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Impact of substrate temperature on rapid solidification of an Al–Cu eutectic alloy

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An aluminium–copper eutectic alloy has been subjected to rapid solidification, utilising the "gun" technique, with different substrate temperatures to evaluate its influence on the cooling rate and microstructure. At all temperatures, the microstructure is essentially non-uniform and consists of metastable solid solution (with decomposition products) as well as eutectic regions. The solid state decomposition of the metastable solid solution is strongly dependent on the substrate temperature and leads to the formation of different metastable precipitates and consequent changes in microstructure. The origin of the different microstructures is discussed.

1. Introduction

Several investigations have been carried out to determine the effect of process variables on the constitution, structure and morphology of rapidly solidified alloys. The results of these have been reviewed by Jones [1]. However, the effect of substrate temperature on rapidly solidified alloys has not attracted much attention so far. Stoering and Conrad [2] studied the effect of substrate temperature in the "gun" technique of rapid solidification by keeping the substrate at 123, 293 and 323 K. The analysis of their results on silver–copper alloys established the presence of different metastable phases at different temperatures and thus brought out the importance of substrate temperature in the formation and stabilization of non-equilibrium phases. Shingu *et al.* [3] investigated the impact of substrate temperature on an aluminium–12 at% silicon alloy solidified by the "piston-and-anvil" technique. They varied the substrate temperature from room temperature to more than 573 K and followed the formation of the metastable solid solution by precise measurements of the lattice parameter. Their results quantitatively establish the decreasing stability of the metastable solid solution with increasing temperature up to 573 K, where the equilibrium solid solution becomes stable.

It is clear from the above investigations that the substrate temperature can be used as an important processing variable for controlling the structure and morphology of rapidly solidified alloys. To explore this interesting possibility, studies have been initiated in our laboratory on the effect of substrate temperature on the structure and morphology of several rapidly solidified aluminium alloys. In the present paper we report the results obtained on an aluminium – 17 at% copper eutectic alloy.

2. Experimental procedure

A substrate which can be heated to the desired temperatures was fabricated, as shown schematically in Fig. 1. Essentially the substrate consists of a small resistance heater over which a ski-slope copper plate is fixed. To avoid oxidation of the copper plate at higher temperatures, it is electroplated with silver. This procedure enables the effective use of the substrate up to 523 K. In each experiment a small amount of liquid metal (50 to 100 mg) was rapidly solidified over this substrate using the "gun" technique, the details of which have been presented elsewhere [4]. The aluminium–copper eutectic alloy was prepared from commercial as well as high purity

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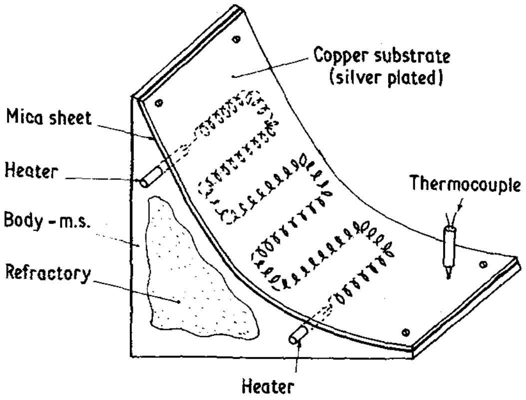


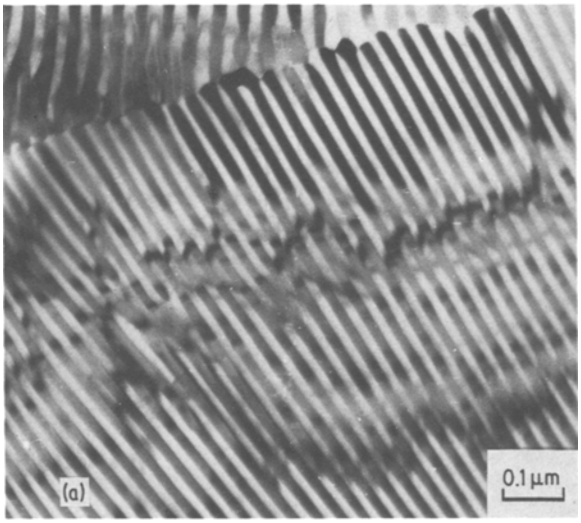
Figure 1 Schematic sketch of hot substrate for gun quenching.

