Estimation of cooling rates in rapid solidification from eutectic cell spacing

Methods for determining cooling rates based on microstructural features in alloys solidified rapidly from the melt have gained considerable popularity [1]. In this context, secondary dendrite arm spacing and lamellar spacing in eutectic alloys are the two most used microstructural features [2, 3]. The relative merits and demerits of these two procedures were debated at some length [4–6]. In the use of lamellar spacing as a parameter for estimating the cooling rate a knowledge of thickness of the foil is essential. As shown by Ruhl [7] the cooling rate varies inversely as the square of thickness under ideal cooling conditions and inversely as the thickness in case of Newtonian cooling. Values of thickness employed in the calculations could thus play an important role in estimating the cooling rates. Thus in the literature, different cooling rates were estimated for identical values of lamellar spacing, owing to vast differences in the value of thickness used in the calculations [3, 8].

In the course of our experiments aimed at determining the cooling rates in melt spinning, we noticed that in an aluminium–copper eutectic alloy made from > 99.99% pure constituents, the eutectic grew in a cellular fashion. This observation has enabled us to develop a method of estimating the cooling rate from the eutectic colony spacing without any knowledge of the splat thickness and the details are reported in this communication.

The Al–$CuAl_2$ eutectic tapes were produced in air on a locally fabricated melt spinning apparatus [9]. The overall thickness of the tapes was in the range 40 to 50 μm when the substrate velocities varied between 30 and 25 m sec^{-1}. On the side of the tape in contact with the wheel, fine axial striations arising from the disc and similar to those reported by Walter [10] were noticed. It was suggested that the striations enable the gases to escape from between the ribbon and the wheel. On examination in a Philips EM 300 electron microscope, continuous thin regions capable of transmitting a 100 kV electron beam were frequently observed near the centre of the tapes. These regions were found to extend along the length of the tape and possibly arise due to the striations. Eutectic in these transparent regions was found to grow cellularly in the plane of the tape (Fig. 1). Often the lamellae in each cell were well aligned along the growth direction and also the cell boundaries were parallel and well delineated. The cell spacings were found to vary between 0.2 and 0.3 μm and the lamellar spacings in the colonies were in the range 8 to 10 nm.

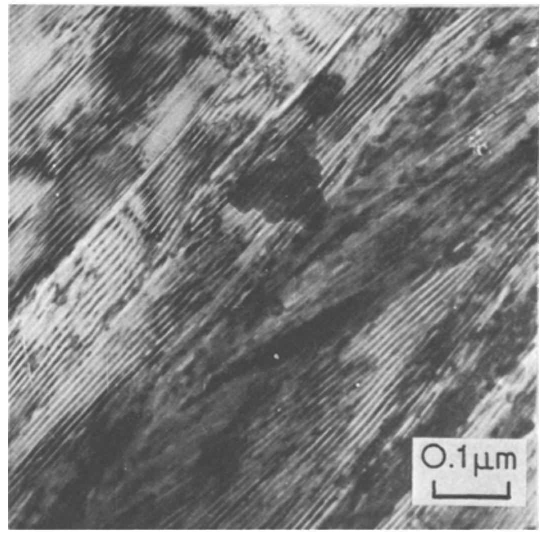

Figure 1 The cellular morphology of Al–$CuAl_2$ eutectic alloy observed in the melt-spun tapes. The parallel cells are used for determining the average cell spacing.

We assume that Newtonian conditions of cooling prevail in melt spinning. Under these conditions, the rate of cooling, $\dot{T}$, and the isothermal freezing time, t_s, are given by [11, 12]:

$$\dot{T} = \frac{hK(T - T_s)}{k \cdot d} \tag{1}$$

and

$$t_s = \frac{k\Delta H^f \cdot d}{hC_p(T_f - T_s)K} \tag{2}$$

where h is the interfacial heat transfer coefficient, K the thermal diffusivity, d splat thickness, k the thermal conductivity of the splat, ΔH^f the latent heat of fusion per unit mass, C_p the specific heat per unit mass, T_f the temperature of solidification, T_s substrate temperature, and T instantaneous temperature of splat.

Rohatgi and Adams [13] studied the growth of cellular Al–$CuAl_2$ eutectic over a range of freezing rates (df_s/dt) where f_s is the fraction solidified at time t. They varied the freezing rates

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over about three orders of magnitude (1.6×10^{-3} $\sec^{-1}$ to $7.3 \sec^{-1}$) by employing diverse solidification methods ranging from freezing in plaster moulds to arc melting thin layers over cast plates of eutectic alloy. They concluded that the colony formation is a heat and/or mass diffusion controlled phenomenon and that the colony spacing, C, is related to the inverse freezing rate by the relation

$$C = 15.5 \left(\frac{\mathrm{d}f_\mathrm{s}}{\mathrm{d}t}\right)^{-\frac{1}{2}} \tag{3}$$

where C is expressed in μm and t in sec. Since $t \to t_\mathrm{s}$ as $f_\mathrm{s} \to 1$, the colony spacings enable the estimation of local freezing times. On the assumption that cooling rate is estimated in the vicinity of freezing temperature, T_f, h from Equation 2 can be substituted in Equation 1 to yield

$$\dot{T} = \frac{\Delta H^\mathrm{f}}{C_\mathrm{p} \cdot t_\mathrm{s}}. \tag{4}$$

