Spray forming, droplet microstructure and impingement behavior

by

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ABSTRACT

An experimental set-up was built to process individual liquid metal droplets with a control of process parameters (flight distance, particle diameter and speed, superheat temperature, inert environment). Microstructural study was performed on the droplets to estimate the cooling rate and undercooling achieved. The cooling rate was deduced from the observation of the secondary dendrite arm spacing in aluminum-copper 4.5% (wt), and the undercooling achieved was estimated from the volume fraction of solid formed at recalescence in aluminum-iron 4.3% (wt).

A cooling model based on the Ranz-Marshall correlation was developed and coupled with a four step solidification description: (1) liquid droplet cooling, (2) nucleation when a given undercooling is reached, (3) recalescence, (4) equilibrium growth following the Scheil equation. This model predicts within an order of magnitude the cooling rate measured on aluminum copper alloy.

The deposition behavior of aluminum 4.5% copper was observed for several impact conditions (warm or cold substrate, semi-solid droplets with various fraction solid) using very high speed imaging (up to 40500 frames per second). The cooling model described above was used to determine the thermal history of a droplet. Several impact categories were observed and classified: thick pancake, thin pancake, spherical pancake, spherical, bilaminate, rigid. Two dimensionless numbers were then defined: the Weber number that gives the tendency to spread in the absence of solidification and the Freezing number, a dimensionless time required to solidify the whole droplet; these were used as axis to build an impingement behavior map. Similar impact types are found in the same domains on this topology. Other experimental results from the literature on lead, tin and copper were plotted on the same map and are in agreement with our results, indicating that this map is universal and versatile, which should make it useful to predict the droplet deposition in spray forming and die casting of a broad range of metal alloys.

Thesis Supervisor: Pr. Merton C. Flemings

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Chapter 1
Introduction

Rapid Solidification Processing

Rapid solidification processing (RSP) has been used in industry for more than 30 years to produce special alloys with outstanding properties regarding temperature resistance, corrosion, mechanical and electrical properties. Such products cannot be achieved by conventional ways where a good control of the microstructure of the materials is difficult due to the occurrence of micro and macrosegregation.

Dendritic growth is strongly affected by the rapidity of the solidification. Numerous works have shown theoretically [1] and experimentally [2,3] that the secondary dendrite arm spacing is related to the cooling rate by a power law, whose exponent is close to \(-1/3\) for aluminum copper alloys. A rapid solidification process leads to smaller dendritic structures and refined grain size. Refined microstructure improves the mechanical behavior of the alloy: yield strength (Hall-Petch equation) and fatigue resistance [4,5].

RSP techniques may involve high cooling rate as, for example, spin casting and spray forming but may also concern low cooling rates in the case of largely undercooled melt. With increasing undercooling, a great driving force toward crystallization is accumulated [6], so that a rapid solidification is realized even if the bulk melt is slowly cooled.

If solidification occurs fast enough, thermodynamic equilibrium may not be achieved. It is possible to solidify alloys in metastable phases that have interesting mechanical properties and significantly increased solubility of alloying elements: for example enrichment of dissolved iron from the equilibrium value of 0.025% up to 4-6% for aluminum / iron alloys [5].

Specific studies on the undercooling of aluminum based alloys have been
conducted [7,8] using a dispersion technique in which temperature was controlled using differential thermal analysis (DTA). The range of spontaneous nucleation temperatures achieved are still above the homogeneous nucleation temperature predicted using the classical nucleation theory [5]. High undercoolings (on the order of 200 °C) were achieved, the nucleation sites were at the particles surfaces and the microstructures observed were similar to that of sprayed droplets. An argument based on impurity level, probability distribution of these impurities and heterogeneous nucleation is presented to explain that the undercooling achieved increases with a reduction of the particle diameter. Undercooling was shown to be a function of the emulsion type, through the surface oxidation kinetic. Another interesting approach was developed to have access to the key mechanism of solidification: high speed imaging.

Numerous techniques have been developed to achieve new structures in metals and lead to improved materials behavior. Such materials are mainly developed to be used in the aerospace and automotive industry [9]. Effective control of the cooling rate, the microstructure of the solid material and the quality is dependent on the chosen heating and melting methods. Information about these methods can be found in reference [10], a comprehensive review which describes many of the methods used in industry, or in reference [11] which is only concerned with aluminum. Spray processing involves two different ways of decreasing the time to solidify: (1) flight cooling where the amount of undercooling before nucleation is increased by decreasing the diameter of the droplets and (2) substrate quenching where the rapid solidification is achieved by increasing the heat extraction rate. These approaches lead to different morphologies due to the dissimilar thermal conditions at the liquid coolant interface.

**Atomization Spray process**

**Interest and challenges**

Processing of plate/sheet based product is traditionally performed by casting liquid alloys in ingots that are then rolling to final shape through hot mills. The foils obtained may be used for subsequent operations such as pressing, forging or cutting. This leads to a high cost product. Deformation, re-orientation of the grains
and coarsening occurs during the shaping. The quality of the product is therefore not easy to control and the microstructure of the final product (and therefore its properties) are dependent on the processing. Furthermore, the shaping operation requires much infrastructure, energy, work and eventually losses in material that makes it expensive.

The atomization spray process is a promising method to produce plate/sheet preforms where small liquid or semi-solid metal particles impinging on a substrate where they are quenched. Typically, the particle size is on the order of several microns and can be controlled. As the deposit is quenched, coarsening is limited and the microstructure achieved is on the order of microns. Macrosegregation is reduced since each droplet partially solidifies on its own. The long term goal is to be able to obtain a near-net shaped product using a shape substrate. The major limitations of this technique are the mastering of tolerances and overspraying. Some estimations by Alcoa [12] give energy savings of the order of 4.2 millions Btu/ton of aluminum sheet produced using spray process rather than hot milling process or continuous casting. Estimating the overspray (part not sprayed on the target and therefore lost) at 10%, Alcoa predicts $15,000,000 per year savings for the US industry [12].

However, since the fraction solid at impact governs the porosity and grain size and therefore the microstructure, to achieve quality control on the product it is necessary to understand and model the heat and mass transport during the whole process: atomization, flight and deposition. Thus it is important to understand the semi-solid state, that is to be able to predict the undercooled liquid metal behavior, the nucleation temperature and the microstructural deformation at impact.

**Technical description and spray study literature review**

The study of atomization spray process can be divided in three distinct parts: (1) atomization where small droplets of liquid metal are formed, (2) flight during which the droplets cool down and partially solidify exchanging heat with the surrounding gas and (3) the impact where the droplet reaches the target and fully solidifies.
Atomization is traditionally obtained with a high pressure gas. This gas is very often the result of a combustion (oxygen, kerosene) but in many cases pressurized nitrogen is used. The gas exits the nozzle through holes surrounding the liquid metal outlet at a high, typically supersonic, speed. The liquid is thus sucked out of the tundish and forms a stream that rapidly breaks down into various size droplets due to the amplification of the Raleigh oscillations [13]. The typical particle speed is 100 m/s. Studies on the shape of the nozzle have been conducted to predict the size and speed of the droplets as a function of the flow rate of gas and liquid metal [14,15,16]. To enhance the droplet formation and get a good control of the droplet size, ultrasonic excitation of the gas flow has also been studied [12]. Typically the gas speed in the spray chamber is in the order of several hundred of meter per seconds and is decreasing.

The flight study deals with the prediction of the heat flow during flight, as well as the distribution of particle velocities and trajectories. Due to the complex geometry of the spray chamber and the high velocities involved, the gas flow has a huge influence on the trajectories and has to be described precisely (the target has to be covered uniformly by the spray, even if the geometry is complex such that overspray may be avoided). Historically, computation results have been compared to experimentally measured gas velocities using Doppler laser velocimetry measurement and these predictions are in good agreement with observed velocities [15,16,17].

Computer models have been developed to predict the in-flight temperature profile and the fraction solid during the flight and especially at impact, however, the prediction of the nucleation temperature is crucial in this modeling work. Experiments conducted in molten salt [8] for Al-Si and Al-Fe droplet ranging from 5 to 150 μm showed that nucleation occurs at the surface of the droplet and that the undercooling was a strong function of diameter and depends on the impurity level of the alloys as well as the surrounding media used due to the surface oxidation kinetic. To estimate the undercooling, several arguments have been proposed. One school concentrates on the effect of nucleation on the kinetics of recalescence initiation through evaluating wetting angle and nucleation site concentration [15], the homogeneous nucleation temperature and nucleation site density [18], or utilizing a constant pre-exponential factor and a linear approximation of the catalytic
efficiency [17]. Empirical work has treated undercooling as an arbitrary constant undercooling whatever the diameter is [16] or as an input parameter that can be tuned [14].

It is possible to measure experimentally the in-flight undercooling using free fall tubes like the 43 meters high CEA tube [19] or the 105 meters NASA facility [20]. However the temperatures are measured using infra-red pyrometry, limiting the alloys studied in those facilities to high melting point materials such that the recalescence events may be accurately measured. Such alloys are Au-Rh, Ta-Zr for example. Unfortunately in the case of aluminum, the infrared temperature measurement is very uncertain due to the low temperature range, the very high reflectivity (more than 99%) and high sensitivity of surface emissivity to the degree of oxidation. Few experimental data are therefore available to confirm the models on low melting point alloy systems such as aluminum.

The impact study deals with the modeling of the heat extraction on the substrate in an effort to predict the final shape of a single droplet and thus estimate the microstructure and porosity of the deposit. The in-flight thermal history of the droplet is thus an important parameter. Models have been developed to predict the temperature profile and fraction solid as a function of time during the impact [14], however the flow behavior of a semi-solid alloy is not yet tractable (in term of viscosity and solid phase deformation) The heat transfer coefficient, which may vary over two orders of magnitude, is in fact derived by inspection so that the computed results fit with observed results when available. Two methods of study have been employed. The first is a microstructural study of the deposit. This approach enables investigation of the cooling rate and coarsening effects on deposit grain size [18]. A more recent approach is high speed imaging, where pictures of a droplet impacting are taken. It is theoretically possible (but practically very difficult on aluminum alloys) to record at the same time the thermal history (using an infra-red measurement technique). Such experiments have been conducted [21] with a relatively slow high speed camera (2000 frames per second) on 5 mm copper superheated drops impinging on copper substrates. The drop profile during impingement is consistent with numerical results when the heat transfer coefficient is well chosen and show an impact characterized by a large splashing to a final pancake shape. However, the impact behavior at this scale is very different that the
one occurring in spray forming: the volume area ratio and the velocity involved are so different that the phenomena are not the same, furthermore the spray forming industry desires semi-solid droplets. Few studies of the deformation mechanism of vertically impinging droplet have been conducted [22]. They were used to predict the final size of a single fully liquid droplet impinging on a cold substrate.

To summarize, computer intensive models have been developed and validated for the flight, though defining the nucleation temperature is difficult. Most of the work concerning the impact has not yet been validated due to the lack of knowledge relative to the impact mass and heat transfer. In particular the role of semi-solid deposition after recalescence has yet to be investigated.

**Aim of the present study**

A set-up has been developed to conduct an experimental study on aluminum droplets in flight and at impact. The droplets are sprayed through a nozzle and each individual droplet is observed with a high speed camera system (up to 40 500 frame per second) to measure its velocity and size or to image the impingement behavior. The high speed system is also used to study the impact of the droplet. Models are subsequently developed to predict the in-flight speed and temperature evolution of the droplet.
Chapter 2
Experimental aspects

Experimental Set up

Facility

The set-up can be divided in several parts: the casing, the furnace and the spray tube and the control panel. Figure 2-1 shows a sketch of the apparatus, control panel not included.