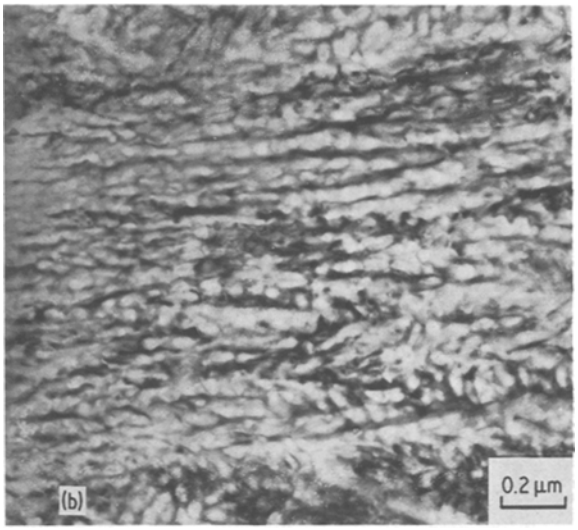
($>$99.999%) metals. The temperature of the substrate was varied, apart from room temperature (303 K), from 323 K to 523 K at 50 K intervals. All observations were made directly on thinner sections of the rapidly solidified foils in a Philips EM300 transmission electron microscope operating at 100 kV.

3. Results and discussion

The microstructures observed in different regions of the same foil were more often than not, non-uniform, irrespective of the substrate temperature. However, the predominant microstructures observed were either single phase (exhibiting different stages of decomposition depending upon the substrate temperature) and/or lamellar or degenerate eutectic. Thus depending upon the local cooling rates, a transition from the normal, lamellar eutectic to a non-equilibrium solid solution could be observed.

Fig. 2 brings out some typical transitions observed in our work. Fig. 2a reveals a fine lamellar eutectic structure. Fig. 2b represents an intermediate stage where primary dendrites of extended solid solution are observed together with microsegregation at the interdendritic regions. From the measurement of secondary dendrites arms spacing [5], the cooling rate could be estimated as $5 \times 10^8\,\mathrm{K\,sec^{-1}}$. (This may be taken to equal or exceed the critical cooling rate for breakdown of the eutectic reaction). Increasing cooling rates





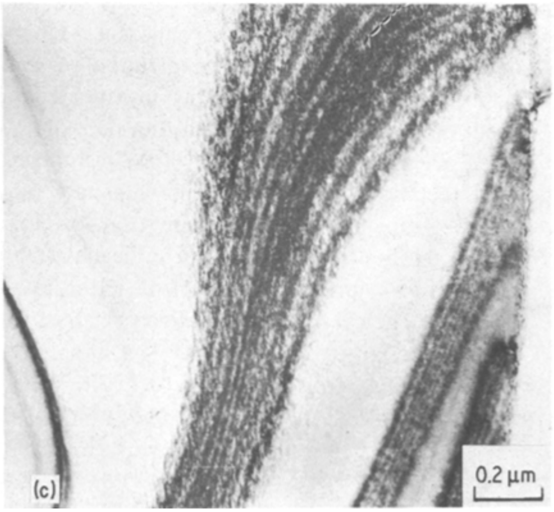


Figure 2 Typical microstructures illustrating (a) fine lamellar eutectic structure; (b) dendritic structure with microsegregation; (c) extended solid solution in splat quenched Al–Cu eutectic alloy.

result in the formation of more solid solution until ultimately only large grains of single phase solid solution without any microsegregation are observed (Fig. 2c). This result is in agreement with the observation of Ramachandrarao *et al.* [6] on this alloy using a diamond substrate at liquid nitrogen temperature to achieve a higher cooling rate than with copper substrate.

