Solidification Rate in Rapid Conduction Cooling

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The ability of rapid conduction cooling to produce new non-equilibrium phases is examined with particular attention on solidification rate. By matching the rate of solidification calculated numerically from the heat flow balance with the crystal growth rate calculated by a kinetic equation, the kinetic undercooling for a given experimental condition is estimated. A limiting condition of cooling is presented in which the cooling rate is so large that the crystal growth cannot cover the whole sample body before it is cooled down to a low temperature where the growth rate of the crystal is negligibly small.

INCREASING attention has recently been paid on the method of splat cooling in producing new crystalline and non-crystalline phases which are not obtainable by conventional techniques. The method of splat cooling,[1] though there are many variations in details, is characterized by the rapid cooling of small amount of liquid material by heat extraction into a cooled substrate by conduction.

Quantitative calculations of cooling rate in splat cooling were performed by Ruhl[2] who analyzed the effects of some ten variables on cooling rate. In order to properly evaluate the ability of splat cooling to produce new structures, however, it appears necessary to estimate not only the average rate of cooling but also the rate of advancement of solid-liquid interface, the solidification rate.

The purpose of this paper is to present the results of calculations of solidification rate based on the heat flow balance during splat cooling and to show how the calculated results can be compared with the rate of crystallization which may be estimated from the molecular kinetic considerations. From such comparisons it is possible to estimate the kinetic undercoolings in the liquid at the solid-liquid interface. A knowledge of such undercoolings should permit the quantitative assessments of the effectiveness of individual splat cooling experiment.

CALCULATION OF SOLIDIFICATION RATE BASED ON THE HEAT FLOW BALANCE

1. Basic Model and Equations for Calculation

Fig. 1 shows a schematic illustration of a model for calculation. It is assumed that the situation may be treated as one of one dimensional heat flow problems. Extraction of heat from a splat into a substrate alone is considered and not the heat lost into the outer atmosphere from the top (farthest from the substrate) surface of the splat. The basic heat flow equation of one dimension to be solved is,

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} \qquad [1]$$

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where

T = temperature
t = time
x = position variable as indicated in Fig. 1
α = thermal diffusivity

Initial and boundary conditions are,

$$T(x, 0) = T_b \qquad x < 0 \qquad [2]$$

$$T(x, 0) = T_0 \qquad 0 \le x \le d \qquad [3]$$

$$T(\epsilon, t) = T_m \qquad [4]$$

$$K_s \left.\frac{\partial T_s}{\partial x}\right)_{x=\epsilon} - K_l \left.\frac{\partial T_l}{\partial x}\right)_{x=\epsilon} = L \frac{d\epsilon}{dt} \qquad [5]$$

where

T_b = initial substrate temperature
T_0 = initial splat temperature
T_m = temperature of solidification
K = thermal conductivity
ϵ = position of solid-liquid interface
L = latent heat of fusion per unit volume
d = splat thickness

subscripts s and l refer to solid and liquid respectively.

Eq. [5] expresses the heat balance at the solid-liquid interface.

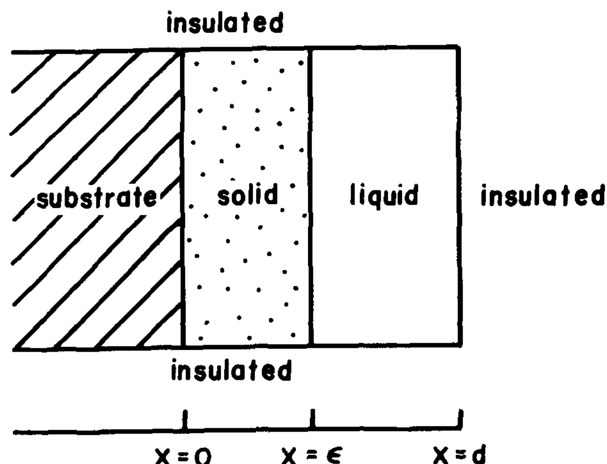

Fig. 1—Model of splat cooling process.

