6. A. J. PERRY, E. D. LAMOTTE, K. PHILLIPS, *J. Mater. Sci.* **5** (1970) 945.
7. A. J. PERRY, K. PHILLIPS, and E. DE LAMOTTE, *Fibre Sci. and Tech.* **3** (1971) 317.

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A Comment on "A Decade of Quenching from the Melt" by T. R. Anantharaman and C. Suryanarayana (J. Mater. Sci **6** *(1971) 1111-1135).*

The authors have produced an interesting and useful review, particularly in respect of their tabulation of information on the structure and properties of a large number of alloys in various metastable conditions induced by quenching from the liquid state. While being among the first to recognise the importance of cooling-rate variations, both within and among specimens, in accounting for variations in structure and properties [1], the authors accept uncritically the proposal of Matyja *et al* [2] that measurements of local dendrite arm spacing can be used to estimate cooling-rates of samples. They reject, on the other hand, another proposal [3] that eutectic interphase spacing be used for this purpose. They support this rejection by a number of incorrect statements and specious arguments. These will be dealt with first, followed by a consideration of the basis of the dendrite spacing method preferred by the authors.

Firstly, they state (p. 1116) that the cooling-rates of 7×10^5 and 3×10^4 K.sec^{-1} derived for two particular conditions in reference 3, are "at least two or three orders of magnitude less than the *usual* cooling-rates associated with the gun technique" (my italics). The higher value is in fact a factor of only three less than that quoted by the authors only two paragraphs earlier as being typical of their own previous experiments [1] on Al-Ge alloys with the gun technique. On the other hand, the authors, not without some justification, imply that all direct measurements of cooling-rates in splat-cooling are unreliable, yet, as we shall see, one such measurement provides the crucial support for the dendrite arm spacing correlation they endorse so enthusiastically. This particular direct measurement by Predecki *et al.* [4] gave 1.5 to 3×10^7 K.sec^{-1} for Al splats cooled on a composite Ni/Ag substrate. The smaller splat thickness obtained in that study would indeed be expected to give a higher cooling-rate than in reference 3, except in the unlikely event of thermal contact being poorer. If we follow Predecki *et al* in assuming Newtonian cooling applied in their experiment, the heat-transfer coefficient they derived is identical within experimental error to that derived in reference 3 for a considerably thicker splat. Even though there is some uncertainty about the significance of directly measured cooling-rates, they can hardly have been overestimates and there is no better alternative at present than to accept them provisionally at their face value. Their consistency with the indirect results of reference 3 is, at least temporarily, reassuring.

Secondly, the authors state incorrectly that a foil thickness of 30 μm was *assumed* in reference 3. This value was in fact directly measured by optical microscopy on the actual local foil cross-sections used for the eutectic spacing measurements. Foil thickness should always be indicated in reports of work on splat-cooling because of its known importance in affecting cooling-rate. Among others, the authors fail to do this in their previous report [1] of the effect of cooling-rate on metastable phase formation in Al-Ge alloys, although this information might have lent support to their cooling-rates derived entirely from measured dendrite spacings.

Thirdly, the authors state that the use of equilibrium eutectic phase proportions and

eutectic temperature in reference 3 is not justified. They assume incorrectly that a drastic undercooling is necessarily involved which will change the phase proportions. There is indeed indirect evidence that certain eutectics such as, Pd-Si, undercool drastically to produce glasses on splat-cooling [5]. The normal lamellar eutectic growth morphology was retained, however, for Al-$CuAl_2$ in reference 3, as in an earlier study [6]. The measured relation between undercooling, growth rate, and eutectic spacing for this eutectic [7] gives undercoolings of 5 and 1K for the spacings of 0.05 and 0.2 μm measured in reference 3. Even if the undercooling were 200 K, the effect on the derived heat transfer coefficients or cooling-rates would be by a factor less than 2. The relative amount of eutectic αAl and $CuAl_2$ observed by transmission electron microscopy was not detectably different from the equilibrium ratio. This is a good illustration of the danger of generalising the finding of a particular splat-cooling experiment or experiments to other studies with different alloys and conditions. This is why such conditions should always be stated as clearly as possible.

