Mono-Size Droplet Production by the Uniform-Droplet Spray Process at High Temperature – with Applications to ASTM F75 and Silicon

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ABSTRACT

The use of the uniform-droplet spray (UDS) process, a controlled capillary jet break-up of molten metal stream at a precise frequency, was extended for the production of mono-sized droplets of high melting-point materials, with particular interest in developing ASTM F75 droplets suitable for the production of bio-implants with porous mating surfaces for effective osseointegration and silicon droplets applicable to efficient photovoltaic energy harvesting.

To facilitate stable UDS spraying of high melting-point materials, charging of UDS droplets at high temperature, required to prevent in-flight merging of droplets, was first investigated through literature survey, theoretical modeling and experiments with copper droplets. Nitrogen gas, a non-attaching gas having a high breakdown temperature, has been successfully used as the chamber gas in which to charge copper droplets effectively. The charging of the droplets, experimentally confirmed by droplet deposition experiments, was in qualitative agreement with model predictions. The model, however, somewhat overestimates the spray width, indicating that ionization of the gas molecules decreases the charge induced on the droplets at high temperatures. Effective droplet charging, nonetheless, can be achieved at temperatures < 1200 °C.

The ASTM F75 and silicon droplets were characterized and their solidification behavior was investigated using theoretical models. A nucleation kinetics model, with the aid of experimentally obtained reference data, was used to construct continuous cooling transformation (CCT) curves for the heterogeneous nucleation of traveling ASTM F75 and silicon droplets. UDS
conditions for the formation of microcrystalline structures in solidified droplets were investigated with the aid of a dendrite fragmentation model and experimentally confirmed. The amount of droplet supercooling, required in the dendrite fragmentation model, was determined on the CCT curves for droplet nucleation, while the dendrite tip radius and the plateau duration, also required in the dendrite fragmentation model, were calculated with a free dendritic growth model and a droplet in-flight solidification model developed in previous studies.

Helium gas-cooled 640 μm UDS droplets of ASTM F75 alloy, which underwent a supercooling of 92 K, solidified to have a well developed dendritic microstructure, whereas smaller 460 μm and 300 μm droplets, cooled in helium gas for supercoolings of 179 K and 377K, respectively, solidified into a fine equiaxed microcrystalline structure, all in line with prediction by the fragmentation model. 550 μm silicon UDS droplets, solidified in helium gas, were characterized by well-developed <110> dendrites showing no indication of fragmentation, which was also predicted by the fragmentation model at the supercooling of 81 K that the 550 μm droplets underwent. Smaller 390 μm silicon UDS droplets cooled in helium gas, which underwent a supercooling of 172 K, were characterized by a finer microcrystalline structure indicative of fragmented orthogonal <100> dendrites, which was also predicted by the fragmentation model. However, in contrast to ASTM F75, marginal conditions for the fragmentation in silicon UDS droplets led to somewhat incomplete fragmentation of the <100> dendrites.
The overall consistency between model predictions and metallographic observations is excellent, indicating that the developed procedure is useful in correlating the microstructure with the process parameters in droplet-based manufacturing processes.
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1. Introduction

1.1 Background

Among different rapid solidification processes, processing through the solidification of molten alloy droplets constitutes an important route to materials processing and manufacturing, as exemplified by water and gas atomization and various forms of spray forming [1-4]. However, almost all of these processes use liquid metal droplets of random sizes, thus making these processes difficult to analyze.

The uniform-droplet spray (UDS) process [5] is a droplet-based manufacturing process where mono-sized or uniform droplets are generated by the controlled breakup of a laminar jet of molten metal ejected through an orifice while applying a regulated perturbation [6]. Such mono-sized droplets may be solidified in a highly controlled manner, either during their flight in a gas or upon deposition onto a substrate, which can be done with droplets in any thermal state. Since the droplets in UDS all have nearly identical size and thermal history, the solidification paths of the droplets during flight can be calculated from the process parameters, such as melt temperature, break-up frequency, orifice diameter and melt ejection pressure [6]. More recently, DiVenuti [7] developed a model that simulates the solidification path of UDS droplets that undergo high supercooling and applied it to Sn-5mass% Pb droplets.
1. Introduction

**High temperature UDS process**

UDS processing has been applied for producing mono-sized droplets of various materials such as tin and tin-lead alloys, aluminum alloys, copper and copper alloys, magnesium alloys and iron-boron alloys, etc. [8-18]. The maximum processing temperature is thus presently limited for the process at 1500 K. To make the process adaptable for a wide variety of materials of higher melting point it needs to be suitably tailored. In this context the production of ASTM F75 and silicon droplets are examined. ASTM F75 is a Co-28mass%Cr-5mass%Mo alloy which has a melting point (liquidus temperature) of 1682 K. The alloy droplets are partially sintered to form a mating surface for osseointegration in implants [103]. Silicon, on the other hand, is an elemental semiconductor which has a melting point of 1687 K. Silicon droplets are used in solar panels and photovoltaic cells to increase the effective surface area for light absorption [124]. Effective application of UDS to these materials would illustrate a much broadened applicability of the UDS process.

The droplets may collide in-flight, which may cause merging in molten or mushy state. This reduces the yield of mono-sized droplets in an experiment. An effective method to prevent the in-flight merging of droplets is to electrically charge the droplets in-flight immediately after they are formed [6]. The charged liquid metal droplets repel each other and thus prevent merging. Charging of UDS tin and tin-lead alloy droplets have been done to prevent in-flight merging of the droplets and hence increase yield of droplets produced [6, 55]. However, at high temperatures the electrical properties of the gas also come into play which renders the process highly unreliable and often even unpractical. Hence it is imperative
that the charging of droplets at high temperatures be examined which would be useful in determining methods to prevent merging for high temperature UDS processes.

**Nucleation studies of UDS droplets**

Moreover, the UDS process is also an effective process to further the understanding of solidification behavior in droplet-based manufacturing processes. It is established that small droplets when cooled rapidly can be highly supercooled in comparison to bulk metallic materials [19-22]. Thus an important key to successful application of droplet based solidification processing is the control of the supercooling that the droplets undergo. This is because the amount of supercooling determines much of the solidification path, particularly the extent of rapid solidification during recalescence. The amount of droplet supercooling depends on the kinetics of nucleation, which in turn depends on the cooling conditions and the density, distribution and potency of the heterogeneous nucleants present in the melt [23-26].

The UDS process has been applied to investigate on the effects of supercooling on the nucleation kinetics of travelling mono-sized droplets. By incorporating a loss-compensated calorimetric technique into UDS experimental procedure, Tuffile et al. [30], Dong et al. [31] and Fukuda et al. [32] were able to determine the supercooling of 155 μm and 185 μm Sn-5mass%Pb uniform droplets. Dong et al. [31] developed a model to predict the nucleation kinetics of travelling mono-sized droplets. This model was successful in predicting the nucleation temperature of droplets that are cooling under known schedule,
However, failed to incorporate the gradual oxidation of the droplets which catalyses surface nucleation. The model was later modified by Wu and Ando [33] to include the effects of gradual surface oxidation on the nucleation kinetics. The model also addressed the internal nucleation in droplets. This nucleation model has been modified by Li, Y. et al. [34] and later by Li, S. et al. [35] for the construction of continuous cooling transformation curves for Sn-5mass%Pb travelling droplets. Bialiauskaya et al. [16, 36] have also effectively used the Wu and Ando model to construct continuous cooling transformation curves for Fe-17mass%B travelling mono-sized droplets by a rotating quencher method, which experimentally determines the nucleation temperature. In this method, the travelling droplets are quenched at various flight distances which determine the nucleation temperature from the morphology of the splats and with the aid of the in-flight simulation model [7]. The method, however, aptly gives the range of nucleation temperature where nucleation probably occurs. The nucleation kinetics model and the rotating quencher method are thus useful in effectively determining the supercooling of the travelling UDS droplets. It is thus motivating to apply them to aid in qualitatively predicting the microstructure in supercooled droplets of other alloys as well.

**Correlation of microstructure to process parameters**

Once a droplet nucleates, subsequent solidification path consists of initial recalescence and post-recalescence plateau, followed by the solid cooling. The recalescence is characterized by the rapid growth of dendrites. The post-recalescence stage is characterized by the rate of solidification limited by the rate of heat removal at a nearly constant temperature just below the liquidus

However, droplets that undergo high supercooling and subsequent rapid solidification may not always exhibit a dendritic microstructure. Instead, highly refined microcrystalline structures are often observed. Formation of such microcrystalline microstructure at high supercoolings was first reported by Walker for Ni [37]. He related the abrupt decrease in grain size at a supercooling of 285 K to the sudden change in pressure in the melt. Recent investigations, however, revealed that the grain refinement is due to the fragmentation of dendrites due to instability in the dendrite trunk. Since Walker, fragmentation of dendrites has also been reported for a number of other alloys. Herlach et al. [38] and Schwarz et al. [39] have reported fragmentation for Ni - 30 at% Cu alloy and have explained the fragmentation behavior by Karma’s model [40]. Wei and Herlach [41] have also reported and similarly explained the fragmentation of supercooled Co- 10 mass% Sb and Co- 60.5 mass% Sb alloys. Ruvalcaba et al. [42] reported in-situ fragmentation of dendrites caused by solute supersaturation during directional solidification of Al- 20mass% Cu alloy. Liu et al. [43] have reported fragmentation of dendrites as the mechanism for grain refinement at high supercooling for Fe- 30 at. % Co alloy. Similarly, Nagashio et al. [44] and Lau et al. [45] have also reported the fragmentation of faceted dendrites in semiconductor based materials such as silicon and germanium. Thus for materials which are highly supercooled, such as small droplets produced by the UDS process, the qualitative prediction of the microstructure would involve predicting the fragmentation of the dendrites.
Although the peculiar phenomenon of unusually highly grain refinement at high supercoolings is a well established fact, there is, however, no consensus on the mechanism and theory to support it. There are a number of theories that attempt to explain this behavior of highly supercooled materials [46-51]. Although, most of these theories are valued for their theoretical soundness, their applicability to most cases of observed dendrite fragmentation is limited. Moreover, they fail to explain the occurrence of grain refinement at both high and low supercoolings as observed by Herlach \textit{et al.} [38], Schwarz \textit{et al.} [39] and Galenko \textit{et al.} [52]. This is more widely and well explained by the fragmentation model by Karma [40]. Thus the fragmentation model by Karma [40] may be used to predict the microstructure in droplet-based manufacturing.

The uniform-droplet spray (UDS) process, in particular is suitable for the production of droplets which may be used to verify the predictions made by the fragmentation model. This is because the process produces mono-sized droplets of nearly identical thermal history and hence, supercooling. The droplet motion has been successfully simulated by the in-flight solidification model for travelling droplets, is well documented and shown to provide good agreement with observed microstructures by many [6-18]. Moreover, the process parameters in the UDS process are decoupled which allows for easy investigation of process parameters on the resulting solidification behavior and microstructure. ASTM F75, a Co-28mass\%Cr-5mass\%Mo alloy, and pure silicon are used in this investigation to show the applicability of the process to high temperature materials.
1. Introduction

Thus, this work aims at producing mono-sized droplets of high temperature materials, such as ASTM F75 and silicon, and characterizing their structures based on the process parameters. It also aims at qualitatively predicting droplet microstructures using the Wu and Ando nucleation kinetics model [53] along with the in-flight solidification model [7] and the fragmentation model by Karma [40].

1.2 Research Goals and Approach

The overall objective of the present research is to produce droplets of high melting point materials in excess of 1500 K, and characterize and relate the process parameters of the droplet-based manufacturing to the structure observed for small droplets with high supercoolings. This involves upgrading the existing experimental set-up suitably for operating at high temperatures and investigating on the charging of droplets at high temperatures to prevent in-flight droplet merging. The emphasis is to illustrate the effects of high supercooling on droplet solidification and hence, on its microstructure, and to further be able to predict the microstructure in a droplet-based manufacturing process with given process parameters.

To achieve the above goals, the following steps are to be adopted:

- Improve the UDS experimental set-up to make it more suitable for processing of high temperature materials.
- Investigate the charging of droplets at high temperatures and verify the experimental results by modeling the behavior of the charged droplets.
1. Introduction

- Investigate establish and optimize the process parameters to for production of UDS droplets of ASTM F75 alloy and silicon.
- Apply the in-flight solidification model to calculate the droplet thermal state and the Wu-Ando model to determine the nucleation kinetics of droplets.
- Apply appropriate model to predict the microstructure for highly supercooled droplets.
- Compare and correlate the calculated results with that obtained from the microstructures of both the materials.

1.3 Overview of Subsequent Chapters

The aim of this section is to provide an overall bird’s eye view of this doctoral thesis. This doctoral thesis is based on the purpose of extending the present UDS process for high temperature materials and utilizing it to produce mono-size droplets. For this purpose droplets of ASTM F75 and silicon are investigated. ASTM F75, a cobalt-chromium-molybdenum biocompatible alloy, is produced as droplets for use in implants as a porous mating surface for the bone tissue to grow into. Silicon droplets are used to manufacture photovoltaic cells for energy harvesting. The introduction outlines the present UDS process and its temperature limitations. The UDS process is made adaptable to high temperatures by incorporating some essential set-up modifications which are provided in chapter 2. It also illustrates the experimental procedures that were used for performing the high temperature UDS experiments with ASTM F75 and silicon.
1. Introduction

The solidification behavior of the mono-sized droplets is computed through applications of the existing models. The existing models that are likely to be used for the computation of the droplet solidification behavior are discussed in detail in chapter 3. This includes the in-flight solidification model developed by DiVenuti [7], the Wu and Ando nucleation kinetics model [33] and Karma’s fragmentation model [40]. The conditions under which the models may be applied in this present work, to both ASTM F75 and silicon, are also presented in this chapter.

One of the goals of the present work is to extend the study of the charging of UDS droplets, as a method to prevent in-flight merging of droplets at high temperatures. Chapter 4 deals with the literature survey done for charging of UDS droplets in various inert atmospheres at high temperatures. The experimental set-up and the experimental procedures for charging are investigated and this is effectively used to charge copper UDS droplets. The effects of charging on the droplet motion are also studied experimentally. The motion of the charged droplets are modeled and compared with the experimental results.

The high temperature UDS process, with the said modifications, is utilized to produce mono-sized droplets of ASTM F75 and silicon. This is discussed in chapters 5 and 6, which deal with the optimization of the process parameters for production of uniform droplets of ASTM F75 and silicon droplets, respectively. Further the application of the models, to both ASTM F75 and silicon, to evaluate their microstructures are also discussed here.
The conclusions of this work are presented in chapter 7. This chapter provides the main conclusions drawn and the central contributions obtained from this research. All the necessary data, formulation, or information related to the calculations presented in this thesis are provided in the appendices.
2. Experimental Procedures

The uniform-droplet spray process was first developed and documented by Chun and Passow [5, 6] in 1993 in M. I. T. They used this process to produce uniform solder droplets of Sn-5 mass% Pb alloy for use in ball grid arrays. Since then it is used extensively to produce mono-sized balls [7-18] of various alloys and metals with improved chemical homogeneity and RSP microstructures [65]. Since the process produces mono-sized droplets with nearly identical thermal history it is used to study the solidification behavior of various metals and alloys in a droplet-based manufacturing process [10-18].

2.1 UDS Process Overview

The UDS droplet process, as developed prior to this work, can easily produce mono-sized droplets ranging from 50 μm – 1000 μm and processing temperatures from 500 K to 1500 K [6-18]. However, production of the smaller droplet sizes entail a lot of difficulty as the orifice is easily clogged by any inclusion in the melt larger than the orifice diameter [14-18]. The photograph in Figure 2.1 shows the unit assembled at the Advanced Materials Processing Laboratory, Northeastern University. It was designed and assembled by former graduate students [8-18]. The droplet generator consists mainly of an inductively-heated melting furnace and a piezoelectric transducer, both used with a gas-filled spraying chamber. Details of the design drawings of the unit are provided in Refs. [9, 12-18].
2. Experimental Procedures

Figure 2.1: High-temperature UDS apparatus at Northeastern University.
2. Experimental Procedures

2.2 UDS Droplet Generator

Figure 2.2 shows a schematic of the droplet generator used in the present research. The top part of the apparatus consists of the piezoelectric transducer and the thermocouple connections. The piezoelectric transducer consists of five PZT-based piezos stacked together and separated by brass spacers. The transducer unit is housed around 20 cm above the induction heating unit, which ensures that the temperature of the piezos do not increase above its Curie temperature (~ 600 K for PZT based piezos). A thermocouple is fed in through the hollow transducer rod (closed at one end) to measure/control the melt temperature. Below the piezoelectric transducer is the induction heating unit. The induction heater coils are positioned so that it encompasses the crucible. A specially designed quartz tube, open at both ends and lined with carbon felt, separates the heater coils from the crucible. A pair of copper tubes running on the outside of the induction heater unit is used to cool it properly.

Figure 2.2: Schematic of the UDS droplet generator.
2. Experimental Procedures

Figure 2.3 shows a schematic of the UDS apparatus indicating the spray chamber, the bottom part of the apparatus used for collecting the droplets. A stainless steel can, containing silicone-based pump oil and fitted with a magnetic stirrer, may be used to collect the sprayed droplets. The sprayed droplets may also be collected as splats and deposits. A motion-controlled table for collecting the splats and deposits is placed in the chamber. The X and Y motions of the table are controlled using a micro-processor and the motion in the Z direction is adjusted manually. In the present work, additional modifications were made to the apparatus to enable working with materials with high melting point (> 1500 K), which are outlined below.

2.3 Modifications to the Set-Up

The use of the apparatus at high temperature was made possible by some additional modifications. The modifications made to the apparatus were done to culminate any hindrances that prevented the production of the droplets and the overall safety of the equipments and personnel involved. The modifications adopted for the UDS experiments for high temperature materials are summarized as:

a) A B-type thermocouple was incorporated in the experimental setup as it has a higher temperature range of operation. The thermocouple is made of Pt-30%Rh / Pt-6% Rh and has an approximate melting temperature (liquidus) of about 2073 K. It is to be noted here that the B-type thermocouple is not sensitive at low temperatures, i.e., for temperatures < 340 K the voltage produced at the thermocouple junction is too low to provide any reading.
b) Insulation lining in the form of high alumina fiber blocks were machined and fitted to the shape of the heating chamber walls, as shown in Figure 2.3. This minimizes the effect of excessive heat produced during the experiment on the top part of droplet generator that contains the piezoelectric transducer.

c) Most molten high temperature materials, such as ASTM F75 alloy and silicon melts, were found to be reactive to the previously used high density graphite crucible. Figure 2.4 shows the design of the alumina insert cemented to the graphite crucible that was used to contain the melt. The melt was also found to react heavily to the boron nitride insert used to hold the orifice and the boron nitride attachment, conventionally used earlier for the transducer insert. Thus, the boron nitride insert was eliminated for these experiments and the orifice was seated directly in the bottom of the alumina insert. The alumina insert was drilled using a diamond drill and the orifice was cemented by high alumina cement, Ceramabond™ 503. For the same reason, a high purity alumina tube, hollow and closed at one end, was used as the transducer rod for the high temperature experiments. To further minimize the corrosive effect of the melt on the crucible at high temperatures, especially for silicon melt, the alumina insert was painted with a thin layer of zirconia wash. The layer of zirconia was stable at high temperatures without having any corrosive effect on the alumina insert or the sapphire orifice.
2. Experimental Procedures

Figure 2.3: Schematic of the UDS droplet generator (not drawn to scale).