The casing is a semi-spherical transparent glass placed on a support plate on the top of a polymer O-ring to limit the leaks. Inside the casing are placed a furnace, the crucible and a thermocouple. The furnace electrical connections, the thermocouple wiring as well as two 1/4 inch diameter gas lines are passed through the plate using special leak-proof seals. The electrical furnace has a cylindrical shape: 2 inch high by 1 inch inside diameter. Its size enables a rapid controlled heating of the sample which is contained in a crucible made of graphite or boron nitride. A connector to the gas line is screwed into the top of the crucible to pressurize the sample at the desired superheat. At the bottom of the crucible is placed a calibrated orifice made of sapphire (see figure 2-2). The droplets are created when the pressurized gas, between 10 and 30 psi, pushes the liquid metal through the orifice. They then fly through a hole drilled in the crucible, through the plate and enter the spray tube. A thermocouple is inserted in the crucible wall and measures a temperature close to that of the crucible chamber exit (calibration is necessary). The second gas line brings in a constant flow of inert gas through-out the set-up to exclude air and preventing oxidation of the metal charge.

The spray tube is a transparent glass tube that goes from the bottom of the plate, down to the place where the droplets are collected. It allows imaging and also contains the inert gas.

The control panel is composed of a temperature display that outputs the
temperature measured in the crucible, a manual valve to control the flow of inert
gas in the casing, the main valve that controls the pressure line opening, a main
valve by-pass valve to purge the system and an electrical switch that controls the
main valve system.

A fast opening valve, model 40-P4K-11AC-SS by Parker, is pressure
triggered by a 50 psi argon pulse resulting from the opening of a solenoid valve
controlled by the electrical switch. The pressuring gas is a mixture of high purity
4% hydrogen balanced with helium or argon to enhance the oxidant scavenging
within the furnace.

**Video imaging**

The data acquisition system is composed of a computer set-up allowing
permanent digital data storage and a very high speed camera. The camera is a
Kodak 4500 high speed digital imaging system which allows acquisition of black
and white pictures at the maximum rate of 40500 frames per second. At this
recording rate the picture size is 64 by 64 pixels. A telescope, model QM1 by
Questar was mounted before the camera to achieve a magnification of typically one
hundred times. The recording time allowed is in the order of 0.2 seconds, which
means that the triggering has to be fast enough not to miss the event. Digitized
images of interest can be down-loaded to the computer hard-drive using a GPIB
interface or in analog mode to a VCR. Image analysis may be necessary to increase
the contrast and reduce the noise.

The higher the recording rate, the more light is required to get sufficient
contrast for analysis. The camera is equipped with amplifiers that can greatly
increase the signal (or brightness) however, the noise is also concurrently
amplified. A special optic fiber lamp, model I-150 by Cuda, was used to focus the
light in a very small area. The back of the spray tube was, when possible, covered
with a reflective material to enhance contrast. It is impossible to know a-priori the
magnification achieved, which is a function of the focal distance. Therefore some
detail of know size has always to be present in the picture, or at least at the
beginning of the recording sequence, to give the scale.
Control ability

The following table details the process control.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Measurement procedure</th>
</tr>
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<tbody>
<tr>
<td>Flight distance</td>
<td>40 to 500 mm</td>
<td>distance between the bottom of the sapphire orifice to the point of interest</td>
</tr>
<tr>
<td>Superheat temperature</td>
<td>Up to 1000 °C</td>
<td>Thermocouple inserted in the crucible</td>
</tr>
<tr>
<td>Particle diameter</td>
<td>From 10 to 200 μm</td>
<td>Measured on quenched droplets. Described in detail in the &quot;measurement and analysis procedures&quot;</td>
</tr>
<tr>
<td>Particle speed</td>
<td>Up to 8 m/s</td>
<td>Using the high speed camera, described in detail in he &quot;measurement and analysis procedures&quot;</td>
</tr>
<tr>
<td>Surrounding gas</td>
<td>From 40 to 500 °C,</td>
<td>Thermocouple placed in the tube at different flight distance.</td>
</tr>
</tbody>
</table>

A correction is necessary to get a correct measurement of the superheat temperature since the temperature at the orifice is not the same as the one seen by the thermocouple. The temperature difference was recorded for each crucible at various temperature. In practice, at the temperature of interest for aluminum based alloys (700-800 °C) the offset is at most 6 °C.

Typical particle diameter distribution and speed profile are presented on Figure 2-3 and 2-4. The speed profile always presents the same characteristics: a maximum speed close to 6 m/s, a large scatter (due to the particle size distribution), artifacts at the beginning of each run probably due to gas resonance with the flexible tubing used.
The ambient temperature of the gas in the spray tube was found to be a strong function of the distance from the orifice. Calibration with a thermocouple enabled to have an estimation of the temperature profile, depending on the gas used. This estimated profile was used in the computations.

Not included in the table, the environment gas is a very important parameter. The inert gases used in this study are argon and helium (plus hydrogen as already described). Their cooling properties are very good compared to other gas usually used like nitrogen or gases resulting from the combustion of oxygen and fuels. This choice of gas combined with the low droplet speed means that the flight distance required to achieve solidification is usually less than one meter, which lead to a reasonable and easy to handle size set-up. This flight length has to be compared with typical industry processes that sometimes requires several meters flight distances.

To conclude the design chosen allows good control on spray parameters. However, this set-up presents two limits: the superheat temperature is limited to 1000 °C (which is the upper limit for a safe use of the furnace) and droplet speed that can reach at most 8 m/s.

**Material selection and preparation**

**Al-4.5 Cu**

This alloy was chosen to validate the models describing thermal history during flight and microstructural evolution because of the numerous studies it has been the subject of. The literature contains good correlation linking cooling rate and secondary arm spacing [2] and its undercooling properties have already been documented [9]. Appendix 1 gives the phase diagram and properties of this alloys.

**Al 4.3 Fe**

This alloy was chosen for its undercooling behavior: it easily undercools and the fraction solidified at recalescence is easy to recognize. The aluminum-iron phase diagram has been difficult to define regarding the behavior at concentration near the eutectic which was defined as about 1.8 % [23], since many metastable
products, like AlFe$_6$, appear during solidification depending on the cooling conditions. Appendix 1 gives the phase diagram and properties of this alloys.

**Alloy piece preparation**

The solid alloy piece inserted in the crucible needs to be shaped so that it has a cylindrical shape and a flat bottom, so that the molten metal will have contact with the orifice. Some trials with spherical pieces have been quite unsuccessful: the gas was flowing around the molten metal that kept its shape due to surface tension and no droplets were sprayed. The alloy was melted and cast in cylindrical rods that were then machined. Prior to casting, the liquid metal was stirred to be sure no gravitational segregation would alter the composition. The microstructure was compared on two different rods to be sure the stirring was sufficient. The final pieces are about 6-7 mm in diameter and 5 mm thick.

The alloys used were provided by Alcoa.

**Spray procedure**

**Preparation**

The orifice is positioned at the bottom of the crucible in the receptacle with orifice cone shape facing upward to prevent big droplet formation when liquid metal sticks to the cone walls. The alloy piece is then added such that the part facing the orifice is flat. Next, the stainless steel gas inlet is screwed in place. There is no need for a tight seal as the crucible dilates less than the metal and the joint will become leak-proof at the pressures of interest. If the gas inlet is tightened too much, cracks may appear in the crucible due to the thermal expansion mismatch. The gas inlet is then connected to the rest of the set-up and the alignment is checked so that the crucible exit is centered on the holding plate hole.

The thermocouple is inserted in the crucible. For reproducibility reasons, one should check it reaches the bottom of the hole. The glass casing is then put in place and the rubber o-ring is inspected to verify the seal. The ambient gas valve is now opened. Only a small flow is required to push the air out of the casing and prevent it from coming back.
The furnace can now be switched on. It takes usually 20 min. to heat up to
the melting point. An ambient gas flow has to be maintained during the heating to
prevent damage to the crucible: graphite consumes itself in air if heated up at more
than 700 °C and boron nitride is more tolerant to rapid heating if surrounded by a
dry atmosphere.

Before reaching the melting point, the spray circuit has to be purged to get
rid of the entrapped air and prevent oxidation of the liquid metal. The inlet pressure
then has to be adjusted prior to pressurization.

**Spray**

For each run, the set-up has to be prepared depending on which data the
experiment was designed to observe. As it is necessary to both keep an inert
atmosphere around the droplet at all time and to be able to visually access the
droplets, the fall was contained in a glass tube. A test tube was placed at the bottom
of the tube and filled with water or a solid substrate. Particular care was attached to
assume proper light quality around the area imaged. If the light is poor, then
pictures will lack contrast and analysis is impossible.

The recording devices (camera, and computerized real time measurements)
have to be ready before the chosen spray temperature is reached. The spray process
starts when the switch is set to ON and will stop when it is set to OFF. The typical
spraying time is less than half a second.

If a camera was used, the interesting images are down-loaded to the VCR
and/or the computer for a further analysis. The set-up can then be prepared for the
next run.

In order to prevent gravitational segregation in the crucible, runs should
follow each other at a reasonably rapid pace. Each spray improves convection, each
waiting period enables segregation. As a general rule, the first spray always
produces big droplets (up to 5 mm in diameter). Afterward, when gas and liquid
metal can flow through the orifice very small droplets are produced. Up to five
successive runs have been made without re-loading the crucible.
Re-loading first means waiting for the set-up to cool down such that the ambient gas flow can be stopped without crucible damage and repeating in the reverse order all the operations described above when equipment has cooled to tolerable level. The orifice is then cleaned by submersion in a bath of aluminum etchant solution, nitric and phosphoric acid, for at least 24 hours. Each orifice can be re-used several times.

**Measurements and analysis procedures**

**Droplet microstructure study**

Microstructure of the droplet was studied to get the secondary dendrite arm spacing as a function of diameter and the fraction solid at recalescence.

The microstructural evolution of the droplet is stopped by quenching in a liquid. Water was used to quench for its ease of manipulation and its ability to evaporate easily. Oil was tried, but it is virtually impossible to clean the droplets for subsequent analysis. It has been observed during the microstructure study that the shape of the droplet is not affected by the impact on the liquid surface. Some small droplets (less than 20 μm) have even been observed to bounce back off the surface.

The test tube containing the droplets is emptied onto a microscope slide. Water is first removed using an absorbing paper wick. The wick should never touch the slide as this could result in loss of the smallest droplets. The remaining water is removed by evaporation augmented by a warm air circulation. The droplets can then be studied to determine the diameter distribution (see below). After being epoxy-mounted (Epoxikit from Struers), the droplets are successively polished with polishing papers (produced by Buehler) from 320, 600, 800 to 1200 grit. Fine polishing is obtained using polishing cloths, water and calibrated alumina powders of 5 μm and then 1μm. The sample is chemically etched with Keller's etch (H₂O: 190 ml, HNO₃ : 5 ml, HCl : 3 ml, HF (48 %): 2 ml) for 10 seconds for Aluminum-Copper alloy and 7 seconds for Aluminum-Iron. After being rinsed and air dried, the sample is ready for metallographic analysis.