Fourthly, the authors challenge the assumption that the heat-transfer coefficient is not appreciably affected by different alloying elements. It is unfortunately necessary to make some assumption if cooling-rates derived by the eutectic method for a particular apparatus and conditions are to be applied to another alloy under nominally the same conditions. This assumption is certainly no less valid than the corresponding one made when dendrite spacing is used, and to which the authors raise no objection. In fact it is known that alloying affects dendrite arm spacing, the effect being *greater* than that of cooling-rate for hypoeutectic Al-Cu alloys [3]. This could be an important effect in the limited range of cooling-rates encountered in splat cooling.

Fifthly, the authors say that Newtonian cooling was *assumed* to prevail in reference 3. In fact, the lack of any detectable systematic variation of eutectic spacing with distance from the substrate side of the splat is a direct indication that ideal cooling was not applicable. The magnitude of the derived heat transfer coefficient confirmed that intermediate cooling applied in one case studied and Newtonian cooling in the other. Predecki *et al* [4] on the other hand, gave no such microstructural confirmation that Newtonian cooling applied in their studies.

It is pertinent to examine the basis of the dendrite-arm spacing method preferred by the authors. This was developed from the correlation found by Spear and Gardner [8] in 1963 for a number of commercial Al-Si and Al-Cu based alloys over a range of dendrite size from ~ 12 to ~ 170 μm and of cooling-rate from ~ 0.02 to ~ 20 K.sec^{-1}. This correlation was subsequently extended to smaller dendrite spacings and high cooling-rates by Dean and Spear [9]. They included data on Al 4.5 wt % Cu collected or determined by Bardes and Flemings [10] (originally for a dendrite size range of 3 to 2500 μm and cooling-rate range of 3×10^{-5} to 400 K.sec^{-1}) and single points for minus 400 mesh atomised Al 5.6 wt % Zn, 2.5 wt % Mg, 1.6 wt % Cu, 0.30 wt % Cr alloy powder (dendrite spacing 10 μm, estimated cooling-rate 4×10^4 K.sec^{-1}) and Al-Cu/Al-Si alloy splats (dendrite spacing 0.2 μm, assumed cooling-rate 2×10^7 K.sec^{-1}). Matyja *et al* added values of dendrite spacing between ~ 0.07 and ~ 0.2 μm for areas of Al 1 at % Fe, Al 6 at % Pd and Al 11 at % Si alloys transparent in the electron microscope. Direct measurements of cooling-rate were made only for the results of Spear and Gardner and for the slower cooling-rates applicable to the results for Al 4.5 wt % Cu collected by Bardes and Flemings. In particular, it is not clear how the cooling-rate of the atomised alloy powder was obtained, or whether, as seems likely [9] it was simply fitted to the data collected by Bardes and Flemings [10]. The cooling-rate of $\sim 2 \times 10^7$ K.sec^{-1} measured by Predecki *et al* for a 1 μm Al splat seems to have been used by Dean and Spear to plot the splat-cooling result they include. Matyja *et al.* assumed that a foil thickness of 2 μm applied for this measurement and assumed their dendrite results were for foils 0.2 μm thick. This enabled them to estimate a cooling-rate of 2×10^8 K.sec^{-1} assuming Newtonian cooling and the same heat transfer coefficient. It is apparent that the extension of Spear and Gardner's correlation from cooling-rates ~ 100 K.sec^{-1} to those applicable in splat-cooling is based entirely on just one isolated cooling-rate measurement, that of Predecki *et al* for a 1 μm Al splat.

The basis of the eutectic method is considerably more secure. Measurements of eutectic spacing as a function of growth-rate have been made independently from experiments using steady state unidirectional growth into the range encountered in splat-cooling [3]. Such controlled

growth has been almost entirely neglected in the study of dendrite arm spacing. Furthermore the relationship determined experimentally agrees very well with theory. A corresponding theory for dendrite arm spacing has yet to be formulated, doubtless because of the complexity of the problem.

