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Splat-quench solidification of freely falling liquid-metal drops by impact on a planar substrate

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Results are presented of a study of the splat-quench solidification of small, freely falling liquid drops of the alloy Nitronic 40W, which were allowed to impact on a solid, planar, horizontal substrate. The principal variable was the substrate material, with substrates of copper, alumina and fused quartz being used. The shapes of the solidified splats were correlated with a simplified model for the energetics of the splatting process and with the thermal conductivity of the substrate. The measured results are qualitatively in agreement with theoretical predictions, and suggestions are offered for a more comprehensive model of splat-quench solidification. A relationship between sessile droplet diameter and parent wire diameter is also presented and discussed.

1. Introduction

Drop-tube experiments represent a useful approach to studying undercooling and solidification of liquid metals [1–7]. In such experiments, droplets that are usually several millimetres in diameter are allowed to fall from rest down a long, vertically mounted tube that is either evacuated or filled to various pressures with an inert gas. Under vacuum operation, droplets are often produced by electron-beam melting the end of a wire of the metal or alloy under examination. Since in-flight cooling and the droplet's eventual solidification in the evacuated tube depend on radiant heat loss, droplet size is an important variable. To be able to produce droplets of preselected sizes, it is useful to have knowledge of a relationship between droplet size and wire diameter. Such a relationship for two representative iron–base alloys is discussed in the Appendix.

An extension of the in-flight solidification experiment is to permit the falling drop to undergo 'splat-quench' solidification by allowing it to impact upon a planar substrate placed in its path. Presented below are the results of a set of experiments on the quenching of droplets, together with correlation of these results with predictions based on a simplified theoretical model. Although preliminary in nature, these studies set the stage for more comprehensive theoretical and experimental analyses of the splat quenching.

2. Theory

2.1. Background

Many different types of rapid solidification processing (RSP) currently exist, and extensive theoretical modelling of RSP, in its various forms, has been carried out. Mathematical modelling is particularly important in the area of RSP, because the very high cooling rates can result in severe difficulties associated with experimental measurements. A comprehensive review and discussion of RSP modelling has been presented by Gutierrez-Miravete [8].

Splat quenching of a liquid drop onto a solid substrate is not a simple form of RSP, despite the apparent simplicity of the physical system. This is due to the kinetic energy of the drop when it strikes the substrate, which can result in complex heat-transfer behaviour because of the time-dependent drop geometry, the intricate internal fluid-flow field, and the fact that the drop undergoes a progressive change of phase.

The general subject of liquid-drop impact onto a solid surface has been studied from a variety of points of view. One early work [9] included an experimental study of the oblique impact of 'large' drops (about 2 mm diameter) onto a solid surface, with adhesion of the drops to the surface being of particular interest. A later study [10] involved a detailed numerical solution of the full Navier–Stokes equations for the impact of a drop onto a flat plate, as well as into a shallow pool and a deep pool. An area of current interest is the erosion of solid surfaces due to liquid-drop impact; along these lines, a model for the collision of a liquid drop with an elastic half-space has recently been reported by Niesytto and Niesytto [11]. As far as RSP is concerned, a relatively advanced model of the splat-quenching process was developed by Madejski [12, 13], involving the impact and solidification of a liquid drop on a solid surface.

The Madejski model [12, 13] included fluid flow (which was treated as being laminar), changes in kinetic and potential energy of the liquid, and energy loss due to friction. In addition, Madejski included the time-dependent rate of advance of the solid/liquid interface into the liquid, beginning at the liquid/substrate interface. He assumed that the thickness of the solidified layer increases as the square root of time, which can be

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shown [14] to be equivalent to assuming that the temperature of the splat at the splat/substrate interface does not vary with time. This would be the case for ideal thermal contact between splat and substrate, with the substrate temperature at the interface remaining virtually constant as solidification proceeds. Some possible generalizations of the Madejski model are suggested in Section 4.2, but are not formally developed in the present work. Instead, a very simple model is constructed based on energy considerations.