2. Analytical Solutions

When the thermal contact at the splat-substrate interface is ideal, for a short time after splat cooling or when d is large, *i.e.*, when a boundary condition $T(d, t) = T_0$ is satisfied, the position of solid-liquid interface may be expressed by a well known simple relation,[3,4]

$$\epsilon = m\sqrt{t} \qquad [6]$$

where m is the solidification constant which may be determined numerically from a relation derivable from Eq. [5] and the error function solutions of Eq. [1]. The rate of solidification is from Eq. [6],

$$v = \frac{m^2}{2\epsilon} \qquad [7]$$

When the thermal contact at the splat-substrate interface is poor, the solidification is limited by the heat transfer at the interface, *i.e.*, the condition of Newtonian cooling is realized. The solidification rate in this case depends on the rate of extraction of latent heat of solidification through the splat-substrate interface,

$$v = \frac{h}{L}(T - T_b) \qquad [8]$$

where h = heat transfer coefficient at splat-substrate interface T in Eq. [8] represents the temperature of a splat at splat-substrate interface. In theory, at the initial stage of solidification, for ideal thermal contact, the solidification rate expressible by Eq. [7] gives infinitely large value. This would not happen in actual experimental condition due to the finite value of h in reality. The thermal conductivities of gases are typically of the order of 10^{-2} W m^{-1} K^{-1}, hence the value of h, which may be calculated by dividing the thermal conductivity by the thickness of the layer of the gas, can hardly be as large as 10^8 W m^{-2} K^{-1} when even a trace of adsorbed gas exists on the substrate surface prior to splat cooling.

3. Numerical Solutions

By solving Eq. [1] by a numerical method it is possible to estimate the solidification rate for any given initial and boundary conditions.

The simple explicit finite difference method is employed in the present work employing proper considerations for the splat-substrate interface, the solid-liquid interface and the top surface of the splat. Time and position increments are chosen with care for proper convergence and accuracy of the calculated results.[5] The number of position increments within the splat varied from 20 for the case of large h value (large temperature gradient) to 5 for the case of small h. The width of position increments is divided by the time duration while a certain position stays at the given solidification temperature to give the average solidification rate at that position. Calculations within the substrate are made until the calculated temperature for a certain position is within 10^{-7} K of the initial substrate temperature.

RATE OF CRYSTAL GROWTH

The rate with which a crystal grows depends on the molecular nechanism of incorporation of molecules from liquid to the crystal surface. The molecular mechanism of growth varies for the change in driving force of growth. Cahn[6] showed that for small driving forces (small undercoolings from the equilibrium melting point) a crystal would grow slowly by layer-by-layer accumulation of new crystal planes (the "lateral" mode of growth) and that for large driving forces, a random way of molecular attachment at the crystal surface (the "continuous" growth mode) would predominate.

Cahn[6] showed that for the "continuous" mechanism of crystal growth the growth velocity would be expressible as,

$$v = \frac{\beta}{a}\left(\frac{D}{RT}\right)\left(L\,\frac{\Delta T}{T}\right) \qquad [9]$$

where

a = inter-atomic distance
β = geometric factor
D = liquid self-diffusion coefficient
R = gas constant
ΔT = undercooling from the equilibrium melting point

Eq. [9] may be interpreted as the equation for the velocity of an interface with a mobility (D/RT) under the influence of a driving force $(L\,\Delta T/T)/a$. The mobility is expressible in terms of viscosity[7] and Eq. [9] may be rewritten as,

$$v = \frac{2\beta a}{9}\left(L\,\frac{\Delta T}{T}\right)\left(\frac{1}{\eta}\right) \qquad [10]$$

where η = viscosity. Calculations of crystallization rate by Eq. [9] or [10] with the data of diffusion coefficient or viscosity would give the results with a maximum at certain value of undercooling as obtained for the solid state phase transformation rate.[8]

RESULTS OF CALCULATIONS

All the calculations were made for the case of splat cooling of aluminum. The physical properties used in the calculations are listed in Table I.