Finally, the authors overlook the real limitation of the eutectic method, which is simply that it can only be used when a sufficient proportion of the microstructure grows eutectically. This is a more restrictive condition than that for the dendrite method because dendrites dominate microstructure under a much wider range of alloy and growth conditions. Against this must be set the fact that the dendrite method is comparatively insecurely based. Until more is known about what controls dendrite arm spacing or until a completely reliable method is devised for measuring high cooling-rates under such conditions as in the gun technique, the preferred course would seem to be to use the eutectic method to calibrate cooling-rates for a particular *apparatus* and use the dendrite method, provisionally, to obtain *relative* cooling-rates for microstructural changes in particular alloys studied.

References

1. C. SURYANARAYANA and T. R. ANANTHARAMAN, *J. Mater. Sci.* **5** (1970) 992.
2. H. MATYJA, B. C. GIESSEN, and N. J. GRANT, *J. Inst. Met.* **96** (1968) 30.
3. M. H. BURDEN and H. JONES, *ibid* **98** (1970) 249.
4. P. PREDECKI, A. W. MULLENDORE, and N. J. GRANT, *Trans. Met. Soc. AIME*, **233** (1965) 1581.
5. H. S. CHEN and D. TURNBULL, *Acta Metallurgica*, **17** (1969) 1021.
6. D. R. SPALDING, R. E. VILLAGRANA, and G. A. CHADWICK, *Phil. Mag.* **20** (1969) 471.
7. A. MOORE and R. ELLIOTT, in "The Solidification of Metals", ISI Publ. No. 110 (1968) p. 167.
8. R. E. SPEAR and G. R. GARDNER, *Trans. Amer. Foundrymen's Soc.* **71** (1963) 209 (*Modern Castings*, **43** (5)).
9. W. A. DEAN and R. E. SPEAR, in "Strengthening Mechanisms: Metals and Ceramics", Ed. J. J. Burke *et al* (Syracuse Univ. Press, 1966) p. 268.
10. B. P. BARDES and M. C. FLEMINGS, *Trans. Amer. Foundrymen's Soc.* **74** (1966) 406 (*Modern Castings*, **50** (3)).

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Reply to "A Comment on 'A Decade of Quenching from the Melt'" by H. Jones

We wish to thank the author at the outset for his complimentary remarks on our Review. His critical comments concern the section of our Review dealing with measurement of cooling-rates. He contends that we accept the dendrite arm spacing method "uncritically", but reject the eutectic interphase spacing method for evaluation of cooling-rates produced in splat-cooling (liquisol-quenching) experiments. We would like to reiterate that every method has its advantages and disadvantages and that there is no single method which can evaluate the very high cooling-rates encountered in liquisol quenching with reliability as well as precision. All methods are, however, generally suited for a comparison of the cooling-rates under different conditions and for a given apparatus and alloy system.

The first point raised by the author is that our cooling-rate of 2×10^6 °C/sec [1] is only three times higher than the values of 7×10^5 and 3×10^4 °C/sec observed by Burden and Jones [2] for Al-Cu alloys quenched on to grit-blasted and mechanically polished copper substrates, respectively. We would like to clarify that our substrate was *mechanically polished* and not grit-blasted. Hence their cooling-rates are not three, but nearly *seventy* times less for the same state of the substrate. In fact, Predecki *et al* [3] report a cooling-rate of 5×10^8 °C/sec for silver solidified on a nickel/silver composite substrate, in which case the cooling-rates of Burden and Jones [2] are about three orders of magnitude lower. Moreover, we believe that the higher values reported by Predecki *et al* [3] are due to their thinner splats. The cooling-rate could perhaps have been even higher, but for the relatively poor thermal conductivity of the composite substrate.

With reference to his second point that the splat thickness was not *assumed*, but actually *measured* by optical microscopy, we wish to point out that it was not clear from the above-referred paper [2], whether it was measured or assumed. Our statement was based on their report that the splat thickness was "taken as 3×10^{-3} cm".