Figure 2.4: Schematic showing position of alumina insert.
It is to be noted here that other suitable crucible materials have been successfully used by researchers, especially for containing silicon melt, are zirconia [135], high purity silica [129,130, 132] and boron nitride [133, 136]. Our initial experiments with binder-less boron nitride showed indications of reaction between boron nitride and silicon melt at high superheats (> 100 K) which is not desirable. Hence, high purity alumina with a lining of zirconia was used throughout for all experiments.

These modifications enabled high temperature materials (ASTM F75 and silicon) to be safely melted and sprayed without affecting the piezos. However, the maximum temperature that may be safely used has been limited to ~ 1923 K. This is due to the use of the quartz tube in the heating unit, which limits the temperature to ~ 1973 K. For temperature > 1973 K it is required that the quartz tube should be upgraded to a more suitable high temperature material.

2.4 Experimental Procedure

The UDS droplet production procedure involved first preparation of the crucible by cementing the insert and orifice as shown in Figure 2.4. The crucible after assembling with the orifice and alumina insert was step-cured at 400 K, 500 K and 600 K for 1 hr at each step. The alumina insulation lining is then provided in the heating unit. Careful cleaning of the inner walls of heating unit and chamber should be done after every experiment to avoid contamination from other metals and alloys being used in the apparatus.
2. Experimental Procedures

Figures 2.2 and 2.3 show schematics of the UDS assembly. The crucible, containing the melt is positioned inside the induction coils. The melt temperature is controlled by the thermocouple inserted inside the hollow alumina transducer rod. Inert gas is supplied to the chamber and the crucible, which is also used to pressurize and eject the melt. The apparatus is sealed gas-tight to ensure no seepage of air into the chamber. The oxygen content inside the chamber is continuously screened by a highly responsive oxygen monitor. For the above crucible assembly, the material here is heated slowly to the desired temperature, at a rate of 10 K/min. This ensures that the alumina insert is heated slowly and does not crack due to thermal mismatch. These procedures were observed for production of droplets for both ASTM F75 alloy and silicon.

2.6 Evaluation of Nucleation Distance

A method for experimentally determining the nucleation temperature of travelling molten alloy droplets was first reported by Tuffile et al. [30] who used a loss-compensated calorimetric technique into the experimental procedure to evaluate the supercooling in 185 μm Sn-5mass%Pb UDS droplets. This method was later used by Dong et al. [31] to calculate the nucleation temperature of Sn-5mass%Pb UDS droplets under various cooling conditions. Dong et al.’s model was further extended by Wu and Ando [33] and Li et al. [35] to address the effects of gradual oxidation of droplet surface on nucleation kinetics. The model by Wu and Ando [33] also permits calculating nucleation temperature caused by internal catalysts. The later models have been used to calculate continuous cooling transformation (CCT) diagrams for the heterogeneous nucleation of Sn-5mass%Pb droplets [33-35]. Later Bialauskaya [36] used the Wu and Ando
model [33] to calculate the supercooling for Fe-17 mass% B UDS droplets from reference data obtained by a splat quenching technique. The same quenching technique is used in the present research to evaluate supercooling of ASTM F75 and silicon droplets.

In the splat quenching technique, the droplets were captured mid-stream on rotating blades placed at various flight distances and examined for evidence of nucleation. Just nucleated droplets are expected to have a splat like morphology with a pronounced hump, characterizing a partially solidified droplet, whereas droplets quenched before nucleation would normally be quenched into flattened splats. However, surface tension and wettability may also affect the splat morphology. Thus the collected splats should be examined for their microstructures to more accurately determine the flight distances at which the droplets nucleate.

Figure 2.5 shows the rotating quencher used for the present work. The method uses blades positioned at different heights from the orifice to catch the droplets. The generated droplets were impinged on the rotating blades as the quencher itself was moved from position \( R_i \) to \( R_f \). The distance between successive blades was approximately 2 cm. The morphologies of the splats collected on the blades were examined for the occurrence of nucleation to determine the flight distance, \( z \), where nucleation occurred.

The rotation of the quencher assembly can be precisely controlled at a desired speed by proper calibration with a pediometer. Figure 2.6 shows such a
calibration curve for the rotational speed corresponding to a pediometer reading [15]. In the present experiments, the pediometer a reading was fixed at 30, which was verified by a digital tachometer to give a frequency of about 550 Hz.

The nucleation temperature was estimated using the temperature profile plot of the droplets calculated using the in-flight simulation model. This method of determining the nucleation temperature using the splat quencher gives a temperature range where nucleation likely occurred. Although an average temperature for the specified range may be used for further simplification, this is strictly an approximation. This method is used in Chapters 5 and 6 to determine the nucleation temperature of ASTM F75 and silicon UDS droplets, respectively.
2. Experimental Procedures

Figure 2.5: Schematic of droplet quenching apparatus \cite{15},
(a) front view, (b) top view.

Figure 2.6: Calibration curve for the quencher \cite{15}.

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3 Prior Models

This chapter describes previously developed models for the simulation of the thermal state in traveling droplets produced by the UDS process. These models are adopted in the present research to calculate the nucleation temperature of the UDS droplets.

3.1 In-Flight Solidification Model

The in-flight solidification model developed in previous studies [6, 7, 14] is used to compute the thermal states of the travelling UDS droplets for ASTM F75 and silicon. The model incorporates the free dendritic growth model developed by DiVenuti and Ando (DA model) [53] to calculate the dendrite tip radius, tip velocity, and alloy partitioning during recalescence. These models are explained below in detail.

The governing equations of the droplet motion and the Newtonian thermal balance in gas atomization were first introduced by Mathur et al. [54]. They were later adopted by Passow [6], Abel [55] and Chen [56] in their UDS process models. The model was further refined by DiVenuti [7] by accounting for the effects of supercooling and rapid solidification experienced by the uniform droplets by incorporating a free dendritic growth model [53] for supercooled melts. Lu [14] modified the latter simulation model by accounting for radiative heat transfer and applied it to droplets of a pure metal, i.e., copper. An overview of the important aspects of the model is explained below.
3. Prior Models

When a jet is forced under pressure through a narrow orifice, the ejected stream breaks down due to surface tension instability into smaller droplets. This is called the Plateau-Rayleigh instability [57, 58]. The wavelength of the instability is related to the jet diameter as,

$$\lambda_m = 4.51d_j$$  \hspace{1cm} (3.1)

The in-flight solidification model [7] uses the initial jet velocity computed as:

$$v_j = \kappa \sqrt{\Delta P}$$  \hspace{1cm} (3.2)

where $\kappa$ is the discharge coefficient of the orifice, = 0.92 for a straight hole sapphire orifice (provided by Bird Precision Co. Ltd) and $\Delta P$ is the pressure difference between the crucible and chamber (obtained experimentally). The targeted droplet diameter is calculated [7]:

$$d_j = \sqrt{\frac{4\dot{m}}{\pi \rho_m v_j}}$$  \hspace{1cm} (3.3)

where, $\dot{m}$ is the mass flow rate of metal and $\rho_m$ is the density of the metal.

3.1.1 Droplet motion

The motion of the droplets is computed by applying Newton’s 2\textsuperscript{nd} law of motion to the force balance of the droplets [7]:

$$m_d \frac{d\vec{v}_d}{dt} = \vec{F}_g + \vec{F}_d + \sum_{i=1}^{n} \vec{F}_{c_i}$$  \hspace{1cm} (3.4)

where $\vec{v}_d$ is the droplet velocity, $\vec{F}_g$ is the gravitational force on the droplet, $\vec{F}_d$ is the drag force on the droplet and $\sum \vec{F}_{c_i}$ is cumblic electrostatic force acting on the $i^{th}$ droplet due to $n$ number of neighboring droplets. A schematic, indicating the force balance on the UDS droplets, is shown in Figure 3.1.
3. Prior Models

3.1.2 Droplet thermal state

The model assumes Newtonian heat transfer by convection and radiation between the droplets and the chamber gas. This is justified on the basis of the small Biot numbers (<0.01) of the UDS droplets [7, 15, 17]. Thus the rate of enthalpy loss, given by Gutierrez-Miravete et al. [59] and Mathur [54], accounts for both effects and is given as:

\[
m_d \frac{dH_d}{dt} = h_{dg} A_d \left(T_d - T_g\right) + \sigma \varepsilon A_d \left(T_d^4 - T_g^4\right) \tag{3.5}
\]

where \(H_d\) is the droplet enthalpy per unit mass, \(T_d\) is the droplet temperature, \(T_g\) is the chamber gas temperature, \(A_d\) is the surface area of the droplet, \(\sigma\) is the Stefan-Boltzmann constant, \(\varepsilon\) is the emissivity of the droplet, \(t\) is the time and \(h_{dg}\) is the convective heat transfer coefficient between the droplets and the chamber gas.
chamber gas. The adjustment parameter for the aligned array of traveling droplets is equal to the ratio of the drag coefficient of the shielded droplets, $C_{d_{\text{sh}}}$, to that of the unshielded droplets, $C_{d_{u}}$, is used to correct the heat transfer coefficient [60]:

$$h_{d_{\text{g, aligned}}} = \frac{C_{d_{\text{sh}}}}{C_{d_{u}}} h_{d_{g}}$$  \hspace{1cm} (3.6)

The rate of the temperature change of a droplet in flight is calculated from [7, 14]:

$$\frac{dT_d}{dt} = \frac{\Delta H_f}{C_p(d)} \frac{df_s}{dt} - \frac{h_{d_{g}}}{\rho_d C_p(d)} \left( \frac{6}{d_d} \right) \left( T_d - T_g \right) - \frac{\sigma \varepsilon}{\rho_d C_p(d)} \left( \frac{6}{d_d} \right) \left( T_d^4 - T_g^4 \right)$$  \hspace{1cm} (3.7)

where $\Delta H_f$ is the latent heat of fusion of the metal or alloy per unit mass, $f_s$ is the fraction solid in the droplet, and $C_{p(d)}$ is the specific heat of the droplet. The rate of solidification of a spherical droplet is given by [7]:

$$\frac{df_s}{dt} = \frac{v_i A^s_i}{V_d}$$  \hspace{1cm} (3.8)

where, $A^s_i$ is the area of the solid-liquid interface, $V_d$ is the droplet volume, and $v_i$ is the interface velocity. Further detailed derivation procedure for all sections of this model can be found in Refs. [7, 14].

3.1.3 Free dendritic growth model

The in-flight solidification model employs the results from a free dendritic growth model to calculate the properties of dendrites that form during recalescence. The free dendritic growth model, developed by DiVenuti and Ando
3. Prior Models

(DA model) [53], is a modification of the popular BCT model [61], to account for curved phase boundaries. Onell and Ando [62, 63] provide an in depth analysis on various important free dendritic growth models and discusses their developments. This section outlines the basic theory that is necessary for understanding the free dendritic growth model.

The dendrite growth properties depend on the supercooling in the melt and the thermal fields across the tip, as shown in Figure 3.2. The total supercooling is defined as the difference between the liquidus temperature of the alloy and the far field temperature in the droplet. The total supercooling has four components, which are given as:

\[ \Delta T = \Delta T_r + \Delta T_t + \Delta T_c + \Delta T_k \]  

(3.9)

where \( \Delta T_r \) is the curvature supercooling, \( \Delta T_t \) the thermal supercooling, \( \Delta T_k \) is the kinetic supercooling and \( \Delta T_c \) the solutal or constitutional supercooling, which is zero for pure metals.
Figure 3.2: Schematic diagram of the thermal and solutal profiles across the tip of a free dendrite. The dendrite tip is approximated by a paraboloid of revolution with radius $R$. 

- $G_s = 0$
- $T_i$
- $G_t < 0$
- $C_i^*$
- $G_c < 0$
- $C_o$
- $T_\infty$
For a dendrite tip approximated as a revolution of paraboloid [64] the components of supercooling are expressed as:

\[ \Delta T_r = \frac{2\Gamma}{R} \]  
(3.10)

\[ \Delta T_c = f^{-1}_L(X_0) - f^{-1}_L(X_L^*) \]  
(3.11)

\[ \Delta T_k = f^{-1}_L(X_L^*) - T_i \]  
(3.12)

\[ \Delta T_i = T_i - T_w = \frac{\Delta H_f}{C_p} Iv(P_t) \]  
(3.13)

where \( R \) is the radius of the dendritic tip, \( \Gamma \) is the Gibbs-Thompson coefficient, \( X_0 \) is the solute concentration of the alloy, \( f_S(T) \) and \( f_L(T) \) are the solute concentrations at the solidus and the liquidus, respectively, \( X_S^* \) and \( X_L^* \) are the solute concentrations at the interface, \( \Delta H_f \) is the heat of fusion, \( C_p \) is the specific heat of the material, \( \frac{\Delta H_f}{C_p} \) is the unit thermal supercooling of the material and \( Iv(P_t) \) is the Ivantsov function of the thermal Peclet number, \( P_t \). [64] For the case of pure metals the curvature supercooling and thermal supercooling remain the same but the constitutional supercooling is zero and the kinetic supercooling reduces to [14]:

\[ \Delta T_k = \frac{V}{\mu} \]  
(3.14)

where \( V \) is the tip growth rate and \( \mu \) is the interface kinetic coefficient. The four supercooling components are illustrated on a schematic phase diagram in Figure 3.3 [7].
3. Prior Models

(a) Components of supercooling shown on a phase diagram.

(b) Components of supercooling across the solid/liquid interface.

Figure 3.3: Bath supercooling and its components in free dendritic growth in an alloy with large deviation from local equilibrium at the tip \[^7\].
3. Prior Models

The difference of the free energy across the solid-liquid interface, $-\Delta G$, provides the driving force for the migration of the interface [7]. Turnbull et al. [19-22] suggested that the rate of migration of the interface may be limited only by the collision rate between the solid and the liquid atoms if the rate is much less than the maximum crystallization velocity, $V_o$, so that the interface velocity, $V_i$, can be expressed as:

$$V_i = -V_o \left( \frac{\Delta G}{RT_i} \right) \quad (3.15)$$

where $R$ is the gas constant and $T_i$ is the temperature of the interface.

DiVenuti and Ando adopted the linear kinetic growth law [7, 53] which expresses the interface velocity as:

$$V_i = -V_o \left[ X_L^*(1-k) + f_s(T_i + \Delta T_i) - f_L(T_i + \Delta T_i) + kX_L^* \ln \frac{k}{k_o} \right] \quad (3.16)$$

where $k'_o$ is the interface curvature-corrected equilibrium partition coefficient, $k$ is the non-equilibrium partition coefficient, which is given by the Aziz equation [67]:

$$k = \left[ \frac{f_s(T_i + \Delta T_i)}{f_L(T_i + \Delta T_i)} \right] + \left[ \frac{2\beta_o P \alpha}{R} \right] \quad (3.17)$$

where $\beta_o$ is the solute-trapping parameter and $\alpha$ is the thermal diffusivity of the alloy.
For pure metals, the driving force is simply a function of droplet temperature, which reduces Equation (3.16) to [14]:

$$V_i = -V_o \left( \int_T^{T_o} \frac{\Delta C_{p(L\rightarrow S)}}{T} dT + \Delta H_f + \int_T^{T_o} \frac{\Delta C_p}{R} dT - \frac{\Delta H_f}{R} \right)$$

(3.18)

where $\Delta C_{p(L\rightarrow S)} = C_{p,S} - C_{p,l}$.

The dendritic tip radius is an important factor that describes the microstructure resulting from rapid solidification. In DA model [53], as in other free dendritic models such as LGK [69], LKT [70], TLK [71] and BCT [61] models, it is obtained by assuming that the tip radius of a growing dendrite is given by the smallest stable perturbation, or the marginally stable wavelength, of the solid-liquid interface [7, 14].

