Deformation and solidification process of a super-cooled droplet impacting on the substrate under plasma spraying conditions

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Abstract

To date, many modelling efforts related to the deformation and solidification processes of a droplet impacting on the substrate under plasma spraying conditions have been reported. However, to the authors’ knowledge, no modelling effort has dealt with the super-cooling effects on the deformation and solidification processes, though much evidence of super-cooling effects has been reported. In this paper, we will show the first results derived from our recent modelling efforts for the case of Al\textsubscript{2}O\textsubscript{3} droplets, which clearly show the strong effects of the super-cooling conditions on the deformation and solidification processes. For example, we predict a significant decrease in deformation degree — defined as the ratio of droplet to splat diameters — to less than 2.0, and also a faster solidification front velocity of up to 5 m/s. Although the small deformation degree is clearly caused by the larger value of viscosity under super-cooled conditions, the rapid solidification is eventually caused by the super-cooling. The model did not predict a dendritic growth, but it clearly suggested that plasma sprayed particles are not all but may be actually in super-cooled state, and any modelling efforts should include the super-cooling effects. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Plasma spraying process has been applied in the manufacture of many new materials such as thermal barrier coatings and solid oxide fuel cells. It is a versatile technology that has been quite successful as a reliable and cost effective method for depositing functional coatings, e.g. wear and corrosion resistant coatings. Thermal spray coatings are formed by heating, melting, and accelerating powdered material in a high temperature and high velocity gas, and depositing them onto a substrate [1,2]. Currently, a variety of heat sources are used to melt and accelerate the powders; these are plasma guns, high velocity oxy-fuel (HVOF) gun, and radio frequency inductively coupled plasma. The produced coatings are formed by the agglomeration of individual droplets (completely melted, partially melted, or unmelted) impacting onto the surface and solidifying. To a large extent, coating properties, e.g. porosity, depends on the shape of individual lamellae, which in turn is dependent on the impact conditions and substrate temperature and topology. Due to experimental difficulties, direct observation of the impact and spreading of a single droplet during thermal spray process has been limited to measuring the radiation of the splat surface during its evolution [3]. More recent work has focused on visualizing the droplet impact during the thermal spray coating process [4]. No experiments have yet been devised to measure details of the solidification process during thermal spray coating.

In this respect, modelling of droplet impact and solidification has seemed to be quite powerful in describing the dynamics of spreading, solidification, and break-up as a function of impact conditions and materials properties of both the droplet and the substrate. The problem of simulating the impact and solidification of a molten droplet onto a solid surface is a coupled fluid flow, heat transfer and phase change problem which includes both a liquid/gas and a liquid/solid interface. For a numerical solution of the fluid flow problem, two general approaches exist for tracking the liquid/gas interface: fixed grid and adaptive grid techniques. Looking back into the past, examples of such numerical techniques applied to the problem of the impact of a liquid
droplet onto a substrate can be seen in Refs. [5–14]. The solidification of a droplet was investigated analytically by Madjeski [15] in as early as 1976. He assumed that upon impact a droplet immediately flattens to form a disk; and by using a simple energy balance and assuming a velocity profile, he found the solution of a one-dimensional Stefan problem. Since then a number of other groups have developed two-dimensional codes. Zhao and Poulikakos [16] used a finite element method to study droplet deposition by assuming that solidification starts after the spreading is complete. They did not, however, consider solidification during spreading. Liu et al. [17] employed RIPPLE [18] and a solidification model to conduct a variety of two-dimensional simulations including impacts onto a wavy surface, and successive droplet impacts. They assumed that the substrate was isothermal and they neglected thermal contact resistance. Bertagnolli et al. [19] employed a finite element model to examine droplet impacts. They implemented a two-dimensional heat transfer model within the droplet and assumed a value for the heat transfer coefficient at the substrate surface. The models discussed above presume equilibrium conditions during solidification. There is however strong evidence that solidification does not occur under equilibrium conditions. Reviews of mathematical modelling of rapid solidification have been done in Refs. [20–22]. As mentioned by Kurz and Fisher [20], by increasing the solidification rate or under-cooling, a description of the interface becomes increasingly more complex. Although not related to the impact of droplets, examples of such phase change problems with super-cooling have been done in Refs. [23–27]. In these studies either a predetermined interface velocity or an explicit relationship between the interface velocity and temperature was used. Moreover, in most cases there was no fluid motion involved and/or the coupling between the fluid motion and solidification was neglected, and cannot be applied directly for the droplet impact cases.

