Single Droplet Formation for a Liquid SnBi Alloy

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Summary

A production process developed to produce tin-bismuth alloy shot particles directly out of the liquid metal phase, appeared difficult to be controlled. Therefore, within this graduation project, the underlying physical principles of droplet formation and the process parameters had to be characterised. After characterisation of the process parameters, the uniform production of spherical particles had to be realised and controlled. A small scale experimental setup was used to test and realise these results.

Periodic single droplet formation at the nozzle was demonstrated to be the most suitable mechanism for uniform shot production. A relation for the maximum uniform production rate was found and evaluated. Both the maximum production rate and the diameter of the produced shot are determined by the nozzle diameter, the metal flow rate through the nozzle, and the metal properties (surface tension and density).

Oxidising gas components cause unstable droplet formation and non-spherical shapes. The viscosity of the coolant is determining for the end shape of the shot particle. Tests with a high viscosity oil (also at elevated temperature) increased the sphericity of the shot particles.

A maximum mean shot diameter of 3.3 mm was produced with a nozzle diameter of 1.5 mm. The tin bismuth alloy showed non-wetting behaviour on the steel nozzle surface. The shape factor, defined as the ratio of the two longest lengths of an ellipsoidal particle, has been determined at 1.05.

Uniform production of tin bismuth shot, directly out of the liquid metal phase is feasible, although it has been shown very sensitive to fluctuations in the operating conditions.
Symbols

Greek symbols

\( \alpha \) = contact angle \quad [\text{rad}]
\( \sigma \) = surface tension \quad [\text{N/m}]
\( \tau \) = time of formation \quad [\text{s}]
\( \gamma \) = angle \quad [\text{rad}]
\( \theta \) = contact angle \quad [\text{rad}]
\( \theta \) = time of constriction \quad [\text{s}]
\( \mu \) = linear damping coefficient \quad [\text{s}^{-1}]
\( \eta \) = viscosity \quad [\text{Pa.s}]
\( \lambda \) = wave length \quad [\text{m}]
\( \Delta \rho \) = density difference between two phases \quad [\text{kg/m}^3]
\( \Delta A \) = small area \quad [\text{m}^2]
\( \Delta G^0 \) = surface free energy \quad [\text{J}]
\( \rho_l \) = liquid density \quad [\text{kg/m}^3]
\( \rho_{\text{metal}} \) = density of the metal \quad [\text{kg/m}^3]
\( \omega_n \) = frequency of small-amplitude oscillations of spherical drops \quad [1/\text{s}]
\( \lambda_{\text{opt}} \) = optimum wavelength \quad [\text{m}]
\( \gamma_{SV,SV',SL'} \) = surface tension of resp. solid-liquid, solid-vapour \quad [\text{N/m}]
\( \varphi_v \) = liquid metal flow rate \quad [\text{m}^3/\text{s}]
\( \phi_{\text{max}} \) = maximum metal flow rate \quad [\text{m}^3/\text{s}]

Roman symbols

\( a \) = jet radius \quad [\text{m}]
\( A \) = pre-exponential constant \quad [-]
\( A_{\perp} \) = cross-section area of the droplet \quad [\text{m}^2]
\( C_D \) = drag coefficient \quad [-]
\( c_{\text{oil}} \) = specific heat of the oil \quad [\text{J/kg.K}]
\( d_0 \) = diameter of jet nozzle (Meesters, 1992) \quad [\text{m}]
\( d_e \) = volume equivalent diameter of the bubble or drop \quad [\text{m}]
\( d_h \) = highest droplet diameter \quad [\text{m}]
\( d_j \) = jet diameter \quad [\text{m}]
\( d_l \) = lowest droplet diameter \quad [\text{m}]
\( d_{\text{max}} \) = maximum nozzle diameter Dosoudil (1971) \quad [\text{m}]
\( D_{\text{nozzle}} \) = diameter of the nozzle \quad [\text{m}]
\( d_p \) = droplet diameter \quad [\text{m}]
\( f \) = Harkins and Brown correction factor \quad [-]
\( f_{\text{bismuth}} \) = mass fraction of bismuth \quad [\text{kg/kg}]
\( f_h \) = highest frequency for uniform jet breakup \quad [1/\text{s}]
\( f_l \) = lowest frequency for uniform jet breakup \quad [1/\text{s}]
\( f_{\text{opt}} \) = optimum frequency \quad [1/\text{s}]
\( f_{\text{tin}} \) = mass fraction of tin \quad [\text{kg/kg}]
\( h \) = heat transfer coefficient \quad [\text{W/m}^2.\text{K}]
\( H_a \) = activation energy \quad [\text{J/mol}]
H_{metal} = \text{height of metal level in metal dosing pot}[m] \\
k = 2\pi/\lambda = \text{wave number}[1/m] \\
L_c = \text{critical cone length}[m] \\
M = \text{mass of falling droplet}[kg] \\
n = \text{the modal of oscillation}[-] \\
Oh = \text{Ohnesorge number}[-] \\
Oh_{\text{min}} = \text{minimum Ohnesorge number (Dosoudil)}[-] \\
r = \text{nozzle radius}[m] \\
Re = \text{Reynolds number}[-] \\
Re_{\text{min}} = \text{minimum Reynolds number (Dosoudil)}[-] \\
t = \text{time}[s] \\
T_{\text{droplet}} = \text{mean temperature of falling droplet}[K] \\
T_m = \text{Tamman temperature}[K] \\
T_w = \text{outside temperature}[K] \\
u = \text{fluid velocity through nozzle}[m/s] \\
u_h = \text{highest liquid jet velocity}[m/s] \\
u_j = \text{jet velocity}[m/s] \\
u_l = \text{lowest liquid jet velocity}[m/s] \\
V_{\text{droplet}} = \text{droplet volume}[m^3] \\
V_{\text{droplet}} = \text{Volume of the droplet}[m^3] \\
W' = \text{real mass of droplet}[kg] \\
W = \text{mass of the droplet}[kg] \\
We = \text{Weber number}[-] \\

\text{Constants} \\
R = \text{gas constant (8.314 J/mol.K)}[m/s^2] \\
g = \text{gravitation constant}
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1 Introduction

1.1 Alternative for lead shot

Lead shot is the traditional ammunition used for sport shooting and hunting activities. However, deposited lead shot on hunting grounds has a detrimental effect on flora and fauna because of its high toxicity. Therefore lead shot as ammunition for sport shooting and hunting activities is prohibited by the European Law since 1994. Obviously, this initiated the search for alternative shot material. Until now steel shot and bismuth shot are used as less toxic alternatives. However, both steel and bismuth are hard metals and erode the inner parts of the shooting equipment. Hunters and sport shooters are still looking for a better alternative. Witmetaal B.V., Naarden, The Netherlands, looks for ways of producing shot based on a tin bismuth alloy. They patented an alloy consisting of 87.5 mass percent tin and 12.5 percent bismuth.

1.2 Production of tin bismuth shot

Lead shot has been produced by a simple process. Molten lead is put through a sieve to create droplets and cooled down while falling through air over 40 – 60 m (shot tower). Rough shaped lead particles are produced. The produced particles widely vary in diameter. The rough shape has no effect on ballistics because of the high density of lead. The tin-bismuth alloy, mentioned above, has a lower density than lead and demands a more spherical shape to enhance ballistics. Witmetaal B.V. developed a production process based on droplet formation directly out of the liquid phase. While testing they ran into several difficulties. To help clearing these difficulties and make the process suitable for production, Witmetaal B.V. turned to the Kramers Laboratorium voor Fysische Technologie of the Delft University of Technology.

1.3 Purpose of the graduation research

The purpose of this graduation project is to characterise the droplet formation process of liquid metal. Different areas are examined: flow phenomena in the nozzle, cooling phenomena, nozzle design, surface tension phenomena and dripping dynamics. After characterisation of the process parameters, the production of spherical particles with a diameter of 3.5 mm and higher has to be realised and controlled.

1.4 Structure of the report

The report is divided in 8 chapters. In chapters 2-4 the appropriate theory for droplet formation will be discussed. Flow phenomena around a free falling particle and the consequent shape of the liquid particle will be outlined. The experimental setup used will be discussed in chapter 5, as well as the measuring techniques used. In chapter 6 the results are displayed and discussed. Chapter 7 and 8 will finish with the conclusions and the recommendations, respectively.
2 Droplet Formation

The production process of tin-bismuth shot particles by droplet formation can be divided in two key areas. These key areas are schematically shown in Figure 2.1. The size and uniformity is determined by the droplet formation process at the nozzle. The sphericity is mainly determined when the droplet falls through the cooling medium while cooling down and solidifying. Liquid metals can be seen as Newtonian fluids.

![Figure 2.1: Key areas droplet production process “Hunting Alloy”](image)

Liquid droplets can be obtained from different mechanisms. In Figure 2.2 these mechanisms are shown schematically. At low flow rates through the nozzle single droplets (I) are formed at the nozzle. The droplets formed by this periodic process are uniform in size. This uniform droplet formation transfers into a quasi-static process (II) when the flow rate reaches a certain critical flow rate. This results in less uniform sized droplets. At even higher flow rates a jet (III) is issuing out of the nozzle. This jet breaks up into droplets due to oscillations triggered by disturbing instabilities from the inside of the jet and its surroundings. The droplets produced have a wide size distribution and even small satellite drops are formed.

![Figure 2.2: Different mechanisms of droplet formation.](image)
At highest flow rates, the semi-dynamic jet breakup (III) transfers into atomization (IV). This dynamic process leads to a wide distribution of small droplets. Going from periodic single droplet formation towards atomization the throughput increases significantly, however, the diameter of the droplets decreases. Both single droplet formation and droplet formation out of jet breakup will be discussed in this chapter. Atomization is only suitable for particle formation with diameters up to 1 mm, and will not be further discussed in this project.

2.1 Single droplet formation

With single droplet formation, the droplets are formed one by one at the nozzle. The limiting case of equilibrium liquid drop detachment is commonly referred to as Tate's Law [Adamson, 1982]. Tate's Law expresses the balance between the gravitational force and the surface tension of the liquid (2.1).

\[
\frac{\pi d_d^3}{6} \rho_l g = \pi D_{nozzle} \sigma
\]

- \(d_d\): equivalent droplet diameter
- \(\rho_l\): liquid density
- \(g\): gravity constant
- \(D_{nozzle}\): inside or outside diameter of the nozzle
- \(\sigma\): surface tension

The "weight" of the droplet is held to the nozzle by the adhesion of the droplet to the nozzle. This adhesion is expressed by the product of the surface tension \(\sigma\) and the perimeter \(\pi D_{nozzle}\) of the nozzle. For wetting fluids, \(D_{nozzle}\) is the outer diameter of the nozzle tip, for non-wetting fluids \(D_{nozzle}\) is the inner diameter (Figure 2.3). Wetting is discussed in chapter 3.
When the droplet detaches from the nozzle, a weight $W'$ is obtained, which is less than the "ideal" weight. Only a portion of the drop that has reached the point of instability actually falls, as much as 40% of the liquid may remain attached to the tip. It is common practice to apply a correction factor $f$ to Equation (2.1). So $W'$ is given by

$$W' = \pi D_{\text{nozzle}} \sigma \cdot f$$

Equation (2.2)

$W'$ = real mass of droplet
$f$ = correction factor

Harkins and Brown (1919) concluded that $f$ should be a function of the dimensionless ratio $r/V^{1/3}$, where $V$ is the droplet volume and $r$ the radius of the nozzle. Correction factors for $r/V^{1/3} < 0.3$ have been determined using mercury drops (Wilkinson and Aronson, 1973). They concluded that the Harkins and Brown tables for $f$ are correct for liquids of high density. For values of $r/V^{1/3} < 0.3$ the correction factors for mercury should be used if the liquid metal is non-wetting with regard to the dropping tip. It is to be noted that the correction factor for a given tip radius depends on the nature of the liquid and also the nozzle parameters. The sharpness of the nozzle edges are of importance for example.