We agree with the author that "foil thickness should always be indicated in reports of work on splat-cooling because of its known importance in affecting cooling-rate". In spite of the contention

that the splat thickness was actually measured in their experiments, Burden and Jones [2] fail to correlate or mention the variation of eutectic spacing (and hence cooling-rate) with foil thickness.

Thirdly, it has been contended that undercooling is not necessarily involved in all cases of splat-cooling. In point of fact, however, the experimental investigations reported so far seem invariably to point to considerable undercooling, e.g. about 200°C in Au-Sb [4], about 135°C in Cu-Ni [5] and appreciable, but unestimated values in other alloy systems. According to the more recent work of Miroshnichenko and Brekharya [6], the degree of undercooling is considerable in Al-base alloys and increases with increase in cooling-rate. Extrapolating the common observation that appreciable undercooling is observed even in conventional quenching techniques and considering the many relevant observations in splat-quenching experiments, one is naturally led to the assumption that substantial undercooling is generally involved in all fast-quenching experiments. In fact, the observed undercooling provides a useful basis for explaining the metastable effects in alloy systems. Giessen and Willens [7] have actually plotted undercooling-composition diagrams to explain the formation of non-equilibrium intermediate phases.

As for "the use of equilibrium eutectic phase proportions and eutectic temperature", it is relevant to mention that Jansen *et al* [8] and more recently Ramachandrarao *et al* [9] have observed supersaturated solid solutions up to the eutectic composition in the Al-Cu system. Spalding *et al* [10] also point out that the phase distribution was non-uniform in splat-cooled Al-Cu alloys. These observations suggest unpredictable changes in the proportion of the microconstituents in splats. Further, although electron microscopy of a few regions might reveal the typical eutectic mixture, it is doubtful whether this technique can give a representative picture, especially as far as quantitative metallography is concerned, in cases of non-uniform distribution of phases.

As for the fourth point, the author himself concedes that "it is unfortunately necessary to make some assumption" in evaluating the cooling-rates. We also appreciate the difficulties and complications involved in this regard. Alexander and Rhines [11] and Ichikawa *et al* [12] have clearly shown that the dendrite spacing is only slightly affected by the nature and concentration of the solute element. Hence the dendrite arm spacing method can safely be applied to all alloy systems. Such a report with regard to the heat transfer coefficient will lend more credence to the reliability of the eutectic phase spacing method.

The fifth point concerns the assumption of Newtonian cooling. The values of the Nusselt number indicate that Newtonian cooling prevails at the mechanically polished substrate, while intermediate cooling prevails in the case of the grit-blasted substrate. Our objection is only to the point that the heat transfer coefficient *and* the cooling-rate are calculated on the basis that Newtonian cooling prevails in *both* cases, which is not strictly true.

We agree that the interlamellar spacing method can be used *only* for eutectic alloys and that too when a sufficient proportion of the microstructure grows eutectically. On the other hand, the dendrite arm spacing method can be applied effectively to all types of alloy systems.

In conclusion, we would like to stress the point that no method is exact and almost any of the methods referred to can be utilised for a comparative study under otherwise identical conditions. The choice of the method will inevitably depend on the individual concerned, the problem on hand and the resources available. In any case, these cooling-rates are at best *estimates* and can never be called *measurements* in the true sense of the term.

References

1. C. SURYANARAYANA and T. R. ANANTHARAMAN, *J. Mater. Sci.* **5** (1970) 992.
2. M. H. BURDEN and H. JONES, *J. Inst. Metals* **98** (1970) 249.
3. P. PREDECKI, A. W. MULLENDORE, and N. J. GRANT, *Trans. Met. Soc. AIME* **233** (1965) 1581.
4. A. K. JENA, B. C. GIESSEN, M. B. BEVER, and N. J. GRANT, *Acta Metallurgica* **16** (1968) 1047.
5. K. LOHBERG and H. MULLER, *Z. Metalk.* **60** (1969) 231.
6. I. S. MIROSHNICHENKO and G. P. BREKHARYA, *Phys. Met. Metallogr.* **29** (1970) 233.
7. B. C. GIESSEN and R. H. WILLENS, in "Phase Diagrams: Materials Science and Technology, Vol. 3" ed. A. M. Alper (Plenum Press, New York, N.Y. 1970) p. 103.
8. C. JANSEN, B. C. GIESSEN, and N. J. GRANT, Fall Meeting of the *Met. Soc. AIME*, Detroit (1968).
9. P. RAMACHANDRARAO, M. LARIDJANI, and R. W. CAHN, *Z. Metalk.* (1971). (In Press).