Mullins and Sekerka [68] first carried out a linear stability analysis of a planar interface to understand the morphological stability of solid-liquid interfaces. Their treatment of marginal stability for low Péclet number conditions was later improved by Trivedi and Kurz [72] who extended the Mullins-Sekerka analysis to fit it for all ranges of Péclet number conditions, including those that apply to rapid solidification occurring at a very high interface velocity. Later, Divenuti and Ando modified the Trivedi-Kurz criterion for curved phase boundaries and added the kinetic supercooling component [53] so that the tip radius is given by:
3. Prior Models

\[ R = \frac{\Gamma/\sigma^*}{P_{\Delta H} \frac{\xi_s}{C_p}} \frac{2 \left( \frac{dT_{L_1}}{dC} \right)_{c=1}^0 P_c C_o (1-k)}{1 - (1-k) \nu(P_c)} \xi_s \]  
(3.19)

and

\[ \xi_s = 1 - \frac{1}{\sqrt{1 + \frac{1}{\sigma^* P_c^2}}} \]  
(3.20a)

\[ \xi_c = 1 + \frac{2k}{1 - 2k \sqrt{1 + \frac{1}{\sigma^* P_c^2}}} \]  
(3.20b)

where \( \sigma^* \) is the stability constant equal to \( \frac{1}{4\pi^2} \), \( P_c \) is the solutal Peclet number, \( \xi_s \) and \( \xi_c \) are the thermal and constitutional stability functions, respectively, and 

\[ \frac{dT_{L_1}}{dX} \bigg|_{x=x_{L_1}} \]  
is the value of the slope of the liquidus function \( T_{L_1} \) evaluated at the interfacial solute concentration \( X_{L_1}^* \). For pure metals, the tip radius is simplified to [14]:

\[ R = \frac{\Gamma/\sigma^*}{P_{\Delta H} \frac{\xi_s}{C_p}} \]  
(3.21)

Thus the following equations, deduced from the considerations of the linear kinetic growth law, the thermal undercooling, the marginal interface stability and solute trapping, constitute a system of equations, which can be solved simultaneously for a given supercooling by any numerical method to obtain \( V_i \) and \( R \):
3. Prior Models

\[ F_1 = -V \frac{\Delta G}{T R} + \frac{2P \alpha}{R_e} = 0 \]  
(3.22)

\[ F_2 = \frac{\Delta H_f}{C_p} \ln(T) + T_e - T_i = 0 \]  
(3.23)

\[ F_3 = k - \frac{\left[ \frac{f_i(T_i + \Delta T)}{f_i(T_i)} \right] + \left[ \frac{2 \beta P \alpha}{R} \right]}{1 + \left[ \frac{2 \beta P \alpha}{R} \right]} = 0 \]  
(3.24)

\[ F_4 = \frac{\Gamma}{\sigma} \frac{P \Delta H_f}{c_p} \xi - \frac{2 P \alpha X_i (1 - k)}{D(T) \ln(1 - k) \ln(T)} \frac{d f_i}{d X} \bigg|_{X = X_i} \xi_e = 0 \]  
(3.25)

3.2 Nucleation Kinetics of UDS Droplets

The model, developed by Dong et al. [31] and Wu and Ando [33], was used to calculate the kinetics of nucleation of travelling droplets and continuous cooling transformation (CCT) curves with the aid of a few experimentally determined nucleation data. The first droplet nucleation kinetics model proposed by Dong et al. [31] addressed the effects of oxidation on the surface nucleation of droplets. Later Wu and Ando [33] proposed a modification of the earlier model to explain the gradual effects surface oxidation on the nucleation kinetics of droplets. This was applied to travelling Sn-5mass%Pb UDS droplets used by Fukuda et al. [32] and Li et al. [35]. A modification of the model for surface oxidation of droplets was provided by Li et al. [34] where the growth and geometry of the oxide particles on the surface are also considered. The kinetics of internal nucleation is given by Wu and Ando [33], which is described in this section.
3. Prior Models

3.2.1 Surface nucleation

Droplet nucleation kinetics relates the nucleation temperature, $T_n$, with the cooling rate, $dT/dt$ using the expression:

$$\int_{T_n}^{T_C} \pi D^2 x \frac{M}{(T_L - T)^2} \exp \left[-\frac{Q}{RT} - \frac{N}{T(T_L - T)^2} \left(\frac{dt}{dT}\right)\right]dT = 1 \quad (3.26)$$

where $M$ and $N$ are material specific constants given by:

$$M = \frac{8\pi C_v^0 (1 - \cos \theta) \gamma^2 T_L^2 D_0}{a_o^4 \Delta H_v^2} \quad (3.27a)$$

$$N = \frac{16\pi \gamma^3 f(\theta)}{k (\Delta H_v^2)^2} \quad (3.27b)$$

where $D$ is the droplet diameter, $T_L$ is the liquidus temperature of the alloy, $Q$ is the activation energy for liquid diffusion, $R$ is the universal gas constant, $t$ is the time, $\theta$ is the wetting angle, $\gamma$ is the interfacial energy, $a_o$ is the lattice parameter, $T_L$ is the liquidus and $\Delta H_v$ is the enthalpy of fusion per unit volume. Here $\gamma$ and $\theta$ are assumed to be independent of temperature. Thus the Equation (3.26) can be calculated using two sets of experimentally determined values of $T_n$. Figure 3.4 shows the scheme of computation adopted by Dong et al. [31]. It is to be noted that the model assumes oxidation would occur instantaneously throughout the surface of the droplet, which gives nucleation temperatures higher than the actual [31, 32].
Wu and Ando [33] thus proposed a modification to this model which addresses the gradual surface oxidation of the droplet, by introducing the fraction oxidized with time, \( x \). The oxidation on the surface proceeds by the reaction:

\[
Sn(l) + O_2(g) = SnO_2(s)
\]  

(3.28)

The surface fraction oxidized is thus calculated as [31]:

\[
x = 1 - \exp\left[-P \cdot [O_2] \cdot \int_{T_0}^{T_f} Q(T) \,dT\right]
\]  

(3.29)

where \( P \) is a constant and \( Q(T) \) is a temperature dependent function.

And the interfacial energy, \( \gamma \), is expressed as:

\[
\gamma = cT + d
\]  

(3.30)

where \( c \) and \( d \) are constants for any alloy system. This introduces a parameter, \( h = c/d \), which conveniently expresses the variation in \( \gamma \) in the final equation. The final expression, which addresses the above changes, is thus given as:
3. Prior Models

\[
\int_{T_0}^{T_s} \pi D^2 \left\{ 1 - \exp \left[ -P \cdot [O_2] \cdot \int_{T_0}^{T_s} Q(T) dT \right] \right\} \times \frac{M'(hT + 1)^2}{(T_L - T)^2} \exp \left[ -\frac{Q}{RT} - \frac{N'(hT + 1)^2}{T(T_L - T)^2} \right] \left( \frac{dt}{dT} \right) dT = 1 \quad (3.31)
\]

Computation of the model to construct the CCT curves for this case needs four sets of experimentally evaluated values of \( T_n \) to calculate \( P, M', N' \) and \( h \).

Li et al. [34] have presented a modification of the above model for droplet surface nucleation caused by oxidation which addresses the rates of nucleation and growth of oxides on the droplet surface. It is assumed that the oxides nucleate and grow as discs shaped islands, with the same thickness and do not impinge on each other. The surface fraction oxidized, \( x \), is thus calculated as [34]:

\[
x = 1 - \exp \left[ \int I(t) \cdot \pi \left\{ \int G(T_x) \left( \frac{dx}{dT} \right) dT_x \right\} \left( \frac{dt}{dT} \right) dT \right] \quad (3.32)
\]

where \( G(T_x) \) is the growth rate of the oxide and \( I(t) \) is the oxide nucleation rate.

The rate of oxidation, \( I \), is given as:

\[
I = I_o P_{O_2} \exp \left( -\frac{E_N}{RT} \right) \quad (3.33)
\]

where \( E_N \) is the activation energy, \( I_o \) is a constant and \( P_{O_2} \) is partial pressure of oxygen in the atmosphere. The oxide growth rate is given by [34]:

\[
G(T) = \left[ T(\Delta S^0 + R \ln P_{O_2}) - \Delta H^0 \right] \frac{M_o}{V} \exp \left( -\frac{E_G}{RT} \right) \quad (3.34)
\]

where \( \Delta S^0 \) and \( \Delta H^0 \) are the standard entropy and enthalpy of formation of the oxide, respectively, \( M_o \) is the pre-exponential constant for mobility of the oxide-gas-liquid triple point, \( V \) is the specific volume of the oxide and \( E_G \) is the
activation energy for oxide growth, which is assumed to be equal to \( E_N - E \).

Therefore, the fraction oxidized is given by [34]:

\[
\chi = 1 - \exp\left\{ -\int_{T_i}^{T} C \cdot P_{O_2} \cdot \exp\left( -\frac{E}{RT} \right) \cdot \pi \cdot \int_{T_i}^{T} \Delta G \cdot \exp\left( -\frac{E}{RT} \right) \cdot \left( \frac{dt}{dT} \right) dT \left( \frac{dT}{dt} \right) \cdot dt \right\}
\]

(3.35)

where \( C \) is a constant defined by: \( C = I_0 \left( \frac{M_0}{V} \right) \) and \( \Delta G \) is the driving force for oxidation per mass, given by: \( \Delta G = T(\Delta S^0 + R \ln P_{O_2}) - \Delta H^0 \). The expression in Equation (3.35) can now be replaced by the fraction surface area oxidized for the droplet obtained by the earlier model in Equation (3.29). This may be suitably used in Equation (3.31) to compute the nucleation kinetics of droplets due to surface nucleation.

### 3.2.2 Internal nucleation

The Wu and Ando nucleation model [33] also addresses the kinetics of heterogeneous internal nucleation. This is based on the formulation that the first event of nucleation occurs:

\[
\int_{T_i}^{T_L} V J \cdot \frac{dt}{dT} dT = 1
\]

(3.36)

where \( V \) is the volume of droplet, \( T_L \) is the liquidus temperature of the alloy, \( J \) is the rate of nucleation at the nucleation temperature, \( T_N \), for the droplet and \( dt/dT \) is the cooling rate for the droplet. The nucleation rate by Perepezko and Uttormark [26] is given as,

\[
J = \frac{4 \pi r^2 D}{a_o^3} \exp\left( -\frac{\Delta G^*}{kT} \right)
\]

(3.37)
where \( r^* \) is the size of the critical embryo, \( D_L \) is the liquid diffusivity, \( a_0 \) is the lattice parameter and \( \Delta G^*_{het} \) is the energy required to form the critical sized nuclei, given as:

\[
\Delta G^*_{het} = \frac{(16/3)\pi \gamma^3 f(\theta)}{(\Delta H_v/\Delta T)^2 \Delta T^2} \tag{3.38}
\]

where \( \gamma \) is the interfacial energy, \( \Delta H_v \) is the enthalpy of formation and \( f(\theta) \) is the shape factor for heterogeneous nucleation.

Wu and Ando [33] proposed that \( D_L \) is exponentially dependent on temperature, which gives \( J_v \) as,

\[
J_v = \frac{8\pi(1-\cos\theta)\gamma^2T_v^2D_v}{a_0^4\Delta H_v^2\Delta T^2} C_v \exp\left(-\frac{Q}{RT} - \frac{(16/3)\pi \gamma^3 f(\theta)}{(\Delta H_v/\Delta T)^2 k_\theta T(\Delta T)^2}\right) \tag{3.39}
\]

where \( D_0 \) is the pre-exponential term for liquid diffusivity, \( Q \) is the activation energy for liquid diffusion and \( R \) is the universal gas constant. Thus substituting Equation (3.39) in Equation (3.36), we have:

\[
\frac{T_v}{t} = \frac{\pi D_v^3 M' (hT+1)}{6 (T_v - T)^3} \exp\left(-\frac{Q}{RT} - \frac{N' (hT+1)^2}{T(T_v - T)^2}\right) \left|\frac{dT}{dt}\right| = 1 \tag{3.40}
\]

\[
M^* = \frac{8\pi(1-\cos\theta)\gamma^2T_v^2D_vC_v}{a_0^4\Delta H_v^2} \tag{3.41a}
\]

\[
N^* = \frac{(16/3)\pi \gamma^3 f(\theta)}{k_\theta (\Delta H_v/\Delta T)^2} \tag{3.41b}
\]

where \( D \) is the droplet diameter, and \( t \) is the time. \( M^* \) and \( N^* \) are material specific constants given by Equations (3.41a) and (3.41b), that depend on the alloy properties; such as \( \theta \), wetting angle, \( \gamma \) interfacial energy, \( a_0 \) lattice parameter, \( T_L \) liquidus, and \( \Delta H_v \) enthalpy of fusion per unit volume. To numerically solve
Equation (3.40) in its entirety, three values of $T_N$ need to be experimentally determined. However, assuming $\gamma$ to be a temperature independent constant, only two sets of experimentally determined values of $T_N$ are sufficient to solve the above equation.

### 3.2.3 Continuous cooling transformation curves

The droplet nucleation kinetics model can be used to construct continuous-cooling curve transformation (CCT) curves for travelling droplets. First the values of $M^*$ and $N^*$ are calculated from Equation (3.40) based on two sets of experimentally obtained nucleation data, e.g., data points 11 and 22 in Figure 3.4. The computed values of $M^*$ and $N^*$ are used in Equation (3.40) to calculate $T_N$ values for any given cooling schedule. This enables computation of CCT curves.

This nucleation kinetics model was used to compute the CCT curves for ASTM F75 and silicon droplets. The nucleation in ASTM F75 droplets and silicon droplets was assumed to be internal from the microstructure of the droplets, as explained and shown in Chapters 5 and 6, respectively. Stringent control of oxygen content during the experiments was ensured, by measuring the oxygen partial pressure, to obtain reliable and reproducible results.

### 3.3 Karma’s Fragmentation Model

The dendrites that form during recalescence may undergo fragmentation during the post recalescence solidification. Whether such fragmentation occurs in travelling droplets may be assessed by applying the model developed by Karma.
3. Prior Models

[40]. This fragmentation model is useful in both, determining the mechanism of fragmentation and predicting the form of dendrites in the solidified microstructure. The model predicts transitions from coarse grained dendritic microstructure to fine grained microcrystalline microstructure with increasing supercooling. Depending on the material properties and alloy composition the model predicts at least one, but also as many as two, three or four such transitions [38, 40]. The first transition is usually observed at low supercoolings, and is reported to be a broad transition [40]. However, for further transitions, the supercoolings are usually highly defined and sharp [39, 40]. Karma assumes that fragmentation completely occurs in the stage following recalescence until complete solidification has occurred, called the post-recalescence plateau stage. This has also been experimentally verified by Nagashio et al. [44] in highly supercooled silicon using time resolved X-ray diffraction. They report that the fragmentation of the dendrites was found to occur in the initial stage (25 ms) of the plateau period (~ 2 s). Karma’s model [40] is based on the assumption that the dendrite fragmentation occurs by the remelting of the dendrite trunks initiated by a wave like perturbation in the dendrite. The fragments then separate from each other and re-orient to form individual dendrites that coarsen as the rest of the inter-dendritic melt solidifies.

In the model time required for break-up of the dendrites is related to the supercooling in the droplet by the dendrite tip radius. Hence, it is also required to calculate the tip radius at various supercoolings. Herlach et al. [38], Schwarz et al. [39] and Galenko et al. [52] have applied the LKT model [70] to compute the dendrite tip radius. The LKT model uses equilibrium interface conditions to
compute the dendrite tip radius for high supercoolings [70, 62]. The LKT model being a non-rigorous model does not address the non-equilibrium kinetics at the interface, which exists in rapidly solidified materials. To make the fragmentation model applicable to highly supercooled droplets produced by rapid solidification, a more rigorous model that addresses the non-equilibrium kinetics needs to be used. In this context, the BCT model [51] and the DA model [53] may be appropriately used. The BCT model addresses the non-equilibrium kinetics but assumes a straight phase boundary for calculations. The DA model, on the other hand, applies both the non-equilibrium interface kinetics and also incorporates curved phase boundaries.

**Formulation**

The fragmentation model assumes that the dendrites fragment in the post recalescence plateau period, only when the time required for dendrite break-up, $\Delta t_{bu}$, is smaller than the plateau period, $\Delta t_{pl}$. The plateau period is calculated from the in-flight solidification model [7] developed for the travelling UDS droplets. The break-up time is calculated using an instability criterion for the dendrite trunk as explained below.

According to the model [40], fragmentation is initiated by a wave like perturbation with an amplitude rate of $\omega(k; R)$, which is related to the break-up time by:

$$\Delta t_{bu} (\Delta T) = \frac{1}{\omega(k_{\text{max}}; R(\Delta T))}$$  \hspace{1cm} (3.42)
where, $k$ is the partition coefficient and $R(\Delta T)$ is the dendrite radius which depends on the supercooling, $\Delta T$. The amplification rate is given by [40]:

$$
\alpha(k; R) = \frac{d^C_0 D_l}{R^3} \frac{K_1(kR)}{K_0(kR)} \left[ 1 + \left( k_0 \frac{D_s}{D_l} + S \right) h(kR) \right] kR - \left( 1 + k_0 \frac{D_s}{D_l} \right) (kR)^3 \times \right.
$$

$$
\left[ 1 + \frac{(\Delta H_f / C_p)(D_l + k_0 h(kR) D_s) \alpha}{\alpha m_l C_0 (1 - k_0)(1 + h(kR))} \right]^{-1}
$$

(3.43)

where $k_0$ is the equilibrium partition coefficient, $d^c_0$ is the capillary length, $D_l$ and $D_s$ are the solute diffusivities in the liquid and solid phases, respectively, $S$ is the amplification factor, $C_p$ is the heat capacity, $\Delta H_f$ is the enthalpy of fusion, $m_l$ is the composition of the binary alloy, $\alpha$ is the thermal diffusivity and $C_0$ is the composition of the binary alloy. The function $h(kR)$ is given by:

$$
h(kR) = \frac{K_o(kR) I_s(kR)}{I_o(kR) K_o(kR)}
$$

(3.44)

The expression for $\Delta t_{bu}$ has been simplified by Karma [40] by assuming that for most metallic systems $k_{max} = 0.5$, independent of $C_0$. This evaluates, $h(0.5) \approx 0.1$ which is small enough to be neglected. For small values of $R$,

$$
K_o(k_{max} R) \sim -\ln k_{max} R, \quad I_o(k_{max} R) \sim e^{i\alpha} \quad \text{and} \quad \frac{K_o(kR)}{K_o(kR)} (kR - kR^3) \approx \frac{2}{3}
$$

Thus the final expression for $\Delta t_{bu}$ is given as [38, 40]:

$$
\Delta t_{bu}(\Delta T) = \frac{1}{\alpha(k_{max}; R(\Delta T))} = \frac{3 R(\Delta T)^3}{2 \alpha \cdot d_0} \left[ 1 + \frac{m_l C_0 (1 - k_0) D_l}{\Delta H_f / C_p \alpha} \right]
$$

(3.45)
The amplification factor, $S$, is a dimensionless number that estimates the relative dominance of the driving forces. Fragmentation can be either driven by the surface tension or supersaturation inside the dendrite trunk. The dominating driving force is estimated from the value of $S$, which is given as [40]:

$$S = -\frac{G_C R}{C_0 (1 - k_0)} \times \frac{D_s}{D_l} \times \frac{R}{d_0^c} \quad (3.46)$$

where $G_C$ is the gradient of solute concentration near the interface in the solid, $D_s$ is the solute diffusivity in the solid and $D_l$ is the liquid diffusivity. For simplification, the model assumed that the solute concentration in the solid is linear which gives [40]:

$$G_C^{max} = -C_0 (1 - k_0) / R^{min}_{tip} \quad (3.47)$$

Thus using the above expression for $G_C^{max}$, the maximum value of $S$ is estimated from Equation (3.46):

$$S \equiv \frac{R \cdot D_s}{d_0^c \cdot D_l} \quad (3.48)$$

The numerical value of $S$ is then calculated using known values of $D_s$ and $D_l$. The value of $R_{tip}$ is estimated from the computation of DA model, which has been explained in Section 3.2. The chemical capillary length is computed from the expression:

$$d_0^c = \frac{\Gamma}{m_l (1 - k_0) C_0} \quad (3.49)$$

where $m_l$ is the slope of the binary phase boundary, $k_0$ is the equilibrium partition coefficient and $C_0$ is the composition of the alloy. The value of $S$ can now be used to determine the mechanism for the fragmentation. For $S < 1$, fragmentation is
driven mainly by the capillary force of the interface, whereas for values of $S > 1$, it is driven by the supersaturation inside the dendrite trunk.

Thus, in the present work, using the expression in Equation (3.45) the break-up time has been calculated for ASTM F75 and silicon, as explained below.