Observing Equation (2.1), it seems that the droplet is not bounded to any maximum. However, the droplet diameter is restricted to capillary length scale ($d_{\text{cap}}$), defined as shown below. When the nozzle diameter exceeds this length scale, the flow through the nozzle starts ignoring the walls. Single droplet formation will not be possible anymore.

$$d_{\text{cap}} = \left( \frac{\sigma}{g \rho_l} \right)^{1/2}$$

Equation (2.3)

The maximum droplet diameter is therefore only related to the properties: surface tension $\sigma$ and the liquid density $\rho_l$ of the fluids.

The quasi-static force balance (Eq 2.4) proposed by Van den Berg (1996), describes the droplet formation at the nozzle in another way. Under quasi-static conditions, flow of momentum associated with the stream of liquid entering the drop is added to the force balance. By taking the flow of momentum into account, the droplets become smaller, when the flow rate is increased.

$$V_{\text{droplet}} \rho_{\text{metal}} g + \frac{4 \rho_{\text{metal}} \phi_v^2}{\pi D_{\text{nozzle}}} = \pi D_{\text{nozzle}} \sigma$$

Equation (2.4)

$V_{\text{droplet}}$ = volume of the droplet
$\rho_{\text{metal}}$ = metal density
$g$ = gravitational constant
$\phi_v$ = liquid metal flow rate

2.2 Dripping dynamics

In section 2.1 force balances were proposed which describe the single droplet formation process. This section gives an insight of what happens physically with a droplet which is formed and detached from a nozzle.

1 In literature no detailed research on metal dripping dynamics has been found. Liquid metal can be regarded as Newtonian fluid. Therefore research on non-metal Newtonian fluids can be reviewed as a guideline for metal dripping dynamics.
Van den Berg (1996) analysed dripping dynamics for water and showed that two basic forms of droplet formation (i.e. dripping) can be distinguished. In Figure 2.4 these two mechanisms are shown schematically.

![Diagram of primary and secondary drop formation]

Figure 2.4: Primary and secondary drop formation

When a drop slowly develops at a nozzle (a), the ongoing supply of liquid makes the droplet grow (b). When the surface tension forces are defeated by gravity (2.1), an almost spherical drop will detach from the nozzle (c), leaving a certain amount of liquid attached to the nozzle tip (d). This amount of liquid has a conical shape. This liquid cone snaps back towards the nozzle. Depending on the length of the cone, it will perform a certain amount of relaxation oscillations. When the remaining liquid cone is smaller than a critical length, \( L_c \) (and therefore a critical volume), the whole process of droplet formation starts again: growth, detachment, left cone, oscillations (a-c). This dripping mechanism is referred to as **primary dripping**.

When the remaining cone exceeds the critical cone length, \( L_c \), a drop is formed, and detaches while the rest of the cone snaps back (d - g). This mechanism is referred to as **secondary dripping**.

Another approach to the mechanism of droplet formation is to describe the different processes of dripping in terms of time intervals (Van den Berg, 1996). In Figure 2.5 the time intervals of the two different dripping mechanisms are shown.

![Diagram of primary and secondary dripping times]

Figure 2.5: Times of formation for primary and secondary dripping [V.d Berg, 1996]

* V.d. Berg, 1996
Primary dripping shows three different time intervals: $T_1$ snapback of the remaining liquid; $T_2$ relaxation oscillations of the cone; $T_3$ necking and constriction of the liquid bridge.

The first interval corresponds with the snapback of the liquid cone after detachment of the previous drop. The second interval is directed to the period of relaxation oscillations of the remaining liquid cone and growing of the new drop. After the drop has reached his critical mass (Eq. (2.1), the liquid bridge between the cone and the drop begins to stretch (i.e. neck) and finally breaks (i.e. constrict), resulting in detachment of the drop. $\theta$ is the time of constriction. The period of snapback with primary dripping is by definition smaller than $G$. Otherwise a secondary drop would be formed. The time of formation of a secondary drop formation equals the time of constriction $\theta$. During upward launching of the liquid cone, detachment takes place since $\theta$ is smaller than the period of snap-back. (Figure 2.4 d-g)

Van den Berg stated that the development of secondary drops was caused by capillary disturbances of the liquid cone. Parameters determining the capillary disturbances are the length and the ultimate volume of the remaining cone. These parameters are to a good approximation proportional to the flow rate of liquid through the nozzle. To investigate how the flow rate is related to the dripping mechanism, Van den Berg varied the flow rate through the nozzle and measured the drop interval time (i.e. the time interval between two consecutive drops). In Figure 2.6 the result of one experiment with water is shown. The drop interval time as a function of the liquid flow rate is shown for a nozzle with diameter $D = 2.0$ mm. Three different regimes were identified.

![Figure 2.6: Different dripping regimes with water and nozzle diameter 2.0 mm [V.d Berg 1996]](image)

At low flow rates, primary dripping is manifest. The time of formation ($\tau$) of the drops is constant, for a given nozzle diameter and flow rate $\phi$. Consequently, the drop volume is also nearly constant, $V_{\text{droplet}} = \phi \cdot \tau$. For this so-called primary dripping regime the periods of oscillation and time of constriction are much smaller than the time of formation. So, the dynamics are generally monotonic. However, when the damping of the relaxation oscillations and the time of formation are small enough, period-2 (Figure 2.6: split lines) and chaotic behaviour (Figure 2.6: scattered areas) can be observed as well at low flow rates. At low flow rates, the fluctuation in drop interval time is small in the first regime. At a critical flow rate of 0.63 ml/s a transition (i.e. bifurcation) to the chaotic regime is observed. The drop interval times are scattered between two lines of almost constant dripping times $t_1$ and $t_2$. Secondary dripping will be manifest next to primary dripping. The dynamics are characterised by an interplay of primary and secondary constriction and relaxation oscillations.
At a flow rate of 0.8 ml/min a second transition is observed. The dynamics of this regime are monotonic again. The dripping mechanism is mainly secondary. The regime is called secondary dripping regime. The volume of the drops are about half the size of the drops of the primary dripping regime.

V.d Berg also stated that the damping of the relaxation oscillations of the liquid cone is proportional to the inverse square of the nozzle diameter \(D_{\text{nozzle}}\), viz. \(\mu \sim D_{\text{nozzle}}^{-2}\). \(\mu\) being the damping coefficient, which describes the damping of the oscillations. Therefore the oscillations will cause "richer dynamics" when the nozzle diameter is increased.

The critical flow rates are proportional to the nozzle diameter. Section 2.3 will demonstrate this as well.

2.3 Transition of static and quasi-static (chaotic) droplet formation

The primary dripping regime is the operating window for producing uniformly sized droplets. So the transition from primary dripping to chaotic dripping has to be examined.

Dosoudil (1971) examined droplet formation for non-wetting Newtonian fluids. Experiments with water, glucose-solution, glycerin and mercury were performed. With a stroboscope and a microscope (40x magnification), the critical flow rates from the primary to the chaotic regime were determined. For water and mercury it showed to be difficult to set the flow rate at critical boundary conditions.

Dosoudil transformed the results of these measurements into the dimensionless numbers of Reynolds (Re) and Ohnesorge (Oh). The results of the transformation were graphically presented in Figure 2.7 (\(K_i=\text{Oh}\)). He defined the Reynolds number according to Eq. (2.5) and the Ohnesorge number to Eq. (2.6) following Weber (1931) who introduced these numbers for determining the optimal wavelength with jet breakup.

Physically the Reynolds number represents the balance between inertia forces and viscous forces through the nozzle. The Ohnesorge number represents the balance between viscous forces, inertia forces and surface tension forces.
\[ \text{Re} = \frac{\rho ud}{\eta} \quad (2.5) \]

\[ \text{Oh} = \frac{\eta}{\sqrt{d \rho \sigma}} \quad (2.6) \]

\[ u = \text{fluid velocity through nozzle} \]
\[ d = \text{nozzle diameter} \]
\[ \rho = \text{liquid density} \]
\[ \eta = \text{viscosity} \]

In lines a - d Figure 2.7, the critical flow rates for different nozzle diameters are shown: a for water, b for the glucose-solution, c for glycerin and d for mercury.

To avoid more future tedious measurements, Dosoudil derived a general relation for the critical flow rate of the transition from primary dripping and the chaotic regime. For stable droplet formation a maximum nozzle diameter exists as discussed in Section 2.2. Dosoudil derived a different relation than Eq. (2.3) for the maximum nozzle diameter. He stated that when the diameter of the produced droplets are equal to the nozzle diameter (normally the droplet diameter exceeds the nozzle diameter), the maximum "stable" nozzle diameter is reached\(^2\). To calculate this he substituted \( d_d = D_{\text{nozzle}} \) and \( d_{\text{max}} = d_d \) in Equation (2.1) and found for the maximum nozzle diameter:

\[ d_{\text{max}} = \frac{6 \sigma}{\rho g} \quad (2.7) \]

With this maximum nozzle diameter, Dosoudil calculated four minimum values of the Ohnesorge number of the different liquids. In Figure 2.7 the intersection between the horizontal lines of these minimum Ohnesorge numbers and the boundary-lines a - d, result in the points 1 - 4, which represent the boundary of primary dripping. The trendline (e) through points 1 - 4 follows the relation

\[ \text{Oh} = 0.9 \text{Re}^{-1.02} \quad (2.8) \]

To compensate for the scatter of the measured points, Dosoudil transferred line e into e' with a security-factor. This line (e') obeys the following relation.

\[ \text{Oh} = 0.6 \text{Re}^{-1} \quad (2.9) \]

Looking closely into equation (2.9), one can recognize the Weber - number (We) which denotes the balance of inertia forces and the surface tension forces. Equation (2.10) gives the definition of the Weber-number.

\[ \text{We} = \text{Re}^2 \cdot \text{Oh}^2 = \frac{\rho u^2 d}{\sigma} \quad (2.10) \]

\(^2\) It must be noted that Dosoudil's motivation for the derivation of Equation (2.7) is doubtful. Section 6.7 will discuss this.
So, Equation (2.9) implies that the general boundary for primary dripping to chaotic dripping is given by \( \text{We}^{1/2} = 0.6 \).