The areas where the eutectic reaction has occurred can be divided into two distinct categories (Case I and II). Both types could be observed at all substrate temperatures.

In Case I fine and perfect lamellae are observed (Fig. 2a). The lamellar spacing in such areas does not change significantly with substrate temperature. Assuming an average thickness of 200 nm for the foil under estmination, the cooling rate calculated from these lamellar spacings [7] yields a consistent average value of about 3×10^8 K sec^{-1}.

Case II generally consists of a degenerate eutectic surrounded by a radial lamellar eutectic (Fig. 3). An examination of the transition interface areas suggests that the $CuAl_2$ particles in degenerate regions nucleate the lamellar eutectic cell. The lamellar spacings obtained from these eutectic regions are larger than those obtained in Case I. Again the values are similar at all substrate temperatures. The cooling rate calculated from these spacings (assuming 200 nm thickness) yields an average value of about 2×10^7 K sec^{-1}. The selected area electron diffraction from degenerate areas gives ring type patterns indicating the absence of any fixed crystallographic relation between the matrix and the $CuAl_2$ particles.

A comparison of the cooling rates obtained from dendrite arms spacings and finest lamellar spacings of Case I leads to the conclusion that the critical cooling rate for the lamellar to single phase transition lies in between 3 to 5×10^8 K sec^{-1}. The sequence of occurrence with increasing cooling rate is as follows: Lamellar eutectic → dendritic with limited solute partitioning → single phase with very little solute partitioning. The complete trapping of solute can be said to occur when the thickness of the solute rich boundary layer in front of the solid–liquid interface is of the atomic order. Using the diffusion data of Cu in liquid Al–Cu alloys [8] the growth rate for complete trapping is found to be an order of magnitude higher than the highest observed eutectic growth rate. Assuming that the thermal gradient does not change significantly gives us a lower limit of cooling rate for the formation of completely single phase homogeneous solid solution to be better than 10^9 K sec^{-1} which is consistent with our observation.

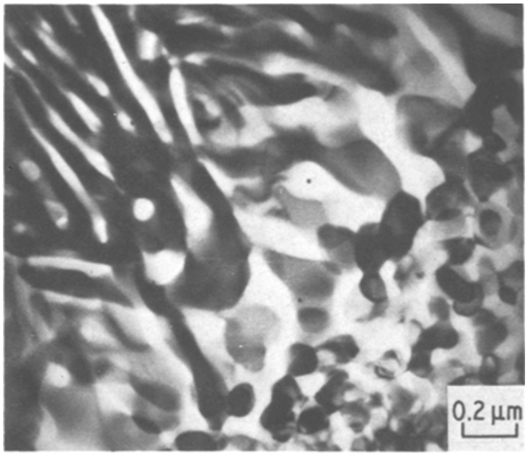


Figure 3 **Degenerate eutectic surrounded by coarse radial lamellar eutectic.**

Several attempts have been made to explain the origin of degenerate regions of Case II and is subjected to some controversy in recent times [9–11]. Though a detailed re-evaluation is outside the scope of the present work, some conclusions can be drawn based on our observation. Solid–solid nucleation theory requires the existence of an orientation relationship [12], and non-existence of such a relation supports the theory that the degenerate region is indeed a solidification morphology, contrary to the proposal of solid state decomposition by Kattamis and Flemings [13]. The observation of $CuAl_2$ particles of these regions nucleating lamellar eutectic colony lends further support to the above conclusion. The cooling rate of the lamellar regions surrounding the degenerate regions is at least an order of magnitude less than the maximum possible for a co-operative growth in other areas. Thus the model of successive transition from lamellar to degenerate to single phase with increasing cooling rate is not valid. However, one often observes a fairly sharp transition from degenerate to co-operative lamellar morphology (Fig. 3). This indicates a different operating growth mechanism. Recently Hillert [14] proposed a model for degenerate eutectic growth involving sidewise growth of the second phase over parent phase. The engulfing $CuAl_2$ phase (dark) in Fig. 4 does support this model.