### 3.4 Application of the Models to ASTM F75 alloy

Published works on thermodynamical assessment of the Co-Cr-Mo system through a first principle method [78, 79] shows that at 28 mass% Cr and 5 mass% Mo, the room temperature stable phase is ε phase (hcp) with a γ phase (fcc) stable at higher temperatures. Figure 3.5 shows the Co-Cr binary phase diagram (generated on Thermo-Calc TCW2) that at a composition of 28 mass% Cr also indicates the ε phase and the γ phase (fcc) at temperatures $> 1100$ K. Thus for such low concentrations of Mo in the alloy ($< \sim 10$ mass%), Co-Cr approximation may apply to the ternary. Such binary approximation was necessary as the DA model applies only to binary alloys. Thus, in this investigation ASTM F75 was approximated as a Co-28mass%Cr binary alloy.

The regular solution model was used to compute the extended metastable solubility of the γ Co phase. The computed plot is provided in Appendix C. The in-flight solidification model of Co-28mass%Cr droplets was simulated using the input parameters for the alloy given in Appendix A. The C++ source codes for computation of the DA model and in-flight solidification model are provided in Appendix D.
Figure 3.5: Binary Phase Diagrams of Co-Cr alloy (generated by TCW 2).
3. Prior Models

Figures 3.6 and 3.7 show the plots the dendrite tip radius and tip velocity, respectively, as a function of supercooling for Co–28mass%Cr. The overall tip radius is found to decrease with increasing supercooling whereas the tip velocity increases monotonically with the increasing supercooling. The mathematical saddle point is found to occur between 50 K and 73 K, corresponding to the solutal-to-thermal transition region [7]. The calculated tip radius and velocity were fitted to polynomials, which were then incorporated in the in-flight solidification model to calculate the solidification.

Figure 3.8 shows the calculated droplet thermal state for UDS droplets of Co-28mass% Cr alloy. In this computation, the nucleation temperature is a user contributed factor. As an example, a supercooling of 100 K is assumed for the computation of these plots. However, the actual supercooling in the droplets will need to be determined experimentally. The solidification rate is observed to increase with the decreasing droplet size.

Figure 3.9 shows the $\Delta t_{bu}$ vs. supercooling curves for the alloy calculated with Equation (3.45). The value of $S$ is calculated with $D_3 \sim 1.27 \cdot 10^{-9} \text{ m}^2/\text{s}$ and $D_l = 3.23 \cdot 10^{-7} \text{ m}^2/\text{s}$ [81]:

$$S_{\text{max}} = \frac{R_{\text{max}} \cdot D_s}{d^{*} \cdot D_l} = \frac{3 \cdot 10^{-6} \cdot 1.27 \cdot 10^{-9}}{4.45 \cdot 10^{-8} \cdot 3.23 \cdot 10^{-7}} = 0.2504.$$  

(3.50)

This suggests that the driving force for fragmentation is dominated by the surface tension of the solid-liquid interface. Similar results are discussed by Wei and Herlach for Co-Sb alloys [41].
Figure 3.6: Computed tip radius vs. supercooling for Co-28wt%Cr alloy.

Figure 3.7: Computed interface velocity vs. supercooling for Co-28mass%Cr alloy.
Figure 3.8: Temperature vs. flight distance for Co-28mass%Cr alloy.

Figure 3.9: Computed break-up time ($t_{bu}$) vs. supercooling for ASTM F75.
3.5 Application of the Models to Silicon

The models are much simplified for the case of pure metals in comparison to that for binary alloys. Lu [14] and later Ranganathan [16] computed for the case of pure copper, the C++ source code can be found in Refs. [14] and [16]. This was used as a basis to compute the relevant results necessary for evaluating the droplet thermal states of silicon droplets using the in-flight solidification model. The input parameters necessary for computation are provided in Appendix A.

Figures 3.10 and 3.11 show the plots of dendrite tip radius and tip velocity, respectively, at various supercoolings computed for silicon. The tip radius is observed to decrease monotonically whereas the tip velocity increases with increase in the supercooling. The tip velocity is observed to increase rapidly by five orders of magnitude for 300 K increase in supercooling. The numerical values of radius and velocity were similarly fitted into polynomial functions that were used in the in-flight solidification model [7].

Figure 3.12 shows the computed droplet thermal states vs. their flight distance for various droplets cooled in helium atmosphere. The plots were computed at an assumed supercooling of 100 K for each of the droplets. However, the actual supercooling of the droplets would differ based on its cooling conditions.
Figure 3.13 shows the computed values of \( \Delta t_{bu} \) against supercooling calculated for the case of silicon using Equation (3.45). The capillary length for pure Si is given as: 

\[ \Gamma^* = \Gamma \sim 1.96 \times 10^{-8} \text{mK} \]

The maximum amplification parameter, \( S \) is calculated as:

\[
S = \frac{R}{d^* \cdot D_s} \cdot \frac{D_s}{D_l} = \frac{10^{-7} \cdot 1.53 \times 10^{-11}}{1.96 \times 10^{-6} \cdot 1.45 \times 10^{-12}} \sim 0.538 \times 10^{-2}
\]

(3.51)

where \( D_s \sim 1.53 \times 10^{-11} \text{ m}^2/\text{s} \) and \( D_l \sim 1.45 \times 10^{-12} \text{ m}^2/\text{s} \) [81]. This indicates the dominating driving force for fragmentation is the surface tension that tends to minimize the surface area. This is expected for pure materials where surface tension is the only driving force for instability of the dendrite.
3. Prior Models

Figure 3.10: Computed dendrite tip radius vs. supercooling for Si.

Figure 3.11: Computed dendrite tip velocity vs. supercooling for Si.
3. Prior Models

Figure 3.12: Temperature vs. flight distance for silicon UDS droplets ($\Delta T = 100 \ K$).

Figure 3.13: Computed break-up time ($t_{bu}$) vs. supercooling for silicon.
4 Charging of UDS Droplets at High Temperature

Charging of droplets is a well-established method for obtaining unmerged UDS droplets of low melting point alloys, e.g., Sn-Pb alloys [6, 13, 55]. It was traditionally used to charge ink/toner droplets in an inkjet printer [82, 83]. The electrostatic force of repulsion between the charged droplets prevents the ink droplet from merging in-flight [83]. This principle has been utilized to prevent merging of metallic UDS droplets. Researchers have successfully charged droplets of Sn and Sn-Pb alloys having a melt temperature up to 800 K [6, 13, 55, 84]. However, at higher temperatures the behavior of the gas also comes into play making it difficult to effectively charge droplets during spraying without any electrical disruption. This chapter explores the charging behavior of droplets at higher temperatures (> 800 K).

4.1 Literature Review

The charging of droplets/particle in an electric field depends on the stability of the gas against ionization at that temperature. To charge droplets, gas between the electrodes should have an ideal dielectric behavior. However, at certain conditions of temperature and pressure, gases begin to conduct electricity and thus cannot sustain to be a dielectric. In this context the breakdown point of the gases, i.e., the condition beyond which they stop behaving as dielectric and conduct electricity, has been studied and compared to obtain information about the use of such gases for UDS charging experiments.
4. Charging of UDS Droplets at High Temperatures

4.1.1 Breakdown mechanism in gases

Inert gases are dielectric and act as insulators in standard conditions of temperature and pressures when an electric field is applied. However, they become conductive and the electric field breaks down when a sufficiently high voltage (breakdown voltage) is applied. This process of breakdown in gases usually occurs by the process of ionization. Ionization at high temperatures can occur by collision, photo-ionization or by secondary emission processes by either photons, metastable or neutral atoms present in the field [85-87]. In these processes the particle would manage to dislodge an electron from a neutral atom and produces a positive ion. By a repetitive process the number of free electrons in the gas increases over time causing an avalanche of electrons to be formed. This increases the electron current reaching the anode. With increasing current the gas breakdowns when a steady stream of current can pass through the gas. This is accompanied by a glow discharge or at sufficiently high voltages an electric arc between the electrodes.

Inert gases can be classified as attaching or non-attaching depending on their mechanism involved for breakdown. For attaching inert gases, the molecules of the gases bind the free electrons present and become negatively charged. This is found to occur in most electronegative gases that have vacant outermost orbitals (such as in oxygen and nitrogen). The negative ion is now too massive to cause further ionization and this thus decreases the probability of breakdown of the field. For non-attaching gases like argon and helium, the electrons are free (as these gases do not have vacant outer orbitals that can bind the electrons) and ionize the gases by collision as described above [85-88]. It is thus interesting to
note that attaching gases have higher breakdown voltages than non-attaching gases [85-87].

Generally the breakdown voltage of the gas depends on its pressure, electrode gap (gap length), temperature, gap geometry and type of gas used. The surface conditions and relative shape of the electrodes also affects the breakdown voltage [87]. Plane parallel plate electrodes have the most stable and uniform electric field and hence less probability of breakdown. UDS has two parallel plates with a line of charges in between the plates. The electric field distribution in such a case is highly non-uniform due to the charge concentrations. The potential across this field has been derived by the method of images as explained in Appendix B.

At higher pressures the gas density is high so that the mean path of the electrons decreases and their potential to ionize the gas molecules decreases [85, 86]. Similarly for increasing gap lengths the breakdown voltage increases. These two factors are related by Paschen’s law which states that the breakdown voltage of a gas, \( V_{br} \), in a uniform field is given as a function of its pressure, \( p \) and gap length, \( d \):

\[
V_{br} = f(p \cdot d)
\]

With increasing temperature the density of the gas decreases and so, for constant electrode gap lengths, the breakdown voltage decreases. This holds true up to the critical temperature, at which point the gas breaks down and no longer behaves as a dielectric. This limit on the voltage owing to thermal instability is termed as the breakdown temperature, \( T_{br} \), which is independent of the gap distance. The
corresponding voltage at which $T_{br}$ occurs is the upper limit for breakdown. The minimum breakdown voltage is called the minimum sparking voltage, $V_s$, and is defined as the lower limit for breakdown. The breakdown of the field is followed by a steady glow discharge across the electrodes. The values of $V_s$ that have been reported for helium, argon and nitrogen are shown in Table 4.1. The suitability of using different gases at high temperature for UDS charging experiments is discussed below.

<table>
<thead>
<tr>
<th>Gases</th>
<th>$V_s$ (V)</th>
<th>pd at $V_s$ (Torr-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>251</td>
<td>0.67</td>
</tr>
<tr>
<td>He</td>
<td>156</td>
<td>4.0</td>
</tr>
<tr>
<td>Ar</td>
<td>137</td>
<td>0.9</td>
</tr>
<tr>
<td>Air</td>
<td>327</td>
<td>0.567</td>
</tr>
</tbody>
</table>

4.1.2 Breakdown behaviors of nitrogen, argon and helium gases

The UDS charging system represents a highly non-uniform field with a varying potential at every point of the gap. Most of the research in this area is concentrated on the breakdown behavior at low temperatures ($\sim 300$-$500$ K) as most applications like switch gears, gas arrestors (gas tube surge protectors) and oscillators operate at these ranges [92, 93]. There are a few fundamental studies which focus on the characteristics breakdown temperature of inert gases which are relevant to the present work.

A study of various inert gases for a uniform field has been done by Bozhko et al. [88]. It shows that, for a uniform field breakdown voltage for
nitrogen, argon and helium gases when compared show $V_{br}^{N_2} > V_{br}^{He} > V_{br}^{Ar}$ [88]. A similar study for comparing argon and helium gases in a non-uniform field shows that for temperatures $<1900$ K $V_{br}^{Ar} > V_{br}^{He}$ but $V_{br}^{He} > V_{br}^{Ar}$ at higher temperatures [89]. This is attributed to the change in nature of breakdown from ionic (characterized by glow discharge between the electrodes) to thermionic (characterized by a steady arc between the electrodes). Similar breakdown behavior in a non-uniform field has also been reported for nitrogen and air at similar temperatures but lower corresponding voltage. Thus, a gas attains breakdown at lower voltages for a non-uniform field compared to a uniform field for the same temperature. A comparison of the breakdown temperature for various gases at different fields has been shown in Table 4.2.
4. Charging of UDS Droplets at High Temperatures

Table 4.2 Comparison of Some Experimental Breakdown Conditions of Inert Gases (d is the gap length and p is the pressure).

<table>
<thead>
<tr>
<th></th>
<th>Gas</th>
<th>Breakdown Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nitrogen</td>
<td>12 kV, 2500 K non-uniform field d=24 mm, p = 0.013 atm</td>
<td>Rothhard et al. [92]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9000 V, 300 K non-uniform field d=0.4 mm, p = 9e-10 atm</td>
<td>Hackham et al. [93]</td>
</tr>
<tr>
<td>2</td>
<td>Helium</td>
<td>150 V, 2000 K non-uniform field d= 5 mm, p = 1 atm</td>
<td>Bozhko et al. [88]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300 V, 1900 K uniform field d= 10 mm, p = 1.6 atm</td>
<td>George et al. [89]</td>
</tr>
<tr>
<td>3</td>
<td>Argon</td>
<td>155 V, 1800 K non-uniform field d= 5 mm, p = 1 atm</td>
<td>Bozhko et al. [88]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>300 V, 1900 K uniform field d= 10 mm, p = 1.6 atm</td>
<td>George et al. [89]</td>
</tr>
</tbody>
</table>
4. Charging of UDS Droplets at High Temperatures

4.2 Experimental Set-Up

Figure 4.1 shows the charging set-up which consists of two rectangular steel plates connected by a steel wire and having a separation of $d$ between them placed directly below the crucible. The charging plates were directly connected to a high voltage generator. The plates were electrically insulated from the rest of the equipment by layers of high alumina insulation. A gap, $h$, between the crucible and charging plate also helped to effectively isolate the charging plate electrically when heated to high temperatures. This gap, for effective charging of the droplets, should lie within the jet break-up distance, $L$. The jet break-up distance for UDS tin droplets was determined by Yim [96] to vary between 2 and 6 mm depending on the experimental parameters such as jet velocity, pressure difference between the crucible and the chamber, oxygen content in the chamber and the molten metal properties such as surface tension, wettability, etc. The details of the experimental set-up of the charging system indicating the position of the charging plates in the UDS set-up are shown in Figure 4.2.

![Figure 4.1: Schematic showing the position of charging plates w. r. t. the jet break-up distance.](image)
4. Charging of UDS Droplets at High Temperatures

Figure 4.2: Details of positioning the charging plate in the UDS chamber; (a) Schematic showing front view set-up of charging set-up, (b) Photograph of top view of charging set-up.
4. Charging of UDS Droplets at High Temperatures

Thus nitrogen may be expected to be stable up to temperatures of 1500 K [86-95]. Other factors such as the uniformity of the electric field, presence of impurities, oil vapors and metal fumes during spraying in UDS experiments may appreciably affect the breakdown conditions. Hence it was difficult to correctly establish a critical breakdown limit from the mentioned literature. For safety, 1500 K (~ 1200 °C) was taken as the upper limit to be used for charging UDS experiments in this investigation.

A voltage between 200 V and 500 V was applied to the charging plates which creates a charge of +q on the charging plates. The droplets, generated within the electric field of the charging plates, acquire a charge -q on them. As they travel away from the charging plates, the repulsion force between the droplets prevents them from merging. Hence, unmerged droplets can be collected. Experiments were performed for various gap distances of 8 mm to 28 mm. To study the charging behavior of droplets, the droplets can either be quenched in oil or collected in-flight on a substrate. In this study the use of oil for quenching droplets was avoided due to issues of possible arcing/discharge aided by oil vapors, between the charging plates. Hence the droplets were collected on a steel substrate as a deposit to study the scatter of the droplets as a function of the charging conditions. Charging was conducted during spraying while the induction furnace was operating. This caused a lag of a few volts, as measured by a multimeter, due to the overlapping electric fields of the charging plates and induction coils. To prevent any interference to the induction heater, the multimeter measured/controlled the current in the charging plates and fixed it at 0.53 A for all experiments.
4. Charging of UDS Droplets at High Temperatures

4.3 Experimental Results

Initial experiments with $\beta$-brass were unsuccessful due to the evaporation of zinc at such high temperature which short-circuited the electrical connections of the charging set up. Thus omitting brass, experiments with copper were only focused.

For optimum charging of the droplets, charging plates need to be placed close to the jet breakup length. Figure 4.3 shows the snapshot of a UDS experiment indicating a jet break-up length of approximately 3 - 5 mm. Thus the distance between the crucible and charging plates was fixed at 3 mm and the thickness of the charging plates at 5 mm for all experiments. Figure 4.4 shows the simulated temperature - time profile of the droplets which indicates that they were mushy at a flight distance of 0.30 m. The simulation was done with the in-flight solidification model described in Chapter 3. They were collected as deposits on a moving substrate with 10 alternating passes. The deposits were collected at various voltages and then the results compared, as discussed below.

Figure 4.5 shows the deposits obtained by charging Cu droplets at various conditions. Table 4.3 shows the experimental parameters used to obtain the deposits. The mushy droplets when collected on a moving substrate form of a deposit. The spread of the droplets due to the charging is clearly observed as the width of the deposit. Thus it is a convenient method to characterize the spread due to charging of the droplets [6, 56]. The width and height of the deposits obtained at various charging conditions were characterized.
4. Charging of UDS Droplets at High Temperatures

Figure 4.3: Photograph of spraying indicating jet break-up distance.

Figure 4.4: Solidification behavior of 300 μm Cu UDS droplets under various conditions of charging (d = 10 mm, N₂ atm).
Figure 4.5: Deposits obtained by charging 300 μm Cu droplet in various conditions (a) deposit at 0 V, (b) deposits for d = 14 mm, (c) deposits for d = 10 mm, (d) deposits for d = 8 mm.
It was observed that even with no charging, as shown in Fig 4.5 (a), the deposits obtained had a minimal width. This natural scatter of the droplets without any charging is mostly due to the gas movements inside the chamber. Since this disturbance may vary with the experimental conditions, a number of such deposits were collected without any applied voltage and average values width and height were obtained. This width, due to the natural disturbance, was subtracted from the width of the deposits obtained with charging to clearly illustrate the effect of applied voltage on the droplets. The experiments with a gap $\geq$ 14 mm yielded deposits which did not show appreciable increase in spray cone width with charging. Figure 4.6 shows the trend of increasing spray cone width with increasing voltage and decreasing gap for experiments performed with a gap $\leq$ 14 mm.

To illustrate the shape of the deposits, the width and height of the deposits were fitted to a Gaussian curve, $y = y_o + Ae^{-0.5 \frac{(x-x_o)^2}{w}}$ where $A$ is the standard deviation in height and $w$ is the variance, which is the width of the deposit at the midpoint of the profile, $(x_o, y_o)$. The spray cone width of the deposit is roughly twice (exactly $2\sqrt{2\cdot\ln 2}$ times) the variance, $w$, of the profile. Figures 4.7 and 4.8 show the profiles of the droplets which indicate an increasing width and corresponding decreasing height with increasing voltage for each of the cases.
4. Charging of UDS Droplets at High Temperatures

Table 4.3  UDS conditions used for charging 300 μm diameter copper droplets.