Observing Figure 2.7 the separate lines a - d and the lines \( \text{Oh}_{\text{min}} = \) constant make an angle \( \gamma \). The \( \tan \gamma \) is about \(-2\). Taking this angle into account, Dosoudil derived a general relation for the boundary between primary and chaotic dripping.

\[
\log \frac{\text{Oh}}{\text{Oh}_{\text{min}}} = 2 \log \frac{\text{Re}_{\text{min}}}{\text{Re}}
\]  

(2.11)

Dosoudil introduced \( \text{Re}_{\text{min}} = 0.6 \text{Oh}_{\text{min}}^{-1} \) into Equation (2.11) resulting into the following general relation:

\[
\text{Re} = 0.6 \text{Oh}^{-0.5} \text{Oh}_{\text{min}}^{-0.5}
\]  

(2.12)

Relation (2.12) holds for \( 10^{-4} \text{<Oh<10} \).

Finally, Dosoudil derived a general relation for the maximum fluid flow rate in the range of the primary dripping regime combining Equations (2.7) and (2.12).

\[
\Phi_{\text{f, max}} = 0.58 \sigma^{0.625} d^{2.25} g^{0.125} \rho^{-0.625}
\]  

(2.13)

Equation (2.13) shows no dependency on the viscosity. Therefore the primary dripping process can be seen as a static and not a dynamic process.

Because this relation is based on a range of Newtonian fluids including mercury, this relation is an interesting guideline for the “Hunting Alloy” research.
2.4 Droplet formation through jet breakup

A second method for producing uniformly sized droplets is droplet formation via jet breakup. Jet breakup into droplets, was first described by Savart (1833) and Plateau (1856). They found that a jet is stable to all but axisymmetric disturbances of wavelengths greater than the circumference of that jet. It was Lord Rayleigh (1878) who first described a mathematical analysis of the jet breakup for inviscid liquids. In 1931 Weber included the effects of viscosity and aerodynamic drag into the analysis. These theories still stand as the principles of jet instability.

In practice it was not possible to use the theories of Rayleigh and Weber for all radii and wavenumbers applied. Often is was seen that satellites accompany the jet break-up, satellites being small droplets formed between the main droplets. This kind of breakup leads to at least two droplets per wavelength, which was not explained by the theories.

At larger wavenumbers the theories were better able to describe the process of breakup. It was Yuen (1968) who by taking into account the non-linear behaviour of jet breakup predicted satellite formation. Goedde and Yuen (1970) verified the theory experimentally. They calculated that at low wavenumbers (\(k.a = \text{dimensionless wavenumber, with } k = 2\pi/\lambda, [m^{-1}] \text{ and } a = \text{jet radius [m]}, \)
\(k.a \sim 0.2\), the volume of the satellites become equal or almost equal to the volume of the main droplet. In practise, however, at these low wavenumbers two droplets per wavelength are formed. What clearly could be seen from these calculations was that at higher wavenumbers, \(k.a > 0.7\), the volume of the satellites becomes zero. So then uniformly sized droplets can be expected at a rate of one per wavelength.
Figure 2.8: Photograph of a breakup process of a 2% alginate solution with a longitudinally vibrated nozzle [Hulst, 1987]
2.5 Vibrating nozzle systems

To promote uniform jet breakup, it is possible to superpose an external vibration onto the liquid jet. It was Sakai et al. (1980, 1982, 1985) who described regions of uniform breakup of liquid jets for a longitudinally vibrated jet. Hulst et al. (1985) produced immobilized biocatalysts with a vibrating jet system. His jet system is showed in Figure 2.8. Meesters (1992) performed jet experiments with water, ethylene glycol 66%, and Na-alginate using a longitudinally vibrating nozzle what resulted in narrow size distributions of droplets. Heinzen and Widmer (1997) produced droplets with a vibrating system as well and specified the region to produce uniform droplets. Up till now this technique seems not to be in practice for fluid metals.

Meesters (1992) performed experiments to verify that uniformly sized droplets are formed only at wavenumbers greater than about \( k.a = 0.6 \) as reported by Yuen in 1968. He also showed the existence of regions of uniform jet breakup and predicted upper and lower limits for these regions. For low viscosity liquids he found that uniform jet breakup was possible for wavenumbers in the range of \( 0.6 < k.a < 1.0 \). For a more viscous jet, he found a maximum value of the wavenumber at about \( k.a = 0.7 \).

The formation of uniformly sized droplets without any satellite formation by using mechanical vibrations has been described by many investigators. It can easily produce uniform droplets of desired size and number.

Both Newtonian and non-Newtonian liquids and slurries of low and high viscosity can be atomised. Although easy production of uniform droplets is reported often, it is still difficult to predict the droplet size of the produced particles. Not only the liquid properties have to be considered, but also the apparatus parameters, the imposed frequency, the amplitude of the disturbance, the liquid flow rate and the nozzle diameter.

An area enclosed by the upper and lower frequencies and the upper and lower liquid velocities represents the region of uniform jet break-up. An example of such a plot is shown in Figure 2.9 for a alginate-solution jet in air.

![Figure 2.9: Example of uniform jet breakup region. \( f_h \) and \( f_l \) = resp. highest and lowest frequency for uniform breakup; \( u_h \) and \( u_l \) = resp. highest and lowest liquid velocity of the jet [Meesters, 1992]](image)

---

3 One relevant article was found: Warner, N.A., Stream breakup in vacuum degassing, J. of the Iron and Steel Institute, Jan 1969. This article was not used in this project.
The transition at the minimum liquid velocity line from dripping to smooth jet is said by Lindbald and Schneider (1965) to occur when the Weber number based on the jet diameter has a value of \( \text{We} = 8 \).

Beyond the higher liquid velocity boundary, the jet transforms from laminar to transitional because of turbulence near the orifice and air friction. Grant and Middleman (1966) found for the transition from smooth to wavy jet the following relationship:

\[
\text{Re} = 325Oh^{-0.28}
\]

(2.14)

The frequency limits shown in Figure 2.9 are not well described. Meesters (1992) showed that the droplets produced have a maximum and a minimum size, determined by the nozzle diameter. The frequency of producing these droplets can be altered by increasing the liquid velocity of the jet. This is graphically shown in Figure 2.10.

Figure 2.10: An experimentally determined region of uniform jet breakup, and the corresponding droplet diameters obtained; \( f_h \) and \( f_l \) = resp. highest and lowest frequency for corresponding droplet diameters obtained; \( d_h \) and \( d_l \) = resp. highest and lowest droplet diameter [Meesters, 1989]

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2.6 Guideline for vibrated jet experiment

The following part will discuss the guidelines to perform a successful vibrating nozzle experiment (Hulst, 1987). The optimum wavelength ($\lambda_{opt}$) for breakup, according to Weber, is given by:

$$\frac{\lambda_{opt}}{d_j} = 4.44(1 + 3Oh)^{1/2} \quad (2.15)$$

The optimum frequency ($f_{opt}$) is related to the jet velocity ($u_j$) and the wavelength by:

$$f_{opt} = \frac{u_j}{\lambda_{opt}} \quad (2.16)$$

When a jet is mechanically vibrated at a frequency based on Equation (2.16), drops of uniform size are formed.

As discussed above, Meesters (1992) found an optimum breakup performance for the range $0.6 < k_a < 1.0$ (corresponding to $5.2d_j < \lambda < 3.14d_j$)

Assuming that one liquid cylinder with length $\lambda$ breaks up in one droplet with diameter $d_p$, it is easily seen that:

$$\frac{1}{4}\pi d_j^3 \lambda_{opt} = \frac{1}{6}\pi d_p^3 \quad (2.17)$$

When the volumetric flow rate is expressed as:

$$\phi_v = u_j \frac{1}{4}\pi d_j^2 \quad (2.18)$$

then the droplet diameter, after substituting equations (2.16) and (2.18) into the mass balance (2.17) is given by:

$$d_p = \left( \frac{6\phi_v}{\pi f_{opt}} \right)^{\frac{1}{5}} \quad (2.19)$$

Substitution of Equation (2.17) into (2.15) gives:

$$\frac{d_p}{d_j} = 1.89(1 + 3Oh)^{1/6} \quad (2.20)$$

Figure 2.11 shows that the influence of the viscosity is negligible when log Oh < 0
Although this guideline suggests an exact vibration frequency, the optimal frequency has to be found by visually fine-tuning with, for example, a stroboscope.

Hulst (1987) used a vibrating nozzle system to breakup a jet producing alginate droplets. He produced droplets with a diameter range of less than 10 per cent. A schematic representation of his nozzle system is shown in Figure 2.12. A metal pin is mounted onto a flexible membrane, which floats onto the liquid and vibrates in longitudinal direction. The vibration is propagated through the membrane into the liquid, and will force the issuing jet to breakup.
3 Wetting

When forming a metal droplet at a nozzle, the degree of wetting of the liquid metal onto the solid nozzle surface is an important parameter. In this chapter surface tension and wetting behaviour will be shortly reviewed. Further, more detailed discussions can be found in textbooks on physical chemistry (Murr, 1975; Adamson, 1982; Hunter, 1993).

3.1 Contact angle and wetting behaviour

When a drop of liquid is placed on a solid surface, the contact angle is a measure of the competing tendencies of the drop to spread out and cover the solid surface and to minimize its surface tension by forming a droplet. Rounding may seem to be the natural process, since it also reduces the area of liquid/solid contact but that neglects the fact that the solid/vapour interface is thereby increased. The contact angle measures the wetting tendency of a liquid on a solid.

![Figure 3.1: Liquid drop formed on a solid surface.](image)

For a brief discussion of wetting behaviour of liquids on solid surfaces, a simple derivation [Adamson, 1982] is given. The change of surface free energy $\Delta G^s$, accompanying a small displacement of the liquid such that the change in area of solid covered is $\Delta A$ (Figure 3.1), and is given by

$$\Delta G^s = \Delta A (\gamma_{SL} - \gamma_{SV}^\circ) + \Delta A \gamma_{LV} \cos(\theta - \Delta \theta)$$

(3.1)

$\Delta G^s$ = surface free energy  
$\Delta A$ = small displacement  
$\gamma_{SL,SV, LV}^\circ$ = surface tension of solid-liquid, solid-vapour  
$\theta$ = contact angle

(\(\gamma_{SV}^\circ\) = in equilibrium with sat vapour pressure) and liquid-vapour resp.
At equilibrium,

$$\lim_{\Delta A \to 0} \frac{\Delta G^S}{\Delta A} = 0$$

Equation (3.1) becomes:

$$\gamma_{SL} - \gamma_{SV} + \gamma_{LV} \cos \theta = 0$$

or:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$

Equation (3.2) is called the Young equation. It is important to keep in mind that the phases are mutually in equilibrium. In particular, the designation $\gamma_{SV}^0$, is a reminder that the solid surface must be in equilibrium with the saturated vapor pressure $P_0$.