As mentioned above, modelling studies have a possibility to provide detailed information on the transport phenomena relating to the deformation and solidification process of impacting droplets; e.g. temperature distribution within the droplet and substrate, deformation and solidification time, and the effects of thermo-physical properties of droplets. The models may also provide insight into microscopic heat transfer at the interface between the droplet and the substrate, which is difficult to be determined experimentally. Actually, we have little knowledge about the microscopic heat transfer for the cases of large temperature difference of over 1000 K, though this heat transfer critically influences microstructure formation of the deposited layers. Moreover, it has been shown that the super-cooling can result in crystal growth initiated by nucleation such as dendrite formation and segregation [28,29]. It can also lead to smaller deformation degree (or splat flattening ratio), defined as the ratio of splat (D) to impinging droplet diameter (d). Note that the splats with deformation degrees of less than 2 are often reported and found, depending on the spraying conditions. This is much smaller than those predicted by the models developed so far. This may be caused by the fact that the reported whole models assumed equilibrium solidification, and the super-cooling effects on the deformation and solidification processes could not be treated.

In this study, we have investigated mainly the super-cooling effects on solidification and will report the preliminary results derived so far. The results clearly show the strong effects of the initial under-cooling degree on the deformation and solidification processes. We also evaluate the effects of viscosity, radiation, contact angle, and substrate temperature and thermal conductivity on the deformation process.

2. The model

Numerical simulations of the droplet splat deposition processes have been conducted by basically solving the full Navier–Stokes and energy equations coupled with the Volume of Fluid (VOF) approach to track the surface of a deforming droplet. We extended the model of Mostaghimi et al. [8,9] and included the super-cooling effects on solidification.

The mathematical model is based on the following assumptions and simplifications:

1. laminar and incompressible fluid flow;
2. two-dimensional, axi-symmetric flow with no slip at the solid substrate;
3. normal impact of a spherical droplet;
4. compared to heat transfer to the substrate, convection and radiation from the droplet surface to the surrounding is negligible;
5. smooth, homogeneous, and insoluble substrate surface;
6. heat transfer between droplet and substrate may be influenced by thermal contact resistance;
7. constant physical properties except for viscosity, which is expressed as a function of temperature;
8. Al2O3 or stainless steel substrates.
The incompressible spherical liquid droplet of Al$_2$O$_3$ with diameter $D_0$, initial temperature $T_{in}$, and velocity $v$ impinges on a flat substrate whose initial temperature is $T_{sub,in}$. Upon impact, the droplet deforms by radial spreading with a phase change process occurring at the splat–substrate interface. The droplet temperature increased continuously along the symmetry axis with its maximum at the solid–liquid interface. The interface specified by symbol “I” shows the solidification front, and a clear recalescence phenomenon is shown. The super-cooled droplet is completely solidified after 250 ms. On the other hand, the deformation of the super-cooled droplet finishes at 4 ms. This is due to the higher viscosity of the relatively colder droplet. The droplet temperature increased continuously along the symmetry axis with its maximum at the solid–liquid interface. The interface specified by symbol “I” shows the solidification front, and a clear recalescence phenomenon is shown. The super-cooled droplet is completely solidified after 125 ms, which is around a half of the superheated case. The deformation degrees for each case are 3.2 and 2.4, respectively. This difference in deformation degrees will substantially alter the final splat thickness. Therefore, the structure of the coatings will be greatly affected by a small difference in the deformation degree.