Obtaining t_s from Equation 3 and substituting the known values of ΔH^f ($342\,\mathrm{kJ\,kg^{-1}}$), C_p ($710\,\mathrm{J\,kg^{-1}\,K^{-1}}$) in the equation above results in

$$\dot{T} = \frac{1.157 \times 10^5}{C^2}. \tag{5}$$

It may be noted that the present approach does not require a knowledge of the splat thickness and is thus similar to the secondary dendrite arm spacing method of estimating cooling rates. The relation $C \propto \dot{T}^{-1/2}$ arises from the empirical observation (Equation 3) in an Al–$\mathrm{CuAl_2}$ eutectic [13]. Alternative equations relating colony spacing and inverse freezing rate, where possible, are equally suitable for the present analysis. An attempt has recently been made by Hunt [14] to obtain such an expression from theoretical considerations. The derived relationship, $C \propto G^{-1/2} V^{-1/4}$ where G is the prevalent temperature gradient and V is the growth velocity, differs from the empirical finding, $C \propto G^{-1/2} V^{-1/2}$ [13]. Theoretical developments could thus alter Equation 5 and make it more generally applicable.

Substitution of observed cell spacings (0.2 to 0.3 μm) in Equation 5 yields cooling rates of 1 to $3 \times 10^6\,\mathrm{K\,sec^{-1}}$. The result is in remarkable agreement with the cooling rates in melt spinning estimated by more direct methods such as calorimetry [15] and high speed photography [10]. Since the cell spacing in the present investigation was obtained from electron transparent regions only, the agreement between the calculated cooling rates and those determined by the use of methods employing bulk samples may be fortuitous. It is possible that h and C may change with thickness. Unfortunately, such variations could not be established due to difficulties in obtaining, by a jet polishing technique, large electron transparent areas amenable for quantitative determination of cell spacing. The central thin areas of the tape back-polished rapidly and interfered in uniform thinning of the tape. Use of ion-beam thinning technique could help solve the problem and aid in obtaining a more characteristic cooling rate.

Following the accepted procedures [3] of estimating cooling rates from the lamellar spacing method and assuming a thickness $\leqslant 0.15\,\mu$m for the transparent regions, we arrive at a cooling rate of $3 \times 10^9\,\mathrm{K\,sec^{-1}}$. The disagreement between the values obtained by the two procedures could be due to an overestimation of the cooling rate by the lamellar spacing method. Where the lamellar eutectic in the thin areas grows in the plane of the tape, and the distance grown is substantially greater than the tape thickness, the cooling rate estimated from lamellar spacing could be considerably lower. However, no exact information regarding the distance of growth is needed for evaluation of cooling rate by the cell spacing method.

Substituting the overall thickness (150 nm) along with other known values [3] of T_f (821 K), C_p ($710\,\mathrm{J\,kg^{-1}\,K^{-1}}$), and P ($3840\,\mathrm{kg\,m^{-3}}$) in Equation 1 gives an h value of $\sim 782\,\mathrm{J\,m^{-1}\,K^{-1}\,sec^{-1}}$ for the cooling rate of $10^6\,\mathrm{K\,sec^{-1}}$ estimated from colony spacing. The Nusselt number is evaluated to be 8.69×10^{-7} using a thermal conductivity value of pure aluminium ($135\,\mathrm{W\,m^{-1}\,K^{-1}}$) [16]. The value obtained justifies the assumption of Newtonian conditions of cooling [7]. It may be remarked that at a cooling rate of $10^6\,\mathrm{K\,sec^{-1}}$ aluminium–copper eutectic tapes of up to $\sim 20\,\mu$m can cool under Newtonian conditions (Equation 1) and we have examined regions of far smaller thickness. It may, however, be pointed out that in all methods utilizing microstructural features, it is implicitly assumed that the heat transfer coefficient estimated from isothermal part of freezing also apply during liquid and solid state cooling.

In practice, the heat transfer coefficient will be temperature dependent and will vary from stage to stage. The cooling rates calculated on the assumption of a constant value of h can only represent the average cooling rate by virtue of h obtained from isothermal freezing being intermediate to those prevalent in liquid and solid state cooling regimes [17].

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Influence of external magnetic and electric fields on sintering, structure and properties

Diffusion processes occurring during sintering can be significantly altered by applied electric or magnetic fields, resulting in novel structures with unique properties. This paper summarizes recent theoretical work by the author on the influence of inhomogeneous temperature distributions arising during electrical sintering on diffusion behaviour, and on the sintering of magnetic materials. Studies by Hermel *et al.* [6] corroborate the theoretical ideas presented here on electric sintering, but the author is unaware of any experiments on the sintering of magnetic materials in a magnetic field with which to compare this aspect of this theory.

1. Influence of uneven temperature distribution on diffusion processes during Joule sintering
The diffusion kinetics of macroscopic lattice defects is not enhanced either by passing direct current through a specimen or placing it in a uniform temperature gradient, *per se*. However, electric (Joule) heating can introduce a spacially varying temperature gradient within the specimen, and this can cause such diffusion. For instance, the temperature distribution, $T(r)$, in a wire under steady electric heating conditions is given by

$$T(r) = (\sigma\langle E\rangle^2/4\kappa)(R^2 - r^2) + T_0 \quad (1)$$

where σ is the electrical conductivity, κ the thermal conductivity, T_0 the temperature of the surface of the wire, $\langle E\rangle$ the external homogeneous