For one droplet, the secondary dendrite arm spacing is measured on at least 3 dendrites in the same droplet and then averaged. For one dendrite, the secondary
dendrite arm spacing is averaged on at least 5 arms [3,23,24]. Computer analysis of the microstructure to define areal fraction is performed on pictures using the software NIH Image, version 1.58.

**Droplet size distribution study**

The droplets are collected in a test tube and put on a microscope slide. Water is removed using the same technique as for the microstructure study. Micrographs of the dried slides are then taken such that the diameter of each droplet may be measured. The droplets can still be mounted and subsequently studied by following the procedure already described.

**Speed distribution study**

Measuring particle velocity involves positioning the high speed camera to look at a precise part of the flight path and choosing the zoom factor so that several millimeters of flight can be observed. The back of the tube was covered with millimeter paper to give a calibration scale in order to facilitate the analysis. For large particles, the depth of field was sufficient to image the calibration screen and the droplet but for smaller droplets a window was required to limit the trajectory as shown in Figure 2-5. The window is a device that closes the tube except for 1 mm wide gap, through which some droplet may go. The droplets not going through the hole impact the entrance and are removed. The droplets going through the window are then imaged. The pictures taken are downloaded to a VCR and videotape is then analyzed: each droplet velocity is estimated measuring the number of frame required for a droplet to travel between two points of known spacing. The time between two frames is given by the recording rate.

**Impingement study**

The impingement behavior is observed by imaging the impact of droplets on a flat surface of a chosen materials (aluminum for example). The substrate must be such that a mark can be seen with the camera to be used as a distance calibration tool. The camera is set at a slightly higher level than the substrate so that it looks down to the substrate with a small angle. The distances are not affected by the angle of vision whereas a 3D vision is achieved and good measurements can be made. A bright but diffuse light is required to get best picture quality. Shading is to be
avoided as it creates an optical illusion in which the apparent size of the droplet is enlarged. The images are downloaded to a VCR (analog data) and to the computer (digital pictures). The digital pictures may be subjected to image processing to increase the contrast. One useful technique involves subtracting intensity values pixel by pixel to track the changes between pictures.
Figure 2-1: Sketch of the apparatus
Sapphire Orifice

Diameter: 50 μm (0.002")

2.2 mm (0.087")

0.63 mm (0.025")

Figure 2-2: orifice used to spray
Figure 2-3: Droplet size distribution as a function of spraying pressure
Figure 2-4: Droplets speed evolution during a run

Droplets speed as a function of time

<table>
<thead>
<tr>
<th>Time (ms)</th>
<th>Speed (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
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<tr>
<td>1000.0</td>
<td>12.0</td>
</tr>
<tr>
<td>1200.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>
Figure 2.5: Window filter
Chapter 3
Cooling Model

The objective of the modeling work was to predict the droplet in flight thermal profile. This model was designed as a tool to study the impingement behavior and understand the phenomena involved at impact. Since, it is virtually impossible to measure the temperature of the aluminum droplet directly when it arrives on the substrate, we needed to predict the deposition temperature as a function of particle diameter and flight distance.

Description

The model is composed of several sets of equations. One set describes the temperature evolution and the other deals with the velocity and the flight distance. The two sets of equation are coupled, since the heat extraction rate is a function of speed and the ambient temperature is a function of the droplet position. As a first approach, the coupling terms could be neglected due to the low velocities involved in our experiments.

The temperature evolution can be divided into three distinct parts, in all of which heat is extracted by the environment. The first part deals with cooling of the liquid droplet. When the temperature reaches the nucleation temperature (mainly function of the alloy and of the droplet diameter), the solidification begins and part of the droplet solidifies at once (recalescence time is about 20 μs and therefore 2 orders of magnitude faster than the other phenomena involved) and the remaining part solidifies under equilibrium conditions governed by the Scheil equation. Once solidification is completed, the solid droplet may continue to cool down.

Cooling rates are computed as the average cooling rate between the beginning of the flight and the end of solidification. All the numbers used in the computation are presented in Appendix 1.

The program was written in C and runs on the MIT workstations. Appendix
2 gives more details about the code and its utilization. The scheme used to solve the equation is first order, with a very small time step (5 μs), so that the numerical integration is stable and gives good results.

**Velocity and flight distance**

A droplet of mass \( m \) is assumed to be falling in the gravity field \( g \) at velocity \( v \) into a surrounding gas with characteristic speed \( v_g \) in the laboratory referential and assumed to be constant. The general equation describing the evolution of the speed is:

\[
m\frac{dv}{dt} = mg - \frac{1}{2} \rho_{\text{gas}} C_D A (v - v_g) \frac{|v - v_g|}{v - v_g}
\]  

(3-1)

In this equation, \( \rho_{\text{gas}} \) is the density if the surrounding gas, \( C_D \) is the drag coefficient and \( A \) is the projected area of the droplet.

The mass \( m \) is given by the product of the liquid metal density and the droplet volume \( V \)

\[
m = \rho_{\text{liq}} \cdot V
\]  

(3-2)

and assuming the droplet is spherical with diameter \( D \), (3-1) can be rewritten

\[
m\frac{dv}{dt} = g - \frac{3 \rho_{\text{gas}} C_D}{4 \rho_{\text{liq}} D} (v - v_g) \frac{|v - v_g|}{v - v_g}
\]  

(3-3)

The drag coefficient is a function of the Reynolds number [25]. In our case the Reynolds number, given by \( Re = \frac{\rho_{\text{gas}} |v - v_g| D}{\mu_{\text{gas}}} \), is 0.2 in the limiting case of a 1000 μm diameter droplet, (largest size investigated) and in general is closer to \( 10^{-2} \). As the Reynolds number is smaller than 1, the Stokes correlation can be used [25]:

\[
C_D = \frac{24}{Re}
\]  

(3-4)
The governing equation is finally:

\[
\frac{dv}{dt} = g - 18 \frac{\mu_{\text{gas}}}{D^2 \cdot \rho_{\text{liq}}} (v - v_g) \tag{3-5}
\]

The analytical solutions of the equation (3-5) are for the speed:

\[v = (v_g + \frac{g}{K'}) + (v_0 - v_g - \frac{g}{K'}) \cdot \exp(-K' \cdot t) \tag{3-6}\]

and for the flight distance:

\[x = (v_g + \frac{g}{K'}) \cdot t + \frac{1}{K'} (v_0 - v_g - \frac{g}{K'}) \cdot (1 - \exp(-K' \cdot t)) \tag{3-7}\]

with \(K' = 18 \frac{\mu_{\text{gas}}}{D^2 \cdot \rho_{\text{liq}}} \tag{3-8}\)

and the initial conditions: \(v = v_0\) and \(x = 0\)

This model requires two parameters that are \(v_0\) and \(v_g\), which are obtained from the analysis of the in-flight droplets speeds. An initial speed of 1.6 m/s independent of the diameter and a gas speed of 5.7 m/s provide a solution in good agreement with the observed speeds.

Equation (3-6) is composed of two terms, the first one is the terminal velocity \((v_g + \frac{g}{K'})\) and the second term is the transient term. It gives the deviation from the terminal velocity and tends to zero. \(K'\) is the inverse of a reaction time and measures how fast the droplet speed reaches the terminal velocity. As \(K'\) is proportional to the inverse of the square of the diameter, the speed profile is a very strong function of the diameter. Small droplets have a very small reaction time which means the terminal velocity is reached almost at once, whereas bigger droplets are going to reach the terminal velocity slower.

Figure 3-1 presents speed profile for two different droplet diameters assuming \(v_0 = 1.6 \text{ m/s}\) and \(v_g = 5.7 \text{ m/s}\)
Temperature profile

Heat extraction and Newtonian cooling

Heat extraction from the droplet occurs as a cooler gas flows around it. The heat transfer coefficient \( h \) can be estimated with the Ranz-Marshall equation [17]:

\[
h = \frac{k_{\text{gas}}}{D} \left( 2 + 0.6 Re^{0.5} Pr^{0.33} \right)
\]

(3-9)

\( Re \) is the Reynolds number of the flowing gas and is much smaller than 1 as already seen, \( Pr \) is the Prandtl number, \( Pr = \frac{C_p \cdot v}{k} \), which a good approximation is 0.7 and \( k_{\text{gas}} \) is the gas conductivity, typically \( 10^{-2} \) W/m/K. Hence, the term containing \( Re \) and \( Pr \) is small compared to the first term and a reasonable estimation of the product \( h \times D \) is

\[
h \times D = 2.1 \times 10^{-2}
\]

(3-10)

The radiative heat extraction rate \( E_R \) is given by \( E_R = \varepsilon \cdot \sigma \cdot (T^4 - T_{\text{amb}}^4) \). \( \varepsilon \) is the reflexivity, between 0.1 and 0.01 for aluminum alloys [26], \( \sigma \) is the Stephan constant and is \( 5.67 \times 10^{-8} \) SI and \( T \) is temperature in Kelvin. Assuming a temperature of 1000 K, \( h_R \) is about 3000 W/m². \( E_R \) has to be compared with the gas extraction which is \( E_{\text{gas}} = h \times (T - T_{\text{amb}}) \). \( h \) can be estimated at 200 W/m² for a 100 \( \mu \)m droplet and \( E_{\text{gas}} \) is then about \( 2 \times 10^5 \) W/m². As a conclusion, the radiative heat transfer can be neglected with a good approximation.

The Biot number compares the heat extraction to the heat conductivity, \( k \) being the heat conductivity in the liquid metal (about 100 W/m/K). In this case, the Biot number is:

\[
Bi = \frac{h \times D}{k_{\text{liq}}} = 2 \times 10^{-4}
\]

(3-11)

As it is less than 0.2, Newtonian cooling is justified [27] so that the temperature in the droplet can be treated as uniform. The droplet are again assumed to be spherical.

In-flight cooling, prior to solidification
During the flight and before solidification the governing equation is:

\[ \rho_{\text{liq}} C_{\text{liq}} \frac{dT}{dt} = A h (T - T_{\text{amb}}) \]  

where \( V \) and \( A \) are respectively the volume and surface of the droplet and \( T_{\text{amb}} \) is the ambient temperature, which is a function of the position of the droplet.

Rewriting (3-12) by replacing \( h \) as given by (3-9), we obtain:

\[ \rho_{\text{liq}} C_{\text{liq}} \frac{dT}{dt} = A \frac{k_{\text{gas}}}{D} (2 + 0.6(\frac{\rho_{\text{gas}} |v - v_{s}| D}{\mu_{\text{gas}}} P r^{0.33})(T - T_{\text{amb}})) \]  

Two coupling terms appear now: one with the velocity, function of time and another one with the ambient temperature which is a function of the position and implicitly of the time. This equation cannot be solved analytically. The computer model built enables to solve it.

Some simplifications help give a meaning to equation (3-13). Assuming that the contribution of the second term in the right-hand member of equation (3-9) is small and that the ambient temperature is constant, (3-13) becomes:

\[ \rho_{\text{liq}} C_{\text{liq}} \frac{dT}{dt} = 2A \frac{k_{\text{gas}}}{D} (T - T_{\text{amb}}) \]  

As in the case of the velocity, the solution is an exponential decay to the ambient temperature. Replacing \( V \) and \( A \) by their expressions for spherical droplets, the parameter \( K = \frac{6h}{\rho_{\text{liq}} C_{\text{liq}} D} \) appears. It is the inverse of the response time toward the final velocity (assuming no solidification). \( K \) varies as the inverse of the diameter which means small droplets cool down much faster than large droplet.