For practical purposes, if the contact angle is greater than 90°, the liquid is said not to wet the solid. In such a case, drops of liquid tend to move about easily on the surface and do not enter capillary pores. On the other hand, a liquid is considered to wet a solid only if the contact angle is zero. It must be understood that this last is a limiting extreme only in a geometric sense.

The difference between the adhesion of, for example, liquid metal to the solid and the cohesion of the metal to itself, is expressed by the term wetting. A liquid will wet another material if its own work of cohesion is less than the work of adhesion between it and the substrate.

The metal used in this project can be considered as non-wetting on steel nozzles. To enhance proper defined droplet formation the nozzle edge has to be sharp and 90°.

---

4 It can be shown, that regardless of the macroscopic geometry of the system, $\Delta \theta / \Delta A$ behaves as second order differential and drops out in taking the limit of $\Delta A \to 0$. 
4 Solidification and Spheroidisation

In this section the solidification and the spheroidisation of the droplets in the cooling liquid is discussed. After the drop is detached from the nozzle, it will fall through the cooling liquid. In this stadium, the droplet will solidify and reach its final shape.

4.1 Spheroidisation

Drops tend to deform when subject to external fluid fields until normal and shear stresses balance at the fluid-fluid interface with surface tension forces. The shape of a free falling (or rising) droplet in another immiscible liquid is determined by three dimensionless numbers. The Reynolds number (Re), the Eötvös number (Eo) and the Morton number (Mo):

\[ \text{Re} = \frac{\rho_L d_e v}{\eta_L} \]  
\[ \text{Eo} = \frac{g d_e^2 \Delta \rho}{\sigma} \]  
\[ \text{Mo} = \frac{g \eta_L^4}{\rho_L^2 \sigma^3 \Delta \rho} \]

\( \rho_L \) = density of the fluid  
\( d_e \) = volume equivalent diameter of the bubble or drop  
\( v \) = rising velocity of the bubble or drop  
\( \sigma \) = surface tension  
\( \eta_L \) = dynamic viscosity of the fluid  
\( \Delta \rho \) = density difference between two phases

In Figure 4.1 the empirical relation between these three parameters is graphically presented. This graph is taken from Clift (1978). The graph is valid for Newtonian liquids. So far liquid metals are considered as Newtonian liquids, this graph is used as a guideline. A drop is approximated closely by a sphere if interfacial tension are much more important than inertia forces.

Looking closely into the Reynolds, Eötvös and Morton number (Equations (4.1), (4.2), (4.3)) in combination with Figure 4.1, the viscosity \( \eta_L \) of the cooling liquid is the controlling parameter to the shape of the falling droplet (as the metal properties are kept constant).
4.2 Fall through the gas atmosphere

The detached droplet starts its fall in a gas atmosphere. Disadvantageous deformation effects caused by the impact of the liquid droplet onto the surface of the cooling liquid must be avoided. The developed fall velocity at the point of impact must be less than the eventual terminal velocity in the cooling oil. Therefore the distance between nozzle and the top surface of the cooling liquid (free fall distance) must be minimized.

The free fall distance is also minimized to avoid early solidification (cooling down) in the gas atmosphere.

So there is no opportunity for the liquid droplet to solidify while falling through the gas.
4.3 Gas atmosphere

Another important aspect of the gas atmosphere is the atmosphere composition. Oxygen and other oxidation components will oxidize the hot surface of the liquid metal droplet. Experiments must give an insight in the influence of the gas composition on the droplet formation (See Section 6.1).

4.4 Solidification of the droplet

The liquid metal droplet submerges in the cooling liquid after detachment and a short free fall through the gas atmosphere. It will start to cool down while it is falling through the cooling medium. Different parameters play a role in the cooling of the droplet towards solidification. Velocity, diameter of the droplet, cooling liquid viscosity, temperature gradient of the droplet and the cooling liquid etc. A short overview will be presented in this section of the physical principles of the cooling process.

For the heat transfer of a falling spherical particle, the following heat balance is presented (Equation (4.4)).

\[
\frac{d}{dt} \left( \frac{\pi}{6} d_p^3 \rho_{\text{metal}} e_{p,\text{metal}} T_{\text{droplet}} \right) = -h \pi d_p^2 (T - T_w)
\]

- \(d_p\) = diameter of the droplet
- \(\rho_{\text{metal}}\) = density of the metal
- \(e_{p,\text{metal}}\) = specific heat of the metal
- \(T_{\text{droplet}}\) = mean temperature during fall
- \(t\) = time
- \(h\) = heat transfer coefficient
- \(T_w\) = outside temperature

For simplicity three assumptions are made. First is assumed that the resistance to heat transfer in the bulk phase is higher than that of the metal particle\(^5\). Therefore, the temperature throughout the particle is considered uniform. Secondly the viscosity of the cooling liquid is replaced by a logarithmic mean value (Equation 4.5).

\[
\eta_{\text{L,ln}} = \eta(T)_{\text{boundary}} - \eta(T)_{\text{bulk}} \ln \frac{\eta(T)_{\text{boundary}}}{\eta(T)_{\text{bulk}}}
\]

- \(\eta_{\text{L,ln}}\) = logarithmic mean viscosity
- \(\eta(T)_{\text{boundary}}\) = viscosity of the cooling liquid at the droplet edge
- \(\eta(T)_{\text{bulk}}\) = viscosity of the cooling liquid of the bulk.

\(^5\) The heat transfer coefficient \(h\) for metals is about 100 times higher than for oils
Figure 4.2: Viscosity ($\eta$) gradient over the boundary layer between the droplet and the cooling liquid.

The temperature of the surrounding "bulk" liquid has a lower temperature than the droplet. A temperature gradient exists over the boundary layer between droplet and cooling liquid. This temperature gradient induces a viscosity gradient as the viscosity of cooling liquid shows a temperature relation. The viscosity gradient is schematically presented in Figure 4.1. The third assumption is that the bulk temperature of the oil is controlled at a constant value.

With the boundary conditions $t = 0$, $T = T_0$, Equation (4.4) is integrated and results into Equation (4.6)

$$\ln \frac{T - T_w}{T_0 - T_w} = -\frac{6h}{\rho_{oil} c_{p,oil} d_d} t$$

(4.6)

$T_0$ = begin temperature  
$x$ = cooling distance  
$v$ = fall velocity

The distance $x$ that the liquid droplet needs to cool down, is defined by Equation (4.6). For the solidification distance, the heat of solidification is required. Equation 4.6 will then be altered. Appendix C will show this and calculations on cooling down and solidification distance are shown as well.

The fall of a particle through the medium is characterized by the following instationary force balance, ignoring all hydrodynamic forces except drag.

$$M \frac{dv}{dt} = Mg - C_D A_\perp \frac{1}{2} \rho_{oil} v^2$$

(4.7)

$M$ = mass of falling droplet  
$v$ = fall velocity  
$g$ = gravity constant  
$C_D$ = drag coefficient  
$A_\perp$ = cross-section area of the droplet  
$\rho_{oil}$ = density of the oil

$C_D$ is a drag-coefficient. This drag-coefficient is related to the Reynolds-number.
The drag coefficient which is needed for these calculations is calculated with Equation (4.8). This relation, valid up till Reynolds numbers of 800, is an approximation of the well known $C_D$-curve.

\[
C_D = \frac{24}{Re} \left(1 + 0.15 \frac{Re^{0.6}}{Re} \right)
\]  

$\text{Re} < 800$

The following relation for the heat transfer coefficient ($h$) is valid

\[
Nu = \frac{h \delta}{\lambda_{\text{vol}}} = 2.0 + 0.66 \left( \frac{Re}{Pr} \right)^{1/3} \left( \frac{P_e}{Pr} \right)^{1/3}
\]  

$10 < \text{Re} < 10^4; \text{Pr} > 0.7; \text{Pe} \gg 1$

Equation (4.9) contains various dimensionless numbers. The Reynolds number, which has been discussed in Section 2.3, Equation 2.5.

The Prandtl number represents physically the hydrodynamic boundary layer balanced by the thermal boundary layer between sphere and bulk cooling liquid.

\[
Pr = \frac{c_p \eta}{\lambda}
\]  

The Péclet number for heat transfer gives the balance between the convective and conductive heat transfer

\[
P_e = \frac{\nu d_s}{a}
\]  

\[
a = \frac{\lambda}{\rho c_p}
\]

$a$ is the thermal diffusivity.

Applying the discussed equations above (Eq. 4.4 - 4.11), an analysis can be made to estimate the solidification distance of the liquid metal droplet. Calculations are shown in Appendix C.
4.5 Oscillations of spherical droplets

When the metal drop has been detached, it falls onto the interface between gas and liquid. Triggered by the deformation caused by the impact on the cooling liquid, it starts performing small-amplitude oscillations, while falling through the cooling medium. Lamb (1945) derived for the frequency of small-amplitude oscillations of spherical drops:

\[
\omega_n = \sqrt{\frac{4\pi}{3} \frac{n(n-1)(n+2)}{m} \frac{\sigma}{a}} \tag{4.12}
\]

\(\omega_n\) = frequency of small-amplitude oscillation
\(n\) = the mode of oscillation, equal to the number of nodal circles on the droplet's circumference
\(\sigma\) = surface tension
\(m\) = mass of the drop

4.6 Free breakup of a falling droplet

A droplet produced at the nozzle tends to breakup in smaller droplets when friction force on the droplet is higher than the surface tension force which promotes the droplet to become spherical. A liquid droplet will not breakup until the Weber number of the droplet exceeds a critical value of 19 [Yule et al., 1994].

\[
We_{crit} = \frac{\rho g d_{\text{d,max}} v^2}{\sigma} \approx 19
\]

This criterion is only valid for Newtonian fluids.
5 The Experimental Setup

This chapter describes the experimental setup which was used to produce the shot particles.

5.1 The overall setup

The shot production device used for the experiments in the Hunting Alloy project is originally designed by Witmetaal B.V. More details of the first design and trials are described by Biglari, Godijn and De Rooij, 1997. For the project at the Kramers Laboratorium voor Fysische Technologie the original design is modified. The modified setup is described here. Technical details are described in the appendix A. In Figure 5.1 the overall scheme of the setup is drawn.

The tin-bismuth alloy is melted in the metal storage vessel (Figure 5.1, A2) by two heating jackets. The metal storage vessel has a capacity of 25 kg metal. The heating system is able to heat the system up to temperatures of 300 °C. The storage vessel is mixed by an air-driven mixer (A1) about at 200 revolutions per minute. The metal storage vessel provides the metal dosing pot (A5) with a controlled amount of metal. A heating jacket heats the metal dosing pot as well. The metal dosing pot is equipped with an electrical level control (A3). Under the metal dosing pot the main part of the device is situated: the nozzle (A7). Under the nozzle, a glass container is fitted. This container is filled with nitrogen to avoid oxidation of the metal. This container also enables an active cooling liquid level control. A pump, which is also responsible for the nitrogen outlet, sustains the cooling liquid level in the glass cylinder (B15). The produced metal particles are collected in a glass cylinder filled with a cooling liquid.