10. D. R. SPALDING, R. E. VILLAGRANA, and G. A. CHADWICK, *Phil. Mag.* **20** (1969) 471.
11. B. H. ALEXANDER and F. N. RHINES, *Trans. Met, Soc. AIME* **188** (1950) 1267.
12. R. ICHIKAWA, T. OHASHI, and N. SKHINODA, *Nagoya Kogyo Daigaku Gakuho*, **21** (1969) 389.

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Comments on Authors' Reply to "A Comment on 'A Decade of Quenching from the Melt' "

It is noteworthy that the authors now admit the applicability of *all* the methods (including the eutectic method [1]) of estimating cooling-rates in splat-cooling, and accept in principle that all of them (including the dendrite method [2]) have drawbacks. It is the nature and force of these limitations which is at issue.

Their reply to my first point obscures the issue. Their clarification of the substrate condition in their experiments [3] is appreciated but it is misleading to compare experiments in terms of this variable in isolation from the splat thickness. While admitting, in their reply to my second point, the importance of this latter, they do not take the opportunity to specify it for their conditions, but presumably it must have been < 0.1 μm to appear transparent to electrons. Such a difference in thickness could entirely account for the factor of seventy difference in cooling-rate they point out. The real issue they raise, however, is what range of cooling-rate is characteristic of splat-cooling? Their review quotes measurements and estimates covering the range 10^5 to 10^8 K/sec, most of the values (including ours [1] and theirs [2]) being at the lower end of this range. The measured value [4] of 5×10^8 K/sec for 1 μm thick Ag splats they select as specially characteristic is in fact the *highest* measured directly to date. As shown previously [1], our cooling-rate estimate of 7×10^5 K/sec for 30 μm thick Al-$CuAl_2$ eutectic splats is fully consistent with the corresponding measurement [4] of $\sim 2 \times 10^7$ K/sec for a 1 μm Al splat, i.e. it corresponds to the same heat transfer coefficient. In fact it is *splat thickness*, varying from < 0.1 μm up to 100 μm within specimens and under different splat-cooling conditions, which is normally the *main* factor determining cooling-rate in practice, and not substrate surface condition (heat-transfer coefficient) invoked by the authors to account for the difference between our [1] and their [2] estimates. In fact, the cooling-rate of 2×10^6 K/sec they estimate for an Al–Ge alloy splat less than 0.1 μm thick, suggests a heat transfer coefficient of $< 10^{-2}$ cal/cm^2 °C sec, which is substantially *lower* than either of our values (3 and 0.2 cal/cm^2 °C sec) or those of Predecki *et al* [4] (3 to 7 cal/cm^2 °C sec). This suggests that thermal contact between splat and substrate was in fact *poorer* in their experiments [2] than in ours [1], and not better as they imply.

In respect of the third point, just because evidence has been found for large undercooling ($\sim$ 100 K) in some splat-cooling experiments, it does not follow that this generally occurs. The expectation is that a sufficiently high cooling-rate would need to be exceeded for a given alloy to undercool substantially and this threshold cooling-rate will vary widely with the alloy constitution. This in no way undermines the usefulness of the undercooling concept in accounting for metastable phase formation. Metastable phases do not always form on splat-cooling and, conversely, some metastable phases require only a few degrees undercooling to form them [5]. The authors' doubts about truly representative measurements being made on limited regions of specimens by electron microscopy apply equally to the dendrite method. Our measurements were deliberately taken in the thicker regions in order to be representative of the splat as a whole, in preference to the established practice with the dendrite method of measuring only the thinnest areas, which are not necessarily representative of the remainder.

