



Figure 3 TEM micrograph of the internal structure of the specimen shown in Fig. 3. Domain structure present.

short-range ordered samples exposed to HBr, revealed a uniform attack of the grains and also a selective attack of some boundaries. Sometimes deformed regions were also observed in the as-quenched specimens through SEM and TEM. In such regions, after suitably chosen exposure times, the close-packed planes were etched by HBr (Fig. 1).

The corrosive attack of long-range ordered Ni-rich Ni-Mo samples depended on whether a domain structure was present in the original  $\alpha$ -grains. The smallest loss ( $\sim 0.15 \text{ mg cm}^{-2}$  for 24 h) was found for samples containing the ordered phase  $\beta$  ( $\text{Ni}_4\text{Mo}$ ) or  $\gamma$  ( $\text{Ni}_3\text{Mo}$ ) not

exhibiting any domain structure. In the grains of such specimens no relevant corrosion pattern was observed by SEM except that some grain boundaries were attacked. On the other hand, any long-range ordered specimen containing a domain structure in the grains showed an enhanced loss and specific corrosion patterns, particularly for the phase  $\beta$  ( $\text{Ni}_4\text{Mo}$ ). Figs. 2 and 3 demonstrate the surface and internal structure of a  $\text{Ni}_4\text{Mo}$  specimen quenched from  $1100^\circ \text{C}$ , long-range ordered at  $850^\circ \text{C}$  for 40 h and then exposed to HBr. By comparing the two micrographs one is led to conclude that the corrosion pattern visible in Fig. 2 is due to an attack on the numerous domain boundaries present in the specimen after the annealing treatment.

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### Cooling-rates in splat-cooling

Being involved in splat-cooling studies and having utilized several different methods to determine the cooling-rate of the splat foils, we were quite interested in the recent exchange of opinions and ideas which appeared in the *Journal of Materials Science* [1, 2]. May we please add our thoughts?

Many attempts have been made to determine the cooling-rates achieved in splat-cooling. These

include theoretical calculations [3] as well as direct [4-6] and indirect [7, 8] measurements. Of all the rapid quenching techniques employed, the gun technique [4, 9] is probably the most difficult technique for measuring the cooling-rate. This is due to the wide range of splat thicknesses found (thicknesses may vary from  $0.05 \mu\text{m}$  to over  $25 \mu\text{m}$  in a single foil) and the variation of heat-transfer coefficients found from splat to splat. As shown by Ruhl [3], the cooling-rate varies inversely with the square of

the thickness in ideal cooling; in Newtonian cooling, the cooling-rate varies proportionately with  $h$ , the heat transfer coefficient, and inversely with the foil thickness. Other techniques, in particular the piston and anvil technique [10], yield much more uniform and reproducible splats, and thus would be more suitable for cooling-rate measurements.

Recently [1, 2] there has been much discussion as to the merits of two indirect methods used in estimating the cooling-rate. Anantharaman and Suryanarayana give arguments supporting the use of dendrite arm spacing (DAS) as an indication of cooling-rate and Jones supports the use of interlamellar spacing in eutectic alloys as a cooling-rate indicator. Both methods have their advantages and disadvantages. With the DAS method, one must first establish a reference curve of DAS versus cooling-rate ( $\dot{T}$ ) for a given solvent metal before cooling-rates can be determined. Secondly, it is not yet clear to what extent, if any, composition within a particular binary affects the DAS versus  $\dot{T}$  curve. Lastly, any measurement of DAS applies for a particular region of a splat, and in general will not give an average cooling-rate for the entire foil, thus necessitating many measurements. Uniform, fine splat foils are a great help in this respect but are difficult to produce.

As for the interlamellar spacing method used by Jones, its applicability may be limited by possible variations in the eutectic phase proportions and solidification prior to eutectic formation. Secondly, the constants involved in the relation between lamellar spacing ( $\lambda$ ) and the freezing rate ( $R$ ) must be determined beforehand for each alloy system. Lastly, as in the DAS method, calculations of  $\dot{T}$  from the lamellar spacing apply to a particular region of a splat foil, and will in general not be representative of the entire foil. Also, the interlamellar spacing method is applicable to eutectic compositions only, and neither the DAS nor the interlamellar spacing method applies to amorphous foils.

Thus, neither method is free from drawbacks. Rather, each must be viewed as a fair estimation of the true cooling-rate. In this light, other methods are also of interest, for example, using the degree of supersaturation of a solute as an indication of cooling-rate [11]. Several other variables besides thickness and the heat-transfer coefficient are important, in particular, the atmospheric conditions, which may lead to variations in the cooling-rate of several orders of

magnitude. This could explain why the cooling-rate calculated by Burden and Jones [8] on Al-Fe splatted in air was rather low, whereas recent work [12] on Al-Cu, under a flushed, high purity argon atmosphere, indicated cooling-rates of the order of  $10^8$  to  $10^9$  °C/sec (3 to 4 orders of magnitude greater) using the same interlamellar spacing method. Jansen [11] found this same increased cooling-rate in aluminium solid solution alloys using a flushed, high purity argon atmosphere at 500 mm Mg pressure as compared to an air atmosphere. Jansen noted that the oxygen partial pressure was reduced to about  $10^{-5}$  torr through the gettering action of the graphite heating element. The effects may be associated with the thickness of oxide films on the splat particles, on the surface condition of the substrate, or both.

For the time being one must treat all current methods of determining cooling-rates as worthwhile estimations. Because of the assumptions involved, one should talk in terms of orders of magnitude of cooling-rate, at best. The fact that most of the methods used thus far have been within one to three orders of magnitude of each other shows that each has its merits; the more crosschecks one can obtain, the greater the confidence factor.

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