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The effect of a glass substrate on cooling rate in splat-quenching

The technique of splat-quenching to produce thin films of rapidly solidified material is well-established. In the Duwez or "gun" technique [1] a small quantity of the molten alloy is ejected in a fine spray against a high-conductivity substrate. The measurement of cooling rate in such experiments is a much debated topic [2, 3]. Both direct measurements using thermocouples [4] and radiation pyrometers [5] and indirect estimates from the scale of microstructure of the solidified film [6, 7] have been employed. Although at best such methods can be described only as estimates they are useful in comparative studies where an absolute value of the cooling rate is not required. With this in mind the eutectic lamellar spacing method [7] was used by the author in a recent study [8] of the effect of various experimental parameters on the cooling rate attainable in a newly constructed controlled atmosphere gun-type splat-quencher. To obtain high cooling rates it is usual to use a substrate of high thermal conductivity. This note discusses the unexpected results obtained when the high conductivity copper substrate was replaced by one of low conductivity material (soda glass).

Specimens of eutectic composition (17.3 at. % Cu) aluminium copper alloy were splat-quenched from 800°C onto a copper substrate roughened with grade 400 emery paper and onto a sheet of 6 mm thick window glass. Care was taken to ensure that in all cases the other experimental conditions such as specimen mass, atmosphere (600 Torr argon), diaphragm rupture pressure etc, were constant. The resulting foils were sectioned and mounted transversely in araldite prior to polishing to a 1/4 μm surface finish and etching in 10% NaOH. Plastic/carbon replicas were then made for electron microscopic examination. These replicas allowed not only the microstructure to be examined but also the local foil thickness to be measured.

Three types of microstructure were observed; lamellar eutectic, degenerate eutectic and radial lamellar arrangements apparently nucleated at primary particles. These morphologies were identical to those observed in a previous study of the same system by Burden and Jones [7]. These authors showed that the relationship:

$$\lambda = AR^{-n}$$

where λ is the lamellar spacing and R the growth rate of a lamellar eutectic, may be extrapolated to the growth rates expected in splat-quenching. For the Al–$CuAl_2$ eutectic values of $n = 0.5$ and $A = 1.04 \times 10^{-8}\ m^{3/2}\ sec^{-1/2}$ were obtained.

Accordingly the finest spacings in each lamellar region were measured, along with the local foil thickness, and hence the appropriate growth rate R (m sec^{-1}) was evaluated. As a consequence of sectioning each lamellar region had a wide range of spacing; in every case the finest observed spacing was taken as the true spacing. (Even if the lamellae with the smallest apparent spacing were inclined at 20° to the normal to the foil section the error in estimating the true spacing by this assumption would be only 6%.)

From a knowledge of the growth rate and foil thickness the cooling rate was calculated as follows. The splat-substrate heat transfer coefficient, h (J m^{-1} K^{-1} sec^{-1}), and growth rate, R (m sec^{-1}), are related by the expression [4]:

$$h = \frac{\rho LR}{\theta_F - \theta_A} = 2.5 \times 10^6 R \qquad (1)$$

where ρ is the density of the splat material, taken as 3.84×10^6 g m^{-3} (assuming the values for Al and $CuAl_2$ [9] and the proportions in the eutectic as in the phase diagram). L is the latent heat of solidification, taken as 340 J g^{-1} on the same basis as ρ, θ_F and θ_A are respectively the freezing and ambient (substrate) temperatures, taken as

548 and 20° C. The cooling rate is then given by [4]:

$$C = \frac{h(\theta_F - \theta_A)}{\rho c d} \tag{2}$$

where c is the specific heat of the material; taken as 0.71 J g^{-1} K^{-1}, using the same assumptions as for ρ and L, d(m) is the foil thickness.

Equations 1 and 2 may be combined to give the required equation for cooling rate in terms of growth rate and foil thickness:

$$C = 4.8 \times 10^2 \frac{R}{d} \cdot \tag{3}$$

A surprising result was that, in general, the specimens quenched onto the glass substrate had finer lamellar spacings than those quenched onto the copper substrate even when comparing regions of the same local thickness. Spacings as fine as 600 Å were observed in the glass-quenched specimens whereas in those quenched onto copper few regions has spacings below 1000 Å. Since the foils were irregular in thickness (local cross-sections varied from as small as 25 μm to as large as 100 μm) direct comparisons of lamellar spacings were of little significance. However, substitution of the appropriate R and d values in Equation 3 showed that the specimens quenched onto the glass substrate had cooled faster than those quenched onto the abraded copper substrate. Specimens quenched onto the copper substrate had an average cooling rate of 3×10^4 K sec^{-1} whilst those quenched onto the glass substrate gave an average of 8×10^4 K sec^{-1}. The maximum cooling rate observed in copper-quenched specimens was 1.2×10^5 K sec^{-1} whereas in the glass-quenched specimens a number of areas with cooling rates in excess of 5×10^5 K sec^{-1} were apparent. (That these values of cooling rate are at the lowest extreme of those often associated with splat-quenching is a consequence of the relatively large amounts of material used (150 mg) and hence the thick foils (mean thickness about 50 μm) produced.) An explanation of these results may be found in the values of h, the splat-substrate heat transfer coefficient, which gives a measure of the degree of thermal contact between the splat and the substrate. The values obtained for the specimens quenched onto the glass substrate (4×10^4 Jm^{-2} K^{-1} sec^{-1}) were higher than those obtained for specimens quenched onto the copper substrate (8×10^3 J m^{-2} K^{-1} sec^{-1}), indicating that better thermal contact was achieved with the glass substrate. This improved thermal contact was manifested physically in that the specimens stuck to the glass after quenching. Closer examination showed the glass surface to have melted slightly on contact with the molten metal, thereby giving good wetting of the metal film and enhanced thermal contact. Further evidence was provided by the extent of degenerate eutectic microstructure; in addition to showing finer lamellar spacings the glass-quenched specimens had a lower proportion of degenerate microstructure than the copper-quenched specimens. A higher proportion of lamellar microstructure has previously been shown to be a function of improved thermal contact [7].