Fig. 2 shows the temperature position profile calculated for the cases of different thermal contact at the splat-substrate interface. The values of dimensionless quantity hd/K_S which determines the mode of cooling of a splat are 3.6, 0.36 and 0.036 for curves 1, 2 and 3 respectively. The steep temperature gradient for curve 1 indicates that the cooling is limited by the heat flow resistance within the splat and substrate whereas the temperature gradient for curve 3 is small indicating that the cooling is nearly Newtonian.

Fig. 3 presents the change of solidification rate within splats. The solidification rate sharply decreases as

Table I. Properties of Splat and Substrate Materials Used in Calculations

Materials	Thermal conductivity (W·m^{-1}K^{-1}) × 100	Density (kg·m^{-3}) × 1000	Specific heat (J·kg^{-1}·K^{-1}) × 1000	Heat of fusion (J·kg^{-1}) × 1000
Liquid Al	0.971	2.4	1.089	397.7
Solid Al	2.303	2.7	0.900	
Solid Cu	3.936	8.92	0.385	–

solidification proceeds toward the top surface for curve 1 (large h) as expected from Eq. [7] given for the case of ideal thermal contact. The small and almost constant solidification rate at all positions within the splat for

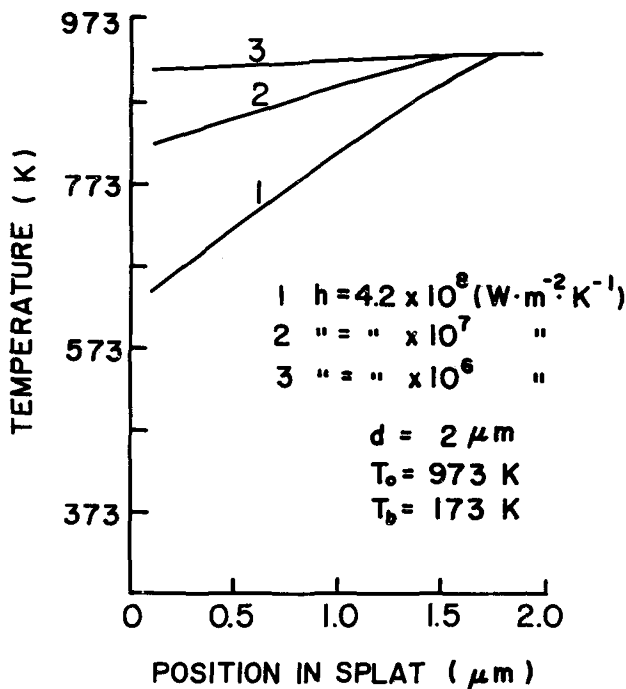

Fig. 2—Temperature vs position in splat when the solid-liquid interface reached the top surface calculated for zero undercooling.