**3. Results and discussion**

Fig. 1 shows the deformation profiles of two droplets with initial temperatures of 3000 K (superheated, Fig. 1(a)) and 2000 K (super-cooled, Fig. 1(b)). The droplet diameter is 100 µm and its impact speed is 30 m/s. The superheated droplet continues to deform by flattening up to 10 µs, and finally solidifies after 250 µs. On the other hand, the deformation of the super-cooled droplet finishes at 4 µs. This is due to the higher viscosity of the relatively colder droplet. The droplet temperature increased continuously along the symmetry axis with its maximum at the solid–liquid interface. The interface specified by symbol “I” shows the solidification front, and a clear recalescence phenomenon is shown. The super-cooled droplet is completely solidified after 125 µs, which is around a half of the superheated case. The deformation degrees for each case are 3.2 and 2.4, respectively. This difference in deformation degrees will substantially alter the final splat thickness. Therefore, the structure of the coatings will be greatly affected by a small difference in the deformation degree.

Fig. 2 shows the summary of deformation degree as a function of the initial temperature of the impinging droplet. The results show that, regardless of the thermal state of the droplet and in spite of the large variation in viscosity, when size and impinging velocity remain constant, the
deformation degree changes linearly with the initial droplet temperature. As expected, droplets with higher impact velocity (Fig. 2, line a) show a higher deformation degree. For the case of droplets of 100 m and 30 m/s (line b), the deformation degree is greater than 2.5 just above alumina’s melting point (2323 K). Higher supercooled droplet showed smaller deformation degree. It is also shown that smaller droplets (line c) are subject to a smaller degree of spreading than that of larger droplet (line b). These results appear to be sound and strongly suggest that super-cooling effects should be the cause of such a small deformation degree.

3.1. Effect of super-cooling and high viscosity

Fig. 3 shows a comparison between solidification velocities for super-cooled ($T_{in} = 1800$ K) and superheated ($T_{in} = 3000$ K) cases. For both cases, droplet diameter and impact speed are $D_i = 100$ m and $V_{in} = 30$ m/s, respectively. The solidification speed of the super-cooled droplet was converged to 5 m/s at the very beginning of the impact, and was asymptotically decreased to 0.2 m/s at 10 µs. Under equilibrium conditions, the results show that the initial solidification speed would be 10 times smaller, and the solidification time of the super-cooled droplet is 2.5 times shorter than that of superheated droplet.

Fig. 1. Solidification process of (a) superheated droplet with $T_{in}$ of 3000 K and (b) super-cooled droplet with $T_{in}$ of 2000 K. Impinging droplet and substrate are Al$_2$O$_3$. Droplet diameter ($d_{in}$), impinging velocity ($V_{in}$), and substrate temperature ($T_{in}$) are 100 m, 30 m/s, and 800 K, respectively.
Fig. 4(a) shows the time dependence of the deformation degree variation and Fig. 4(b) shows the solidification time versus droplet temperature. Droplet diameter and impact speed were either $D_i = 100 \, \mu m$, $V_i = 30 \, m/s$, or $D_i = 30 \, \mu m$, $V_i = 100 \, m/s$, which results in a constant Reynolds number at the impact. Interestingly, the deformation degree is greatly affected by initial temperature, and the difference increases more and more as the initial temperature increases. This is mainly caused by considering the viscosity’s dependence on the temperature (Fig. 2). Actually, when superheating is not large, e.g. $T_i = 2500 \, K$, the difference is not so large. The correlation between deformation and solidification and

![Graph showing deformation degree variation and solidification time.](image)

**Fig. 2.** Variation of deformation degree with the initial impinging temperatures for the droplets of (a) $d_i$ of 30 $\mu m$ and $V_i$ of 100 $m/s$; (b) $d_i$ of 100 $\mu m$ and $V_i$ of 30 $m/s$; and (c) $d_i$ of 30 $\mu m$, $V_i$ of 30 $m/s$.

![Graph showing solidification velocity.](image)

**Fig. 3.** Comparison of solidification velocity of a super-cooled and superheated droplet with $d_i$ of 100 $\mu m$ and $V_i$ of 30 $m/s$. 
initial droplet temperature is maintained, provided the size and impact velocity are constant regardless of superheated or super-cooled conditions. Judging from the linearity of deformation and solidification times as well as deformation degree (Fig. 4(b)) versus droplet initial temperature, the effect of high viscosity of the super-cooled droplet may be compensated by the recalescence effect.