An improved treatment of heat transfer across the splat/substrate interface was used by Evans and Greer [15] in their modelling study of splat quenching. They assumed that the rate of heat transfer across the interface is proportional to the temperature difference, at this position, between the splat and the substrate. They did not, however, include effects of liquid spreading on the substrate surface.

2.2. Simplified considerations of energy in the splat-quench process

In this section, we present some highly simplified, but nevertheless useful, considerations of the energetics of the splat-quench process. Although the treatment of Madejski [12, 13] is far more detailed, a simpler approach is adequate for present purposes.

Upon impact on a cold substrate, assumed here to be horizontal, the drop often spreads and solidifies as a thin splat. We assume that an initially spherical drop of density ϱ and radius r solidifies as a very thin cylindrical splat of radius R. If the drop falls from rest, with its centre initially at height h above the substrate, then the maximum value, R_{max}, that R can attain is that for which all the kinetic energy of the drop upon impact has been used to alter the various surface and interfacial energies of the system, except for some energy being dissipated by friction through viscous flow of the liquid. For the assumed geometry, an approximate energy-balance expression is

$$\frac{4\pi}{3}r^3\varrho gh + 4\pi r^2\gamma_l \simeq \pi R_{max}^2(\gamma_l + \gamma_{ls} - \gamma_s) + E_f \quad (1)$$

where γ_l, γ_s, and γ_{ls}, are the respective surface tensions of the liquid/vapour interface, substrate/vapour interface, and the liquid/substrate interface, g is the acceleration due to gravity, and E_f is the total energy dissipated in frictional forces during spreading. The first term on the left-hand side of Equation 1 is the initial potential energy of the drop (measured relative to the substrate); the second term is the surface energy of the initially spherical drop, which is generally small compared to the potential energy term and is henceforth neglected. Since the splat is assumed to be very thin, no account is taken of the surface energy associated with its edge, nor of its gravitational potential energy relative to the substrate.

The interfacial energy terms on the right-hand side of Equation 1 account for creation of liquid/vapour and liquid/substrate interfaces as a result of spreading, as well as loss of a solid/vapour interface as the liquid spreads. An upper limit for R_{max} can be obtained by neglecting E_f, which we shall do.

Equation 1 can be simplified through application of the Young and Dupré equation [16]:

$$\gamma_s = \gamma_{ls} + \gamma_l \cos\theta \quad (2)$$

where θ is the equilibrium contact angle between the liquid and the substrate. We then obtain, neglecting the surface-energy term on the left-hand side of Equation 1 and dropping the dissipation term on the right-hand side,

$$\frac{4\pi}{3}r^3\varrho gh > \pi R_{max}^2\gamma_l(1 - \cos\theta) \quad (3)$$

the inequality arising from dropping the E_f term.

The contact angle is an important consideration in the application of Equation 3. For example, a gas layer may separate the spreading liquid from the substrate: in this case $\theta = \pi$ would be appropriate. On the other hand, for experiments done in a vacuum with clean, smooth, and insoluble surfaces, the value of θ would be the equilibrium contact angle for the particular liquid/substrate combination. The question of contact angle 'hysteresis' [17] is one which should be addressed in a more detailed analysis.

Assuming that $\theta = \pi$, Equation 3 can be used to obtain the following upper limit for γ_l:

$$\gamma_l < \frac{2r^3\varrho gh}{3R_{max}^2} \quad (4)$$

Estimates of γ_l obtained using Equation 4 would be significantly higher than the actual value if large amounts of energy are dissipated during flow or if the measured splat radius is smaller than R_{max}. Significant energy dissipation by viscous flow is not likely, however, since solidification probably occurs too quickly, as discussed below. Moreover, if some wetting of the drop on the substrate does occur in practice (i.e. $\theta < \pi$), then the upper limit for γ_l calculated from Equation 4 would be smaller than it would have been if the correct contact angle had been assumed in Equation 3. If some wetting does occur, part of the overall driving force for spreading of the drop on the substrate would arise from the wetting process, in addition to that arising from the kinetic energy existing upon impact.