**In-flight Solidification**

Equation (3-13) is used to get the solution until the nucleation temperature is reached. To evaluate the nucleation temperature, the program needs to be given the specific law that represents the best the highly probabilistic nucleation temperature. In the results presented below, the nucleation temperature was estimated from the
droplet diameter using the experimental results described in the undercooling section.

Once nucleation occurs spontaneously in the undercooled droplet, recalescence is observed as the heat of fusion is rejected from the growing solid into the undercooled liquid. The recalescence event is so fast that we can consider an adiabatic treatment as correct, so that the heat released by the solidification is used to heat up the droplet to the liquidus temperature. The fraction solid \( f_{s,r} \) right after recalescence can be estimated using equation (3-15), derived in the next section, where \( H_{\text{fus}} \) is the heat of fusion, \( C_p \) is the specific heat, \( T_L \) is the liquidus temperature and \( T_N \) is the nucleation temperature.

\[
f_s \times H_{\text{fus}} = C_p (T_L - T_N) \tag{3-15}
\]

The remainder of the solution is given by the Scheil equation [28], which in differential form is:

\[
(C_i - C_s) \frac{df_s}{ds} = (1 - f_s) dC_i \tag{3-16}
\]

where \( C_i \) is the composition of the liquid, \( C_s \) the composition of the last solid formed and \( f_s \) the solid fraction.

Several cases then arise, of which we are treating here only two kinds. The first case is when the alloy is an hypoeutectic one, for example Al/Cu 4.5 %. In this case the Scheil equation can be integrated to give equation (3-17)

\[
C_s = k C_0 (1 - f'_s)^{k-1} \tag{3-17}
\]

where \( C_s \) is the concentration of the solid fraction just deposited, \( k \) is the partition coefficient (ratio between the solidus and liquidus slopes), \( C_0 \) is the original concentration of the alloy and \( f'_s \) is a corrected fraction solid and presented in equation (3-18):

\[
f'_s = \frac{f_S - f_{s,r}}{1 - f_{s,r}} \tag{3-18}
\]

in which \( f_{s,r} \) is the fraction solid at recalescence and \( f_s \) is the actual solid
fraction computed using equation the argument that the heat extracted during \( \delta t \) is equal to the heat released by the solidification of \( \delta f_s \), equation (3-19).

\[
A h (T - T_{\text{amb}}) \, dt = \rho_{\text{liq}} \, V \cdot H_{\text{fus}} \cdot df_s
\]  

(3-19)

The temperature is then obtained using the phase diagram, more specifically the liquidus slope \( m \) and the partition coefficient introduced in equation (3-17).

\[
T = T_m - \frac{m}{k} \, C_s
\]  

(3-20)

The other case is the case of an hyper-eutectic alloy that solidifies in a phase of constant composition \( C'_E \) and the eutectic, for example Al/Fe, 4.3 % that solidifies in AlFe\(_3\) and the eutectic. The integrated Scheil equation is then:

\[
C_i = (C_0 - C'_E) \frac{1 - f_s, r}{1 - f_s} + C'_E
\]  

(3-21)

where \( f_s \) is given by equation (3-19).

And the temperature is then given by:

\[
T = T_E + m(C_i - C_E)
\]  

(3-22)

where \( T_E \) is the eutectic temperature and \( C_E \) is the eutectic composition.

In both cases, if during the solidification, the solid or the liquid concentration reaches the equilibrium eutectic composition, we assume it remains at this value until the end of the solidification, meaning that the temperature is stationary at the eutectic temperature. No modeling of the eutectic undercooling was included. Solidification ends when fraction solid reaches unity.

**In-flight cooling, after solidification**

After the end of the solidification, the temperature follows the same equation as (3-11) replacing the liquid properties by the solid ones. However, this case is of limited interest, since the purpose of this work is to model spray forming of liquid or semi-solid particles.
Results and Validation

Validation of the flight model was conducted using several approaches. First, comparison with other published models shows that the assumptions made, the equations used and that the shape of the solutions are coherent with previous works.

Experimental observation of impingement behavior shows that the model predicts reasonably accurately whether a droplet should be solid or not when it reaches the substrate. The error is within the imprecision range induced by the modeling process. For example, two parameters to which the model was particularly sensitive are the ambient temperature profile, influencing directly the heat extraction, and the gas velocity, influencing directly the flight distance. However, these functions are difficult to measure precisely and errors are induced as we model them respectively with a linear temperature profile and a constant gas velocity.

The last part of the validation process was to compare the computed cooling rates with the one observed experimentally. The experimental procedure was to spray droplets that were quenched in water, and observe the microstructure as described in the experimental procedures part. Figure 3-2 shows some of the micrographs used to get the data points. Some previous work [2] established a correlation between the secondary dendrite arm spacing (DAS) $\lambda_2$ in $\mu m$ and the cooling rate $\dot{T}$ in K/s:

$$\lambda_2 = 50(\dot{T})^{\frac{1}{3}}$$

(3-21)

The computed DAS were compared with the measured one (Figure 3-3). The agreement is good, below one order of magnitude.

The validated model was used to get results for the impingement behavior of droplets. Solutions giving the temperature and the fraction solid as a function of flight distance for two different alloys, Al-Cu 4.5% and Al-Fe 4.3 %, are presented in Figures 3-4 to 3-7. The conditions are in the case of the Al-Cu alloy : sprayed in Helium-Hydrogen 4% at the temperature of 720 °C and in the case of the Al-Fe...
alloy: sprayed in Helium at the temperature of 830 °C.

As already noted, although liquid undercooling of the melt was assumed to be considered, no undercooling was assumed for the semi-solid during eutectic solidification which explains the unusual aspects of the prediction for the Al/Fe alloy. This assumption affects the computed temperature and composition during solidification, therefore the cooling rate given by the model have to be taken with caution. As the fraction solid is computed from the heat extraction, this result is correct.
Figure 3-1: Predicted speed profile of two different droplet diameters assuming $v_0 = 1.6 \text{ m/s}$ and $v_g = 5.7 \text{ m/s}$
Figure 3-2: Microstructure of aluminum copper 4.5% (wt) droplets of respective diameter 200 μm and 93 μm
Figure 3-3: Comparison between predicted and measured dendrite arm spacing in the cases of flight in helium and argon.
Figure 3-4: Predicted temperature profile as a function of distance for various aluminum copper 4.5 % (wt) droplet diameters
Figure 3-5: Predicted fraction solid profile as a function of distance for various aluminum copper 4.5 % (wt) droplet diameters.
Figure 3-6: Predicted temperature profile as a function of distance for various aluminum iron 4.3 % (wt) droplet diameters
Figure 3-7: Predicted fraction solid profile as a function of distance for various aluminum iron 4.3 % (wt) droplet diameters.
Chapter 4
Undercooling measurement

Principle

The undercooling measurements were based on an analysis of the microstructure of the droplets. The droplets are quenched and then studied using the method described in the experimental aspects chapter.

The rapid solidification of a liquid metal proceeds in 2 steps. The liquid is cooled below the liquidus temperature until the temperature reached is such that nucleation occurs due to the high driving force toward the solid phase existing at this temperature. The nucleation can be homogeneous (when a self assembly of atoms reaches a critical size, the addition of a new atom to the solid germ is energetically favorable and growth can proceed) or heterogeneous (a foreign particle triggers the nucleation at a lower undercooling by decreasing the amount of energy required to attach new atoms to the existing surface, thus creating a critical nuclei). In some cases, undercooling may be negligible and solidification is limited by the heat extraction rate. The difference between liquidus temperature and nucleation temperature is the undercooling. When nucleation occurs, the first step of solidification begins; it is called recalescence. In a very short time, a few microseconds, part of the droplet solidifies. The second step is an equilibrium solidification growing from the originally solidified mass and finishing when the whole sample is solid.

The microstructures created by these two solidification processes are very different since the microstructure morphology is related to the time necessary to achieve solidification. The recalescence event occurs so fast that at the scale of the droplet, a few microseconds, the diffusion phenomena are too slow to allow a redistribution of the atoms and solidification occurs far from the thermodynamical equilibrium. A feature-less structure results. On the contrary, the part that solidifies afterward, solidifies following the equilibrium diagram in such a manner that a
dendritic structure can usually be observed.

The shape and growth of the part solid at recalescence (PSAR) is still subject to study: reference [29] shows a change in the growth mechanism after a critical undercooling is reached for pure nickel samples. Some models have been developed [20] to predict the PSAR shape evolution in time. It appears that the solidification front is unstable and may lead to a structure with a disc shape as well as to a structure where only a few branches develop. This unstable behavior of the solidification front and the resulting microstructure have been observed for Al/Fe 4%. Figure 4-1 (Al/Cu 4.5 %) and Figure 4-2 (Al/Fe 4.3 %) show undercooled droplets processed during this study. Some branched SPAR can be observed in Figure 4-2. Figure 4-3 is a schematic description of the solidification process for the droplet seen in figure 4-1; for the liquid droplet (a), nucleation occurs (b), leading to the recalescence (c). Afterward equilibrium solidification continues creating a dendritic structure growing from the SPAR (d) as well as from the outer surface (e).

To estimate the undercooling achieved by the droplet, it is necessary to relate the undercooling with a microstructural characteristic. At recalescence, part of the droplet solidifies and releases heat. As the recalescence is an extremely fast process, we can neglect the heat extraction from the environment and consider the recalescence event to be adiabatic. The energy released increases the temperature until it reaches the liquidus temperature. It is then impossible for the solidification to proceed further at this rate: any new mass solidifying would increase the temperature above the liquidus which would lead to an unstable solid phase. For the solidification to continue, it is necessary to remove heat from the droplet surface, which is much slower and proceeds by another solidification mechanism. Equation (4-1) can be deduced from a heat balance on the droplet: the heat released by the solidification of the SPAR is equal to the heat required to increase the temperature from the nucleation temperature to the liquidus temperature.

\[ f_s \times H_{\text{fus}} = C_p (T_L - T_N) \]  \hspace{1cm} (4-1)

where \( f_s \) is the fraction solid at the end of the recalescence, \( H_{\text{fus}} \) is the heat of fusion and \( C_p \) the specific heat of the alloy, \( T_L \) is the liquidus temperature and \( T_N \)
is the nucleation temperature. In equation (1), \(H_{\text{fus}}\) and \(C_p\) are thermodynamic constants available in the literature. If \(f_s\) can be measured, the undercooling \((T_L - T_N)\) is known.

Two methods to estimate the fraction solid at recalescence (FSAR) have been developed and are now presented.

