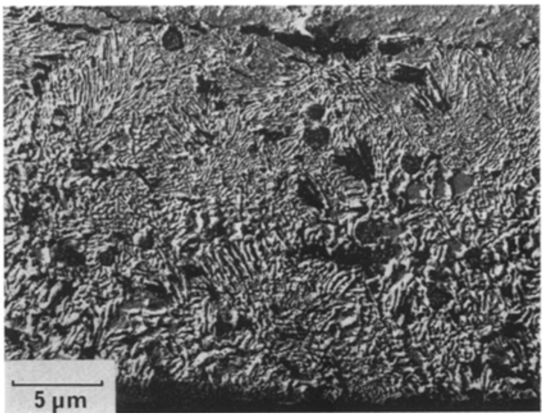

Figure 5 Low magnification replica to show entire foil cross-section.

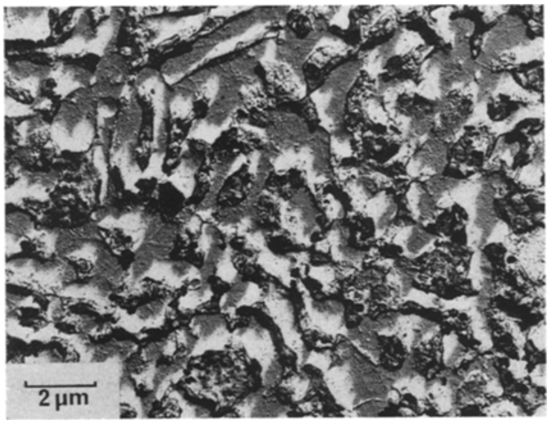

Figure 3 Replica showing degenerate morphology.

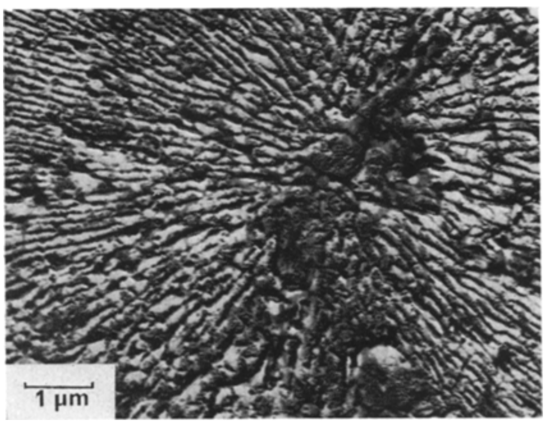

Figure 4 Replica showing radial lamellar morphology.

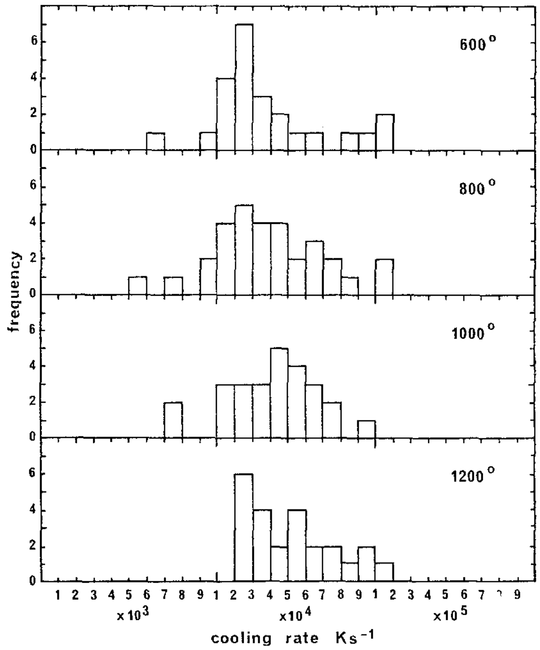

Figure 6 Histograms to show cooling rate measurements in the splat-quenched foils.

attached to the relative proportions of degenerate to lamellar microstructure, which increased from about 30% at 600°C to about 60% at 1200°C. At high cooling rates the normally lamellar Al–$CuAl_2$ eutectic may become degenerate [24]. Thus the observation cited above may be indicative of an increase in cooling rate with increasing temperature of quenching. Alternatively the formation of a degenerate morphology may depend on the contact between the splat and the substrate. With perfect thermal contact ($h = \infty$) heat flow should be normal to the substrate surface at all points, solidification should occur unidirectionally from the substrate and lamellar growth be easily established. With a reduction in the thermal contact lamellar growth would become more difficult to establish and a degenerate morphology may result. Thus in a number of cases improved thermal contact between splat and substrate has been accompanied by an increase in lamellar morphology [6, 17]. However, the values of h obtained in the current work show no obvious dependence on the temperature from which the specimens were quenched and thus a change in thermal contact with melt superheat cannot be established.

5. Conclusions

The foils obtained in the gun splat-quencher were shown to be very irregular in thickness. The two phase eutectic structure was retained at cooling rates up to about 2×10^5 K sec^{-1} although it often adopted a degenerate morphology. The effect of the initial melt temperature on the cooling rate as deduced from lamellar spacing measurements was small. Foils quenched from just above the melting point were generally thicker than those quenched from higher temperatures under otherwise similar conditions and consequently there was a slight increase in cooling rate with increase in melt superheat. The proportion of degenerate eutectic microstructure increased with increase in the initial melt temperature.

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