On the fourth point, the authors select from several available, the two references which happen to support their belief that dendrite spacing is only slightly dependent on alloy constitution. Of these, that by Alexander and

Rhines [6] has been criticised on experimental grounds [7]. Furthermore, the work by Spear and Gardner [8] originating the dendrite spacing/cooling-rate correlation the authors advocate, *itself* contains unambiguous evidence of a marked effect of alloy constitution. When expressed as a power relation, in line with other measurements [1], the effect of composition, they [8] find, for example, is at least as great as that of cooling-rate. The authors' unqualified statement that "Hence the dendrite arm spacing method can safely be applied to all alloy systems" seems precipitate in relation both to this evidence and to all that is available, amounting to measurements on just a few (mainly Al-base) systems over restricted ranges of variables.

On the fifth point, the Nusselt number of 0.03 for the grit-blasted substrate indicates that cooling is only just within the lower bound [9] of the intermediate cooling-range. Ruhl's calculations [9] show [10] that the assumption of Newtonian conditions under such circumstances* introduces an error of considerably less than a factor of two which is certainly not greater than other sources of error and uncertainty in this and in other methods.

The attraction of the dendrite method is undoubtedly its ease of application and wide opportunity for use. This is no reason for disregarding the limitations of its present basis and for advocating its universal use without qualification. Obviously, spot checks by alternative methods are a minimal safeguard and there is clearly a general need to check one method against another on common systems. This is the approach which will enable present *estimates* to be improved, and, ultimately, to be superseded by *measurements*.

References

1. M. H. BURDEN and H. JONES, *J. Inst. Metals* **98** (1970) 249.
2. H. MATYJA, B. C. GIESSEN, and N. J. GRANT, *ibid* **96** (1968) 30.
3. C. SURYANARAYANA and T. R. ANANTHARAMAN, *J. Mater. Sci.* **5** (1970) 992.
4. P. PREDECKI, A. W. MULLENDORE, and N. J. GRANT, *Trans. Met. Soc. AIME* **233** (1965) 1581.
5. B. C. GIESSEN and R. H. WILLENS, in "Phase Diagrams: Materials Science and Technology", vol. 3, Ed. A. M. Alper (Plenum Press, New York, 1970), p. 103.
6. B. H. ALEXANDER and F. N. RHINES, *Trans. AIME* **188** (1950) 1267.
7. J. A. HORWATH and L. F. MONDOLFO, *Acta Metallurgica* **10** (1962) 1037.
8. W. E. BROWER, R. STRACHAN, and M. C. FLEMINGS, *Cast Metals Res. J.* **6** (1970) 176.
9. R. C. RUHL, *Mater. Sci. Eng.* **1** (1967) 313.
10. H. JONES, *ibid* **5** (1970) 297.
11. R. E. SPEAR and G. R. GARDNER, *Trans. Amer. Foundrymen's Soc.* **7** (1963) 209; (*Modern Castings* **43** (5)).

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*Brower *et al* [8] reached the same conclusion for an even higher Nusselt number (0.5) observed in splat-cooling

*Observations during Annealing of Cold-Drawn Polyethylene**

This letter describes some preliminary observations made during cold drawing and subsequent annealing of bulk-crystallised linear polyethylene. The structures that are observed to develop during annealing on a microscope heating stage are probably due to the presence of low molecular weight fractions.

Sheet specimens, 0.2 mm thick, of compression moulded Rigidex 2 high-density polyethylene were observed during cold drawing by a micro-tensile machine fitted to a Zeiss photomicroscope. The polyethylene contained particles of silica catalyst, ranging up to 25 μm diameter, which initiated the formation of cavities during the cold-drawing process. The natural draw ratio of 8 resulted in considerable elongation of the cavities, and the influence of the transverse tensions associated with the cold-drawn neck boundary are evident from the fact that the voids were very much wider in the plane of the sheet than perpendicular to it. Fig. 1a shows the outline of a void in as-drawn material and 1b a view of another void in a section perpendicular to

*This work was carried out at the University of Surrey, Guildford.