5.2 The heating system

Two heating jackets heat the metal storage vessel. Both are separately temperature controlled (A6). When the metal level drops under the top jacket this one is automatically shut off to avoid overheating. Both jackets are controlled at a temperature between 250 °C – 300 °C. The transfer pipe from the metal storage vessel to the metal dosing pot is heated by an electrical heating wire. The transfer has to be heated to avoid solidification and obstruction of the metal supply into the metal dosing pot. The wire temperature is also controlled at a temperature between 250 °C – 300 °C. The metal dosing pot is heated by one heating jacket. The temperature is controlled stand alone. The temperature of the metal dosing pot is controlled between 250 °C – 300 °C. All temperature controls have an control accuracy of ± 5 °C. The temperatures are measured with standard thermocouples.

5.3 The metal dosing system

The gravitational force of the liquid metal above the nozzle induces the metal to flow through the nozzle. Therefore, the metal level in the metal dosing pot directly controls the droplet formation. The maintenance of this level is an important operating parameter. The relation of the metal flow through the nozzle and the height H in the metal dosing pot is illustrated in Figure 5.2.
Figure 5.1: (A) Shot production device; (B) Magnification of metal dosing pot.
Figure 5.2: Illustration of the metal liquid height in the metal dosing pot in relation with the metal flow rate.

The metal pen (B10) is made variable in height by a screw thread. The metal pen that is drilled into the metal dosing pot is connected with the valve of the metal storage vessel through an electronic circuit. When the pen contacts the liquid metal surface the valve (A4) of the metal storage vessel is closed and vice versa when the pen looses contact, the valve is opened to fill the dosing pot again until the contact is reestablished. The height of the screw thread is proportional to the height of metal above the nozzle. The metal flow is proportional to the metal height in the metal dosing pot.

The flow is adjusted by manually altering the height of the screw thread.

5.4 The nozzle

The single droplet formation mechanism, discussed in Sections 2.2 - 2.4, was applied to produce the particles directly out of the liquid phase. The formation was promoted through a nozzle system.

Different nozzles could be mounted into the metal dosing pot. The different nozzles geometries are summarised in Table 5.1 and shown in Figure 5.3. The nozzles made for the non-wetting trials were manufactured of stainless steel type 1.8504. The stainless steel was nitratated up to a depth of 0.2 mm to assure non-wetting conditions. For the non-wetting trials, nozzles of different inside diameter were used. The nozzles made for the wetting trials were made of copper.

Table 5.1: Different nozzle types

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Figure</th>
<th>Diameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitreerstaal 1.8504</td>
<td>I</td>
<td>Figure 5.3 type I</td>
<td>D₁ = 1.0 mm</td>
</tr>
<tr>
<td>Nitreerstaal 1.8504</td>
<td>II</td>
<td>Figure 5.3 type II</td>
<td>D₁ = 1.5 mm</td>
</tr>
<tr>
<td>Copper</td>
<td>III</td>
<td>Geometry as Figure 5.3 type I</td>
<td>D₁ = 1.0 mm</td>
</tr>
</tbody>
</table>
5.5 The nitrogen atmosphere system and oil level system

To create a non-oxidising atmosphere around the nozzle, the setup is equipped with nitrogen atmosphere system. The glass container (B15) around the nozzle is filled with 99.999% nitrogen. A constant flow nitrogen is put through the chamber. The inlet flow is set at 215 ml/min and monitored by a mass flow controller. (See Appendix A for details) The outlet flow is proportional to the inlet flow.

The combined nitrogen and cooling liquid flow is removed by the action of a displacement pump (A8, B13). The outgoing flow is set at 215 ml/min. The cooling liquid/nitrogen mixture is recycled back to the glass cylinder. A constant oil level is reached. However sometimes cooling liquid fluctuations in the level are seen due to the peristaltic movement of the pump.

To avoid oxidation on the top of the metal surface in the metal dosing pot, a diluting nitrogen flow is added on top of the metal surface. This flow is monitored by a flow meter as well. This flow is set at 175 ml/min.

5.6 The cooling liquid

The cooling liquid is contained in a glass cylinder. The height of the cylinder is 0.60 m. The outside diameter is 0.134 m. The thickness of the glass is 0.07 m. The glass cylinder is equipped with an overflow pipe to relieve the increasing level of cooling liquid by submerged metal droplets and increasing temperature during production. The glass has been chosen to enhance visibility of the metal particles falling through the liquid.

First Serdox NOG 440 was used as the cooling medium. Serdox is an ester of polyethylene glycol (10 units) and oleic acid.

The last trials were executed with Madrela T. Madrela T is a compressor oil of Shell. Madrela T was used to enhance the spheroidization of the particle through the high viscosity index of the oil. Further detailed physical properties are described in Appendix B.
5.7 Visualisation technique

A high speed camera system was used to visualise the dripping dynamics of the "hunting alloy" setup.

Two different cameras have been used. One camera with a maximum frame rate of 750 Hz (128 x 126 pixels per frame) and a camera with a maximum frame rate of 200 Hz (256 x 256 pixels per frame) camera were available for visualisation.

The field of view of the 750 Hz camera is about 1 cm². The field of view of the 200 Hz camera is 3 cm².

The dripping dynamics at the nozzle were filmed as well as the cooling droplet falling through the nozzle. A 500 Watt halogen-lamp has been used to illuminate the setup. (Front-lighted). To enhance the contrast a white paper screen was set behind the nozzle.

A 105 mm objective has been used to assure the magnification.

The frames were further processed with the software application SCILIMAGE.
6 Results and Discussion

In this chapter, the results of the different trials are discussed. The metal properties were held constant at the same values within all trials. The metal temperature was set at 275 °C. This temperature was found suitable for stable production by Biglari et al. (1997).

6.1 Oxidation at the nozzle

The first test trials were executed to investigate the influence of air oxidation of the liquid metal on the droplet formation process. To obtain detailed information, a high speed CCD camera was used. For investigation of the influence of air oxidation, two different trials were performed. In both trials a nozzle diameter of 1.0 mm was used. Comparable conditions as temperature and metal flow rate were applied.

The first trial was executed in an air atmosphere. The results are shown in Figure 6.1. The pictures were obtained with a frame rate of 500 Hz (128x126 pixels per frame). The actual size of the frame is shown in the first frame. The outside nozzle diameter is 4 mm.

The air oxidation is assumed to react fast with the surface of the liquid metal droplet. The oxidation takes place in 0.03 seconds. The created "rigid" oxidized layer disturbs the normal droplet formation mechanism. The wobbling movement (towards sphericity) of the detached droplet is not strong enough to counteract this rigidity and a sharp point-tail shaped droplet is formed.

Figure 6.1: Droplet formation with air atmosphere (D\textsubscript{nozzle} = 1.0 mm, 500 frames/sec)

The resulting shot particles are displayed in Figure 6.2. The point-tail shape is easily recognized.

---

6 CCD = Charged Coupled Device
The second trial was executed in a nitrogen atmosphere. The CCD camera was used again with a frame rate of 500 Hz (128x126 pixels per frame). The obtained pictures are shown in Figure 6.3. In frame 8 of this figure, the flexible oscillation (i.e. wobbling) towards sphericity is executed. Nitrogen protects the fluid metal surface from oxidation and becoming "rigid".

Figure 6.2: Result of droplet formation with air-oxidization

Figure 6.3: Droplet formation with nitrogen atmosphere (D_{nozzle} = 1.0 mm, 500 frames/sec)
The resulting shot particles from the nitrogen trial are displayed in Figure 6.4. Their spherical shape is recognized.

![Figure 6.4: Shot particles produced with nitrogen atmosphere Mean $d_p=2.8$ mm](image)

### 6.2 Oil vapor oxidation

Later trials showed another disturbing side effect. With long duration trials ($t > 2$ h) the oil was deposited on the metal surface around the nozzle (in the glass container). This oil was evaporated by the high temperature of the steel metal surface ($275$ °C) or even disintegrated to high reactive radicals. This oil vapor was not immediately removed by the oil/nitrogen outlet. The resulting shot particles had an ellipsoid form (Figure 6.5). The time scale of this oil vapor oxidation is apparently larger than the time scale of air oxidation.

![Figure 6.5: Result of droplet formation with oil-vapor](image)

### 6.3 Pressure instabilities

The droplet production is very sensitive to pressure build-up in the nitrogen chamber. When a certain overpressure is reached, the droplet formation stops abrupt. Trials with the Madrela T oil ($D_{\text{nozzle}} = 1.5$ mm) revealed that instabilities began to play a role when the overpressure exceeded 1 cm oil column. Figure 6.6 shows the overpressure situation schematically.
Pressure ($\Delta P$) can be presented by the height of a liquid column ($\Delta h_{oil}$). Equation (6.1) shows the relation.

$$\Delta P = g \rho_{oil} \Delta h_{oil} \quad (6.1)$$

The glass cylinder of the setup (Figure 6.6) makes it possible to measure the difference in height of oil ($\Delta h_{oil}$) inside and outside the tube. When the inner level is lower than the outside level there is an overpressure in the glass cylinder. With Equation (6.1) the critical overpressure based on 1 cm oil column, equals 0.1 kPa ($\rho_{oil} = 1050 \text{ kg/m}^3$).

For the experiments with the 1.5 mm nozzle, the metal height $H$ was 8 mm. This $H$ corresponds with a "hydrostatic" pressure on the nozzle of 0.57 kPa ($\rho_{metal} = 7252 \text{ kg/m}^3$). See Figure 5.2 for the relation of the metal height with the metal flow rate.

The pressure drop caused by capillary rise ($\Delta P = \sigma/r$) is 0.249 kPa. Thus the "hydrostatic" pressure is counteracted by the capillary rise and the overpressure in the glass cylinder.

For pressure instabilities around 0.1 kPa, the droplet formation process becomes unstable and can stop.

### 6.4 Droplet formation mechanisms for a tin-bismuth alloy

After the oxidation trials, which are discussed in the previous sections, trials were performed to visualise the different droplet formation mechanisms for tin-bismuth. For Newtonian fluids these mechanisms have been discussed in Section 2.1. The CCD high speed camera was used to enhance visibility (500 frames/s). A 105 mm camera objective assured the satisfactory magnification.

To get an overview of the different mechanisms, the droplet formation dynamics at the nozzle were filmed at a range of metal flow rates. As discussed in chapter 5, the metal flow rate was controlled by the height of the metal level in the metal dosing pot. It appeared to be impossible to keep the metal flow rate constant for a set height of the metal pen (Figure 5.1, 10B). The metal feed from the metal storage vessel into the small metal dosing pot was too high to assure a constant level. Therefore the filmed mechanisms could not be accompanied with the appropriate quantitative flow rates. The next section shows that the critical flow rates were determined alternatively.