3.1. The single phase regions

Single phase regions are observed only occasion-

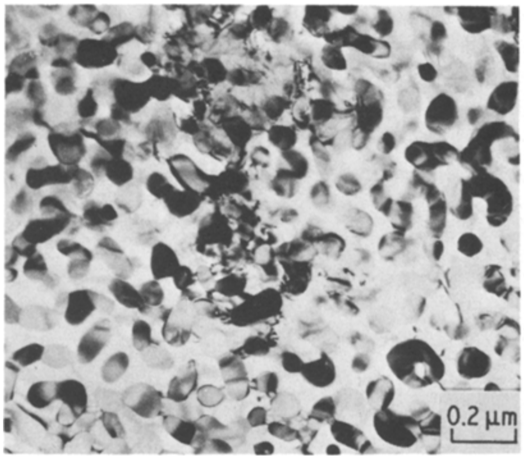


Figure 4 Degenerate eutectic structure illustrating α-aluminium surrounded by $CuAl_2$ phase.

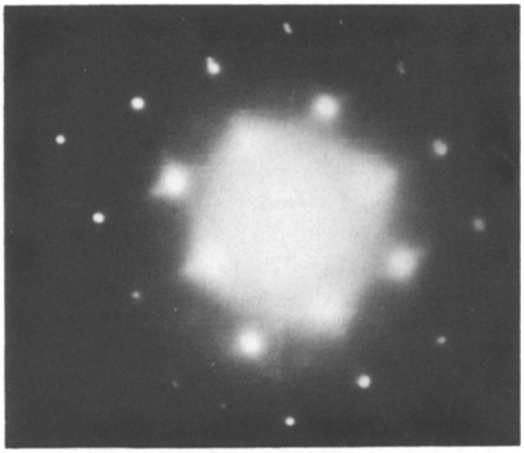


Figure 5 Diffraction pattern from single phase region showing streaking along ⟨1 0 0⟩ directions (substrate at room temperature).

ally in foils obtained from the substrate kept at room temperature (303 K). For all other substrate temperatures, we have invariably observed a decomposed structure, the nature and extent of the decomposition being a strong function of the substrate temperature.

A majority of the regions of the solid solution type obtained with a substrate at room temperature contain a very fine distribution of Guinier–Preston (GP) zones. These can be best seen near bend contours (Fig. 2c). The diffraction patterns from such regions show diffuse streaks along ⟨1 0 0⟩ directions (Fig. 5). In conformity with the earlier observation [15] on rapidly solidified Al–Cu alloys, the shape relrods are broader than those observed in solid quenched alloys due to higher copper concentration which in turn leads to thicker GP zones. At a substrate temperature of 323 K, the microstructure predominantly features a very high density of plate–shaped precipitates (Fig. 6a). The diffraction patterns from these areas clearly establish the precipitates to be θ'' (Fig. 6b) having the usual orientation relationship. In a few regions, θ' precipitates, which had nucleated either on the surface of the foils or at grain boundaries (Fig. 7), were also present.

At 373 K, the predominant precipitating phase is θ'. However, diffuse spots due to θ'' could be seen in diffraction patterns from some areas indicating its existence in smaller quantities. Frequently, extra reflections which were not due to θ'', θ' or θ precipitates were also present.