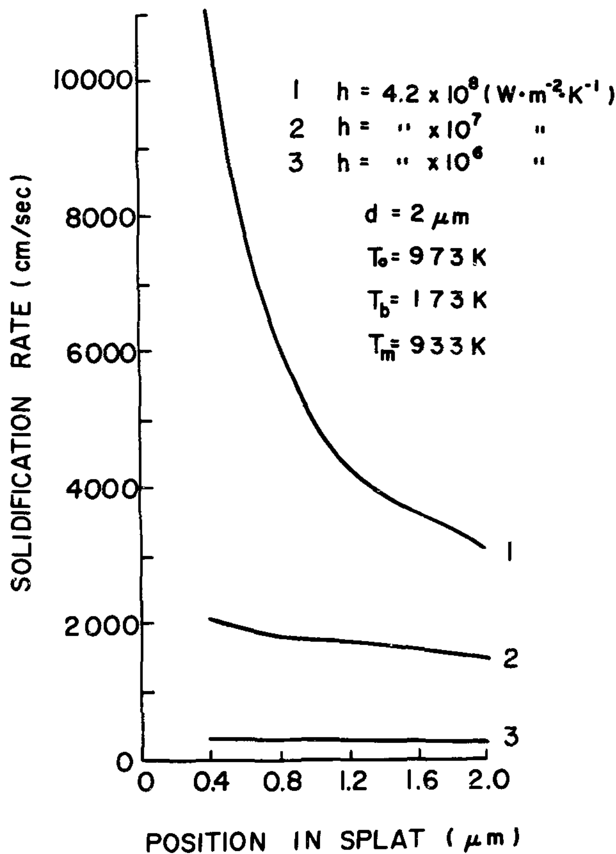

Fig. 3—Rate of solidification vs position for different thermal contacts at the splat-substrate interface calculated for zero undercooling.

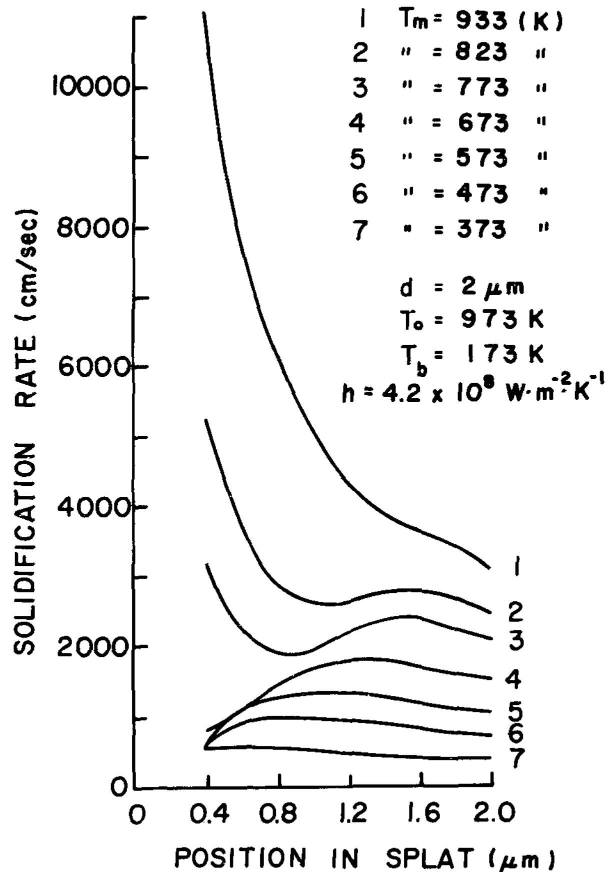

Fig. 4—Rate of solidification vs position for different solidification temperatures.

curve 3 (small h) may well be understood by Eq. [8] given for Newtonian cooling case.

The effects of undercooling below equilibrium melting point on the rate of advancement of solidification front are presented in Fig. 4. As the solidification temperature, T_m, decreases, the amount of heat to be extracted before solidification temperature is reached becomes large and also the temperature difference between the splat and substrate during solidification becomes small, hence the rate of solidification decreases. In Fig. 4 it is seen that for large undercoolings the solidification proceeds in an almost Newtonian manner even for a good thermal contact at the splat-substrate interface.

The rate of crystallization as a function of undercooling calculated from Eq. [10] using the viscosity data by Wilson[9] and putting $\beta/a = 0.3 \times 10^8\ cm^{-1}$ is shown in Fig. 5 together with curves for the rate of solidification at the top surfaces of splats calculated from the heat flow balance. For a given set of initial and boundary conditions, the crystallization would proceed at a temperature for which the crystallization rate coincides with the rate of solidification determined from the heat flow balance. Consequently, the actual crystallization temperatures may be found from the intersection points of the solid curves and the dashed curve in Fig. 5. The differences between these actual solidification temperatures and the equilibrium melting point represent the kinetic undercoolings for solidification of splats.