3. Experimental procedure

Liquid metal drops of the alloy Nitronic 40W were formed by heating the end of a wire of this material. (The principal ingredients of Nitronic 40W in weight per cent are 20.8 chromium; 6.5 nickel; 9.3 manganese; balance iron.) The drops were allowed to fall approximately 0.5 m in a room-temperature environment of argon at a pressure of 1 atm. They fell onto horizontal plates of polished (1 μm) copper, alumina, and fused quartz. The morphologies of some resulting splats are shown in Fig. 1.

4. Results and discussion

4.1. Experimental results

The principal features of the solidified splats are as follows. For the copper and alumina substrates, roughly flat circular splats were formed with radii of ~8 mm. On the other hand, for the fused silica substrate, the drops solidified as roughly hemispherical

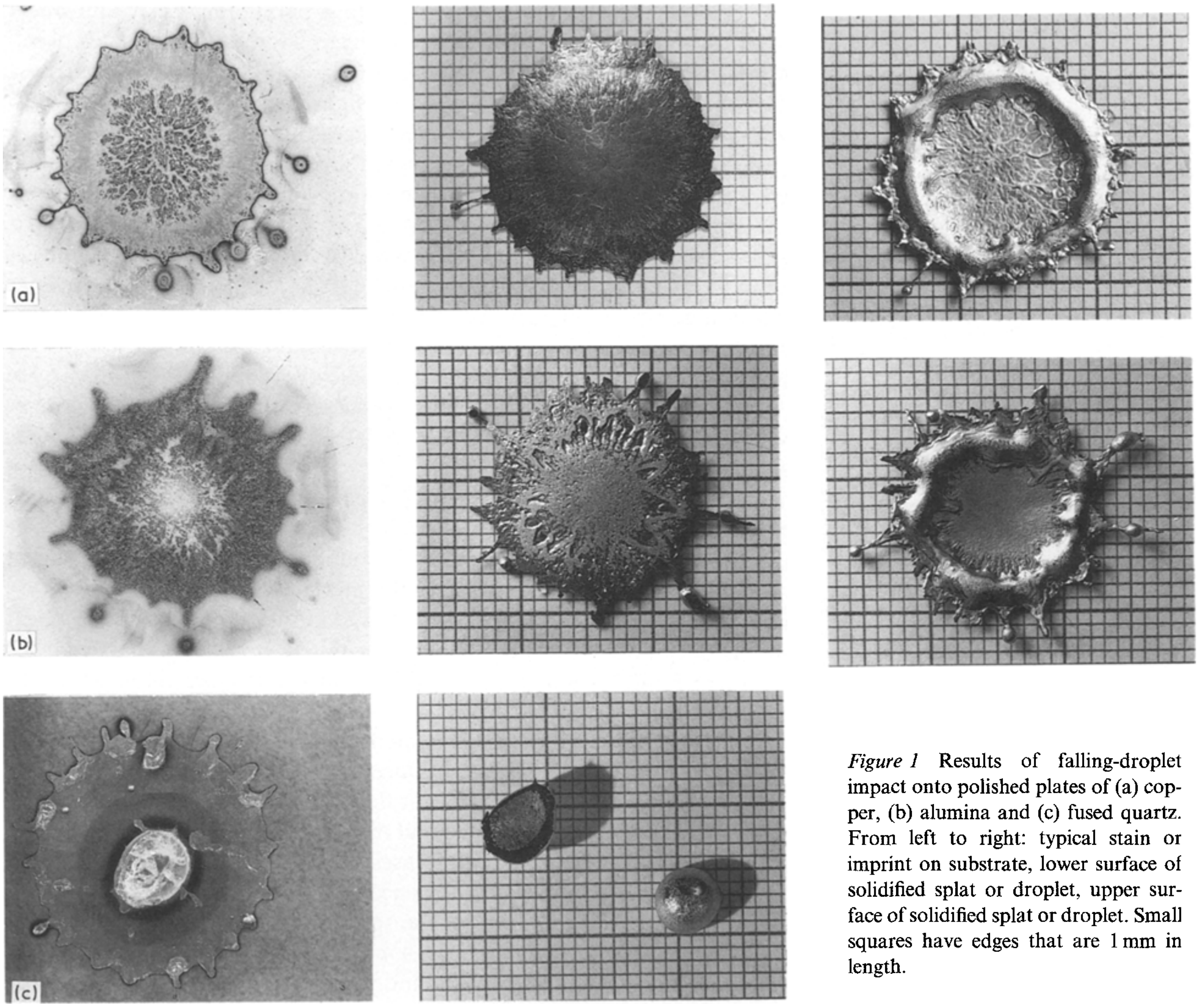

Figure 1 Results of falling-droplet impact onto polished plates of (a) copper, (b) alumina and (c) fused quartz. From left to right: typical stain or imprint on substrate, lower surface of solidified splat or droplet, upper surface of solidified splat or droplet. Small squares have edges that are 1 mm in length.

masses. The results for copper and alumina are consistent with the observation of Madejski [12] that the splat radius is largely independent of the substrate material.

The result for fused silica suggests that solidification on this substrate took place much more slowly, such that the liquid metal attained an approximately equilibrium shape (that of a 'sessile drop' on a flat solid surface) before solidifying. This would mean that the thermal contact at the metal/substrate interface was not as good as for the other two cases and/or that conduction of heat away from the drop through the substrate took place more slowly. The latter explanation is consistent with the thermal conductivities of these materials which, at 300 K, are roughly 400, 30, and 2 $W/m\,K^{-1}$ for copper, alumina and fused silica, respectively [18]. Thus heat would be conducted through the fused silica much more slowly than for either of the other two materials. The observed similarities between splats on copper and alumina, despite the large difference in thermal conductivities for these two materials, may imply that, at least over this range of conductivities, heat transport away from the drop is controlled by transport across the liquid/substrate interface. It may be that, for conductivities as low as that of fused silica, conduction through the substrate becomes rate-controlling.