Although the flow rate was not determined parallel with the filming, the different theoretical mechanisms could be visualised. Primary single droplet formation could be distinguished from secondary single droplet formation. In Appendix D, the obtained films of different droplet formation mechanisms are displayed.
6.5 Static and quasi-static (chaotic) droplet formation

As discussed in Section 2.3, a sharp transition for static to quasi-static droplet formation exists for Newtonian fluids. The critical flow rate, which accompanies this transition, is an important process parameter, as we aim to produce at maximum production rate in the periodic droplet formation regime.

To determine this critical parameter for the tin bismuth alloy, trials with a nozzle diameter of 1.0 mm were performed. A metal flow rate range of 0 up to 0.3 ml/s was applied.

![Graph](image)

Figure 6.7: Results of trials at various metal flow rates (0-0.3 ml/s)

The flow rates were measured directly using a spoon to collect a sample, while timing the collection-interval with a stopwatch. The mechanism of droplet formation was determined visually. Afterwards, the weight, size and shape factor of the collected particles were determined (see Chapter 5). The obtained results of two trials are shown in Figure 6.7.
It can be observed, that the data points\(^7\) of both trials lie under the theoretical values of the quasi-static equation of Van den Berg (1996), Eq. (2.4). The scatter of the mean diameters for different metal flow rates is explained by the rough experimental method of measuring the metal flow rate. The manual interval time measurement introduces an error of maximum 10\%. Despite this deviation, a qualitative interpretation of the results is allowed. The quasi-static equation of Van den Berg is valid as a maximum boundary of the dripping mechanism. Due to dynamic instabilities, the real diameter of the obtained shot particles will deviate from the ideal. The volume of the cone that remains at the nozzle after detachment, is also responsible for the discrepancy between the Van den Berg relation and the data points.

The critical flow rate for the transition of static to quasi-static droplet formation was examined through measuring the diameter distribution of each solidified sample. This diameter distribution is defined as the diameter range:

\[
\text{Diameter range} = \frac{D_{\text{max}}}{D_{\text{min}}}
\]  

(6.2)

The diameter range of the two trials are shown in Figure 6.8. When the critical flow rate is exceeded, the droplet formation mechanism transits towards quasi-static droplet formation. This transition should result in a higher diameter range because, as discussed in section 2.3, the droplet formation is not uniform anymore and leads to a range of different diameters. This effect is observed with metal droplet formation as well. In Figure 6.8 this could be observed. When the metal flow rate exceeds the value of 0.16 ml/s, the diameter range increases dramatically.

As discussed in section 2.3, Dosoudil derived a relation for Newtonian fluids for the critical flow rate. When applying Eq. (2.12) here, the calculated value of the critical flow rate is 0.162 ml/s. This corresponds with the experimental value of 0.16 ml/s. This excellent agreement suggests that Eq. (2.12) is valid for the liquid tin-bismuth alloy as well.

---

\(^7\) All data points are means of 10 (14/4/1998) or 15 (20/4/1998) shot particles
In Figure 6.8, the bifurcation (0.16 ml/s and higher) towards quasi-static droplet formation seems to be accompanied by a split into two extremes, as in Figure 2.3 of Van den Berg. The presumed extremes could indicate the primary (being the low diameter range) and secondary dripping dynamics (being the high diameter range).

6.6 Correction factors

In Section 2.1, the correction factor of Harkins and Brown (1919) was introduced. This correction factor compensates for the discrepancy between the real volume of the detached droplet and the theoretical volume. Wilkinson and Aronson (1973) investigated the validity of the correction factors for low $r/V^{1/3}$ values < 0.3.

Figure 6.9: Comparison of Wilkinson & Aronson correction factors with tin-bismuth trials

Here is tried to evaluate the correction factors for the tin-bismuth case. The data are presented in Figure 6.9. The data for different nozzle diameters of Wilkinson and Aronson (1973) are displayed as three lines for three different mercury surface tension values. For the tin-bismuth case, the correction factor is calculated for the mean diameter and shown for the 1.0 mm and 1.5 mm nozzle. No correlation of the tin bismuth factors with the mercury correction factors is found. The high flow rate level of the tin bismuth shot production process compared to the low flow rate system for precise measurement of surface tensions, does not allow correction by these factors which are determined in these latter processes. Therefore the tin-bismuth process can not be evaluated with the modified Tate equation (Eq.(2.2)).

6.7 Results of trials with $D_{nozzle} > 1.0$ mm

To increase the produced droplet diameter, the nozzle diameter has to be increased. Trials were executed using a nozzle with internal diameter of 1.5 mm. Unfortunately, due to difficulties concerning oil vapour oxidation as discussed in section 6.2 no metal flow rates were measured as was done with the 1.0 mm trials. Critical flow rates could therefore not be determined.

The overall result of one trial (i.e. the collected shot particles) was examined. To determine the mass equivalent diameter, 100 particles were weighed. Particles with point-tail shape were neglected, because their shape is not well defined. The results are summarized in a distribution diagram.
The sample is classified in classes of 0.1 mm. The diagram is shown in Figure 6.10.

![Mass equivalent diameter distribution](image)

Figure 6.10: Classification of the mass equivalent diameters of 1.5 mm nozzle trial

Tate's law (Eq. (2.1)) suggests that by just increasing the nozzle diameter, the diameter of the produced droplet will increase. This is valid until the capillary boundary is reached. When the capillary length scale (Eq. 2.3) is reached, the droplet is not determined by the nozzle diameter anymore. For the tin-bismuth system the capillary length scale is reached at an internal nozzle of 2.3 mm.

A test performed with a nozzle diameter of 2.0 mm, revealed that single droplet formation was no longer possible. The Dosoudil maximum capillary length scale (Eq. 2.4) is not valid in this system. It suggests a maximum nozzle diameter of 5.6 mm.

6.8 Spheroidisation

It is assumed, that the solidification of the liquid metal droplet takes place in the cooling liquid. To prove this statement, films of the liquid droplet falling through the upper part of the cooling liquid (Serdox NOG 440), obtained by the high speed CCD camera, were inspected closely. At frame rates above 600 Hz, nodal oscillations (n=1) of the falling droplet were observed.
As described in section 4.5, a liquid droplet performs oscillations when falling through a Newtonian liquid [Lamb, 1945]. The oscillation frequency for tin-bismuth droplets in Ser­dox NOG 440 oil was determined with Eq. (4.12). The oscillation frequency was 594 Hz (n=1). This high frequency explains why at lower frame rates than 600 Hz, no oscillations were observed.

It is thus justified to state that the solidification mainly takes place in the oil under normal operating conditions. See Appendix D-3 for the film of oscillating droplets.

The viscosity of the cooling liquid is the main control parameter for the spheroidisation of the liquid shot particle, as has been described in section 4.1. To evaluate the shape of the produced shot particles, the shape factor is introduced. The shape factor is the ratio of the largest diameter (L) and shortest diameter (W):

\[
\text{Shape factor} = \frac{L}{W} \quad (6.3)
\]

Figure 6.11: Definition of the shape factor of the mainly ellipsoid shot particles.

The shape of the trials with nozzle diameter 1.0 mm and Ser­dox NOG 440 as coolant, was mainly ellipsoid. Reviewing Figure 4.1: *Shapes of free falling drops in Newtonian liquids* (Clift et al., 1978), this shape corresponds with the "ellipsoid" area in the graph. The calculated Re, Eo and Mo- number agree with the aspected spot in the graph. It indicates an ellipsoid shape. The shape factor of two trails with the 1.0 mm nozzle diameter were determined. A slide gauge was used to measure the lengths of W and L. In Figure 6.12 the determined shape factors are displayed. With increasing droplet diameter, the shape factor increases as well. The sphericity deteriorates, when producing larger droplets.

---

8 Prior solidification than solidification in the oil is caused by oxidation.
Figure 6.12: Determined shape factors of the 14/4 and 20/4 trials

To improve this characteristic of shape factor and droplet diameter, Figure 4.1 was used to choose an oil with a higher viscosity and also a better temperature-viscosity characteristic. The viscosity of the first used Serdox NOG 440 dropped very fast at elevated temperatures. Shell Madrela T was chosen for new trials. The trials with Madrela T were performed with the 1.5 mm nozzle.

The trials with high viscosity oil Madrela T resulted into the following conclusions:

- The sphericity of the shot produced in Madrela T is better than in Serdox NOG 440
- The shot of diameter higher than 3.0 mm produced in Serdox exceeded shape factor = 1.15
- A sample of shot produced in Madrela T with a nozzle of 1.5 mm and a mean diameter of 3.5 mm, had a mean shape factor of 1.045.

Figure 4.1 seems to be valid for tin-bismuth alloy. Both Serdox NOG 440 and Shell Madrela T oil showed Newtonian behaviour. The test results of both oils are shown in Appendix B.
6.9 Maximum production

To indicate where the boundaries of the periodic single droplet formation lie for production directly out of the metal liquid phase, this section summarises the results. The results are listed in Table 6.1. The theoretical critical flow rates [Dosoudil, 1971] and the theoretical volume equivalent droplet diameter [Van den Berg, 1996] for the three tested nozzle diameters are shown. The experimentally determined mean mass equivalent diameters are shown as well. For the 1.0 mm nozzle diameter trials, the critical flow rate (0.16 ml/s) was experimentally determined, and agreed well with the theoretical value (0.162 ml/s). For reference, the maximum production capacity is shown in the last column based on the critical flow rate. In Figure 6.13 the theoretical critical flow rates and volume equivalent droplet diameter are shown graphically.

Table 6.1: Summarized theoretical and experimental results

<table>
<thead>
<tr>
<th>Nozzle diameter (mm)</th>
<th>Critical flow rate (ml/s) [Dosoudil, 1971]</th>
<th>Theoretical volume eq. Droplet diameter (mm) [V.d. Berg, 1996]</th>
<th>Experimental mean mass eq. droplet diameter (mm)</th>
<th>Maximum production rate for 1400 prod. h/y (tons/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.162</td>
<td>2.9</td>
<td>2.7</td>
<td>5.92</td>
</tr>
<tr>
<td>1.5</td>
<td>0.269</td>
<td>3.4</td>
<td>3.3</td>
<td>9.83</td>
</tr>
<tr>
<td>2.0</td>
<td>0.385</td>
<td>3.8</td>
<td>Unstable</td>
<td>14.1</td>
</tr>
</tbody>
</table>

Figure 6.13: Theoretical critical metal flow rates and maximum volume equivalent droplet diameter.
6.10 Statistical Background

An important remark has to be made about the quantitative reliability of the results, reviewed in the above. All trials have in common, that they are produced with a setup, which was unstable. Different process parameters were difficult to control during one trial:

1. The metal flow rate was not constant, due to a fluctuating metal level.
2. The composition of the gas atmosphere of the nozzle chamber was not constant, through blockage of the gas and oil outlet, by temporary present oil slugs.
3. Metal-oxides caused blockage of the nozzle and pressure buildups (section 6.3) in the gas chamber caused cessations of the process. Nozzle blockage, through presumably metal-oxides, showed to be irreversible and necessitated total restart of the process. (cool down, clean, melt-in..). Cessations caused by pressure instabilities showed to be reversible.