**Surface based method**

**Principle**

From the study of the droplets micrograph, it is possible to measure the area of both the droplet \(A_{\text{droplet}}\) and of the PSAR \(A_{\text{solid}}\) in the plane of cut. A simple estimation of \(f_s\) (based on areal fraction) is then:

\[
f_{\text{area}} = \frac{A_{\text{solid}}}{A_{\text{droplet}}} \quad (4-2)
\]

However, this solid fraction is based on area measurement and is different from the volumic one (or fraction solid deduced from the ratio of the volume of the SPAR to the total volume of the droplet). To correct for that, it is possible to estimate, using a few assumptions, what would be the volumetric ratio for a droplet with a known areal ratio. We assume the volume elements involved are spherical; this assumption is a good one for the droplet, however it is more difficult to justify it for the solid part. A discussion of the validity of the method is done below. We then assume the plane of cut is passing through the center of both spheres. Denoting by \(R_1\) the radius of the droplet and \(R_2\) the radius of the solid part we have:

\[
A_{\text{droplet}} = \pi R_1^2 \quad \text{and} \quad A_{\text{solid}} = \pi R_2^2 \quad (4-3)
\]

Equation (4-2) can then be rewritten in:

\[
f_{\text{area}} = \frac{R_2^2}{R_1^2} = \left(\frac{R_2}{R_1}\right)^2 \quad (4-4)
\]

The volumic fraction solid \(f_s\) can be written:
It is then possible to relate (4-4) and (4-5):

\[ f_s = \left( \frac{f_s^{\text{area}}}{A_{\text{droplet}}} \right)^{\frac{3}{2}} = \left( \frac{A_{\text{solid}}}{A_{\text{droplet}}} \right)^{\frac{3}{2}} \]  

(4-6)

The undercooling is therefore given by:

\[ \Delta T = \frac{H_{\text{fus}}}{C_p} \left( \frac{A_{\text{solid}}}{A_{\text{droplet}}} \right)^{\frac{3}{2}} \]  

(4-7)

This last equation (4-7) was used to compute the undercooling of aluminum-copper droplets.

**Results and validity**

Experiments with Al/Cu 4.5% were run to study the relationship of the undercooling achievable and when the droplet diameter, the cooling rate and gas atmosphere are changed. It is experimentally [8] and theoretically known (classical theory of nucleation, [5]) that a large droplet may undercool much less than a small one because it is statistically more probable that it contains more impurities than the small one and therefore the probability it nucleates at a given undercooling is much higher than for a small droplet. Undercooling is therefore a probability related phenomena, usually described by Poisson distribution and large scatter is inherent.

The diameter of the droplets was, when possible, not estimated from the micrograph: using the fact that the epoxy substrate is transparent it is possible to focus on the periphery of the droplet below the surface and to estimate with a better accuracy the real diameter of the droplet. The micrographs obtained were scanned and the area of interest measured using the software NIH Image. Numerous runs were performed under different conditions of superheat and gas type (which affects the cooling rate). From each run, hundreds droplets were collected, of which only several displayed significant undercooled behavior, some rare times because the
metallographic section did not intersect the solid core or more often because the droplets did not undercooled significantly.

Results for Al/Cu 4.5 % are reported in Figure 4-4. A lot of scatter is observed, resulting from the probabilistic behavior which rules the nucleation as well as from our measurement method. Increasing the number of points gives a better idea of the general trend. It is impossible to track the effects of superheat and gas type variations on undercooling as seen in Figure 4-5 and 4-6, which indicates that nucleation statistic are more important than processing conditions in the term of superposed variability, provided that the method variability is small. Improvement of this technique is necessary to get this kind of information. The distribution was fitted by Equation (4-8) with a correlation coefficient of 85.7 %.

\[
\log (\Delta T) = 3.86 - 1.75 \log D
\]  
\quad (4-8)

In equation (4-8), D is the diameter in \( \mu m \) and the temperatures are in °C.

It is interesting to compare the undercooling measured with the homogeneous undercooling predicted by the classical theory of nucleation as presented in (A11). These homogeneous undercooling are the largest undercooling achievable. Solving for equation (4-9) with a solid-liquid interface energy of 0.158 J/m2 from (A9), estimation of the maximum undercooling achievable were performed.

\[
\Delta T = \frac{16 \pi \sigma^3 \nu^2 T_f^2}{3kT_N H_f^2 \ln(10^{-3} \frac{d^3}{\Omega} (\frac{\alpha}{\Omega}) D \frac{\Delta T}{T})}
\]  
\quad (4-9)

where D is the diffusion coefficient of Cu in Al, \( \alpha \) the atomic spacing.

Figure 4-7 compares the undercooling observed to the one predicted with the theory. As expected, the undercoolings achieved with the apparatus are smaller than the homogeneous predicted one, in the better case one third of the maximum. The reason for that is likely to be the presence of numerous nucleation sites: either impurities coming from the alloys or being introduced in the apparatus, or oxidation that create impurities on the surface.
In order to evaluate the imprecision introduced by this method, the same droplets were examined after several polishing sequences to check on the validity of the assumption that the section is done through both the center of the droplet and of the solid core. Some differences arise the position of the plane of cut that may intersect the SPAR in such a way we only see a small amount of it (underestimation of FSAR) or it may cut the droplet in such a way the diameter is underestimated (overestimation of the FSAR). The undercooling values deduced for the same droplet could vary by one order of magnitude and therefore, to get more accuracy, another method was developed.

**Volume based method**

**Principle**

The volume based method is also based on metallographic examination. Observing the droplet microstructure along several parallel cut planes, it is possible to reconstruct a 3 dimensional map of the droplet. Studying this map, we estimate the SPAR volume and the droplet volume and therefore the volume fraction solid and the undercooling with a very good precision. This treatment allows for analysis of non-spherical volume elements and simplification are minimized. Figure (4-8) shows the principle of the method.

The experimental procedure was exactly the same as presented before, except the end of the polishing sequence was repeated several times (1200 grits, 5 μm, 1 μm and etching). Micrographs were taken after each polishing sequence. The studied droplets were chosen very close to each other to be sure the thickness grinded during one polishing sequence was the same for all of the droplets.

Each micrograph is scanned, the shape and the dimensions of each area of interest are measured. Distances between each polishing plane are deduced from the analysis of the droplet radius evolution: assuming each droplet is spherical we know that the apparent radius of the section, \( r \), is related to the radius of the droplet, \( R \), and to the distance between the cutting plane to the center of the sphere, \( z \), by

\[
r^2 = R^2 - z^2
\]  

(4-10)
Using several successive measurement of the apparent droplet radius, we solve for the real droplet radius and the distance to the center. Comparing the results for each droplet, and giving more weight to the droplet whose shape is really spherical as indicated by consistent circular cross-sections, the distance between each cut plane is assessed as well as the dimensions of the droplets. A 3D model of each droplet is then built. The next step is to estimate the volume of the SPAR, whose shape can be very distorted. Each droplet requires a different treatment and volumic integrals are written and solved according to the shape encountered.

Some droplets appear to have had several nucleation points, which lead to several discontinuous SPAR. In these cases, the fraction solid was computed as the sum of all the SPAR volumes divided by the total volume of the droplet.

Results

This method was used to study the undercooling behavior of Al/Fe 4.3%. The SPAR is very easy to recognize. Figure (4-9) shows the micrographs taken for a single droplet. The SPAR parts are the bright and featureless area, whereas the darker parts are the equilibrium solidified alloy. These darker parts show features if observed under a very high magnification. The undercooling as a function of droplet diameter is presented in figure (4-10). This figure shows two interesting trends. For droplets with a small number of nucleation sites (below 3), it appears that the points are pretty much aligned. However, in the case of droplets presenting numerous nucleation points, as that of figure (4-11), it appears the undercooling is huge with regard to the diameter and does not fit at all in the previous line. A maximum undercooling of 232 K was recorded for a 43 μm diameter droplet. This result is close to the highest undercooling value found in literature 260 K [8].

To explain the multiple nucleations and unify the undercooling results, a theoretical explanation is now presented. It is very unlikely that all the nucleation sites triggered solidification at the same time. A specific site must have nucleated first. As the first solid is formed, shrinkage creates a pressure variation. Solidification is so fast that this pressure variation behaves a Heavyside wave and conveys energy to other parts of the droplet. This energy wave touches other nucleation sites such that the undercooling was not sufficient to override the
nucleation barrier energy. However, the undercooling plus this wave energy is now
enough and nucleation occurs. Solidification proceeds and a new wave is created.

To respect the Newtonian cooling assumption, new nucleation sites produce smaller
solid parts. This model assumes implicitly that heat diffuses slower than the wave.
Typical sound speed in liquids is above 1000 m/s, it is reasonable to evaluate the
velocity of the wave in this range. The solidification front velocity is in the order of
10 m/s, which means that the wave could travel much faster than the solidification
front.

When local recalescence (for one nucleation site) occurs, the growth of the
local solid part is limited by the heat that can be released in the surrounding liquid.
This behavior is not influenced by the neighboring domains, which allow us to
assume that each of the small domains surrounding the nucleation sites behaves
independently and should be treated as a single droplet. An apparent volume is then
defined as the total volume of the droplet divided by the number of nucleation sites.
This apparent volume is the volume that each domain would occupy if they all were
of the same size. From this apparent volume, an apparent diameter is computed as if
the domain was spherical. Figure (4-12) presents the undercooling as a function of
the apparent diameter. This time the point are almost aligned on a curve which fit
equation is:

\[ \Delta T = 348.4 - 2.55 D \]  \hspace{1cm} (4-11)

with a correlation coefficient of: 93.3 % and D in μm.

Equation (4-11) gives the undercooling as a function of diameter in the case
of single nucleation, which is a lower estimation of the undercooling achievable.
The maximum undercooling extrapolated from this equation is close to 350 K.
Which is close to the figures given by the classical theory of homogeneous
nucleation (Figure 4-13). This figure was computing assuming the cooling rates
given by the model are valid for the Al/Fe alloy.

**Future work**

This technique is a precise tool to study the undercooling behavior of
droplets. However, its use is limited to alloys where the SPAR is really distinct
from the equilibrium solidification part. In this respect Al/Fe is a very interesting alloy to work with.

This technique could be used to study the influence of the superheat, of the surrounding gas through the surface oxidation kinetics and of the process parameters such as materials used for the crucible and the nozzle.
Figure 4-1: Aluminum copper 4.5% (wt) undercooled droplet. Diameter is 94 μm and undercooling in the order of 5 K.
Figure 4-2: Aluminum iron 4.3% (wt) undercooled droplets. Diameter are respectively 117 µm and 72 µm, undercooling are respectively 43 K and 166 K.
Figure 4-3: Droplet Microstructure evolution during solidification

a) The droplet is fully liquid and undercooled

b) Nucleation occurs inside the droplet

c) Part of the droplet solidifies at recalescence

d) Equilibrium growth from the part solid at recalescence

e) Final structure, with at the end growth from the surface (where heat is extracted)
Figure 4-4: Undercooling vs. diameter for aluminum copper 4.5% (wt) droplets. The first attribute in the legend gives the gas type: He for helium and Ar for argon. The second attributes is the superheat in K.
Figure 4-5: Undercooling vs. diameter for aluminum copper 4.5% (wt) droplets. The first attribute in the legend gives the gas type: He for helium. The second attributes is the superheat in K.
Figure 4-6: Undercooling vs. diameter for aluminum copper 4.5% (wt) droplets. The first attribute in the legend gives the gas type: He for helium and Ar for argon.
**Figure 4-7**: Comparison between predicted homogeneous undercooling and observed undercooling for aluminum copper 4.5% (wt)
Figure 4-8: Microstructure of an undercooled droplet (the equilibrium grown part is not represented.)
Figure 4-9: Successive section of a 130 μm diameter aluminum iron 4.3% (wt) droplet. Undercooling was estimated to be 73 K.
Figure 4-10: Undercooling achieved in aluminum iron 4.3% (wt) droplets as a function of diameter.
Figure 4-11: Multiple nucleation sites aluminum-iron 4.3% (wt) droplet.
Figure 4-12: Undercooling achieved in aluminum iron 4.3% (wt) droplets as a function of apparent diameter.
Figure 4-13: Comparison between predicted homogeneous undercooling and observed undercooling for aluminum iron 4.3% (wt).
Chapter 5
Impingement behavior

The aim of the impingement study was to predict the deformation behavior and the final shape of a deposited droplet as a function of parameters to be defined. The method was to image the impingement behavior of semi-solid droplets, whose thermal history was well-known (using the model developed), with a very high speed camera. A descriptive theory was developed to take into account the results given by the analysis of the droplet behavior.