With increasing temperature up to 473 K, the

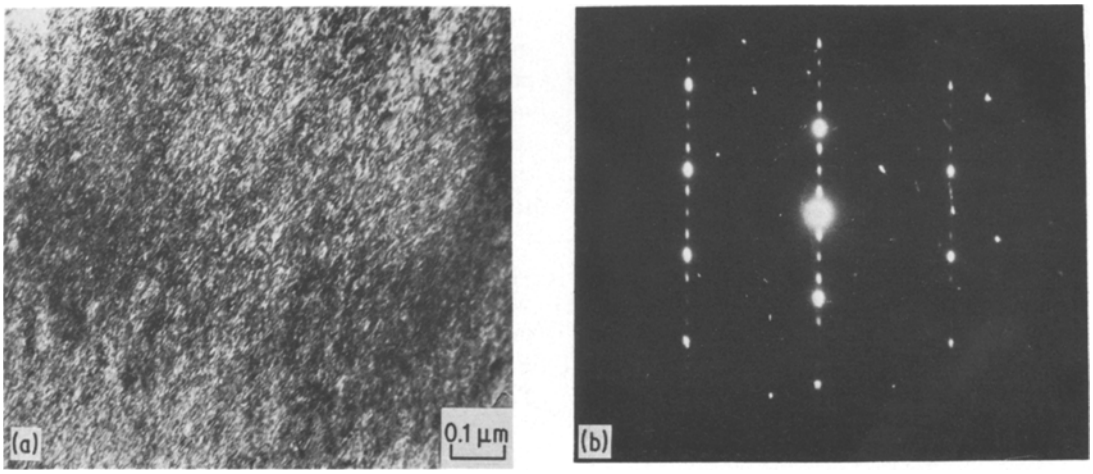


Figure 6 (a) Plate shaped θ'' precipitates and (b) corresponding SAD pattern (substrate at 323 K).

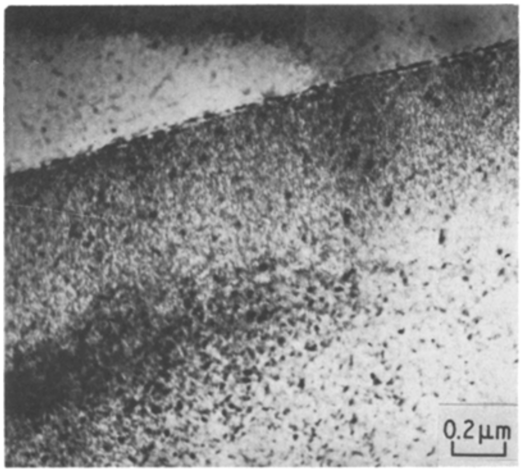


Figure 7 Surface or grain boundary nucleated globular θ' precipitate (substrate at 323 K).

same phases co-exist. While it was not possible to obtain unambiguous diffraction patterns to identify the extra phase(s) at substrate temperatures of 373 K and 423 K, the extra spots in patterns from foils with the substrate at 473 K could be indexed on the basis of a CsCl type of structure with $a \simeq 0.285$ nm (Fig. 8). At this stage diffraction patterns also show occasional occurrence of θ phase. It is worth noting that the morphology of θ' even at 473 K is essentially globular (Fig. 9) indicating predominant surface nucleation. Surprisingly, the usual lath-like θ' precipitate could be observed only at a substrate temperature of 523 K. However, very few foils could be examined at this temperature due to the oxidation of the substrate and sticking of the foils to it.

The partial decomposition of solid solution is clearly a solid state process. In typical experiments the foils were observed within 2 to 4 minutes of rapid solidification and were stripped from the substrate within 30 to 45 sec. Therefore, the question that needs answering is when the decomposition has occured. Besides the fact that the time available during cooling in the solid state is still too small in comparison to reduced diffusivity in the solid state, the observation of different morphologies at different substrate temperatures led us to conclude that the decomposition occured after the foils have attained the substrate temperature. Thus the present investigation indicates that the GP zone forms only at room temperature in the metastable 17 at% Cu solid solution. The predominant phase up to 373 K is θ'' though it can exist in small quantities up to 473 K. From 373 K to 523 K, the highest substrate temperature employed in the present investigation, the major decomposition product is θ' while θ can be observed occasionally only at the highest temperature.