Fig. 6 presents the kinetic undercoolings in the liquid at the solid-liquid interface when the solidification front

reached the top surfaces of splats as a function of thermal contact by plotting the intersection points of curves in Fig. 5.

The rates of solidification calculated at the top surfaces for various splat thicknesses are compared with

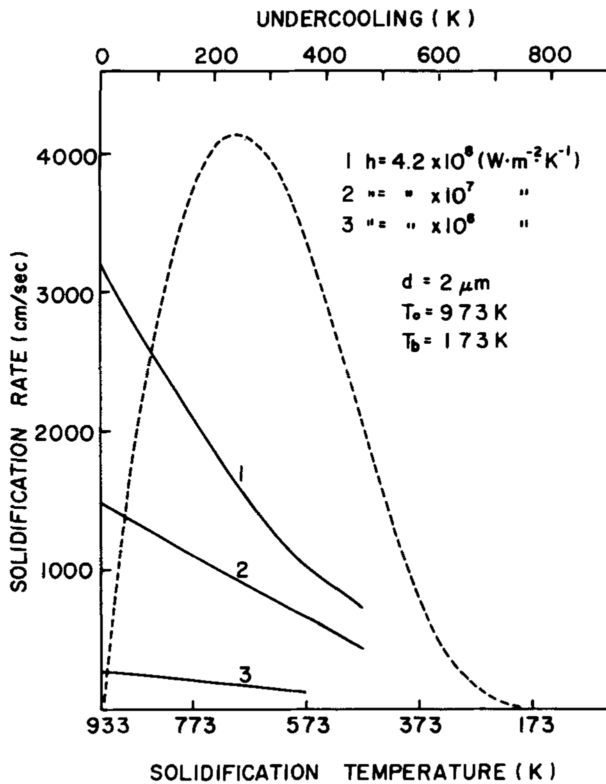

Fig. 5—Comparison of the solidification rate and the crystal growth rate for different thermal contact at the splat-substrate interface. Solid lines: Rate of solidification vs undercooling, when the solid-liquid interface reached the top surface of splats, calculated from the heat flow balance. Dashed line: Rate of crystal growth vs undercooling calculated from the kinetic equation, Eq. [10].

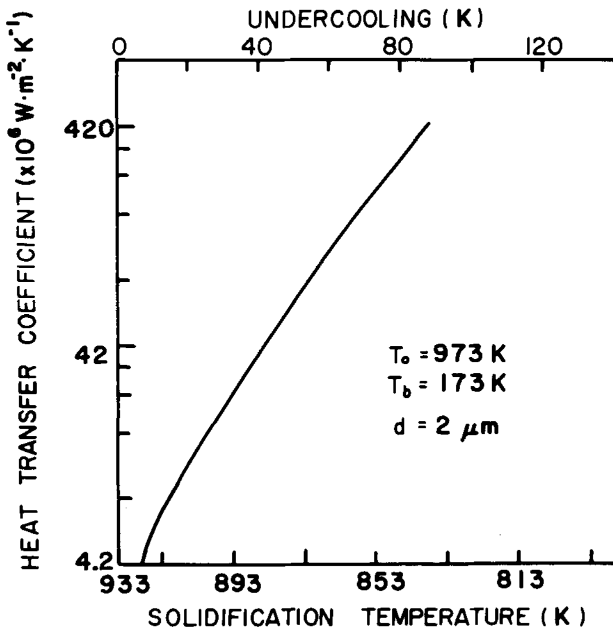

Fig. 6—Thermal contact at the splat-substrate interface vs kinetic undercooling in the liquid at the solid-liquid interface when the solidification front reached the top surface of splats.