Theory

Introduction

Without solidification, the deformation behavior of an impinging droplet can be described in term of competition between kinetic energy and surface energy. At impact, because of the revolution symmetry of the system, the droplet deforms into a disc shape. The kinetic energy of the falling droplet is converted into lateral motion by deflection off the surface. As the deformation progresses, the surface area is increased by progressive flattening of the spherical droplet into a disc. Thus the kinetic energy is converted to surface energy. Viscous forces are also present and tend to dissipate the kinetic energy in the form of heat. Oscillations may arise before an equilibrium state is reached. A good analogy to describe the phenomena is the movement of a spring with weak viscous damping. The final shape depends on the solid/liquid and liquid/solid surface energies.

With solidification, the problem is much more complex. First, heat is extracted from the bottom of the disc such that temperature is changing which leads to a large variation in physical properties (such as viscosity) over short distances. Second, depending on the solidification rate, the equilibrium shape of the droplet may differ from that predicted by purely molten droplet impinging theory. Modeling approaches [22,31] are based on a diffusion treatment of the heat. However, as already seen in the model chapter, the cooling of the droplet is assumed Newtonian
and the rate limiting step is more probably the heat transfer coefficient between the substrate and the droplet.

**Physical dimensionless approach**

In this analysis, some parameters have been defined as governing the impingement behavior:

- \( D \), droplet diameter (m)
- \( \rho \), liquid metal density (kg/m\(^3\))
- \( v \), impact speed (m/s)
- \( \sigma \), surface tension of the liquid metal (J/m\(^2\))
- \( \mu \), viscosity of the liquid metal (J.s/m\(^3\))
- \( H_f \), heat of fusion (J/kg)
- \( h\Delta T \), heat extraction flux (J/m\(^2\)/s). \( \Delta T \) is the difference between the droplet temperature at impact and the substrate temperature.
- \( C_p\Delta T' \), specific heat (J/kg). \( \Delta T' \) is the difference between the liquidus temperature and the droplet temperature. It may be positive (undercooling) or negative (superheat).
- \( f_s \), fraction solid just before impact (no units)

The case of an undercooled droplet reaching the substrate without nucleating is very interesting. Impact will trigger the recalescence. If the undercooling is large, the solidification front velocity can reach high numbers (up to 20 m/s). If this front velocity is much larger than the droplet speed, we can treat the problem as if the droplet had nucleated in flight and is semi-solid when arriving on the substrate. This means explicitly that it will solidify, impact and eventually deform. However, if the undercooling is small or the droplet speed very fast, the solidification front velocity will be smaller than the droplet velocity and the dendrite array will impact and deform or break faster than it is created, leading to multiple nucleation site. The
droplet will change shape and then solidify.

We have then to consider nine physical quantities, that can be described with three basic units: kg, m and s. The Buckingham-PI theorem [32] tells us that we can describe the problem with six independent dimensionless numbers. These numbers can be chosen arbitrarily but have to be independent.

The four dimensionless numbers were chosen as follow:

- fraction solid, \( f_s \)

- Reynolds number, \( \text{Re} \), given by equation (5-1), that compares the inertia to the viscous forces.

\[
\text{Re} = \frac{\rho D v}{\mu}
\]  

(5-1)

- Weber number, \( \text{We} \), given by equation (5-2), that compares the kinetic energy to the surface energy. The Weber number gives the relative spreading. A high Weber number means a high relative kinetic energy and thus a large spreading of the droplet.

\[
\text{We} = \frac{\rho D v^2}{\sigma}
\]  

(5-2)

- Freezing number, \( F \), given by equation (5-3), is a dimensionless time comparing the time to solidify and the time to impact. The heat extraction rate is determined by the contact area \( A_c \). \( F \) is of course related to the fraction liquid \((1-f_s)\) as well as the droplet temperature. In the case of semi-solid droplet, the specific heat related term is zero.

\[
F = \frac{v \rho D^2}{A_c h \Delta T} (H_f (1-f_s) - C_p (T_L - T))
\]  

(5-3)

- \( N_2 \), given by equation (5-4), that compares the kinetic energy to the heat extraction rate.

\[
N_2 = \frac{A_c h \Delta T}{\rho v^3} (1-f_s)
\]  

(5-4)
-N₃, given by equation (5-5), that compares the heat of fusion to the specific heat.

\[ N₃ = \frac{H_f}{C_p\Delta T} \quad (5-5) \]

The estimation of \( A_c \) is done using the solution of the non-freezing problem given by reference [B12]. In the case of a high Reynolds number (which is always the case for liquid metals, the relative spreading \( \xi \) (ratio of the disc diameter to the original droplet diameter) is given by:

\[ \xi = \sqrt{\frac{\text{We}}{3}} \quad (5-6) \]

Using this equation, and forgetting the numerical constant, we can write

\[ A_c = \xi^2 D^2 = \text{We} D^2 \quad (5-7) \]

and the freezing number \( F \) can be rewritten as:

\[ F = \frac{1}{\text{We}} \frac{v \rho}{h \Delta T} (H_f(1-f_s) - C_p(T_L - T)) \quad (5-8) \]

or writing explicitly the Weber number:

\[ F = \frac{\sigma}{D v h \Delta T} (H_f(1-f_s) - C_p(T_L - T)) \quad (5-9) \]

A comparison between equations (5-1) and (5-2) shows the Reynolds number and the Weber number are strongly correlated, hence it is not necessary to use both of them. The Weber number is more related to the topic of interest, so that it will be used. The number named N₂ is of limited interest since its physical meaning is not obvious, neither is N₃ which is a material property. In consequence, to describe the final shape of the impinged droplet, only the freezing number and the Weber number will be used in the following description.

This dimensionless approach is used to map the morphology of the impact as a function of the experimental conditions. Figure 5-1 shows a four quadrant prototype of this map, where the numbers on the axis are We and F and each impact category will be represented differently.
Impingement morphology

Experiments were performed, during which high speed imaging of the impingement of semi-solid droplets was accomplished. Figure 5-2 to 5-5 presents examples of the digital impingement images taken, respectively a spherical solidification of a 200 \( \mu \text{m} \) droplet, a rigid impact for a very small droplet, a spherical pancake for a 500 \( \mu \text{m} \) droplet, and another rigid impact for a 200 \( \mu \text{m} \) droplet. Each impact was classified depending on the deposition behavior. A summary of these categories is given in Figure 5-6. The transition from one category to another is difficult to define precisely.

For each impact event, F and We are computed. Physical constants such as \( \sigma, \rho, H_f, C_p \) or \( \mu \) are found in the literature, \( D \) and \( v \) are deduced from the picture analysis, \( h \) is estimated as \( 10^5 \text{ W/m}^2 \) [14]. The physical values used are presented in Appendix 1. The substrate temperature is measured and the droplet temperature and fraction solid are given by the model described in the model chapter. The dependence of thermo-physical properties was ignored. Viscosity is taken as that of the liquid at the melting point.

The substrate temperature was measured by a thermocouple touching the substrate 2 mm below the top surface. Enough time is allowed for the substrate temperature to be uniform. The substrate was in some cases heated.

The results are presented in Figure 5-7 (a). No results concerning droplets smaller than 100 \( \mu \text{m} \) were reported since it is difficult to observe their behavior (too low magnification and not enough light). Additional points are plotted in Figure 5-7 (b). The thin pancake results were taken from experimental results on two large copper [21] droplets and from experiment on lead [22]. Three points were obtained during a private communication with Chen-An Chen (Professor Chu's group at MIT) on Sn - 5\% \text{ wt Pb}. These last points are in the semi-solid pancake or pancake category. The points denoted by spray industry are computed using the typical processing parameters [12] encountered in the spray forming industry.

All impacts presenting the same behavior end up separated on the map. The spherical impacts are in the first quadrant as expected (high F and low We). When
F is even larger, the droplet does not freeze at all and bounces back fully liquid. The flat pancake type impacts are located in the small F and high We region. Rigid impact results from droplets almost solid at impact that undergo slight deformation and spreading before being totally frozen. Other semi-solid droplets observed in this study solidify in a form of thick pancake and present some oscillations before freezing. Some of the droplets were observed to burst, the fragment solidified as thick pancake.

Due to the limitation of the facility, it was not possible to explore the whole surface, especially the high We part or the very low F part.

**Fraction solid dependence and shape**

Figure 5-8 gives the typical shape evolution of a droplet impinging a substrate as a function of its fraction solid at impact. The Weber number is about 70 and the Freezing number ranges from 0.86 (fully liquid droplet) to 2.0 (90 % solid droplet). This figure was derived from observation of the final shape of Sn-Pb droplets produced under the direction of Chen-An Chen.

When the droplet is fully liquid, the deformation is that of a pancake with a relative spreading of 2 and an aspect ratio (thickness divided by diameter) of 40. As the fraction solid increases, the pancake increases in thickness and the relative spreading decreases. When the droplet is 70 % solid at impact, it keeps it spherical shape; for even higher fraction solid, it may bounce back.

As the fraction solid increases, the deformation of the droplet becomes more difficult. The mushy zone gets denser and stronger. Dendrites that are small and weak around 20 % solid are much stronger at 70 % and may not break at impact. The fluid flow is hindered by the presence of a large amount of solid material so that the droplet do not deform as easily. This could be explained by an increase of the apparent viscosity of the whole droplet.

It would be interesting to estimate the apparent overall viscosity of the droplet. Knowing the diameter and the speed we can deduce the kinetic energy and the deformation necessary to dissipate the kinetic energy, from that we could estimate the viscosity profile as a function of solid fraction.
Discussion

Analysis of the results

The map presented earlier can be divided into several different areas. Figure 5-9 gives a sketch of these different areas. The border between each of them are not yet precise and more points are necessary to define them.

The spherical droplet region is characterized by low We (less than 20), large F (more than 3.8) and a fully liquid droplet. Without solidification, the droplet would tend to become spherical (low We). As the heat extraction process is very slow (F large), the droplet has almost enough time to take its equilibrium shape and therefore solidifies in a spherical shape. Very close to that behavior is the case where the droplet does not have time to reach the spherical shape (little lower F, around 4.4) and solidifies as a spherical pancake shape. In one case, a huge droplet, fingers stretching from the base of the spherical pancake have been observed to lift up, retract, then remelt and finally retract into the droplet bulk. Another interesting case is when the F number is so large (around 16) that the droplet not only reaches its equilibrium shape but does not freeze at all and bounces back.

The thick pancake type represents the case where the heat extraction rate is fast enough to freeze the bottom of the droplet while the upper part still moves and oscillates due to the kinetic energy/surface energy competition. This occurs for a We number around 80 and F number around 2. The typical maximum spreading is around 2 and is little less in the final shape. Some of the droplets were semi-solid at impact. The burst behavior seemed to be related to the fraction solid: the droplets with a fraction solid less than 10% burst whereas those with a fraction solid larger than 10% stayed in one piece. This could mean that the fraction solid present at impact would prevent the liquid movements and therefore decrease the kinetic energy to a level low enough not to split the droplet. Unfortunately, the imprecision on the fraction solid is such that this interpretation may be wrong. Bursting is of course facilitated by a high temperature (lower viscosity) droplet and high kinetic energy at impact (Daimler Benz source).
The bilaminate type is characterized by a large We number (around 300). However as the F number is small (around 0.6), solidification is very fast and the droplet does not have time to spread out. No solid is present before the impact. The base of the droplet freezes very fast. Liquid floats on the top and solidifies at a slower rate controlled by the interface heat extraction rate. The upper part of the liquid is allowed to shrink whereas the lower part is constrained by the already solid metal and has a higher viscosity. This leads to the creation of bending stresses strong enough to lift the edges up.