These control problems lead to a great number of malfunctions. Successful trials were small in numbers.
The results of the successful trials (read solidified shot particles), reviewed in this report, must be evaluated with care. Because of the small number of trials, only precautious qualitative conclusions can be drawn from them.

To get an idea of the stability of the process during one trial of 3 hours, the results of two separate trials with the same process settings are compared. The nozzle diameter was 1.0 mm and the metal level $H_{metal}$ was set at 15 mm. To compare both trials, 100 particles were taken from the collected shot. These samples were weighed one by one. The separate weights were converted in mass equivalent diameters. Figure 6.14 shows the classification of the mass equivalent diameters of the two identical trials.

![Mass equivalent diameter distribution](image)

Figure 6.14: Classification of 1.0 mm nozzle diameter trials (14/4 & 20/4); $H = 15$ mm.
Both figures give about the same mean diameter with a high standard deviation. The standard deviation for the 14/4 trial is 9% and 7% for the 20/4 trial. The standard deviation gives an indication of the wide distribution of the diameter produced. Generally, this is explained by the discussed metal level (i.e. metal flow rate) fluctuations. Both figures show another aspect as well. At the diameter class 2.5 - 2.6 mm and 2.9 - 3.0 mm they show a peak. It looks bimodal distributed. An explanation for this phenomenon could lie in the fluctuation of the metal height in the metal dosing pot between a fixed maximum and minimum value. The maximum level causing a higher momentum through the nozzle and thus a lower diameter (2.5 mm) and the minimum level causing a more static droplet formation and thus a higher diameter.

As discussed in the comment on Figure 6.8, these bimodal distribution could be explained as well by the two extreme dripping mechanisms (Van den Berg): primary dripping responsible for the high diameter peak (2.9 - 3.0 mm) and secondary dripping responsible for the low diameter peak (2.5 - 2.6 mm).

Van den Berg (1996) claimed (section 2.2) that the damping of the relaxation oscillations of the liquid cone is proportional to the inverse square of the nozzle diameter $D_{\text{nozzle}}$, viz. $\mu \sim D_{\text{nozzle}}^{-2}$. Increasing the nozzle diameter should result in a wider distribution of droplet diameter. Comparing Figure 6.10 to Figure 6.14, the 1.5 mm nozzle diameter trial shows a standard deviation of 0.21 mm to 0.19 mm and 0.24 mm of the 1.0 mm nozzle diameter trials. No significant increase in distribution width is observed.

### 6.11 Wetting trials

One trial has been executed using the wetting metal copper as nozzle material. The internal nozzle diameter of 1.0 mm has been applied. The geometry of the nozzle is type I, as shown in Figure 5.3. Unfortunately, the copper was not resistant to the tin bismuth alloy at 275 °C. It was dissolved totally within 30 minutes. Despite the disintegration of the nozzle, some results were obtained. As described in section 0, the tin-bismuth showed wetting behaviour, resulting in constriction phenomena onto the outer diameter of the nozzle. No metal creeping upwards at the sides of the nozzle was observed. In the first few minutes, static single droplet formation was observed with the eye. The mean droplet diameter has been determined at 3.8 mm (shape factor 1.15). After 5 minutes, the droplet formation mechanism transformed gradually into jet breakup. Presumably this effect was caused by the slow dissolution of the inner wall of the copper nozzle. Further investigations towards wetting behaviour were not done.
7 Conclusions

The droplet formation process for the tin-bismuth alloy was characterised. The important process parameters were determined.

The static single droplet formation mechanism has been demonstrated to be the most suitable for uniform shot particles production.

7.1 Instability of the Process

- A relation for the maximum stable production rate during single droplet formation has been found and evaluated. This boundary is determined by the nozzle diameter, the metal flow rate through the nozzle and the metal properties (density, surface tension).
- The electrical level system to control the metal flow rate has been demonstrated to be too rough to ensure stable uniform droplet formation, as the dripping mechanism is very sensitive to metal flow rate fluctuations (± 0.05 ml/s).
- Mass production directly out of the liquid phase is feasible, although it has been shown very sensitive to process instabilities, such as fluctuations in the atmosphere composition and metal flow rate.
- Cessations of the droplet formation at the nozzle seem to be explained by pressure build-ups in the gas chamber.

7.2 Process Parameters

- The diameter of the produced particle is determined by the nozzle diameter, the metal flow rate through the nozzle, and the metal properties.
- The gas atmosphere surrounding the nozzle has to be non-oxidising. Oxidising gas components cause unstable droplet formation and non-spherical shapes.
- The viscosity of the coolant, and its temperature - viscosity characteristic is determining the spheroidisation of the liquid metal droplet before solidification.
- Non-wetting nozzle conditions have been proven more stable than wetting nozzle conditions. A wetting nozzle material copper has been tested, but proved to be soluble in tin-bismuth.
- A maximum mean shot particle diameter of 3.3 mm has been produced with a nozzle diameter of 1.5 mm.
- The mean shape factor of this sample has been determined at 1.05. This shape factor is affected by using the compressor oil Madrela T as coolant. An improvement over the results obtained with the former coolant Serdox NOG 440 of 10 % was reached.
8 Recommendations

8.1 Future research

- Determination of the maximum stable nozzle diameter (1.5 mm < D\text{nozzle} < 2.0 mm)
- Find a suitable coolant, which obeys SHE - standards, has a sustainable temperature resistance and assures spheroidisation with a proper viscosity - temperature dependence. Suggestion: DOW CORNING 710 (good thermal stability, good temperature-viscosity characteristics)
- Droplet formation through triggered jet breakup speeds up the production. Therefore it is worthwhile to investigate the possibilities.

8.2 Technical recommendations

- Constant metal flow rate is crucial
  - more sensitive metal level control
  - buffer vessel
- Smooth and well-defined internal nozzle geometry
  - polish internal surfaces
  - sharp 90 degree edge
  - non-wetting material
- Anti-oxidation measures
  - Glove-box principle (total setup in nitrogen atmosphere)
  - Separate oil and vapour outlet
- Appropriate coolant (Suggested: DOW CORNING 710)
  - HSE-standard
  - low vapour pressure at elevated temperatures
  - constant physical properties even at elevated temperatures
  - high viscosity > 200 mPa.s
- Temperature control on vessel
- Minimum free fall through gas atmosphere
- Prevention of pair coupling of liquid droplets
  - acentric turning of metal nozzle system or coolant vessel
9 Literature


Appendix A  Technical Data

A-1 Experimental Setup

<table>
<thead>
<tr>
<th>Detail</th>
<th>Part</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating jackets</td>
<td>Metal storage vessel</td>
<td>Sinus – Aben (Zeist, Holland) 1500 W x 220 V</td>
</tr>
<tr>
<td>Heating jacket</td>
<td>Metal dosing pot</td>
<td>Smit Sinus 595 W x 230 V</td>
</tr>
<tr>
<td>Gas flow meter</td>
<td>Atmosphere around nozzle</td>
<td>Bronkhorst High-tech B.V., SN 86.12.4787.B, Type F-201-EA, $P_{\text{max}}$ 64 bar, $P_{\text{in}}$ 3 bar, $P_{\text{out}}$ 1 bar</td>
</tr>
<tr>
<td>Gas flow meter</td>
<td>Nitrogen flow onto metal surface</td>
<td>Bronkhorst High-tech B.V., SN 87.02.5039.A, Type F201C-FA, $P_{\text{max}}$ 64 bar, $P_{\text{in}}$ 3 bar, $P_{\text{out}}$ 1 bar</td>
</tr>
<tr>
<td>Oil pump</td>
<td>Oil level system</td>
<td>Watson-Marlow 502 S, Slangenpomp, Max fluid flow: 500 ml/min</td>
</tr>
<tr>
<td>Mixer device</td>
<td>Mixing system</td>
<td>Gast Model nr 1AM-NRV-60-GR11</td>
</tr>
</tbody>
</table>

A-2 Mass Balance
"Substitutie balans B5", Mettler, Zürich, Switzerland

A-3 Rotational Viscometer
Contraves Rheomat 115

A-4 Wetting Balance (at Witmetaal B.V.)
GEC Meniscograph Solderability Tester
Appendix B  Physical properties

B-1 Melting Point

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting point [°C]</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Tin (Sn)</td>
<td>232</td>
<td></td>
</tr>
<tr>
<td>Pure Bismuth (Bi)</td>
<td>271</td>
<td></td>
</tr>
<tr>
<td>Alloy Sn 87.5 % Bi 12.5 %</td>
<td>231 (End traject)</td>
<td>DSC</td>
</tr>
</tbody>
</table>

B-2 Density

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature [°C]</th>
<th>Density [kg/m³]</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn 87.5 % Bi 12.5 %</td>
<td>230</td>
<td>7282</td>
<td>Linear estimation with mixing rules*</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>7269</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>275</td>
<td>7252</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>7235</td>
<td>&quot;</td>
</tr>
<tr>
<td>Serdox NOG 440 Oil</td>
<td>20</td>
<td>1020</td>
<td>N.A.</td>
</tr>
<tr>
<td>Madrela T</td>
<td>15</td>
<td>1050</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

* Linear estimation with mixing rules:

When Tin and Bismuth are mixed, the total volume is almost equal to the sum of the separate volumes (no contraction or expansion) (Klein Wassink, 1984). So it is fair to state that the alloy density is a linear function of the volume fractions (or mass fractions):

\[
\frac{1}{\rho} = \frac{f_{\text{tin}}}{\rho_{\text{tin}}} + \frac{f_{\text{bismuth}}}{\rho_{\text{bismuth}}} \tag{B-1}
\]

\[f_{\text{tin}} = \text{mass fraction of tin}
\]

\[f_{\text{bismuth}} = \text{mass fraction of bismuth}
\]

For the temperature dependence of the density, a relation is taken from Smithell Metals Reference Book (1976):

\[
\rho = \rho_0 + (t - t_0) \left( \frac{d\rho}{dT} \right) \tag{B-2}
\]
### Pure Metals

<table>
<thead>
<tr>
<th></th>
<th>$t_0$ [°C]</th>
<th>$\rho_0$ [g/cm³]</th>
<th>$\frac{dp}{dT}$ [mg/cm³.K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth</td>
<td>271</td>
<td>10.07</td>
<td>-1.33</td>
</tr>
<tr>
<td>Tin</td>
<td>232</td>
<td>7.285</td>
<td>-0.613</td>
</tr>
</tbody>
</table>

### B-3 Surface tension

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temperature [°C]</th>
<th>Surface Tension [N/m]</th>
<th>Measurement technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn 87.5 % Bi 12.5 %</td>
<td>250</td>
<td>0.351</td>
<td>GEC Meniscograph</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.396</td>
<td>&quot;</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>0.413</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

### B-4 Viscosity

#### B-4.1 Metal viscosity

<table>
<thead>
<tr>
<th>Metal</th>
<th>Temperature [°C]</th>
<th>Viscosity [mPa.s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn 87.5 % Bi 12.5 %</td>
<td>232</td>
<td>1.969</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.882</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>1.792</td>
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<tr>
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<tr>
<td></td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>330</td>
<td>1.591</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>1.419</td>
</tr>
</tbody>
</table>

The viscosity values for the SnBi-Alloy are obtained from an estimation based on theoretical viscosity relations:

For the viscosity - temperature dependence of liquid metals the following relation is valid:

$$\mu = A \cdot \exp \left( \frac{H_\mu}{RT} \right)$$  \hspace{1cm} (B-3)

$\mu$ = viscosity [Pa.s]  
$A$ = pre-exponential constant [-]  
$H_\mu$ = activation energy [J/mol]  
$R$ = gas constant (8.314 J/mol.K)  
$T$ = absolute temperature [K]
Tin and Bismuth belong to the semi-metals group. For this group holds:
\[
H_\mu = 0.75T_m^{1.2}
\]  
(B-4)

\[T_m = \text{Tamman temperature [K]}\]

The activation energy for the alloy can be calculated using the relation (B-4). For \(T_m = 505 \text{ K (232 °C)}\), \(H_\mu\) becomes \(5.51 \times 10^7 \text{ J/mol}\).