<table>
<thead>
<tr>
<th>Gap, d (mm)</th>
<th>Orifice Diameter (μm)</th>
<th>Spraying Temp (K)</th>
<th>Frequency (kHz)</th>
<th>ΔP (kPa)</th>
<th>O₂ content (ppm)</th>
<th>Voltage (V)</th>
<th>No. of Passes</th>
<th>width (mm)</th>
<th>height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>168 μm</td>
<td>1470</td>
<td>3.05</td>
<td>89.6</td>
<td>12</td>
<td>200</td>
<td>10</td>
<td>3.5</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>10</td>
<td>3.7</td>
<td>7.8</td>
</tr>
<tr>
<td>10</td>
<td>165 μm</td>
<td>1450</td>
<td>3.08</td>
<td>89.6</td>
<td>10</td>
<td>300</td>
<td>10</td>
<td>4.8</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400</td>
<td>10</td>
<td>5.8</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>10</td>
<td>6.7</td>
<td>5.7</td>
</tr>
<tr>
<td>8</td>
<td>167 μm</td>
<td>1450</td>
<td>3.05</td>
<td>90.2</td>
<td>9.5</td>
<td>300</td>
<td>10</td>
<td>7.1</td>
<td>5.2</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>400</td>
<td>10</td>
<td>9.9</td>
<td>3.4</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>500</td>
<td>10</td>
<td>11.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Figure 4.6: Width of the deposit for various charging conditions.
4. Charging of UDS Droplets at High Temperatures

Figure 4.7: Profile of deposits made by 10 passes of 300 μm Cu UDS droplets for various voltages collected at z = 0.3 m ($\Delta T = 100$ K, $d = 10$ mm).

Figure 4.8: Profile of deposits made by 10 passes of 300 μm Cu UDS droplets for various voltages collected at z = 0.3 m ($\Delta T = 100$ K, $d = 8$ mm).
4. Charging of UDS Droplets at High Temperatures

4.4 Simulation

The in-flight solidification model [7] was used to calculate the thermal state of pure copper droplets. The effect of charging the droplets was incorporated as explained below. The parameters for calculating the charge on the droplets was adapted from Abel [55], who used a similar in-flight solidification model to simulate the behavior of charged Sn droplets. The inputs used for the model and the simulation results are discussed below.

The charging set-up is considered here as a parallel plate capacitance with a distance, \( d \), between the parallel plates. The charge per droplet, in this case, was calculated as:

\[
q_d = \frac{2\pi \varepsilon_0 \lambda_d V}{\kappa + \ln \left( \frac{d}{d_d} \right)}
\]  

(4.2)

where \( \kappa \) is the correction factor for the parallel plate arrangement (\( \kappa = 0.423065 \) for \( d_d = 300 \mu m, d = 8 \text{ mm} \) and \( \kappa = 0.430500 \) for \( d_d = 300 \mu m, d = 10 \text{ mm} \)), \( \varepsilon_0 \) is the permittivity of free space, \( \lambda_d \) is the wavelength of perturbation and \( V \) is the voltage applied. The correction factor was derived by using the method of images (see Appendix C) provided for a line of charges between two parallel conducting plates [55, 82, 96]. The correction factor depends on the droplet diameter and the gap between the plates and must be calculated individually for each experimental condition.
The motion of the charged droplet was modeled using the force balance equation following the scheme used in previous studies. The columbic force between the droplets is given as:

$$\vec{F}_c = \frac{1}{4\pi\varepsilon_0} \sum_{j=1}^{n} \frac{q_i^2 q_j^2}{r_{ij}^2} |\vec{r}_{ij}|$$  \hspace{1cm} (4.3)

The electrostatic force will scatter the droplets equally in both x and y direction which gives a spray cone, i.e., the droplets tend to move away from each other in a spray cone as they travel away from the orifice. The scatter in the x-direction can be calculated from

$$m \frac{dx_i^2}{dt} = \frac{1}{8} C_s \pi \rho_s d_j^3 \frac{dx_j}{dt} \sqrt{\left(\frac{dx_i}{dt}\right)^2 + \left(\frac{dy_i}{dt}\right)^2 + \left(\frac{dz_i}{dt}\right)^2} + \frac{1}{4\pi\varepsilon_0} q_i^2 \sum_{j=1}^{n} \Delta x_{ij}$$  \hspace{1cm} (4.4)

where $\Delta x_{ij}$ is the x-distance between the $i^{th}$ and $j^{th}$ droplets. The droplets scatter as they travel away from the orifice. The pattern for scattering has been assumed as random. Patterns for scattering may also be considered to be sinusoidal as done by Passow [6] for Sn-5mass%Pb droplets.

Figures 4.9 and 4.10 show the calculated spray cone width plotted against the flight distance for various voltages. It is observed that the predicted spray cone width increases slowly with the flight distance initially and reaches a somewhat steady state with almost constant velocity for longer flight distances. The simulated results, however, neglect the small flattening effect of the droplets due to deformation as they impinge on the substrate as it is negligibly small in comparison to the spray cone width.
4. Charging of UDS Droplets at High Temperatures

Figure 4.9: Spray cone width vs. flight distance of 300 μm Cu UDS droplets for various voltages (ΔT = 100 K, d = 10 mm).

Figure 4.10: Spray cone width vs. flight distance of 300 μm Cu UDS droplets for various voltages (ΔT = 100 K, d = 8 mm).
4. Charging of UDS Droplets at High Temperatures

4.5 Discussion

The experimental results, as expected, show an increase in deposit width with increasing applied voltage and decreasing charge plate gap. This indicates that the droplets were charged and thus affected by the variations in charging conditions. Thus it was indeed possible to charge copper droplets in nitrogen atmosphere at around 1473 K (melt temperature). This indicates that with suitable charging conditions it is possible to prevent in-flight merging in copper. Due to the limitations of the chamber height it was not possible to carry out complete solidification of copper droplets in-flight, without oil, and hence this was not attempted.

Figures 4.11 and 4.12 show the spray cone width vs. voltage for d = 8 mm and 10 mm to compare the simulation results against the experimental results. The simulated spray cone width increases rapidly with increasing voltage. The experimental results, on the other hand, show a much restrained increase in the deposit width with increasing voltage for both cases, d = 8 mm and 10 mm. This deviation of the experimental and simulated results could be attributed to the ionization of nitrogen at the operating temperature.

Gases at room temperature contain some amount of free electrons due to cosmic rays and natural radioactive degeneration which increases with increasing temperature by collision and photo emission. It has been reported that the ionization probability of nitrogen molecules increases with increasing temperature (heated iron surface) [97]. This may have caused a weak non-sustaining discharge
that disrupted the potential between the electrodes [98]. Other minor causes of deviation may be due to insufficient charging of the droplets by the electrostatic field or loss of charge of the droplets as they travel away from the charging plates. The induced charge on the droplets may have been reduced due to the alteration of the charging field due to the presence of the electro-magnetic field of the induction heater and/or presence of impurities (like oxides and soot) on the charging plates which act as protuberances and somewhat distort the field [98]. It is expected that in actual practice, due to the above mentioned reasons, the results deviate from the simulated results with increasing spraying time and spraying temperature.
4. Charging of UDS Droplets at High Temperatures

Figure 4.11: Spray cone width vs. voltage for 300 μm Cu UDS droplets collected at F.D. = 0.3 m (ΔT = 100 K, d = 10 mm).

Figure 4.12: Spray cone width vs. voltage for 300 μm Cu UDS droplets collected at F.D. = 0.3 m (ΔT = 100 K, d = 8 mm).
4. Charging of UDS Droplets at High Temperatures

Thus the results of the experiments to charge copper droplets in nitrogen indicate an increased spray cone width with increasing applied voltage and decreasing gap between the electrodes. For 300 μm droplets, an appreciable increase in spray cone width was obtained for a charging potential 200 V – 500 V and gap < 14 mm. This indicates that the copper droplets were successfully charged by the applied voltage. Thus in-flight merging of copper droplets may be prevented by suitably charging them in nitrogen atmosphere.

The spray cone width of the droplets was simulated using the in-flight solidification model for pure metal UDS droplets. The experimental results were in the same order as the simulated results and agreed well with the predictions made by the model, although the predicted results overestimated the spray cone width. This is expected as the model does not address the ionization probability of the gas molecules with increasing temperature.

The results confirm that charging of copper droplets can be safely done up to 1473 K (melt temperature) in nitrogen gas. To avoid issues with arcing/discharge in the charging field, oil was not used to quench the droplets rather the spray cone width was measured by collecting deposits on a moving substrate.
5 Production & Characterization of ASTM F75 UDS Droplets

ASTM F75 alloy is a bio-compatible cobalt-chromium-molybdenum alloy having the chemical composition shown in Table 5.1. It has high wear resistance, good strength and excellent biocompatibility and is used to manufacture artificial dental, hip and knee replacements [99-101].

A novel method for using the alloy as a bio-implant involves fabricating a porous mating surface for the bone tissues to grow into for enhanced osseointegration (attachment of the bone to the implant). The osseointegration surface is fabricated by sintering balls of diameter 300-700 μm to obtain a porous surface [102]. It thus anchors the implant firmly and makes its density and strength similar to that of the human bone. This study establishes the parameters needed for the production of these balls by the UDS process.

| Table 5.1 Chemical composition of ASTM F75 alloy (in mass %). |
|-----------------|-------|---------|----|---|---|---|---|---|
| Cr   | Mo   | Mn    | Si  | Ni | Fe | C  | Co |     |
| 28   | 5    | 1     | 1   | 0.5| 0.35| 0.3| Balance |

5.1 Literature Survey

Implants using ASTM F75 alloy are typically metal-on-metal (MOM), ball and socket type of joints. In spite of improved implant designs for reduced wear and good lubrication, there are clinical reports for the implants that show an appreciable amount of Co and Cr ions that have been leached into the body due to corrosion and mechanical wear [101, 105, 106]. Although the wear in the
osseointegration surface is limited, the amount of metal ions strayed into the human body, even due to chemical activity, is significantly beyond the permissible upper limit [101, 106]. Thus, implants with higher strength and better wear resistant properties need to be developed. For porous implants, the droplets need to possess higher strength and smoother surface morphologies that reduce the MOM wear [101, 106].

The Co-based alloys are used to produce not only balls for biomedical applications but are also drawn into wires and ribbons [107, 108] and forged into shapes [109]. Chiba et al. produced fine wires of Co-29mass% Cr-8 mass% Mo by a melt spinning method which show good mechanical strength and an effective method to produce the alloy for bio-medical applications [107]. Owing to the popularity of Co-based alloys in bio-medical implants a number of investigations have been published to date, an overview of which is presented below.

Rapid quenching of the Co-28 mass% Cr-5 mass% Mo alloy usually results in the formation of the metastable γ phase and the room temperature-stable ε phase is usually suppressed [78, 79]. However, the formation and stability of the phases depend on the specific alloying composition, processing conditions and the final microstructure. Escobedo et al. have reported on the formation of γ phase with two kinds of carbides precipitated in the matrix, M₆C and M₂₃C₆, due to dissolution of nitrogen in the matrix which stabilizes the formation of both types of the carbides in ASTM F75 alloy [110]. Ramirez et al. [111] have similarly shown the precipitation of M₂₃C₆ carbides in σ phase (tetragonal) when the alloy was quenched during directional solidification. Chiba et al. [107] have reported a
rapidly quenched microstructure with mostly $\gamma$ phase strengthened by precipitates of carbides at grain boundaries in melt spun wires of the alloy. The effects of microstructure on the mechanical properties of Co-Cr-Mo alloys have also been investigated by many researchers in this area. Varano et al. [112] have reported on the effects of carbon addition in the Co-Cr-Mo alloy which apparently strengthens the matrix due to carbon dissolution. The Co-Cr-Mo implants under both static and dynamic loading conditions show a significantly increase in strength due to an increase in the amount of carbides and simultaneously decreased size of carbide precipitates in implants manufactured by forging and sintering [113, 116]. The fatigue strength of the implants, however, depends on the surface conditioning such as polishing and shot peening [113]. Semlitsch [113] provides a thorough study on the processing, structure and properties of commercially available Co-Cr alloys for bio-medical applications.

Recent investigations with Co-Cr-Mo alloys show that there are some studies on powder production techniques for the alloys but most of the literature is concentrated towards using the alloys in cast, wrought or forged form. This is mostly because these are the commercial production routes preferred by the industry. However, production of porous implants does require formation of balls or spheres. Droplets are commercially manufactured through a centrifugal atomization technique, particularly the plasma rotating electrode process (PREP) [103, 104]. This process produces droplets in a narrow but still non-uniform size distribution. However, more importantly it is difficult to control the thermal history, supercooling and microstructure of the droplets. Thus, desired properties such as homogeneity, refined grain size and strength are not properly reflected in
the droplets. To this end, mono-size droplets produced by the uniform-droplet spray (UDS) process may prove better suited because of the uniform rapid solidification microstructure expected in them. Thus it is most useful to establish the experimental process parameters and characterize the microstructure. The present work is also aimed at investigating the solidification behavior of the alloy by considering the nucleation kinetics and dendrite fragmentation behavior of the droplets.

5.2 Experimental Procedure

The experimental set-up used for the production of ASTM F75 droplets is discussed in detail in Chapter 2. The modifications outlined in the chapter enabled the apparatus to work at around the melting point of ASTM F75, 1682 K, without any problem. Charging of the droplets in He atmosphere at these temperatures, 1600 – 1800 K, is not safe owing to the possibility of ionizing the gas and causing break-down of the gas, as explained in Chapter 4. Hence, charging of the ASTM F75 droplets was not been attempted here.

Table 5.2 lists the relevant conditions used for obtaining the mono-sized droplets. The alloy, obtained in the form of an ingot, was cut into small pieces ~ 25 mm x 25 mm x 10 mm. The pieces are ultrasonically cleaned with acetone and charged into the crucible. Approximately 100 g. of the material was used for each experiment. The droplets were quenched in silicone-based vacuum pump oil.
Table 5.2 Experimental Conditions for Production of ASTM F75 Droplets.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Droplet size</td>
<td>640 μm</td>
</tr>
<tr>
<td></td>
<td>300 μm</td>
</tr>
<tr>
<td>Orifice diameter</td>
<td>381 μm</td>
</tr>
<tr>
<td></td>
<td>168 μm</td>
</tr>
<tr>
<td>Melt temperature</td>
<td>1520 °C</td>
</tr>
<tr>
<td></td>
<td>1520 °C</td>
</tr>
<tr>
<td>Frequency of perturbation</td>
<td>3.01 kHz</td>
</tr>
<tr>
<td></td>
<td>3.50 kHz</td>
</tr>
<tr>
<td>Gas</td>
<td>He</td>
</tr>
<tr>
<td></td>
<td>He</td>
</tr>
<tr>
<td>Oxygen content</td>
<td>9.60 ppm</td>
</tr>
<tr>
<td></td>
<td>10.50 ppm</td>
</tr>
<tr>
<td>Ejection pressure</td>
<td>90 kPa</td>
</tr>
<tr>
<td></td>
<td>94 kPa</td>
</tr>
<tr>
<td>Flight distance</td>
<td>0.36 m</td>
</tr>
<tr>
<td></td>
<td>0.36 m</td>
</tr>
</tbody>
</table>

The droplets quenched in oil were ultrasonically cleaned in acetone, sieved, sectioned, polished and etched to observe their microstructures. The droplets were cold-mounted and ground systematically using 300 to 2000 grit emery paper and final-polished with 0.05 μm alumina powder to examine their microstructure. An etching solution of HNO₃, CH₃COOH, HCL and H₂O in the volume ratio of 1:1:4:1 was swabbed for 30 seconds on the cross-sections to reveal their microstructures.

The experimental evaluation of the nucleation temperature was done as explained in Chapter 2. Table 5.3 shows the blade positions used for the quenching experiments. Two sets of quenching experiments were performed to determine the nucleation temperatures of 300 μm and 640 μm droplets. A third verification experiment, with 460 μm droplets, was performed to verify the predicted results by the nucleation kinetics model [33], as described in Chapter 3.
### Table 5.3 Blade Positions and Respective Droplet Conditions.

<table>
<thead>
<tr>
<th>Flight distance</th>
<th>Remarks</th>
<th>Flight distance</th>
<th>Remarks</th>
<th>Flight distance</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expt. – I (640 μm droplets)</td>
<td>15.0 cm</td>
<td>molten</td>
<td>14.5 cm</td>
<td>molten</td>
<td>15.0 cm</td>
</tr>
<tr>
<td></td>
<td>16.5 cm</td>
<td>molten</td>
<td>16.0 cm</td>
<td>molten</td>
<td>17.0 cm</td>
</tr>
<tr>
<td></td>
<td>18.0 cm</td>
<td>partially solidified</td>
<td>18.0 cm</td>
<td>partially solidified</td>
<td>19.0 cm</td>
</tr>
<tr>
<td></td>
<td>20.5 cm</td>
<td>partially solidified</td>
<td>20.0 cm</td>
<td>partially solidified</td>
<td>21.0 cm</td>
</tr>
<tr>
<td></td>
<td>22.0 cm</td>
<td>partially solidified</td>
<td>22.0 cm</td>
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<td>23.0 cm</td>
</tr>
<tr>
<td></td>
<td>24.5 cm</td>
<td>partially solidified</td>
<td>24.0 cm</td>
<td>-</td>
<td>25.0 cm</td>
</tr>
<tr>
<td></td>
<td>26.5 cm</td>
<td>-</td>
<td>26.0 cm</td>
<td>-</td>
<td>27.0 cm</td>
</tr>
<tr>
<td></td>
<td>28.5 cm</td>
<td>-</td>
<td>28.0 cm</td>
<td>-</td>
<td>29.0 cm</td>
</tr>
<tr>
<td></td>
<td>40.5 cm</td>
<td>partially solidified</td>
<td>43.8 cm</td>
<td>completely solidified</td>
<td>43.8 cm</td>
</tr>
</tbody>
</table>
5.3 Results

5.3.1 Characterization of Droplets

Figure 5.1 shows the optical micrographs of 300 μm and 640 μm uniform droplets produced by the UDS process. The droplets are shown to be uniform in size with smooth external surfaces, which is usually observed with UDS droplets.

The surface morphology of the droplets was examined by secondary electron imaging in a scanning electron microscope (SEM). The 640 μm and 300 μm droplets, shown in Figures 5.2 (a) and (b), are both characterized by dark spots on the surfaces of the droplets. Presumably, these are surface carbides as reported in a previous characterization study of this alloy [113, 115]. The exact composition of these carbides is not known, although M_{23}C_{6} is highly likely from the previous study [115].