Rigid pancake is the last type of deposition observed with this set-up. The droplet solidifies presenting few deformation during the deposition and shape oscillation as in the case of the thick pancake. In this case, the freezing number is small (F number about 1), the We number is small (around 10) and the fraction solid large (more than 50%). The low F results from the fact that the droplet is partly solid and less heat needs to be extracted. The droplets do no spread and the final shape is a thick pancake. A more detailed discussion is given in the faction solid part.

The thin pancake is another deposition class that has been reported in the literature. The We number is quite big, in the order of 5, allowing for a large relative spreading and solidification is really fast (F number around 0.08); the liquid freezes as soon as it touches the substrate. The remaining liquid flows out due to the conservation of momentum which creates a radial flux. This outward flow freezes as soon as it contacts exposed substrate. This leads to the formation of large pancakes.

Figure 5-10 summarizes all these descriptions, adding the estimated solid part (darker parts) to the Figure 5-6. One can observe that a spherical pancake become a pancake with oscillation by increasing the We number. A bilaminate type impact becomes a flat pancake type impact if the F number is smaller, i.e. if the heat is extracted much faster.

The map seems to be coherent and promise to be very useful for the process design engineer.
Utilization by the industry

This deposition topology can be useful for several engineering design problems. Porosity, grain size and oxidation level are among the problems that are to be solved to promote spray forming to an economically efficient process. Die-casting designs are also concerned with this droplet deposition problem in the sense that at high injection speed, the metal stream decomposes into discrete droplets.

Porosity has two origins. It either results from the trapping of gas between the impinged droplets or from formation of very small voids inside the grains due to shrinkage known as gas and shrinkage porosity, respectively as shown on Figure 5-11. Shrinkage porosity is related to metal contraction and grain boundary strength and has no direct relationship with droplet shape. This is of no interest for this study. To reduce the gas porosity, it is convenient to use the fact that a liquid metal will fill up the holes, thus a higher F number, that would allow liquid to flow before freezing, could decrease the porosity. This was confirmed by Alcoa that observed an increase of porosity when the heat transfer coefficient was increased (substrate conductivity was increased, for example using Steel instead of Ceramic type substrates).

This approach is, however, dependent on the size of the porosity to be eliminated. To reach our conclusion in the former paragraph, we assume the liquid would flow in the holes which is true only for large surface cavities. Reference [33] concludes, from a mathematical analysis and some experimental results, that increasing the speed would decrease the porosity and that the porosity is minimum in the center and maximum in the outer region of the splat. Increasing the speed leads to an increase in the We number and decrease the F number leading to a faster solidification. However, increasing the speed means forcing the contact between the droplet and the substrate creating more solid/liquid interface where the surface curvature tends to prevent such a contact. This explains why porosity is smaller in the center: the gas is pushed away where the liquid has enough inertia to override the curvature effects. Our analysis does not take this curvature effects into account. It is, however, possible to decrease both large and small porosity by decreasing the heat transfer coefficient and increasing the velocity while maintaining constant F number.
Reference [21] proposes a qualitative model to explain the commonly observed equiaxed structure. At impact, the solid dendrite arrays break in small pieces that promote growth and lead to the equiaxed microstructure after coarsening. To conclude, grain size is then a function of fraction solid, particle diameter, number of nucleation sites present in the melt and coarsening time. The substrate temperature and the production rate gives the coarsening effect, knowing the target grain size we can estimate the droplet diameter and define the others process parameters to access in the correct domain.

Oxidation is also a problem in the case of mass production units; the ambient gas cannot always be inert. Oxidation level is proportional to the surface exposed to the gas. A small droplet is therefore, in proportion, more prone to oxidation than a large droplet since it has a higher area/volume ratio. In industrial processes with very high velocities, the flight time is smaller than the deposition time so that the deposit shape has a huge influence on the oxidation level. It has been observed that bursting is responsible in a large extent for the oxidation level because it creates several very small droplets (source: Daimler Benz). Therefore speed has to be adjusted so that the flight time is short but also so that it does not provoke bursting.

From the established map, one may try to predict what happens in industry. The Weber number is larger than most of what we observe, meaning that the droplet will spread. At the beginning of the process, when the substrate is still relatively cold, the F number is of the same order as that of the bilaminate, meaning freezing is fast but not instantaneous. When the substrate heats up, the F number increases to the level of the pancake with oscillation. A reasonable prediction would then be that at the beginning, the droplets would form thin pancakes with eventually some porosity and after warming set-up, one would observe slightly thicker pancakes and less porosity. Due to the higher temperature some coarsening would occur and grains would be bigger than at the beginning of the process. Some bursting may also happen if the liquid part is too superheated (lower viscosity and no fraction solid) leading to a lot of oxide trapped.
Conclusion

The major interest of this map is that it is a universal one, in the sense that it is expected be valid for any kind of liquid metal solidifying during deposition onto a cold substrate. If more points could be added, it would become a useful tool to predict the porosity and the shape of the grain, and their variation through the process. It would be of interest to understand in detail the bursting behavior. Gathering all the experimental results obtained in the laboratories or in the industry could perhaps enable to fill up the whole surface. The map suggests new areas of research to develop practical solution to problems such as selecting microstructure, improving process design and controlling key operating parameters for spray forming and die-casting.

Future work on this map, would widen the window of parameters investigated by increasing the speed of the droplet (for example by having them falling in a moving gas), by adding the capability to offer cryogenic cooling of the substrate to increase heat extraction rate, and by improving the observational technique to allow work on 20 µm or less droplets. Another area of research would be to improve the viscosity model of liquid flow in the broken mushy zone.
Figure 5-1 : Sketch of the impingement topology
Figure 5-2: Impingement sequence of a 100 μm droplet, impact speed was 4 m/s. The time between each frame is 75 μs.
Figure 5-3: Impingement sequence of a 240 μm droplet, impact speed was 4.7 m/s. The time between each frame is 75 μs.
Figure 5-4: Impingement sequence of a 550 μm droplet, impact speed was 2.3 m/s. The time between each frame is 110 μs.
Figure 5-5: Impingement sequence of a 210 μm droplet, impact speed was 4.2 m/s. The time between each frame is 37 μs. The last frame has been taken 370 μs after the previous one.
Figure 5-6: Impingement classification

- Bounce back
  - droplet fully solid
  - droplet fully liquid

- Thin pancake
  - Solid

- Oscillation
  - Thick pancake
  - Or
  - Burst
  - Solid

- Spherical pancake
  - Solid

- Spherical
  - Solid

- Bilaminate
  - Solid

- Or
  - droplet less than 50% solid
  - droplet more than 50% solid

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**Figure 5-7**: Impingement topology. (a) All points were obtained using our apparatus, (b) some points on copper, tin and lead have been added. Points denoted industry represents the typical spraying conditions in aluminum industry.
Figure 5-8: Influence of fraction solid on shape

Fraction solid = 0
Aspect Ratio = 40

Fraction solid = 0.40
Aspect Ratio = 7

Fraction solid = 0.8
Aspect Ratio = 1.1
Figure 5-9: Schematic impingement topology
Figure 5-10: Impingement classification

- **Droplet fully solid**
- **Droplet fully liquid**
- **Bounce back**
- **Thin pancake**
- **Solid pancake**
  - Oscillation
  - Thick pancake
    - Or
    - Burst
  - Solid
- **Spherical pancake**
- **Spherical**
- **Bilaminate**
- **Solid**
- **Rigid**
  - No oscillation
  - Or
  - Rigid
    - Droplet less than 50% solid
    - Droplet more than 50% solid
Figure 5-11: Porosity in deposited material
Conclusion and suggestions for future work

A method to determine undercooling in spray forming from microstructure analysis has been developed and appears to be accurate. Further work on the undercooling behavior of droplets would involve defining quantitatively the influence of cooling rate, superheat temperature and gas environment on the maximum undercooling reached.

A model describing the solidification behavior in apparatus employed is presented. Further improvement is possible by refining the empirical description of the gas temperature and by including thermo-dependent physical characteristics (gas viscosity, conductivity...).

An impingement map is proposed to describe the deposition behavior of droplets, depending on the process parameters. This map may find large practical interest in the spray forming and die casting industry. Testing of other metal alloys, increasing the droplet speed and improving the droplet formation are among the options available to continue the work on the impingement behavior topology. Other axes of research could also be to evaluate the viscosity behavior of a semi-solid droplet as a function of the solid fraction by estimating the amount of deformation necessary to dissipate kinetic energy during impact. Computer modeling could also be developed to explain and describe the observed domains.

To conclude, this work proposes a way of estimating the undercooling of liquid metal droplets and a new qualitative approach of the description of the impinging behavior of aluminum droplets. Even though a first approximation in many respects, the coherency observed all along this study encourages further work in this direction.
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Appendix 1 : Physical data used

This appendix lists all the physical constants used in the models presented in this work. In the case of thermo-dependent data, the value presented is an average on the temperature range of interest.

**Aluminum 4.5 % Copper**

<table>
<thead>
<tr>
<th>Physical constant</th>
<th>Value</th>
<th>Unit</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific mass</td>
<td>2400</td>
<td>kg/m³</td>
<td></td>
</tr>
<tr>
<td>Specific heat</td>
<td>880</td>
<td>J/kg/K</td>
<td>Obtained using the lever rule</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>390.5 x 10³</td>
<td>J/kg</td>
<td>idem</td>
</tr>
<tr>
<td>Liquidus Temperature</td>
<td>647</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Eutectic temperature</td>
<td>548</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>partition coefficient, k</td>
<td>0.171</td>
<td>no unit</td>
<td></td>
</tr>
<tr>
<td>m (- liquidus slope)</td>
<td>3.4</td>
<td>K/wt%</td>
<td></td>
</tr>
<tr>
<td>Surface tension</td>
<td>0.86</td>
<td>J/m²</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>1.3 x 10⁻³</td>
<td>Pa.s</td>
<td></td>
</tr>
</tbody>
</table>

The phase diagram of the aluminum copper system is presented next.
Aluminum 4.3% Iron

<table>
<thead>
<tr>
<th>Physical constant</th>
<th>Value</th>
<th>Unit</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific mass</td>
<td>2560</td>
<td>kg/m³</td>
<td></td>
</tr>
<tr>
<td>Specific heat</td>
<td>932</td>
<td>J/kg/K</td>
<td>Obtained using the lever rule</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>391.6 x 10³</td>
<td>J/kg</td>
<td>idem</td>
</tr>
<tr>
<td>Liquidus Temperature</td>
<td>757</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Eutectic temperature</td>
<td>655</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>m (- liquidus slope)</td>
<td>40.8</td>
<td>K/wt%</td>
<td></td>
</tr>
</tbody>
</table>

The phase diagram of the aluminum copper system is presented next.
Other metals related to the impingement study