Following the analysis presented in Section 2.2, an upper limit for the surface tension of the liquid splats on copper and alumina substrates was calculated and found to be approximately 3 $J\,m^{-2}$, which is roughly twice the actual value. In view of the uncertainties associated with this greatly simplified analysis, this figure is reasonable. As discussed above, the most likely explanation is that the shape of the solidified drop was not one of maximum surface area.

4.2. The Madejski model

The Madejski model [12, 13] provides a relatively advanced description of liquid-drop splat-quench kinetics. Nevertheless, a number of extensions could be included which would enable it to describe more closely the actual physical process; such extensions, as well as other aspects of the model, are discussed in this section.

First, spreading of liquid on the substrate, following impact, is assumed by Madejski to be laminar, i.e. possible transition to turbulent flow at high Reynolds number is ignored. In order to determine if turbulence may be important, we follow Madejski [12] and define a characteristic Reynolds number as $Re \equiv vD/\nu$, where v is the drop velocity upon impact, D is its diameter prior to impact, and ν is the kinematic viscosity of the liquid metal. Noting that $v = \sqrt{(2gh)}$, and applying representative conditions for our experiments, i.e. $h = 0.5$ m, $D = 2$ mm, and $\nu = 1.4 \times$

$10^{-7}\,\mathrm{m^2\,sec^{-1}}$, we obtain $Re \simeq 4 \times 10^4$. This high value for Re would appear to indicate that turbulent flow is likely to occur; however, since solidification takes place so quickly, it is probable that what actually does occur consists of highly unstable velocity fluctuations that would otherwise eventually lead to turbulence. The high value for Re obtained above also indicates that inertial forces are much larger than those associated with viscous damping, at least until the characteristic speed becomes considerably smaller. This, combined with the fact that solidification occurs very rapidly, makes it unlikely that significant viscous losses take place. However, more detailed theoretical studies along these lines are needed.

Another fluid-flow effect that could be considered is related to the Rayleigh instability [19]: the circular periphery of the drop breaks down in a relatively complex, although fairly regular, manner. This instability is clearly illustrated in Fig. 1 for the copper and alumina substrates, but not for the fused silica substrate. Presumably the low thermal conductivity of fused silica provided enough time for the drop to achieve a minimum interfacial energy configuration before solidification. Madejski's figure 1 [12] also illustrates the existence of this instability, which he attributed to "drop vibrations".