The occurrence of a CsCl type of phase has already been reported by our laboratory in rapidly solidified aluminium–copper alloys with higher solute content [16]. This phase does not form in the present system under equilibrium conditions. However, the equilibrium phase AlCu (r) has been shown to be a derivative of the observed CsCl structure [17]. It is worth noting that the latter is an equilibrium phase in many of the transition metal–aluminium binary systems. Thus the metastable existence of this phase at higher substrate temperature is not surprising. However, the stabilization of this phase at eutectic composition alloys remains to be explained.

4. Conclusions

The following conclusions can be drawn from the present investigation.

(a) At all substrate temperatures, the aluminium–17 at% copper eutectic alloy undergoes

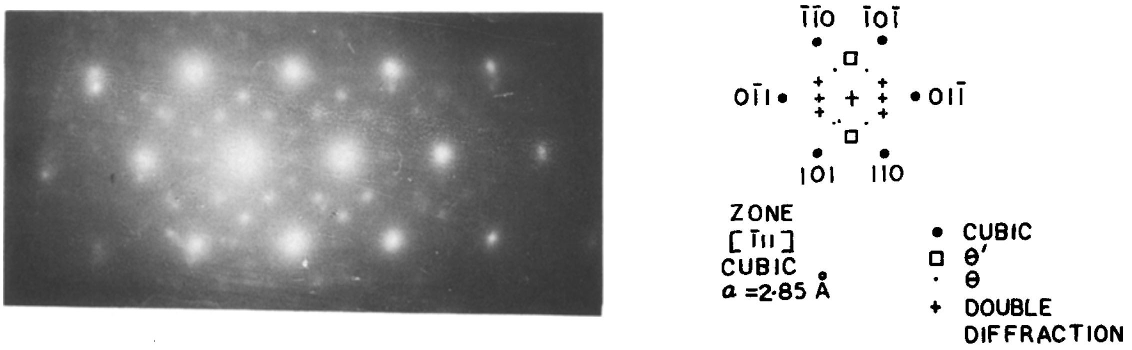


Figure 8 SAD of "X" phase with CsCl structure (substrate at 473 K).

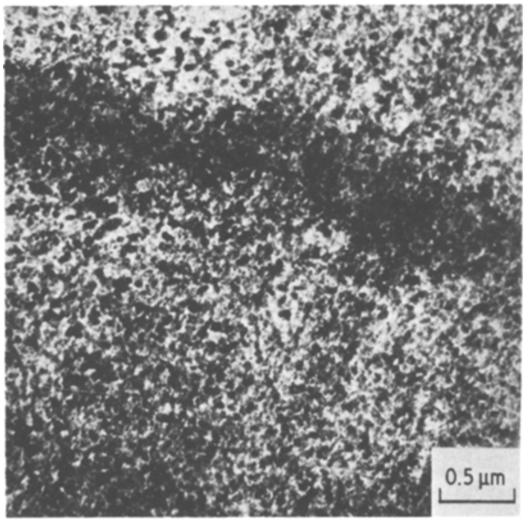


Figure 9 Globular θ' at 473 K substrate temperature.

the following morphological changes with cooling rate.

$$\text{The lamellar eutectic} \xrightarrow{\sim 10^{8}\,\text{K sec}^{-1}} \text{Dendritic with interdendritic segregation} \xrightarrow{>10^{9}\,\text{K sec}^{-1}\text{ (estimated)}} \text{single phase homogenous solid solution.}$$

(b) The degenerate eutectic forms from liquid by an uncoupled growth mechanism and may not represent regions undergoing higher cooling rate than the lamellar regions.

(c) The solid solution regions decompose under the influence of substrate temperature. The phases which co-exist at different temperatures are

$$\underset{+\text{ GP zones}}{\overset{303\text{ K}}{\text{solid solution}}} \longrightarrow \overset{323\text{ K}}{\theta'' + \theta'} \longrightarrow \overset{373\text{ to }423\text{ K}}{\theta'' + \theta' + \text{“X”}} \longrightarrow \overset{473\text{ K}}{\theta' + \theta + \text{“X”}}$$

(d) At 473 K, the "X" phase has a CsCl type crystal structure with a lattice parameter of approximately 0.29 nm.

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