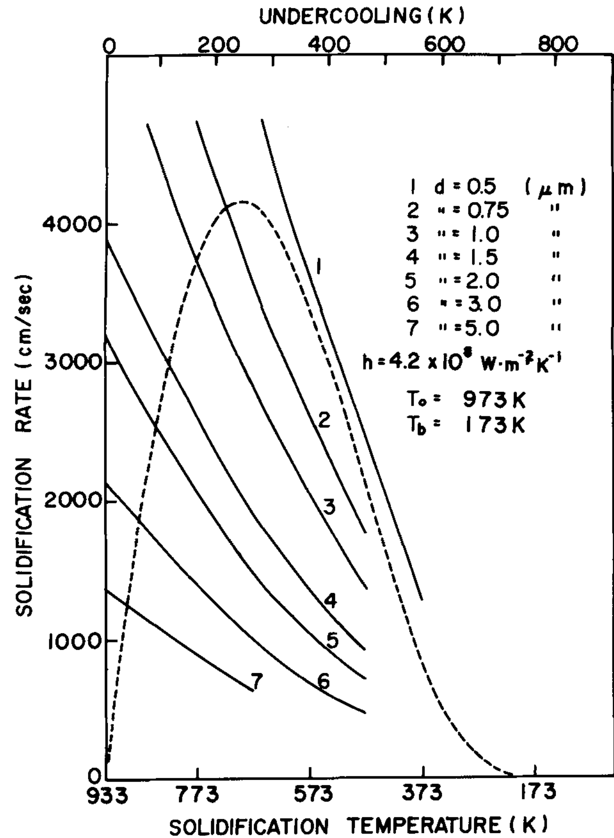

Fig. 7—Comparison of the solidification rate and the crystal growth rate for different splat thicknesses. Solid lines: Rate of solidification vs undercooling, when the solid-liquid interface reached the top surface of splats, calculated from the heat flow balance. Dashed line: Rate of crystal growth vs undercooling calculated from the kinetic equation, Eq. [10].

the rate of crystallization as a function of undercoolings in Fig. 7. The intersection points of curves again give the temperatures at which actual solidification would take place. The intersection points in Fig. 7 are plotted in Fig. 8 to give the kinetic undercoolings in the liquid at the solid-liquid interface when the solidification front reached the top surface of splats, for various splat thicknesses.

DISCUSSION

The effectiveness of splat cooling in producing new micro-structures may be discussed in terms of average cooling rate of a splat as it was performed by Ruhl.[2] However, the estimation of solidification rates would give more direct informations of the abilities of splat cooling since one of the most important factors in producing new structures by splat cooling is the forced change in atomic arrangements from equilibrium ones at solid-liquid interface due to the rapid advancement of the interface.

Soldification rates calculated from the heat flow balance depend greatly on the nature of thermal contact at the splat-substrate interface, as shown in Fig. 3, and also on the splat thickness as shown in Fig. 7. These results, naturally, support the conclusions given by Ruhl[2] from the cooling rate considerations.

The solidification rate also changes significantly with the change in solidification temperature. The im-