Vibrational energy of the splat may indeed represent an important contribution to its overall mechanical energy, one which Madejski did not consider. Some of the initial kinetic energy of the drop may thus be transformed to vibrational energy of the liquid rather than contributing directly to spreading.

The fact that a solid/liquid interface is progressing into the splat would also affect fluid flow within the liquid. (Conversely, the fluid-flow field would affect the morphology of the solidified material.)

Madejski also ignores the contribution of gravitational potential energy (GPE) to the total energy of the spreading drop. To estimate the overall magnitude of this factor, let ΔE_g be the net change, of GPE, defined as the potential energy of a spherical drop of diameter D, just before impact, minus that of a drop after spreading to a very thin disc. Since the potential energy of the disc relative to the substrate is small compared to that of the drop, we have $\Delta E_g \simeq \pi \varrho g D^4/12$. The concomitant change of surface energy, ΔE_s, is roughly equal to $2\pi R^2 \gamma_l$ for $\theta = \pi$. For the case $\varrho = 7000\,\mathrm{kg\,m^{-3}}$, $\gamma_l = 1.5\,\mathrm{J\,m^{-2}}$, $D = 2\,\mathrm{mm}$, and $R = 8\,\mathrm{mm}$, we obtain $\Delta E_g \simeq 3 \times 10^{-7}\,\mathrm{J}$ and $\Delta E_s \simeq 6 \times 10^{-4}\,\mathrm{J}$, so that the total surface energy change in this case is indeed large compared to the change of GPE, which would justify its neglect.

It is noted that an alternative description of capillarity-versus-gravitational forces is through use of the Bond (or Eötvös) number, Bo, which is the ratio of gravitational or accelerational forces to surface-tension forces acting on a fluid particle, and is defined as [20] $Bo = \varrho L^2 a/\gamma_l$, where L and a are characteristic values for length and acceleration, respectively, and ϱ and γ_l are as defined above. Considering the drop at impact, at which point one would expect the largest relative effect due to gravitational forces, we take $a = g$ and $L = D$, and using the numerical values assumed in the previous paragraph, we obtain $Bo \simeq 0.2$, which is indicative of forces that are still dominated by capillarity.

As an aside, one might question the extent to which capillarity-related forces compare with inertial or flow forces. In this regard, one can use the Weber number, We, which is the ratio of inertial forces to capillarity forces, and is defined as [20] $We = \varrho v^2 L/\gamma_l$ where v is a characteristic speed of the fluid and other quantities are as defined above. Again considering the drop at impact, we take $v^2 = 2gh$, $L = D$, and obtain, using the above-noted numerical values, $We \simeq 92$. Thus, inertial forces dominate over capillarity forces early in the splat-quench process. However, capillarity forces will dominate at later stages, as the flow speeds decrease.

An extension of Madejski's heat transfer analysis would be desirable. Of particular value would be relaxation of the assumption of ideal heat transfer at the splat/substrate interface, as well as consideration of the effects of the solidification process itself on heat transfer. The former might, for example, involve the approach used by Evans and Greer [15], described above. The latter would include effects resulting from release of the latent heat of fusion at the advancing solid/melt interface.

Effects of heat flow from the drop to regions of the substrate beyond the drop periphery might be important in some cases. It is noted that Madejski did attempt [12] to account for intensive cooling on the boundary of the splat.

In summary, some possibly important extensions of the Madejski model could be made. Nevertheless, the present model does provide a useful, semi-quantitative description of splat-quench kinetics.

5. Conclusions

The results of some introductory experimental and modelling studies of the splat-quench solidification of freely falling liquid-metal drops onto a solid substrate are reported. The observed shapes of solidified splats can be reasonably well explained, at least in a qualitative sense. However, more detailed comparisons between theory and experiment will require a more comprehensive theoretical treatment of the splat-quench process, which would extend the work of Madejski [12, 13] and include effects of both laminar and nonlaminar fluid flow within the drop after impact, nonideal thermal contact between drop and substrate, and advance of the solid/liquid interface.