Figures 5.3 and 5.4 show the microstructures of 640 μm and 300 μm droplets, respectively. The microstructure of 640 μm droplet is characterized by well-developed dendrites. Figure 5.3(b) present a high magnification micrograph which shows dendritic grains of size about 270 μm. The microstructure of 300 μm droplets is characterized by highly refined grains. The average grain size determined from Figure 5.4 (b) is around 4 μm.
Figure 5.1: Optical Micrographs of ASTM F75 UDS droplets, (a) UDS 640 μm droplets, (b) UDS 300 μm droplets.
Figure 5.2: SEM micrographs of UDS droplets, (a) 640 μm droplets, (b) 300 μm droplets.
Figure 5.3: Dendritic microstructure of 640 μm UDS droplets quenched in He, (a) low magnification, (b) high magnification.
Figure 5.4: Microcrystalline microstructure of 300 μm UDS droplets cooled in He (a) low magnification, (b) high magnification.
5.3.2 X-Ray diffraction patterns of droplets

The phases present in the solidified droplets were identified from the X-ray diffraction patterns obtained from the polished cross-sections of the droplets. Figure 5.5 shows the XRD patterns of the sectioned UDS 640 μm and 300 μm. The dominant phase (matrix) is the γ-Co (fcc) with interdendritic M23C6, cobalt-chromium-molybdenum carbide phase and bcc Cr solution. It is observed for 300 μm droplets that the γ-Co peaks are much broader and smaller than for 640 μm droplets, indicating a high degree of grain refinement in the smaller droplets.

The γ-Co peaks for 300 μm droplets are also shifted to lower angles by 2 - 5°, with respect to those for 640 μm droplets, indicating an increase in lattice parameter due to supersaturation of chromium in the 300 μm droplets crystal lattice. This is also shown by the fact that the Cr peaks are very prominent in 640 μm droplets. However, they are either absent or indistinguishable in 300 μm droplets, indicating increased solubility of Cr in Co for 300 μm droplets than in 640 μm droplets. The M23C6 metal carbide is present in both 640 μm and 300 μm droplets although its formation in the 300 μm droplet is suppressed as seen from the much smaller carbide peaks for the smaller droplets.
Figure 5.5: XRD patterns for UDS droplets cooled in He.
5. Production & Characterization of ASTM F75 UDS Droplets

5.3.3 Nucleation distance

Figures 5.6, 5.7 and 5.8 show the splats collected from the quenching experiments for 640 μm, 460 μm and 300 μm droplets, respectively. The flight distance at which the droplets nucleated is estimated from their typical morphologies. It is observed that the splats collected at shorter flight distances are elongated without any particular shape due to the deformation caused by the rotational effect of the quenching blades. However, those at longer flight distances have a pronounced hump with a somewhat elongated tail. The hump is found to increase proportionately with increasing flight distance. Thus it is indicative that the splats with the hump and tail morphology indicate a semi-solid state while the elongated morphology indicates completely molten state of the droplet when it impinges on the rotating blades.

Table 5.4 shows the ranges of nucleation distances of the droplets determined from the splat morphologies. At the upper bound of the range (0.16 m) for 300 μm droplets, the collected splat, Figure 5.8(a), does not have as much elongation as that of the splats of 460 μm or 640 μm droplets. Yet it is highly likely that the 300 μm droplet was fully molten at 0.16 m. It was most probably supercooled to a much greater degree than the 460 μm or 640 μm droplets. Such a supercooled state would cause very rapid solidification before allowing the droplets to undergo complete deformation into an elongated shape.

The nucleation distances for 640 μm and 300 μm droplets are used to numerically evaluate the nucleation kinetics model explained in Chapter 3. The nucleation distance determined experimentally for 460 μm droplets was used to
verify the results predicted by the nucleation model. The simulation model, as described in Chapter 3, is used below to determine the supercooling in these droplets.

Table 5.4 Nucleation Distances Determined for Splat Morphologies.

<table>
<thead>
<tr>
<th>Droplet Diameter</th>
<th>Nucleation Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>640 μm</td>
<td>0.17 ± 0.013 m</td>
</tr>
<tr>
<td>460 μm</td>
<td>0.18 ± 0.010 m</td>
</tr>
<tr>
<td>300 μm</td>
<td>0.17 ± 0.010 m</td>
</tr>
</tbody>
</table>
Figure 5.6: Microstructure of splats obtained by quenching 640 μm droplets
(a) z = 0.165 m, (b) z = 0.18 m, (c) z = 0.225 m.
5. Production & Characterization of ASTM F75 UDS Droplets

Figure 5.7: Microstructure of splats obtained by quenching 460 μm droplets, (a) z = 0.17 m, (b) z = 0.19 m, (c) z = 0.23 m.
Figure 5.8: Microstructure of splats obtained by quenching 300 μm droplets (a) $z = 0.16$ m, (b) $z = 0.18$ m, (c) $z = 0.22$ m.
5. Production & Characterization of ASTM F75 UDS Droplets

5.4 Simulation

The simulation models explained in Chapter 3 were used to predict the solidification path of the droplets. The initial liquid cooling and the temperature at which nucleation takes place in the droplet were simulated with the droplet nucleation model by Wu and Ando [33] with the aid of an in-flight droplet cooling model, which is a part of the in-flight solidification model [7]. The procedure for the above is explained in Chapter 3. The droplet nucleation model, with the aid of a few sets of reference data, can predict nucleation temperature under any cooling conditions, producing continuous cooling transformation (CCT) diagrams of internal nucleation of droplets.

With the predicted nucleation kinetics, the subsequent paths of droplet solidification were calculated with the in-flight droplet solidification model [7] described in Chapter 3. The dendrite growth behavior during the recalescence was predicted with the DA model [53] by approximating ASTM F75 as a Co-28mass%Cr binary alloy, and the calculated growth kinetics were incorporated in the in-flight droplet solidification simulation.

5.4.1 Droplet nucleation kinetics

Figure 5.9 shows the nucleation temperatures of the 640 μm, 460 μm and 300 μm droplets, estimated from the nucleation distances in Table 5.4, using the cooling schedules generated from the in-flight solidification model [7]. Table 5.5 gives the nucleation temperatures of the droplets numerically. The nucleation temperatures, evaluated experimentally for two sets of data for 640 μm and 300 μm.
5. Production & Characterization of ASTM F75 UDS Droplets

\[ \mu m, \text{i.e., Expts. I and II, respectively, were used to solve Equation (3.40). Table 5.6 shows the values of the material specific constants } M^* \text{ and } N^* \text{ obtained.} \]

![Figure 5.9: Simulated cooling schedule indicating nucleation temperature.](image)

<table>
<thead>
<tr>
<th>Droplet Size</th>
<th>Nucleation Temperature</th>
<th>Supercooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>640 ( \mu \text{m} )</td>
<td>( \sim 1590 \pm 10 \text{ K} )</td>
<td>92 K</td>
</tr>
<tr>
<td>460 ( \mu \text{m} )</td>
<td>( \sim 1503 \pm 15 \text{ K} )</td>
<td>179 K</td>
</tr>
<tr>
<td>300 ( \mu \text{m} )</td>
<td>( \sim 1305 \pm 22 \text{ K} )</td>
<td>377 K</td>
</tr>
</tbody>
</table>
Figure 5.10 shows the CCT curves calculated for the heterogeneous nucleation of 300 μm and 640 μm droplets of the alloy. It is assumed that the nucleation of the droplets is internal and that the interfacial energy, γ, is temperature independent. Also shown in Figure 5.10 are the ranges where the CCT curves should be as calculated from the ranges of the experimentally determined nucleation distances.

Data from experiment III, with 460 μm droplets, were used to verify the predicted nucleation temperature by the computed CCT curves. The predicted nucleation temperature determined from the nucleation model [33], $T_{N(\text{cct})}^{460\mu m}$, is $\sim 1522 \pm 15$ K which matches closely with the experimentally obtained nucleation temperature, $T_{N}^{460\mu m} \sim 1503 \pm 15$ K. Hence the model predictions are cross-verified and the calculated CCT curves likely give nucleation temperatures for other droplet diameters and cooling conditions as well.

Table 5.6  Computed Values of $M^*$ and $N^*$.

<table>
<thead>
<tr>
<th>Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M^*(K^2m^3s^{-1})$</td>
<td>$7.590\times10^{18}$</td>
</tr>
<tr>
<td>$N^*(K^3)$</td>
<td>$4.206\times10^7$</td>
</tr>
</tbody>
</table>
Figure 5.10: CCT curves drawn for ASTM F75 droplets.
5. Production & Characterization of ASTM F75 UDS Droplets

### 5.4.2 Fragmentation Behavior

The fine equiaxed microstructure found in the 300 μm droplets is indicative of dendrite fragmentation that may result at certain ranges of droplet supercooling. Thus the fragmentation of dendrites in ASTM F75 alloy was investigated using the fragmentation model by A. Karma [40]. The details of the model and its application to ASTM F75 alloy are explained in Chapter 3.

The break-up time is calculated using Equation (3.45). The amplification parameter, $S$, is calculated to be $\sim 0.25$, which suggests that surface tension is probably the dominant driving force for fragmentation. The value of $R(\Delta T)$ is estimated for each of the droplets from the average dendrite radius observed in the microstructure of the droplets in Figures 5.11 and 5.12. The geometrical parameter, $z^*$, is the ratio of the trunk radius to the tip radius of the dendrites. Since coarsening of the fragmented droplets is inevitable there is some variance between the calculated $z^*$ and that which correlates in the calculation of the model. The parameters used in the calculation of the $\Delta t_{bu}$ values are listed in Table 5.7. The $\Delta t_{pl}$ values are calculated from the in-flight solidification model [7]. The predictions were verified against the microstructures observed in the droplets as explained below.

<table>
<thead>
<tr>
<th>$\Delta T$ (K)</th>
<th>640 μm (He)</th>
<th>300 μm (He)</th>
<th>460 μm (He)</th>
<th>300 μm (Ar) Verify</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta T_p$ (K)</td>
<td>92 K (exp)</td>
<td>377 K (exp)</td>
<td>179 K (exp)</td>
<td>132 K (CCT curve)</td>
</tr>
<tr>
<td>$R_{tip}$ (m)</td>
<td>$1.43 \times 10^{-7}$</td>
<td>$5.58 \times 10^{-8}$</td>
<td>$1.03 \times 10^{-7}$</td>
<td>$1.19 \times 10^{-7}$</td>
</tr>
<tr>
<td>$R(m)$</td>
<td>$3 \times 10^{-6}$</td>
<td>$1 \times 10^{-6}$</td>
<td>$2 \times 10^{-6}$</td>
<td>$2 \times 10^{-6}$</td>
</tr>
<tr>
<td>$z^*$</td>
<td>21</td>
<td>18</td>
<td>19</td>
<td>16</td>
</tr>
</tbody>
</table>
5. Production & Characterization of ASTM F75 UDS Droplets

Figure 5.11: Optical micrographs of 640 μm droplet cooled in He gas.

Figure 5.12: Optical micrographs of 300 μm droplets cooled in He gas.
Figures 5.13 and 5.14 show the combined plots of $\Delta t_{bu}$ and $\Delta t_{pl}$ vs. supercooling for 640 μm and 300 μm droplets cooled in He atmosphere, respectively. The plots show four distinct regions. The plot in Figure 5.13 shows that at very low supercoolings, < 30 K, and intermediate supercoolings, 70 – 140 K, $\Delta t_{bu} > \Delta t_{pl}$ indicating the droplets nucleating in these ranges of supercooling do not have sufficient time to undergo fragmentation. However, at supercoolings between 30 – 70 K and > 140 K, $\Delta t_{bu} < \Delta t_{pl}$, which indicates the dendrites would fragment when nucleating in these ranges of supercooling. Similar interpretations can be made from Figure 5.14.

The calculated supercooling of 92 K for 640 μm droplets thus predicts no fragmentation of dendrites, whereas, the supercooling of 377 K for 390 μm droplets predicts fragmented dendrites. These predictions agree with the metallographic observations shown in Figures 5.11 and 5.12 which confirm the prediction of no fragmentation in 640 μm droplets whereas complete fragmentation of dendrites in 300 μm droplets.
5. Production & Characterization of ASTM F75 UDS Droplets

Figure 5.13: Computed dendrite break-up time vs. supercooling for 640 μm droplets cooled in He gas.

Figure 5.14: Computed dendrite break-up time vs. supercooling for 300 μm droplets cooled in He gas.
Figure 5.15 shows plots of $\Delta t_{bu}$ and $\Delta t_{pl}$ vs. supercooling for 460 $\mu$m droplets. At the experimentally determined supercooling of 179 K, $\Delta t_{pl} > \Delta t_{bu}$, which indicates a fragmented dendritic microstructure. Figure 5.16 shows the actual microstructure of 460 $\mu$m droplets cooled in helium atmosphere. The microstructure does indicate complete fragmentation of dendrites throughout the droplet volume.

The predictions have been further verified for 300 $\mu$m droplets cooled in argon atmosphere. Figure 5.17 shows the calculated plots. At the estimated supercooling of 132 K the model predicts no fragmentation. This is verified by the optical micrographs of 300 $\mu$m droplets, shown in Figure 5.18, which does show well developed dendrites in the droplet. This cross-verifies that the values of supercooling predicted by the nucleation kinetics model are correct.
5. Production & Characterization of ASTM F75 UDS Droplets

Figure 5.15: Computed dendrite break-up time vs. supercooling verified for 460 μm droplets cooled in He gas.
Figure 5.16: Optical micrograph of 460 μm droplets cooled in He gas, (a) low magnification, (b) high magnification.
Figure 5.17: Computed dendrite break-up time vs. supercooling verified for 300 μm droplets cooled in Ar gas.
Figure 5.18: Optical micrographs of 300 μm droplets cooled in Ar gas.
5.5 Discussion

This investigation provides an analysis on the rapid solidification behavior of ASTM F75 droplets through microstructural evaluation and comparison with simulated results to predict the microstructure of droplets for any cooling condition.

The characterization of the droplets show that the X-ray diffraction patterns of the droplets show increased supersaturation for 300 μm droplets than 640 μm droplets due to the effects of rapid solidification, as also reported by Chiba et al. [107]. Thus the UDS droplets are expected to have increased strength due to the effects of solid solution strengthening. The UDS ASTM F75 droplets were characterized essentially by γ-Co as the dominant phase with no presence of ε-phase. For the application of these droplets in implants, the ductile γ (fcc) phase is preferred rather than the ε (hcp) phase [112]. However, secondary processing such as heat treatment may partly or completely transform the γ phase to ε phase [114, 116].

Moreover, the microstructure also shows presence of metal carbides (M23C6) which is typically observed in high carbon Co-Cr-Mo alloys. The XRD indicates smaller and reduced volume fractions of carbides in 300 μm droplets than 640 μm droplets. The M23C6 interdendritic carbides are hard and stable in the matrix and thus when distributed in the UDS droplets provide increased strength to the droplets due to dispersion strengthening [113]. They also act as sites for grain boundary pinning which greatly reduces the probability of fcc to hcp
transformation [113]. The blocky surface carbides, also observed on the SEM micrographs of the droplets, on the other hand are more prone to third body abrasive wear and pull out and are thus undesirable. However, the use of the droplets to make a porous osseointegration site of the implant does not entail metal-on-metal wear action and thus the presence of the surface carbides is not expected to be a problem. Many researchers [114] advocate to reduce the C content in the alloy (< 0.5 mass %) which would suppress the formation of the blocky surface carbides [103, 114] However, this results in the formation of $\varepsilon$ phase, indicating that the effect of carbon supersaturation in the matrix is significant in stabilizing the $\gamma$ phase [103, 110].

The application of the nucleation kinetics model [33] to ASTM F75 UDS droplets shows that they can easily be supercooled to about 300 K resulting in microcrystalline grain structure. This was confirmed, by the fragmentation model [40], to occur due to the fragmentation of dendrite in the post-recalescence plateau period. The fragmented dendrites may act as growth centers of the equiaxed grains [38]. It was observed that for 300 $\mu$m droplets when cooled in helium produced completely fragmented dendrite whereas when cooled in Ar produced well-developed dendrites. The heat conductivity of He gas is almost four times higher than that in Ar which can supercool the droplets to a higher degree [14].

The consistency between predicted and metallographic observations suggests that the formation of microcrystalline microstructure in ASTM F75 droplets is indeed caused by fragmentation of dendrites. The fragmentation of
dendrites around the second transition supercooling was observed for ASTM F75. The transition is found to be sharp with completely fragmented dendrites occurring beyond the predicted transition supercooling and well developed dendrites found for supercoolings below that. The dominant driving force for fragmentation is found to be the surface tension in the solid-liquid interface. A number of papers report on the highly refined grain structure in rapidly solidified ASTM F75 alloy [102-116], but the fragmentation behavior of the dendrites has not been addressed by any.

The application of the nucleation kinetics model [33] and dendrite fragmentation model [40] to ASTM F75 UDS droplets shows good consistency between the predicted and experimentally obtained results. Thus by the application of experimental data to the nucleation kinetics model [33], CCT curves constructed for ASTM F75 may be applied to cooling conditions for droplet based manufacturing process such as gas atomization. And with the application of the fragmentation model [40] the droplet microstructure can also be predicted in such droplet-based manufacturing processes.
6 Production & Characterization of Silicon UDS Droplets

6.1 Background

Silicon is a widely studied material for its applications in the computer and semiconductor industry. The solid silicon in its natural state is a semiconductor with an energy band gap of 1.17 eV. However, in its liquid state it behaves like a metal, i.e., it conducts electricity and is strongly electro-magnetic [117]. Detailed molecular dynamics studies of supercooled silicon reveals that a liquid-liquid transitions occurs around 1100 -1200 K, below which a high density liquid with high co-ordination number transforms to a low density liquid with nearly tetrahedral structure [118, 119]. Although simulations have proved the existence of such transitions in silicon, experimental verification has not been achieved yet. Although the study of the solidification of silicon is pursued by many to understand the science better, the commercial focus on silicon revolves around low cost manufacturing methods of silicon for use in IC chips, transistors, photovoltaic cells, LCD displays, etc [120].

Recently, interest in silicon processing has grown with the concern for finding alternative energy sources. Solar energy is a clean and cheap form of energy that can be used to solve part of the energy crisis. Silicon in solar cells is used to trap the solar energy which is then converted to electrical energy and used as a DC power supply. Recently other materials such as cadmium telluride (CdTe) [121] and sulfosalts [122] such as copper indium/gallium diselenide (CIGS) are also being used in the production of thin-film solar cells. Conventionally, silicon is used in photovoltaic cells in the form of wafers. Silicon
single-crystals are theoretically the most efficient for energy harvesting. The production technique to grow perfect single crystals is thus sought after in research labs due to this. Whereas polycrystalline silicon wafers easily have an efficiency of approximately 17% [123], they are produced by slicing polycrystalline silicon ingots into thin wafers, approximately 100 μm thick [124]. Thin film solar cells, on the other hand, are more efficient with almost 20% efficiency but require a more extensive deposition process like PVD, etc., to grow them [123]. Although high efficiencies in silicon solar cells are certainly advantageous, the ease and low cost of production on the other hand are what draw the manufacturing companies to these technologies. Thus, although monocrystalline silicon is more efficient for use in solar cells they are not a necessity and are usually ditched in preference to polycrystalline or even amorphous (thin film) silicon for a better cost to efficiency ratio [144].