Next the pre-exponential factor \(A\) has to be calculated. With a known viscosity for the SnBi alloy (1.42 mPa.s at 673 K from lida, 1970) equation (B-3) gives the pre-exponential factor \(A\). \(A = 5.3 \times 10^3 \text{ mPa.s}\)

Both constants for Equation (B-3) are known. The viscosity of the SnBi alloy is calculated and displayed in the table above. This estimation holds up to 473 K, because then the Bismuth solidifies in the alloy.

In Figure B-1 the temperature dependence of the viscosity of the SnBi alloy is shown graphically.

![Viscosity of liquid Sn-Bi alloy (12.5 mass % Bi)](image)

Figure B-1: *Temperature dependence of the viscosity for the SnBi-alloy*
B-4.2 Serdox oil viscosity

The temperature dependence of the viscosity for Serdox NOG 440 oil used, was measured using a rotational viscometer. Through extrapolation of the experimental viscosity data (Figure B-2), a relation was fitted for the temperature dependence of Serdox NOG 440 (Equation B-5). For the viscosity's that were experimentally determined, Serdox NOG 440 showed Newtonian flow characteristics. For the extrapolated values Newtonian behaviour is presumed as well.

\[
\ln \eta = \frac{3.95 \cdot 10^3}{T} - 15.51
\]  

(B-5)

<table>
<thead>
<tr>
<th>Oil</th>
<th>Temperature [K]</th>
<th>Viscosity [mPa.s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Serdox NOG 440</td>
<td>20</td>
<td>131.5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>53.6</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>24.3</td>
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<td></td>
<td>100</td>
<td>6.44</td>
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<tr>
<td></td>
<td>150</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Figure B-2: *Viscosity Temperature characteristic of Serdox NOG 440 oil*
B-4.2 Madrela T oil viscosity

The temperature dependence of the viscosity for Madrela T oil used, was measured using a rotational viscometer. Through extrapolation of the experimental viscosity data (Figure B-3), a relation was fitted for the temperature dependence of Madrela T oil (Equation B-6). For the viscosity's that were experimentally determined, Madrela T oil showed Newtonian flow characteristics. For the extrapolated values Newtonian behaviour is presumed as well.

$$\ln \eta = \frac{5.62 \cdot 10^3}{T} - 19.73$$  \hspace{1cm} (B-6)

![Viscosity of Madrela T oil graph]

Figure B-2: Viscosity Temperature characteristic of Madrela T oil
B-5 Phase diagram

Figure B-3: Phase diagram of tin-bismuth alloy
Appendix C  Calculations

C-1 The frequency of an oscillating liquid drop in a surrounding liquid

From Lamb, 1945:

\[ \omega_n = \sqrt{\frac{4\pi}{3} \frac{n(n-1)(n+2)}{m} \frac{\sigma}{m}} \]

\( \omega_n \) = frequency of small-amplitude oscillations
\( n \) = the mode of oscillation, equal to the number of nodal circles on the droplet's circumference
\( \sigma \) = surface tension
\( m \) = mass of the drop

The common mode of oscillation is \( n = 2 \)
For the surface tension, the surface tension of the metal is taken into account only. The influence of the oil is neglected.

Thus:

\( n = 2 \)
\( \sigma = 0.374 \text{ N/m} \)
\( d_p = 3 \text{ mm} \)
\( m = \rho_{\text{metal}} V_{\text{droplet}} = 7252 \times \frac{1}{6\pi d_p^3} = 0.103 \times 10^{-3} \text{ kg} \)

Thus: the frequency of an oscillating droplet is \( 349 \text{ Hz} \)
C-2 Estimation of the solidification distance

Some simplifications were made:

* The resistance to heat transfer lies in the oil (h_{oil} is about 100 times lower than for the metal)

* The viscosity gradient over the boundary layer between droplet surface and bulk cooling liquid is replaced by a logarithmic mean value:

$$
\eta_{L,ln} = \frac{\eta(T)_{boundary} - \eta(T)_{bulk}}{\ln \frac{\eta(T)_{boundary}}{\eta(T)_{bulk}}}
$$

$$
T|
\eta(T)_{boundary} = \text{viscosity of the cooling liquid at the droplet edge}
\eta(T)_{bulk} = \text{viscosity of the cooling liquid of the bulk.}
$$

* The oil does not warm up (20 °C).

For theoretical details see Section 4.4

Heat balance over the spherical droplet

$$
d\frac{\pi d^3 \rho_{metal} c_{p,metal} T\text{droplet}}{6} = -h\pi d^2 (T - T_w)
$$

$$
T_{droplet} = \text{mean temperature during fall}
T_w = \text{outside temperature}
$$

After integration with t = 0 -> T = T_0 , Equation 4.4 turns into Equation 4.6

$$
\ln \frac{T - T_w}{T_0 - T_w} = -\frac{6h}{\rho_{metal} c_{p,metal} d_d}
$$

$$
T_0 = \text{begin temperature}
x = \text{cooling distance}
v = \text{fall velocity}
$$
Because the temperature of the droplet decreases, we have an instationary problem. Therefore some more simplifications are made:

* $h$ is presumed constant in the temperature
* $T$ is seen as the mean temperature over the fall

Heat transfer coefficient $h$ of the oil

$$Nu = \frac{hd_p}{\lambda_{oil}} = 2.0 + 0.66 \left( Re \right)^{\frac{1}{3}} \left( Pr \right)^{\frac{1}{3}} < 10^4; \; Pr > 0.7; \; Pe \gg 1$$

$$\eta = 0.131 \; (20 \; ^\circ C, \; Serdox \; NOG \; 440)$$

$$\lambda = 0.17 \; W/mK \; (estimated)$$

$$C_{p, oil} = 2 \times 10^3 \; J/kgK \; (estimated)$$

$$\rho_{oil} = 1020 \; kg/m^3$$

$$d_p = 3.0 \times 10^{-3} \; m$$

$$h_{oil} = 1380 \; W/m^2K$$

stationary fall velocity

The following relation was used to estimate the $C_D$ coefficient. It is valid up till Reynolds numbers of 800, and it is an approximation of the well known $C_D$-curve.

$$C_D = \frac{24}{Re} \left( 1 + 0.15 \; Re^{0.687} \right)$$

$Re < 800$

Out of a iteration calculation, with the logarithmic mean value for the oil viscosity a stationary velocity of 0.20 m/s was found.

Calculation of the solidification distance

The cooling down and the solidification of the liquid metal droplet falling through the oil is subdivided in three temperature tracts:

Traject 1 275 °C - 231 °C cooling down
Traject 2 231 °C - 170 °C solidification tracjet

(At 170 °C, the end of the solidification tracjet, the metal is supposed to be soldified enough, to be incompressible)
First the distance $x_1$ for Traject 1: the cooling down towards the solidification temperature, is calculated:

\[ T_W = 20 \degree C \]
\[ <T> = 231 \degree C \]
\[ C_p, \text{metal} = 0.133 \text{kJ/kgK} \]
\[ \rho_{\text{metal}} (275 \degree C) = 7252 \text{kg/m}^3 \]

Equation (4.6):

\[ x = -\frac{\rho_{\text{metal}} C_p, \text{metal} d_p v_{\text{stat}}}{6h_{\text{coll}}} \ln \frac{(T) - T_W}{T_0 - T_W} \]

\[ x_1 = 0.0132 \text{ m} \]

Secondly, the distance $x_2$ for Traject 2: the solidification, is calculated:

Pose: The heat of solidification $\Delta H_{\text{solidification}} = 57.7 \text{ J/g}$ over $\Delta T = 231 \degree C - 170 \degree C (55 \degree C)$.

\[ \Rightarrow C_p, \text{metal linear} = \frac{\Delta H_{\text{solidification}}}{\Delta T} = 1.05 \text{ J/g.K} \]

\[ x_2 = 0.165 \text{ m} \]

The estimated solidification distance upto a temperature of 170 \degree C is

\[ X = 0.18 \text{ m} \]

This distance corresponds with experimental measurements. When droplets are collected at this distance, they stay spherical and do not collapse.
Appendix D  Films of Droplet formation

D-1 Quasi-static droplet formation

CCD camera frame rate: 750 frames/sec
128x126 pixels
Metal height: $H_{\text{metal}} = 15$ mm
$D_{\text{nozzle}} = 1.0$ mm
Time interval between two frames: 0.0027 sec (i.e. 1 frame)
Oxidation: normal droplet formation
D-2 Uniform periodic droplet formation

CCD camera frame rate: 750 frames/sec
128x126 pixels
Metal height: $H_{\text{metal}} = 10$ mm
$D_{\text{nozzle}} = 1.0$ mm
Time interval between two frames: 0.0013 sec (i.e. 1 frame)
Oxidation: normal droplet formation
Production rate: 28 shot particles/sec
D-3 Droplet falling through first 5 cm oil

CCD camera frame rate: 600 frames/sec
128x126 pixels
Metal height: $H_{\text{metal}} = 8$ mm
$D_{\text{nozzle}} = 1.0$ mm
Time interval between two frames: 0.0016 sec

Comment: The interface between gas atmosphere and oil surface is not displayed. The topside of the frame is 1 cm under the gas/oil interface. The droplet is clearly disturbed by the impact on the interface. After it is submerged in the oil, it performs a wobbling motion while falling. As discussed in Section 4.5, the frequency of the nodal oscillation is near the predictions of Lamb (Equation (2.14)). In this trial at least more than 350 Hz.
A close look to the frames 1 - 20 show this wobbling motion. This motion demonstrates that the droplet is still liquid after being submerged in the liquid.