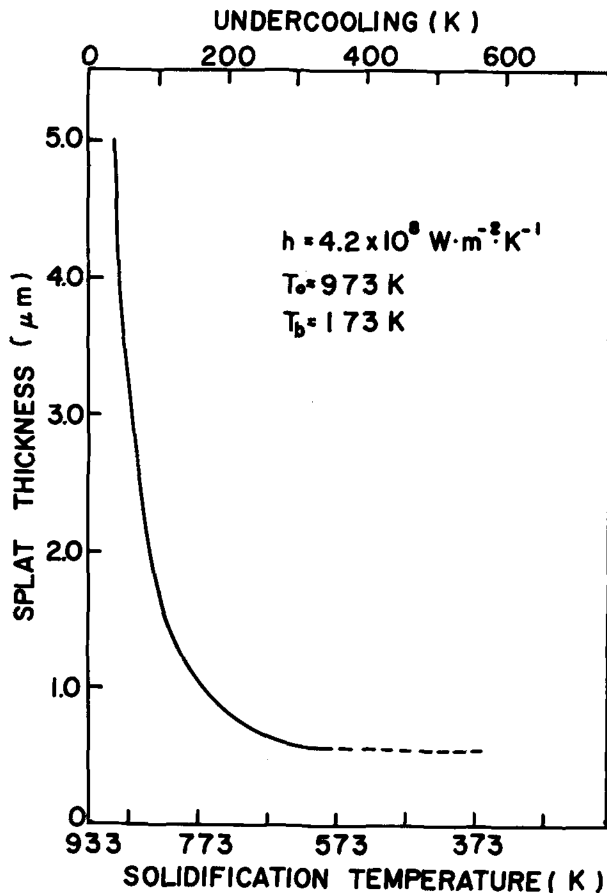

Fig. 8—Splat thickness vs kinetic undercooling in the liquid at the solid-liquid interface when the solidification front reached the top surface of splats.

portance of the solidification temperature lies on the fact that the crystallization rate is a function of the solidification temperature also. As shown in Figs. 5 and 7, the solidification rate calculated from the heat flow balance decreases with undercoolings whereas the crystallization rate first increases sharply and then decreases at larger undercoolings. At a moderate rate of heat extraction, there is an undercooling at which thermal and kinetic conditions are both satisfied as represented by the intersection points of curves in Figs. 5 and 7. These intersection points show the actual temperatures at which solidification would proceed. Figs. 6 and 8 show how the actual solidification temperature varies with the changes in the thermal contact at the splat-substrate interface and in the thickness of a splat. When the heat extraction rate exceeds a certain value, a splat will be cooled so rapidly that the crystal growth, wherever the site of nucleation will be, cannot cover the whole splat body before it is cooled down to a low temperature where the crystal growth rate is negligibly small. An example of such case is shown in curve 1 in Fig. 7. The case for curve 1 may be thought as the limiting condition which determines the possibility of producing an amorphous phase. In the case of pure aluminum, however, the rate of crystallization is still large at the temperature of liquid nitrogen and it will be difficult to produce amorphous structure by a standard splat cooling technique.

The substrate temperature which is described as having no primary importance by Ruhl[2] become crucial when the kinetic undercooling becomes large because the difference between actual solidification temperature and substrate temperature should stay large down to low temperatures in order to ensure large solidification rate. It is the large kinetic undercooling which determines the effectiveness of splat cooling.

CONCLUSIONS

The solidification rate in splat cooling is influenced most strongly by splat thickness, splat-substrate interfacial thermal contact and the difference between initial and freezing temperatures of splat. In addition to keeping these factors favorable, the substrate temperature must be set low in order to create a kinetic undercooling, at the solid-liquid interface, large enough to suppress the occurrence of crystal growth.

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REFERENCES

1. P. Duwez: *Trans. ASM,* 1967, vol. 60, pp. 607-33.
2. R. C. Ruhl: *Mater. Sci. Eng.,* 1967, vol. 1, pp. 313-20.
3. R. W. Ruddle: *The Solidification of Castings,* 2nd ed., pp. 79-80, Institute of Metals, London, 1957.
4. H. S. Carslaw and J. C. Jaeger: *Conduction of Heat in Solids,* 2nd ed., pp. 282-96, Oxford Univ. Press, 1959.
5. G. E. Forsythe and W. R. Wasow: *Finite-Difference Methods for Partial Differential Equations,* pp. 88-139, J. Wiley and Sons Inc., New York, 1960.
6. J. W. Cahn, W. B. Hillig and G. W. Sears: *Acta Met.,* 1964, vol. 12, pp. 1421-39.
7. J. Frenkel: *Kinetic Theory of Liquids,* p. 193, Dover Pub. Inc., New York, 1955.
8. M. E. Fine: *Phase Transformations in Condensed Systems,* p. 49, Macmillan Co., New York, 1964.
9. J. R. Wilson: *Metal. Rev.,* 1965, vol. 10, p. 552.