6. Acknowledgement

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Appendix: Relationship between sessile droplet size and parent wire diameter

In drop-tube experiments, it is important to be able to produce sequences of droplets of pre-selected size. A convenient method of producing such droplets is to form them by melting the tip of a wire prepared from the material under study: for example. Lacy *et al.* [1]

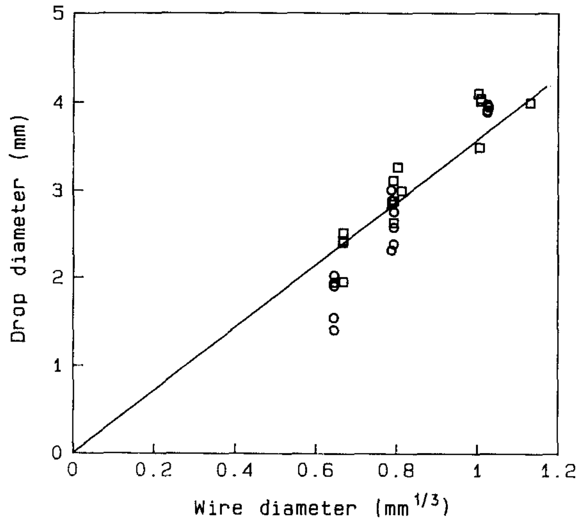

Figure 2 Drop diameter against cube root of wire diameter for music wire (circles) and Chromel A (squares), together with regression line (Equation A3) fitted to combined data.

have described a sophisticated method based on the pendant drop technique and using omnidirectional electron bombardment.

The approach used in the studies reported here was conceptually quite simple but did yield satisfactory results. The end of a metal wire was torch-heated, resulting in the formation of a drop of molten metal which remained adhered to the wire. The drop grew, with continued heating, and the torch was turned off when the drop appeared to be about to fall. Tests of the technique were performed using music wire and Chromel A.

This general approach is similar to the familiar drop weight method [21] used to measure the surface tension of a liquid, in which liquid drops are formed at the end of a tube from which they fall, after reaching a certain size, and are collected in a container. The surface tension is deduced from the weight of a series of collected drops. The method can be described in terms of Tate's law [21]:

$$W = \pi d \gamma_l \tag{A1}$$

where W, d, and γ_l are the weight of the falling drop, the diameter of the tube, and the surface tension of the liquid, respectively. In practice, part of the volume of the liquid drop tends to remain attached to the tube, which is less than or equal to unity. Values of f, as a function of the ratio of wire radius to the cube which is less than or equal to unity. Values of f, as a function of the ratio of wire radius (or d) to the cube root of drop volume, have been reported [21].

The simple form of Tate's law, as given by Equation A1, yields the following relationship between d and the diameter, D, of the drop:

$$D = \left(\frac{6\gamma_l d}{\varrho g}\right)^{1/3} \tag{A2}$$

where ϱ is the density of the liquid as defined above.

A test of the applicability of this simple expression to the present method of drop production was made by plotting data for measured values of D, as a function of $d^{1/3}$ for the two types of wire. The data are plotted in Fig 2 together with a linear least-squares fit to the combined set of data, obtained by minimizing the sum of squares of deviations in D about the regression line, which, as illustrated in Fig. 2, was forced to pass through the origin.

The calculated value of the regression-line slope ($3.566\,\mathrm{mm}^{2/3}$) yielded

$$\left(\frac{6\gamma_l}{\varrho g}\right)^{1/3} = 3.566\,\mathrm{mm}^{2/3} \tag{A3}$$

As above, we take ϱ to be $7000\,\mathrm{kg\,m^{-3}}$, and thus obtain $\gamma_l \cong 0.52\,\mathrm{J\,m^{-2}}$. This value of γ_l is too low by roughly a factor of three, so it would appear that, on average, a substantial portion of the molten liquid remains attached to the heated end of the wire when the drop falls. However, this is unimportant for present considerations, since we are not interested here in making surface-tension measurements. What is important is the fact that the data in Fig. 2 do exhibit, on the whole, a systematic relationship between D and d characterized by a roughly linear variation of D with $d^{1/3}$. The scatter in measured values of D, for any fixed value of d, most probably reflects some lack of control arising from the simplicity of the method. However, the drop sizes that are obtained are within desired limits, so the method is appropriate for our present purposes.

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