In making polycrystalline silicon wafers more efficient, research efforts are aimed at reducing point defects and dislocation density in them which act as recombination sites for the minority carriers [125, 126]. However, a more recent approach (1990’s) is to use silicon spheres produced directly from their melt. The spheres have higher surface area for exposure and are more economical in production without producing any of the waste that slicing wafers produces. The melt is atomized into spheres which are then cooled and assembled together with metallic contacts and used as a module in solar cells. However, producing completely spherical droplets of silicon has not been so easy and entailed a number of difficulties. Silicon, like water, expands on freezing, i.e., it has a negative volume change (10%) during solidification. This produces solidified
droplets that are highly deformed and sometimes broken due to the stress produced during crystallization. A number of research groups have investigated on this topic of the solidification behavior of silicon and correlated experimental findings and theoretical analysis on the anomalous solidification behavior of semiconductors. A brief discussion of their findings is presented below in Section 6.2. However, the use of spherical silicon droplets in solar photovoltaic cells is limited due to the dearth of development of droplet based manufacturing suited for this purpose. Thus it is useful to investigate on the solidification behavior of silicon UDS droplets, which depending on their size and process conditions may undergo solidification in a range of different paths.

6.2 Literature Survey

Typically semiconductors are non-metallic and they normally show facetted grain boundaries due to their high entropy of fusion, \( \sim 30 \text{ JK}^{-1}\text{mol}^{-1} \) [127, 81]. The first instance of metal like behavior of semiconductor materials was observed by Billig in molten germanium [128]. He found that by increasing the supercooling of the melt prior to solidification the microstructure of the solidified Ge showed less faceting. This was attributed to the change in the dendrite growth mechanism from lateral growth of \(<110>\) dendrites to continuous growth mode of \(<100>\) dendrites [128]. This was later also found in silicon solidification [129-139].

Investigations in this area have yielded much needed information about the solidification behavior of silicon. It has been observed by many that silicon droplets when solidified from the molten state have a non-spherical and irregular
6. Production & Characterization of Silicon UDS Droplets

shape [129]. It is generally observed that with increased supercooling the silicon droplets are more spherical in shape albeit with a horn-like structure. Nagashio et al. [129-131] have reported that splats quenched on silicon single crystalline wafers are polycrystalline and depending on the cooling conditions have various microstructures. The horn-like protrusions are also found to change with the prior supercooling. Lui et al. [132] have reported that highly supercooled boron-doped silicon droplets, with \( \Delta T > 250 \) K, exhibit a “tear” shape while droplets with lower supercooling are shaped like a “horn”. Jian et al. have discussed the effects of supercooling on the shape and deduced similar results with pure silicon [133].

The electromagnetic levitation studies of silicon were done to correlate the microstructure observed at various supercoolings [129-131, 134]. Since these studies are designed to get a broader picture of the solidification behavior of silicon, it is interesting to observe the actual solidification behavior that may be found in common thermal spraying processes. A study by Zeng et al. [135] shows the occurrence of twins in silicon droplets atomized in nitrogen. A similar study by Miller et al. [136] discusses on the experimental production of silicon droplets by the plasma rotating electrode process. They clearly establish the process parameters for obtaining silicon, but fail to characterize the droplet solidification behavior.

More importantly, these studies fail to completely evaluate the parameters for the formation of spherical silicon droplets produced by a thermal spray process. The present investigation thus addresses the conditions for dendritic growth in silicon droplets in a droplet based manufacturing process and also
evaluates the fragmentation behavior of the dendrites in silicon droplets with interest in finding conditions for the production of spherical silicon balls. The UDS process, ideally suited for such investigations, was employed in the present work.

6.3 Experimental Procedure

The experimental set-up described in Chapter 2 was used to produce the uniform droplets. The experimental parameters used to generate the uniform droplets are listed in Table 6.1. High purity (99.999%) silicon wafers were used as feed material for the experiment. The wafers were broken into small pieces, approximately 15 mm x 25 mm, and charged into the crucible. A charge of approximately 25 gm was used for each experiment. The pieces were ultrasonically cleaned and charged into the crucible.

It is to be noted that for smaller orifice sizes, a much higher superheat is needed to be able to spray the liquid silicon. For an orifice size of 252 μm, a superheat of ~ 150 °C and differential pressure of ~ 28 psi is needed to eject the molten material and for 168 μm, a differential pressure of 33 psi and a superheat of 220 °C are required. Liquid silicon has an anomalous increase in viscosity, from 0.7 mPa·s to 0.9 mPa·s in the temperature range 1420 – 1450 °C [141]. Thus a sufficiently high superheat is required to spray the melt easily.

The droplets were prepared for characterization by cleaning with acetone, mounting in epoxy and systematically grinding and polishing using emery paper. Cross-sections were mirror polished using a nap-less cloth (to minimize grain
6. Production & Characterization of Silicon UDS Droplets

pull-out by the fibers in the cloth) in 0.3 μm alumina slurry. The microstructure of
the droplets was revealed by etching with a mixture of HNO₃, HF and CH₃COOH
in the ratio (volume) 2:1:1 by swabbing it with a cotton tip for 5 - 7 seconds.

6.4 Results

6.4.1 Characterization of droplets

The surfaces of the silicon UDS droplets are not as smooth and spherical
as those observed for ASTM F75 UDS droplets in Chapter 5. The 550 μm
droplets are found to have jagged surface structure with pronounced faces and
edges and horn-like protrusions on the surface, Figure 6.1. The uneven and
irregular surfaces are commonly found in all silicon droplets formed by similar
rapid quenching methods [135, 136]. Silicon droplets, as explained before expand
on solidification (resulting in the formation of the protrusion) and thus have a lot
of internal stress which when released results in formation of cracks along the
surface of the droplets. These features are clearly seen in Figures 6.2 and 6.3,
which show SEM micrographs of 550 μm and 390 μm Si droplets, respectively.
6. Production & Characterization of Silicon UDS Droplets

Table 6.1  Experimental Conditions for Production of Si UDS Droplets.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Droplet size</td>
<td>550 µm</td>
</tr>
<tr>
<td></td>
<td>390 µm</td>
</tr>
<tr>
<td>Orifice diameter</td>
<td>252 µm</td>
</tr>
<tr>
<td></td>
<td>168 µm</td>
</tr>
<tr>
<td>Melt temperature</td>
<td>1580 °C</td>
</tr>
<tr>
<td></td>
<td>1640 °C</td>
</tr>
<tr>
<td>Frequency of perturbation</td>
<td>2.89 kHz</td>
</tr>
<tr>
<td></td>
<td>3.55 kHz</td>
</tr>
<tr>
<td>Gas</td>
<td>He</td>
</tr>
<tr>
<td></td>
<td>He</td>
</tr>
<tr>
<td>Oxygen content</td>
<td>9.60 ppm</td>
</tr>
<tr>
<td></td>
<td>10.50 ppm</td>
</tr>
<tr>
<td>Differential pressure</td>
<td>193 kPa (28 psi)</td>
</tr>
<tr>
<td></td>
<td>227 kPa (33 psi)</td>
</tr>
<tr>
<td>Flight distance</td>
<td>0.35 m</td>
</tr>
<tr>
<td></td>
<td>0.36 m</td>
</tr>
</tbody>
</table>

Figure 6.1:  Optical micrograph of 550 µm UDS silicon droplets.
6. Production & Characterization of Silicon UDS Droplets

Figure 6.2: SEM micrograph of 550 μm Si UDS droplet.

Figure 6.3: SEM micrograph of 390 μm Si UDS droplet.
Figures 6.4 and 6.5 show the cross-sectional microstructures of 800 μm and 550 μm droplets. The micrographs show grain boundaries in the droplets to consist of ledges that are indicated as sharp corners and lines in the microstructures. Literature shows that these are <110> dendrites that often nucleate as twin boundaries [129-136]. The <110> dendrites are sometimes reported also as H shaped, where the major growth direction is the direction of the arms [137]. In contrast, Figure 6.6 shows 390 μm droplets that have an microcrystalline grain structure with indications of formation of orthogonal <100> dendrites. Also, the 390 μm droplets show growth striations in the grains which indicate direction of the migrating interface in the droplets [137, 138]. The growth striations are usually found in Ge and Si crystals grown by the Czochralski method where the striations are believed to occur due to the presence of oxygen interstitials along the growth directions [138]. However, at low cooling rates the grains are reported to be free of striations [139] as observed for 800 μm and 550 μm droplets.

The microstructure of UDS droplets depends widely on their supercooling and hence on the size of the droplets for a given cooling media. It is generally accepted that smaller droplets cool faster and can be supercooled to a higher degree than larger droplets. Thus the smaller 390 μm droplet would supercool to a higher degree than the 800 μm and 550 μm droplets. With increasing supercooling the growth mode changed from lateral to continuous, which resulted in the formation of twinned <110> dendrites in 550 μm but orthogonal <100> dendrites in 390 μm droplets [131]. The nucleation temperature of the droplets is further evaluated in Section 6.6.
Figure 6.4: Optical micrograph of 800 μm (triplet of 550 μm) UDS Si droplet, (a) low magnification, (b) high magnification.
Figure 6.5: Optical micrographs of 550 μm UDS Si droplet, (a) low magnification, (b) high magnification.
Figure 6.6: Optical micrograph of 390 μm UDS Si droplet, (a) low magnification, (b) high magnification.
6. Production & Characterization of Silicon UDS Droplets

6.4.2 Nucleation distance

To determine the nucleation kinetics of silicon UDS droplets, splat quenching experiments were conducted for droplet sizes of 390 μm and 550 μm. Table 6.2 shows the blade positions used for the quenching experiments.

Figures 6.7 and 6.8 show the cross-sections of the splats obtained at various flight distance of the droplets. The splat morphology is observed to change with the flight distance. At short distances, the splat is seen to have an elongated tail-like feature, which is due to the fully molten state of the droplet before landing on the quenching blades, where the rotating motion of the blades sheared the molten droplet to produce the elongated feature. In contrast, the splats collected at longer flight distances exhibit a pronounced hump-like feature which increases with increasing flight distance. This indicates that these droplets were in a semi-solid or mushy state when they impinged on the rotating blades, thus indicating that nucleation probably occurred at a flight distance between these two stages. The later transition occurred at about 0.26 ± 0.01 m for the 550 μm droplets and at about 0.23 ± 0.01 m for the 390 μm droplets. It follows that these droplets nucleate within the respective ranges of flight distances.
Table 6.2 Blade Positions and Respective Droplet Conditions.

<table>
<thead>
<tr>
<th>Flight distance</th>
<th>Remarks</th>
<th>Flight distance</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0 cm</td>
<td>molten</td>
<td>20.0 cm</td>
<td>molten</td>
</tr>
<tr>
<td>22.5 cm</td>
<td>molten</td>
<td>22.0 cm</td>
<td>molten</td>
</tr>
<tr>
<td>25.0 cm</td>
<td>molten</td>
<td>24.0 cm</td>
<td>partially solidified</td>
</tr>
<tr>
<td>27.0 cm</td>
<td>partially solidified</td>
<td>26.5 cm</td>
<td>partially solidified</td>
</tr>
<tr>
<td>29.0 cm</td>
<td>partially solidified</td>
<td>28.0 cm</td>
<td>partially solidified</td>
</tr>
<tr>
<td>31.0 cm</td>
<td>-</td>
<td>30.0 cm</td>
<td>partially solidified</td>
</tr>
<tr>
<td>32.5 cm</td>
<td>partially solidified</td>
<td>32.0 cm</td>
<td>-</td>
</tr>
<tr>
<td>40.0 cm</td>
<td>partially solidified</td>
<td>35.0 cm</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 6.7: Splats obtained by quenching 550 μm droplets (Expt. I) (a) $z = 0.25$ m, (b) $z = 0.27$ m, (c) $z = 0.40$ m.
Figure 6.8: Splats obtained by quenching 390 μm droplets (Expt. II)
(a) z = 0.22 m, (b) z = 0.24 m, (c) z = 0.30 m.
6. Production & Characterization of Silicon UDS Droplets

6.5 Simulation

The solidification behavior of silicon is quite different and unusual in comparison to that of metals and alloys. The growth mode is reported to change with increasing supercooling, from lateral mode (advancement of interface by formation of ledges, commonly found in solidification of non-metallic materials) to continuous mode (continuous movement of interface, commonly observed in metallic materials) [137]. Jian et al. [133] have reported on the direct observation of solidification in supercooled silicon by a high speed camera. They observe that for low supercooling, the droplet is observed to nucleate and grow laterally from a plate-like structure. At high supercooling, however, the plate-like structures are absent and nucleation takes place copiously throughout the melt. The transitional supercooling for this change is believed to about 100 K.

Recent investigations with molecular dynamics simulation of liquid silicon show that, a liquid-liquid transition may occur at temperatures in the range 1000 – 1200 K [118, 119]. The liquid phase at higher temperature is simulated to have a highly dense and coordinated atomic structure which transforms to a nearly tetrahedral structure with increasing supercooling [119]. This transformation is believed to correspond to the transition (at supercooling of about 400 K) from metallic to non-metallic behavior in liquid silicon [119]. Experimental results have not confirmed this, primarily due to the high supercoolings involved. However, in spite of such anomalies in silicon, its solidification behavior has been effectively simulated by Aoyama et al. [134] and others [129-131] using the BCT free dendritic growth model [61], which have given agreeable results of interface velocity with those measured experimentally.
by Aoyama et al. [134]. Thus, supercooled silicon may be simulated using the solidification models commonly used for simulating the solidification behavior in metallic materials.

### 6.5.1 Droplet nucleation kinetics

Kinetics for internal nucleation of molten silicon droplets was investigated using the nucleation model proposed by Wu and Ando [33] with the aid of the droplet cooling curves generated by the in-flight solidification model [7]. Figure 6.9 shows the droplet cooling curve generated for 550 μm and 390 μm droplets silicon. The nucleation temperatures of the 550 μm and 390 μm droplets were estimated as $T_N = 1606 \pm 8$ K for 550 μm droplets and $T_N = 1515 \pm 17$ K, for 390 μm droplets.

Thus the larger 550 μm droplets have supercooling of 81 K, whereas the smaller 390 μm droplets have a higher supercooling of 172 K. With these experimental data for 550 μm and 390 μm droplets and their simulated cooling schedules, the material specific constants, $M^*$ and $N^*$, are calculated using Equation (3.40). The values of $M^*$ and $N^*$ represent the potency of nucleant catalysts present in the melt. The potency may depend on the initial melt temperature, if the catalysts are likely to dissolve into the melt at high temperatures. However, the calculation of $M^*$ and $N^*$ values assumes that the catalysts are stable and independent of the initial melt temperature. Table 6.3 shows the calculated values of $M^*$ and $N^*$. Once the values of $M^*$ and $N^*$ are determined, the model permits calculating the nucleation temperatures of droplets of any size under any cooling conditions. Figure 6.10 shows the CCT curves
6. Production & Characterization of Silicon UDS Droplets

calculated with the model for 550 μm and 390 μm silicon droplets cooling under various conditions.

Table 6.3 Computed Values of $M'$ and $N'$.

<table>
<thead>
<tr>
<th>Constants</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M'$ (K²m⁻³s⁻¹)</td>
<td>$3.858 \times 10^{18}$</td>
</tr>
<tr>
<td>$N'$ (K⁵)</td>
<td>$3.326 \times 10^{7}$</td>
</tr>
</tbody>
</table>

Figure 6.9: Simulated cooling schedule for Si indicating nucleation temperature.
Figure 6.10: Computed CCT curves for Si droplets.
The droplet nucleation kinetics model [33] can now be used to predict nucleation temperature for droplets of any diameter. Although the present work did not produce mono-sized droplets finer than 390 μm, some satellite droplets (which were finer than the primary droplets) were produced. Of such satellite droplets, a 200 μm droplet and a 275 μm droplet were examined by optical microscopy to verify the predictions by the model.

Figures 6.11 and 6.12 show the cross-sections of the 200 μm and 275 μm satellite droplets, respectively. Both droplets show a multi-grained microstructure with traces of <100> dendrites within the droplets. In these small droplets, probably a single event of nucleation produced subsequent <100> growth. As the <100> dendrites grew, some of the arms detached produced the multi-grained microstructure. The smaller 200 μm droplet, however, has fewer grains, indicating that more marginal conditions for fragmentation applied to this droplet. The supercoolings predicted by the nucleation kinetics model are 226 K for 275 μm droplet and 320 K for the 200 μm droplet. At these high supercoolings, previous studies [44, 19] have also reported formation of <100> orthogonal dendrites.

Thus both microstructures correspond well with their range of predicted supercoolings. However, a more rigorous verification of the actual numerical values was not possible due to the height and temperature limitations of the present UDS apparatus.
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Figure 6.11: Optical micrograph of 275 μm satellite droplet.

Figure 6.12: Optical micrograph of 200 μm satellite droplet.
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6.5.2 Fragmentation behavior

The observation of multi-grained microstructure in the droplets suggests the possibility of fragmentation of the silicon dendrites, which is commonly observed in alloys like ASTM F75. This phenomenon is observed by Nagashio et al. [44], using a high speed camera, for the silicon droplets substantially supercooled above 261 K. Thus it is likely that the dendrites in silicon UDS droplets may undergo fragmentation. Hence the fragmentation behavior for pure silicon droplets is modeled using Karma’s fragmentation model [40], which is explained in detail in Chapter 3.

The thermo-physical constants used for the calculation are listed in Appendix A. The driving force for fragmentation of pure silicon dendrites must necessarily be the capillary force of the solid-liquid interface. The ratio of the trunk radius, \( R(\Delta T) \), estimated from the microstructures to the calculated tip radius, \( R_{\text{tip}}(\Delta T) \), is used to estimate the geometrical parameter, \( z^* \). Figure 6.13 shows the optical micrographs of the microstructures of the droplets used to estimate the trunk radius of the droplets. Table 6.4 shows the values of \( z^* \) calculated for each of the droplets. The expected coarsening of the dendrites in the last stages of solidification may produce some variation in the calculated value of \( z^* \). The coarsening is much more prominent for pure materials which produce nearly same trunk radius for all the solidified droplets.
6. Production & Characterization of Silicon UDS Droplets

Table 6.4 Parameters Used for Computing the Fragmentation Model.