<table>
<thead>
<tr>
<th>Physical constant</th>
<th>Unit</th>
<th>Tin</th>
<th>Lead</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific mass</td>
<td>kg/m³</td>
<td>7000</td>
<td>11340</td>
<td>8000</td>
</tr>
<tr>
<td>Specific heat</td>
<td>J/kg/K</td>
<td>240</td>
<td>142</td>
<td>494</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>J/kg</td>
<td>58.9 x 10³</td>
<td>24.6 x 10³</td>
<td>205 x 10³</td>
</tr>
<tr>
<td>Liquidus Temperature</td>
<td>°C</td>
<td>232</td>
<td>327</td>
<td>1084</td>
</tr>
<tr>
<td>Surface tension</td>
<td>J/m²</td>
<td>0.55</td>
<td>0.45</td>
<td>1.285</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Pa.s</td>
<td>5.38 x 10⁻⁴</td>
<td>2.5 x 10⁻³</td>
<td>4.3 x 10⁻³</td>
</tr>
</tbody>
</table>

Gas properties

<table>
<thead>
<tr>
<th>Physical constant</th>
<th>Unit</th>
<th>helium-hydrogen 4%</th>
<th>argon - hydrogen 4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific mass</td>
<td>kg/m³</td>
<td>1.56 x 10⁻³</td>
<td>1.65 x 10⁻³</td>
</tr>
<tr>
<td>Viscosity</td>
<td>Pa.s</td>
<td>36 x 10⁻⁶</td>
<td>40 x 10⁻⁶</td>
</tr>
<tr>
<td>Conductivity</td>
<td>W/m/K</td>
<td>0.270</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The temperature profile in the set-up was approximated for Helium by $T = 570 - 4500 \times x$ and for Argon by $T = 400 - 3200 \times x$, where $x$ is the flight distance in meter.
Appendix 2 : Computer model

The program, whose listing is presented next, reads the gas type, the metal type, the speed calibration parameters, the spray temperature and the flight distance from a file named data. It outputs several files: output contains the cooling rate for different diameters, temp contains the temperature profile of the droplet as a function of the distance from the nozzle for different diameters and fsfd gives the temperature, speed and fraction solid after the precise flight distance entered as a parameter in the data file for various diameters.

Listing of the program:

/* Spraying modelisation
by M.R. September 95
integration of the heat equation
analytical solution for the speed */

#include <stdio.h>
#include <stdlib.h>
#include <math.h>

main()
{
    double g;

    /* gaz variable */
    double rog, vig, kg, pr;

    /* liquid metal data*/
    double rol, cpl, tm, hf;
    double kscheil, ml, tmal;

    /* ... other code ... */
double cs,csr,clr,tr,c0,fs,fsr,fsunder,cse,teutec,ce,cep,cl;
int metal;

/* variables */
double vi, vg, ti,ti0,a,b,d;
double t,v,xi,temp[100000], x[100000], fsarray[100000];
int i,ii,iii,gaz,niter,indic3;
int recalesc, solidif,fdcheck;
double fd;
double h,k,kp,re,tamb,dt;
double dtemp;
double j;

double cr,tn,t2,t1,t3,das,capa,x2,x3;
int i2,i1,i3; /* same as t2 in lab book page 131*/
int inc;

FILE *tuko,*tuki,*data,*tempe;

tuki=fopen("output","w");
data=fopen("data","r");
tempe=fopen("temp","w");
tuko=fopen("fsfd","w"); /* gives the fs and T for a given fd */

if ((tuki== NULL) || (data==NULL) || (temp==NULL))
{
    printf("Sorry, something is wrong with the files.\n\n");
    exit(0);
}

/* initialization-----------------*/

niter =100000; /* should be less than the size of the array !!!*/
fscanf(data,"%d",&gaz);
fscanf(data,"%d",&metal);
pr = 0.7;
if (gaz==0)
{ /*helium*/
a=570;
b=4500;
rog=1.56e-4;
vig=36e-6;
kg=.270;
fprintf(tuki,"gas : helium + H2\n");
}
else
{ /*argon*/
a=400;
b=3200;
rog=1.65e-3;
vig=40e-6;
kg=0.06;
fprintf(tuki,"gas : argon + H2\n");
}

if (metal==0)
{
fprintf(tuki,"metal : Al/ Cu 4.5 % \n");
rol = 2400.0 ;
cpl = 880 ;
tm = 647 ;
hf = 390.5e3;
c0 = 4.5;
ml = 3.4;
tmal = tm + ml * c0;
kscheil = 0.171;
teutec = 548 ;
else
{
    fprintf(tuki,"metal : Al/ Iron 4.3 \%\n");
    rol = 2560 ;
    cpl = 932.14;
    tm = 757 ;
    hf = 391.6e3;
    c0 = 4.3;
    ml = 40.8;
    tmal = 662;
    kscheil = 0;
    teutec = 655;
    ce = 1.8;
    cep = 36.5;
}

 g = 9.81 ;

 fscanf(data,"%lf %lf %lf", &vi, &vg, &ti0);
/* ti is not really used right now */
fprintf(tuki,"Init vel : %lf\nGas vel: %lf\n", vi, vg);

/* flight distance to get the temp and fs*/
 fscanf(data,"%lf", &fd);

/* Loop on Temperature*/

 for (ti=ti0 ; ti <= ti0; ti+=50)
{
    fprintf(tuki,\nInitial Temperature : %lf\n", ti);
    fprintf(tuki," Diameter Cooling D.A.S Time Distance\n");
    fprintf(tuki," (um) Rate (um) (ms) (mm)\n");
/* Loop on diameter */
for (j=3 ; j<=5 ; j+=.25)
{
    d=pow(10,-j);
/* nucleation temperature from experience*/
    if (metal==0) /* al copper*/
        tn=tm-pow(10,(3.86-1.75/2.30258*log(d*1e6)));
    else
        tn =tm-(328-2.5*d*1e6);
    if (tn>tm) tn=tm-0.01;
    /* log gives In !!!*/

    fsr = (tm-tn)*cpl/hf;
    if (kscheil ==0 )
        { /* hyper eutec*/
            clr = (c0-cep*fsr)/(1-fsr);
            if (clr<ce) clr=ce;
            tr = teutec + ml*(clr - ce);
        }
    else
        {
            csr = kscheil*c0/(1-((1-kscheil)*0));/* new scale */*
            tr = tmal - ml / kscheil * csr;
        }
    temp[0]=ti;
    v=vi;
    x[0]=0;
    t=0;
    recalesc=0;
    solidif=0;
    indic3=0;
    i2=0;
    i3=niter;
fdcheck=0;

/* Loop on time*/

for(i=1; i<niter ; i++)
{
    dt=0.000005; /* increment in second */
    t=dt*i;

    re=rog * d * abs (v-vg)/vig;
    h=kg/d*(2+0.6*(pow(re,.5)*(pow(pr,0.333) ) ));
    k=6*h/rol/cpl/d;
    kp=18*vig/rol/d/d;

    v=(vg+g/kp)+exp(-kp*t)*(vi-vg-g/kp);
    x[i]=(vg+g/kp)*t+1/kp*(vi-vg-g/kp)*(1-exp(-kp*t));

    tamb=a-b*x[i];
    if (tamb<70) tamb=70;

    dtemp = k*dt*(temp[i-1]-tamb);

    /* solidification treatment*/

    if (recalesc==0) /* still undercooling*/
    {
        if (((temp[i-1]-dtemp) <=tn)
        { /* at recalssence*/
            capa = fsr*hf + cpl*(tn-(temp[i-1]-dtemp));
            temp[i]=tr;
            temp[i-1]=tn;
            fsarray[i]=fsr;
            if (fsarray[i]<0) fsarray[i]=0;
            i1=i;
    
    Page 100
t1=t;
recalesc=1; /*!< recalescence */
}
else
{
  temp[i]=temp[i-1]-dtemp;
  fsarray[i]=0;
}
}
else
/* recalescence already occured */
if (solidif==0)
{
  /* solid non completed */
  capa +=dtemp*cpl;
  if (capa < hf)
  {
    /* new : use scheil equation */
    fs = capa/hf;
    fsarray[i]=fs;
    fsunder = (fs-fsr)/(1-fsr);
    if (kscheil==0)
    { /* hypereutectic case */
      cl = (c0-cep)*((1-fsr)/(1-fs)+cep;
      temp [i] = teutec + ml * (cl-ce);
    }
    else
    { /* hypoeutectic case */
      cs = kscheil*c0*pow((1-fsunder),(kscheil-1));
      temp [i] = tmal - ml / kscheil * cs;
    }
  
  if (temp [i]<= teutec) temp[i] = teutec; /*!< eutectic */
else
    { /* end of solidification */
    i2=i;
    t2=t;
    solidif=1;
    fsarray[i]=1;
    temp[i]= teutec - (capa-hf)/cpl;
    }
}
else
    { /* solification finished*/
    temp[i]=temp[i-1]-dtemp;
    fsarray[i]=1;
    /* I assume Cp solid = Cp liquid !!! */
    if (indic3==0)
        { /* find a point such that...*/
        if (temp[i]<200)
            { 
            i3=i;
            t3=t;
            indic3=1;
            }
        }
    }
}

/* output the solution in t (temp, fs) of x[i]=fd in file */
if (fdcheck==0)
    {
    if (fd <=x[i])
        {
        fdcheck=1;
        fprintf(tuko,"%lf %lf %lf %lf %lf %lf %lf

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/* cooling rates*/

if (i2==0)
    {cr=(temp[0]-temp[niter])/niter/dt;
     i2=niter-1;
    } /* in this case I have a bad approximation*/
else
    {
     cr = (temp[0]-temp[i2])/(i2*dt);
    }
das = 50 * pow (cr,-.33);
    fprintf(tuki," %5.0lf %8.0lf %5.2lf %6.1lf %6.2lf %6.2lf

%6.2lf\n",d*1e6,cr,das,t2*1000,x2*1000,t1*1000,t3*1000);

/* Output of temperature */

    fprintf (tempe," %lf\n",d);

/* begining */
    xi = i1*1.0/8;
    inc = (int) xi;
    if (inc <1) inc =1;
    for (ii=0 ; ii < i1 ; ii+=inc)
    {
     fprintf(tempe,"%lf %lf %lf\n",x[ii],temp[ii],fsarray[ii]);
    }

/* solidification */
    xi = (i2-i1)*1.0/10;
inc = (int) xi;
if (inc < 1 ) inc=1;
for (ii=i1 ; ii <= i2 ; ii+=inc)
{
    fprintf(tempe,"%lf %lf %lf\n",x[ii],temp[ii],fsarray[ii]);
}

/* end */
xi = (i3-i2)*1.0/5;
inc = (int) xi;
if (inc<1) inc = 1;
for (ii=i2 ; ii < i3 ; ii+=inc)
{
    fprintf(tempe,"%lf %lf %lf\n",x[ii],temp[ii],fsarray[ii]);
}

} /* end of loop on diameter */
} /* end of loop on temperature */
fclose (data);
fclose (tuki);
fclose (tempe);

} /*end*/
Biographical note

The author was born in Bourges, France on October 6, 1972. He graduated from the Lycee Blaise Pascal (Clermont-Ferrand, France) in June 1989 and received the Baccalaureat C with honors (Tres Bien) the same month. During 1989, he also won the first prize in the chemistry contest "Olympiades de la Chimie, Region Auvergne". He graduated from l'Ecole Centrale (Paris) in June 1994, with a major in Ocean Engineering and after internships in Michelin, Dumez (civil engineering in Argentina) and Elf Aquitaine (study of the propagation of cracks in off-shore platform legs). He entered graduate school at the Massachusetts Institute of technology in September, 1995.