Although no previous quantitative measurements have been made on the effect of a glass substrate, qualitative observations from the extent of supersaturation obtained in aluminium solid solutions [10, 11] have suggested that the cooling rates are lower on glass substrates than on copper. It should be noted, however, that in one case [11] comparison was made with a grit-blasted copper substrate for which it is known that high thermal contact ($h = 1.2 \times 10^5$ J m^{-2} K^{-1} sec^{-1}) results. The values of h obtained in this work were consistent with those reported earlier for a polished copper substrate [7].

In these experiments values of the dimensionless Nusselt number ($N = hd/k$, where k is the thermal conductivity of the splat material) ranged between 0.002 and 0.020 indicating the cooling to be essentially Newtonian, and confirming the theoretical prediction of Ruhl [12] that the cooling rate is independent of substrate conductivity except in conditions approaching ideal cooling. Since in many rapid-solidification experiments ideal cooling conditions are not achieved the above observations are important. They serve to emphasize both the importance of good contact between the solidifying alloy film and the substrate and the danger of assuming that a low conductivity substrate will necessarily produce slower cooling. In the case discussed a three hundred fold decrease in substrate conductivity was compensated by improved thermal contact. That this improved contact resulted from surface melting of the substrate suggests there might be some value in using substrates of a low melting point material. In any event, if the highest cooling rates are to be obtained in any given apparatus, attention should be paid to all factors which give improved heat transfer, e.g., grit blasting of the substrate [7] and quenching in an inert atmosphere [13]. With poor thermal contact a high-conductivity substrate is wasted.

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LPE growth of garnets from the barium oxide–boric oxide flux

Thin films of magnetic garnet are important for both magneto-optic and magnetic "bubble" domain applications. The films are commonly grown from solution in a PbO–B_2O_3 flux onto non-magnetic garnet substrates by the liquid phase epitaxy (LPE) dipping method, as reported by Levinstein *et al.* [1]. In order to provide the required properties, bubble domain garnet materials are necessarily multicomponent, e.g. $Eu_{0.6}Y_{2.4}Fe_{3.9}Ga_{1.1}O_{12}$[2].

However, PbO–B_2O_3 fluxes have a number of undesirable features; they are toxic, corrosive and slightly volatile at the growth temperature. To obtain garnet as the primary phase, the (Fe + Ga):rare earth ratio must be greater than 12:1, which rapidly increases for subsequent growth runs from the same melt and also lowers the garnet solubility by the "common-ion effect". Lead is incorporated into the garnet lattice on the rare earth (dodecahedral) sites, particularly at lower growth temperatures. The incorporation of lead is detrimental to both the optical and magnetic properties of the garnet and because of its large ionic radius, affects the epilayer/substrate lattice mismatch. Furthermore the ratio of the Ga:Fe segregation coefficients is approximately 2.0 and varies with both temperature [1] and growth rate [3].

Linares [4] has grown yttrium iron garnet (YIG) from the BaO–B_2O_3 flux and has shown that it is congruently saturating (i.e. garnet can be crystallized when the Fe:Y ratio is the stoichiometric 5:3) when the molar ratios of BaO:B_2O_3 are between 67:33 and 58:42. Recently Hiskes and Burmeister [5] have demonstrated the use of this flux for garnet LPE. The advantages of BaO–B_2O_3 fluxes are that they are non-volatile, less corrosive and have both a higher garnet solubility and temperature coefficient of solubility. Divalent barium has a large ionic radius (1.35 Å) and is, therefore, unlikely to be accommodated in the garnet lattice.

According to the phase diagram of Levin and McMurdie [6], the melting points of BaO–B_2O_3 fluxes vary almost linearly between 950°C for the 58:42 composition to 1100°C for the 67:33 composition. Compositions with lower B_2O_3 contents have even higher melting points. Low growth temperatures are desirable since the epilayers produced have a higher growth-induced magnetic anisotropy, which is essential for the formation of stable bubble domains, especially as the trend towards smaller bubbles continues.

The melt composition used is given in Table I.