Our results have shown that super-cooling leads to a small deformation degree. However, we must clarify which factor, viscosity or super-cooling effect namely the

Fig. 4. (a) Time dependence of the deformation degree and (b) solidification and deformation time with a parameter of initial temperature. The droplet and substrate are Al₂O₃ and \( T_{\text{sub}} \) is 800 K.
solidification speed, is responsible for the small degree of deformation. To clarify, we calculated two cases: (a) dynamic solidification case by assuming actual melting temperature of 2323 K; and (b) equilibrium solidification by assuming a virtual melting temperature of 1500 K. For both cases, the same initial conditions were adopted, i.e. $D_i = 100 \, \mu m$, $v = 30 \, m/s$, and $T_i = 1800 \, K$. Fig. 5 shows the result, which clearly reveals the difference of the deformation and temperature profiles for both cases, though the deformation degree difference is not so large: 1.8 and 2.0, respectively. Fig. 6 shows the temperature profiles along a vertical centreline as a function of elapsed times for both cases. The negative and positive values of the abscissa reveal the insides of the substrate and the droplet, respectively. The substrate heating effect is very large in the case (a) compared with the case (b). Moreover, complete solidification periods for each case are about 100 and 900 $\mu$s. We may thus conclude that rapid solidification is eventually caused by super-cooling, and the small deformation degree is due to the larger values of viscosity under super-cooled conditions. These differences relating to the substrate heating and recalescence effects should greatly affect the adhesion strength and the microstructure of the coatings.

### 3.2. Effect of other parameters

Fig. 7 shows the effect of substrate temperature on the deformation and solidification times for the cases of superheated and super-cooled droplets. We find that the deformation time does not depend upon the substrate temperature, but the solidification time is greatly affected by the temperature.

Fig. 8 shows the deformation degree of superheated and super-cooled droplets of diameter 30 $\mu m$ and impact speed of 100 $m/s$ as a function of thermal conductivity of the substrate. In the superheated case, the deformation degree decreases slightly with increasing thermal conductivity of the substrate. However, such dependence is not found for the super-cooled case. Accordingly, the selection of a substrate would not be so sensitive for the deformation process under the simulated condition investigated here.

Fig. 9 shows the effect of thermal contact resistance on the deformation degree, which shows the deformation process is not so largely dependent on the resistance except for the resistance less than $1 \times 10^{-6} \, W/m^2/K$. It may however be noted that the available literature suggests the range of thermal contact resistance to be between $10^{-6}$ and $10^{-7} \, W/m^2/K$ [31].

### 4. Conclusions

Numerical and analytical studies of the droplet splat processes have been performed for a better understanding of the solidification process focused on super-cooling effect. The super-cooled droplets showed a low deformation degree, less than 2.2. Therefore, we suggest that plasma sprayed particles are not all but may be actually in the super-cooled state, and the super-cooling effect will have to be considered to explain the deformation process of droplets with a small deformation degree, and modelling efforts should include the super-cooling effects in the future.
Fig. 6. Temperature profiles along the centerline within a super-cooled droplet (broken line) and superheated droplet (bold line) with $d_{in}$ of 100 $\mu$m, $V_{in}$ of 30 m/s, $T_{in}$ of 1800 K, and $T_{sub}$ of 800 K. Impinging droplet and substrate are Al$_2$O$_3$.

Fig. 7. Deformation/solidification time for the droplet with $d_{in}$ of 100 $\mu$m, $V_{in}$ of 30 m/s, and $T_{sub}$ of 800 K. Impinging droplet and substrate are Al$_2$O$_3$. 
Fig. 8. Deformation degrees of (a) superheated droplet and (b) super-cooled droplet with $d_{in}$ of 30 $\mu$m and $V_{in}$ of 100 m/s as a function of thermal conductivity of substrate.

Fig. 9. Deformation degrees of (a) superheated droplet and (b) super-cooled droplet with $d_{in}$ of 100 $\mu$m and $V_{in}$ of 30 m/s as a function of thermal contact resistance of substrate.
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