<table>
<thead>
<tr>
<th></th>
<th>550 μm droplets</th>
<th>390 μm droplets</th>
<th>275 μm droplets</th>
<th>200 μm droplets</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔT (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(exp)</td>
<td>81 K</td>
<td>172 K</td>
<td>226 K (CCT curve)</td>
<td>320 K (CCT curve)</td>
</tr>
<tr>
<td>R_{tip} (m)</td>
<td>7.2 x 10^{-6}</td>
<td>1.7 x 10^{-7}</td>
<td>5.0 x 10^{-8}</td>
<td>7.74 x 10^{-8}</td>
</tr>
<tr>
<td>R(m)</td>
<td>15 x 10^{-6}</td>
<td>10 x 10^{-6}</td>
<td>10 x 10^{-6}</td>
<td>10 x 10^{-6}</td>
</tr>
<tr>
<td>z'</td>
<td>2</td>
<td>10</td>
<td>50</td>
<td>75</td>
</tr>
</tbody>
</table>

Figure 6.13: Optical micrographs of Si UDS droplets, (a) 550 μm droplets, (b) 390 μm droplets, (c) 275 μm droplets, (d) 200 μm droplets.
Figures 6.14 and 6.15 show the computed $\Delta t_{bu}$ vs. supercooling for 550 $\mu$m and 390 $\mu$m droplets, respectively. The $\Delta t_{pl}$ vs. supercooling line, as shown on the plots are not as steep as that observed for the case ASTM F75 in Chapter 5. This is due to the high latent heat of fusion of which makes the amount of liquid left in the droplet at the end of recalescence very large, unless the supercooling is comparable to the hypercooling limit, $\Delta T_{hyp}$ ($= 1977$ K for silicon). Thus a supercooling of 400 K is about $0.2 \cdot \Delta T_{hyp}$, which leaves 80% of the droplet volume still molten at the end of recalescence. Since the solidification rate in the post recalescence period is limited by the rate of heat extraction, droplets with low to moderate supercoolings would all have similar values of $\Delta t_{pl}$.

The model predicts no fragmentation for 550 $\mu$m droplets at the determined supercooling of 81 K. This is verified by the microstructure of 550 $\mu$m droplets which essentially shows large grains with occurrence of elongated, twinned $<110>$ dendrite, as shown in Figure 6.5. For the 390 $\mu$m droplets with a supercooling of 172 K, the model predicts fragmented dendrites. The micrograph for 390 $\mu$m, shown in Figure 6.6, does indicate a microcrystalline microstructure indicative of fragmentation of dendrites. Figure 6.16 shows another 390 $\mu$m droplet that more clearly shows fragmented dendrites. The cross-like features (highlighted in Figure 6.16) are observed to be fragments of orthogonal $<100>$ dendrites. Nagashio et al. [44] have reported on fragmentation of dendrites occurring at a supercooling 261 K, where cross-like dendrite fragments were observed to detach in the initial post-recalescence plateau period. Thus, the microstructure does confirm the occurrence of fragmentation in 390 $\mu$m droplets.
as predicted by the model. The chance of finding a fragmented dendrite in these droplets would in fact depend on the direction of cross-sectioning the droplets and the orientation of the dendrites in the droplets. However, fragmentation itself is considered to have occurred in all 390 µm droplets regardless of the sectioning and orientation, as predicted in Figure 6.15 and metallographically verified in Figures 6.6 and 6.16.
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Figure 6.14: Computed $t_{bu}$ vs. $\Delta T$ for 550 $\mu$m Si UDS droplets cooled in He gas.

Figure 6.15: Computed $t_{bu}$ vs. $\Delta T$ for 390 $\mu$m Si UDS droplets cooled in He gas.
Figure 6.16: Optical micrographs of 390 μm Si UDS droplet showing fragmented dendrites (a) low magnification, (b) high magnification.
Figures 6.17 and 6.18 show the calculated break-up time against supercooling plots for 275 μm droplets and 200 μm droplets. At the calculated supercoolings of $\Delta T = 226$ K for 275 μm droplets and $\Delta T = 320$ K for 200 μm droplets the fragmentation model predicts fragmented dendrites in both cases. Careful examination of the optical micrographs does indicate some fragmented orthogonal dendrites in 200 μm droplets. Figure 6.19 shows optical micrographs of such a 200 μm droplet, clearly revealing fragmented dendrites in the plane of polish in the droplet. Although metallographic evidence of fragmented dendrites was not found for 275 μm droplets, the microcrystalline microstructure in Figure 6.11 provides indirect evidence for dendrite fragmentation. It is also expected that the number of fragmented dendrites are very few in the above droplets, which makes it difficult to accurately pin-point the location of fragmented dendrites in the smaller droplets. Moreover, the uncertainties associated with the metallographic determination of the trunk radius also make the values of $z^*$ used in the computation somewhat tentative.
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Figure 6.17: Computed $t_{bu}$ vs $\Delta T$ for 275 $\mu$m Si droplets cooled in He gas.

Figure 6.18: Computed $t_{bu}$ vs $\Delta T$ for 200 $\mu$m Si droplets cooled in He gas.
Figure 6.19: Optical Micrographs of 200 μm droplets indicating fragmented dendrites at, (a) low magnification, (b) high magnification.
6.7 Discussion

Comparing the microstructures of silicon droplets in Figures 6.4 – 6.6, it is observed that the smaller 390 μm droplets have well developed orthogonal <100> dendrites at a ΔT = 172 K whereas the larger 550 μm droplets with lower supercooling, ΔT = 81 K, have twinned <110> dendritic microstructure. This indicates that the transitional supercooling for formation of <100> dendrites is in the range 82 – 171 K. An earlier work with B-doped Si shows this transition to be ~100 K [130].

The nucleation model [33] with the aid of experimentally obtained data is successful in predicting the nucleation temperatures of UDS silicon droplets. It predicts that 275 μm droplets have a supercooling of 226 K and 200 μm droplets have a supercooling of 320 K. This shows that small UDS droplets, around 200 μm in diameter, can easily be supercooled to a very high degree of about 300 K. The successful verifications of the microstructures for 275 μm and 200 μm droplets at the supercoolings calculated by the nucleation model, cross-verifies the predictions made by using the model.

Silicon droplets with supercoolings of at least 172 K have been shown to have an orthogonal <100> dendritic microstructure. The fragmentation of the <100> dendrites was clearly observed for 390 μm droplets supercooled to 172 K, as predicted by Karma’s fragmentation model. However, complete fragmentation of the orthogonal dendrites is not observed for 390 μm droplets due to the marginal conditions for fragmentation of the UDS droplets as predicted by Karma’s model [40], Figures 6.15, 6.18 and 6.18. In contrast UDS droplets of
ASTM F75 show complete fragmentation of dendrites. Moreover, the error associated with the calculation of $z^\ast$ is less for the alloy than for pure materials as the solute rejected by the growing dendrite restricts coarsening. Thus the computed values of $t_{bu}$ for silicon would probably give more marginal conditions for the actual values of $z^\ast$. Also the hypercooling limit for silicon is large ($\Delta T_{hyp} = 1977$ K), the maximum supercooling observed for silicon UDS droplets is only $0.16\cdot\Delta T_{hyp}$ ($320$ K for $200$ $\mu$m droplets). Thus droplets with sufficiently higher supercooling would probably show more extensive fragmentation of dendrites. Similarly studies by Devaud and Turnbull [140] and Lau and Kui [145] have observed equiaxed microcrystalline grains due to extensive fragmentation of dendrites in germanium droplets ($300$ - $700$ $\mu$m diameter) only when supercooled above $300$ K ($\Delta T_{hyp} \sim 1200$ K).

However, the model correctly estimates the occurrence of microcrystalline microstructure for $390$ $\mu$m and $275$ $\mu$m and $200$ $\mu$m at their respective supercoolings. Thus, this model when applied for the case of pure silicon is useful in predicting the occurrence of microcrystalline microstructures due to the fragmentation of dendrites. Although there are very few reports [44, 145] on the fragmentation of highly supercooled Si dendrites, there has been no general consensus on the conditions required for fragmentation in Si. Thus, this study is helpful in establishing the conditions for fragmentation of silicon <100> dendrites in droplets $800$ to $200$ $\mu$m diameter.
7 Conclusions

The UDS apparatus was suitably upgraded for performing high temperature experiments by altering the design of the crucible and the charging set-up. The maximum UDS processing temperature for droplet production was increased from 1500 K to 1923 K and that for charging droplets was increased to about 600 K to 1473 K. Experiments with ASTM F75 and silicon were successfully used to produce mono-sized droplets at various cooling conditions. The following conclusions are central to this research:

- The design of the charging set-up was suitably improved by separating the charging plates from the crucible to enable safe application of high voltages and charge copper droplets at high temperatures. The charging of copper UDS droplets in nitrogen atmosphere using a voltage of 200 to 500 V and a separation of 8 to 14 mm between the charging plates was successfully performed at 1473 K without any arcing or glow discharge between the electrodes. However, in the present work, the upper limit for processing temperatures with droplet charging was fixed at 1500 K, due to the instability of gases at higher temperatures.

- The measured spray cone width of the charged droplets was found to increase with increasing voltage and decreasing gap between the charging plates. The motion of the charged droplets was simulated with the use of an in-flight simulation model modified for the charging set-up geometry used. The simulated results overestimate the spray cone width compared to that observed experimentally. This is considered to be caused by the probable ionization of the
nitrogen gas molecules at high temperature. Effective droplet charging, nonetheless, was proved.

- The ASTM F75 UDS droplets primarily exhibit the $\gamma$ Co (fcc) phase with interdendritic $\text{M}_{23}\text{C}_6$ carbides. The 300 $\mu$m droplets, cooled in helium gas, showed higher supersaturation of Cr in $\gamma$ solid solution than 640 $\mu$m droplets. Further, the interdendritic carbides decrease in size and volume fraction for 300 $\mu$m droplets relative to 640 $\mu$m droplets, indicating improved mechanical properties of 300 $\mu$m droplets.

- The nucleation temperature of the 640 $\mu$m and 300 $\mu$m ASTM F75 droplets were estimated by splat quenching experiments with the aid of a droplet in-flight cooling model. From these reference nucleation data, CCT curves were calculated for the heterogeneous nucleation of ASTM F75 droplets cooling under various conditions.

- The 640 $\mu$m ASTM F75 droplets cooled in helium gas to a supercooling of 92 K had a well-developed dendritic microstructure whereas 460 $\mu$m and 300 $\mu$m droplets cooled in helium gas to a supercooling of 179 K and 377 K, respectively, had a microcrystalline microstructure. 300 $\mu$m droplets, when cooled in argon atmosphere had a well-preserved dendritic microstructure.

- The application of Karma’s dendrite fragmentation model revealed that the occurrence of microcrystalline microstructure in ASTM F75 droplets was caused by dendrite fragmentation during the post-recalescence plateau stage of
droplet solidification. The model also predicts the observed preservation of dendrites in other droplets.

- The mono-sized silicon UDS droplets of 550 μm and 390μm diameters exhibited cracked surfaces with horn-like protrusions formed due to the volume expansion of the silicon during solidification.

- The droplet nucleation temperature was experimentally determined by a splat quenching technique with the aid of the in-flight cooling model. These nucleation data were used in the nucleation kinetics model to obtain CCT curves for heterogeneous nucleation of silicon droplets.

- The 550 μm droplets cooled in helium atmosphere to a supercooling of 81 K showed microstructures of twinned <110> dendrites. While the 390 μm droplets cooled to a supercooling of 172 K showed a microcrystalline microstructure with traces of orthogonal <100> dendrites. The 275 μm droplets cooled in helium atmosphere at a supercooling of 226 K and 200 μm droplet at a supercooling of 320 K also showed microcrystalline microstructure with traces of orthogonal <100> dendrites. Hence with decreasing droplet size and increasing supercooling the growth mode changed from lateral (forming <110> dendrites) to continuous (forming <100> dendrites). The change of growth mode for silicon droplets occurs between 81 K and 172 K supercooling.

- The microcrystalline microstructure of the 390 μm, 275 μm and 200 μm droplets indicates fragmentation of the dendrites. Application of the fragmentation model proves that the microcrystalline microstructure observed for
droplets with high supercooling (> 172 K) was caused by the fragmentation of dendrites. However, for the smaller 200 μm droplets the fragmentation was not complete as indicated by the fewer number of grains observed in the droplets.

- Comparison of ASTM F75 and silicon droplets shows that the fragmentation of the dendrites at high supercoolings in silicon droplets was not complete as observed for ASTM F75 droplets. This was attributed to the marginal conditions for fragmentation in silicon UDS droplets as predicted by the fragmentation model.

- UDS processing enables stringent control of the nucleation and microstructure evolution during solidification of alloy droplets in a thermal spray process, leading to the development of advanced technology for droplet-based manufacturing.
8 Appendices

8.1 Appendix A: Input Parameters for the Model

Table 8.1 presents the input parameters used for computation of the in-flight solidification model, DA model, nucleation kinetics model and the fragmentation model. The values have been used from Refs. [80] and [81]. For ASTM F75 when values for the alloy parameters (indicated) were not available, pure cobalt was used as an approximation.

Table 8.1 Thermo-Physical Constants Used For Computation.

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Thermo-physical Constants</th>
<th>ASTM F75</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Thermal Diffusivity</td>
<td>$3.12 \times 10^{-6}$ m$^2$/s</td>
<td>$8.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Gibbs Thompson parameter</td>
<td>$4.45 \times 10^8$ mK</td>
<td>$1.96 \times 10^{-7}$</td>
</tr>
<tr>
<td>$\Delta T$</td>
<td>Unit undercooling</td>
<td>509 K</td>
<td>1977 K</td>
</tr>
<tr>
<td>$\Delta S_f$</td>
<td>Entropy of fusion,</td>
<td>0.4846 J K$^{-1}$</td>
<td>1.05 J K$^{-1}$</td>
</tr>
<tr>
<td>$Q$</td>
<td>Activation enthalpy,</td>
<td>33200 J mole$^{-1}$ (Co)</td>
<td>44500 J mole$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>Enthalpy of fusion</td>
<td>18940 J/mole</td>
<td>50208 J/mol</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Specific heat capacity at $T_m$</td>
<td>37.18 J/molK</td>
<td>25.39 J/molK</td>
</tr>
<tr>
<td>$a$</td>
<td>Characteristic diffusion distance</td>
<td>3.54 Å ($\gamma$ Co)</td>
<td>5.34 Å</td>
</tr>
<tr>
<td>$T_L$</td>
<td>Liquidus temperature, (K)</td>
<td>1682</td>
<td>1687 K</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Equilibrium partition coefficient,</td>
<td>0.83</td>
<td>-</td>
</tr>
<tr>
<td>$V_0$</td>
<td>Maximum interfacial velocity</td>
<td>4000 m/s</td>
<td>5000 m/s</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Emissivity</td>
<td>0.33 (Co)</td>
<td>0.20</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Interfacial energy</td>
<td>0.15 Jm$^{-2}$ (Co)</td>
<td>0.38 Jm$^{-2}$</td>
</tr>
</tbody>
</table>
8.2 Appendix B: Charge Induced on a Droplet

The expression for parallel plate capacitor with a line of charges between them has been obtained from a similar derivation for Maxwell gratings [96] which is similar to that of a concentric cylindrical capacitor with a correction factor ($\kappa$). This correction factor has been evaluated by solving the equations obtained by the method of images. This method has been similarly used to by Fillmore et al. [82] calculate the charge on inkjet droplets and by Abel [55] to calculate the charge on Sn droplets.

It is based on the concept of imaginary line charges not located within the region of field evaluation but so chosen that together with the original point or line charges all boundary conditions in this region can be satisfied. Figure 8.1 shows the charging plates, I and II, which act as mirror planes and cast an image of opposite charge at an equal distances ($x_1$ and $x_2$) from the plate. So assuming the droplets have a point charge $+q$, $-q$ charges can be assumed to exists at a distance $x_1$ and $x_2$ from plates I and II, respectively.

![Image of line charges for parallel plate charging set-up.](image-url)

Figure 8.1: Image of line charges for parallel plate charging set-up.
The potential between the points a and b is calculated as:

$$\Phi_{a-b} = \frac{q'}{2\pi\varepsilon_o} \left( \int_{x_1}^{r} \frac{dr}{r} - \int_{2x_1-x_1}^{2x_1+r-x_1} \frac{dr}{r} + \int_{2x_1-x_1}^{2x_2+2x_1-x_1} \frac{dr}{r} ight)$$  \hspace{1cm} (B.1)$$

$$\Phi_{a-b} = \frac{q'}{2\pi\varepsilon_o} \left( \ln \frac{r}{x_1} - \ln \frac{2x_1-r}{x_1} + \ln \frac{2x_2+r}{2x_2+x_1} - \ln \frac{2x_2+2x_1-r}{2x_2+x_1} \right)$$  \hspace{1cm} (B.2)$$

Charge induced on a line of droplets is

$$q' = 2\pi\varepsilon_o \Phi \left( \ln \frac{r}{x_1} - \ln \frac{2x_1-r}{x_1} + \ln \frac{2x_2+r}{2x_2+x_1} - \ln \frac{2x_2+2x_1-r}{2x_2+x_1} \right)^{-1}$$  \hspace{1cm} (B.3)$$

Charge per droplet,

$$q_d = q' \lambda_d$$  \hspace{1cm} (B.4)$$

where $\lambda_d$ is the wavelength for uniform break up obtained experimentally.

The charge induced in such a system has been given by Maxwell [96] to be of form

$$q_d = \frac{2\pi\varepsilon_o}{\kappa + \ln \frac{d}{2r}}$$  \hspace{1cm} (B.5)$$

where $\kappa$ is a factor which depends on $r$, $x_1$ and $x_2$. In this work $x_1 = x_2 = \frac{d}{2} = 4$ mm and $r = 150$ µm the equation converges at $\kappa = 0.423065$. Similarly for any other charging set-up (even with an off center jet) the charge induced can be calculated.
Appendix C: Computation of the Metastable Liquidus

Extensions in Co-Cr phase diagram

The metastable phase diagram was constructed using the regular solution model provided by DiVenuti [7]. The thermo-physical constant used for its calculation are given in Table 8.1.

Figure 8.2: Computed metastable extension for Co-Cr binary alloy using the regular solution.
8.4 Appendix D: Source Codes for Computation of the DA Model and the In-flight Solidification Model.

The C++ source code by DiVenuti [7, 53] and Lu [14] has been used as a basis for computation of the DA model and the in-flight solidification model for the Co-28mass% Cr alloy and pure silicon. The source codes have been provided separately for convenience.
9 References


36. Bialiauskaya, V. V.; Ando, T., “The nucleation kinetics of travelling Fe-17at%B droplets produced by the uniform-droplet spray process”, to be published.


References


