INVESTIGATION OF LIQUID FILLER METAL FLOW

PROCESS THROUGH A BRAZE GAP

by:

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ABSTRACT

The main objective of this study was to investigate the molten filler metal flow in a parallel braze gap. A search of the brazing literature showed that molten brazing filler metal flow at high temperatures has not been extensively studied. Most of the research work in the field of microfluid mechanics was performed at or near room temperature. In brazing, the molten filler material flows through the braze gap by capillary action, but the dynamic characteristics that develop between the molten filler and the base metal surface have a significant effect on the flow mechanics. Factors such as surface roughness of the substrate, the direction of the surface finishing conditions, the pressure head, the density and viscosity of the fluid, and the chemical reactions at the substrate/filler metal interface are important to consider.

Well focused experiments were designed for this research, with two braze systems. The first system had type 304 stainless steel base metal, while the second had pure nickel as base metal; in both cases, the filler metal was pure copper. The experiments were carried out varying the surface roughness and the direction of the surface finish with respect to the direction of the filler metal flow. In half of the experiments the flow was perpendicular and in the other half, parallel to the finishing direction. Also, titanium coated base materials and copper filler metal were used for
additional experiments. All the experiments were carried out in an ultra high purity argon gas environment.

The present work included the development of an experimental technique to study the molten filler metal flow in brazed joints. This experimental method provides an important tool to analyze in-situ the flow properties, producing more realistic data than the traditional laboratory methods used in analyzing filler metal flow, such as sessile drop technique and other destructive methods.

Experimental results indicate that the average filler metal velocity increases as the surface roughness decreases. When the flow is parallel to the surface finishing direction, molten copper on type 304 stainless steel base metal flowed at an average velocity of 275 mm/s (SFC=240 grit), and 318 mm/s (SFC=600 grit), which are slower than in nickel base metal, 324 mm/s (SFC=240 grit) and 341 mm/s (SFC=600 grit). When the flow is transverse to the surface finishing direction, molten copper on 304 stainless steel base metal flowed at an average velocity of 250 mm/s (SFC=240 grit), and 296 mm/s (SFC=600 grit), these values are also slower than in nickel base metal, 305 mm/s (SFC=240 grit) and 327 mm/s (SFC=600 grit). In polished surfaces with 6 μm diamond slurry, molten copper on 304 stainless steel base metal flowed at an average velocity of 321 mm/s, slower than in nickel base metal, 350 mm/s. In the case of the 304 stainless steel and copper braze system, the dynamic characteristics at liquid/solid interaction is more significant on the rougher surfaces, reducing the average velocity drastically,
following a near quadratic curve. For the nickel and copper braze system, the average velocity of the filler metal increases as the surface roughness decreases, following a linear behavior. In general, the average filler velocity is higher for the Ni-Cu system than for the 304SS-Cu system.

In addition, it was also determined that surface roughness has a significant effect on the local contact angles, wetting and filler metal velocity. Rougher surfaces such as a surface finished with a 240 grit size SiC grinding paper develop contact angles constantly changing reaching high (40°) and low values (10°). When the fine base metal surfaces contain defects, such as thin nooks and crevices, they behave like individual capillary tubes on the base metal surface, which promote fine void formation. These types of surfaces are referred to as hydrophobic surfaces. Large voids are promoted in the middle of the vertical direction along the braze joint when the filler metal flows in rougher surfaces perpendicularly to the finishing direction.

A mathematical model based on order of magnitude scaling was developed. An equation that is able to predict the fluid velocity in braze gaps was obtained. The most important factor included in the model is the interaction of the molten filler with the base metal surface, which is represented by the contact angles at the two walls, top and bottom, of the braze gap. Results indicate that the calculated average fluid velocity agrees well with previously developed models.
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DEDICATION

To my parents Raymundo and Maria Teodocia Madeni.

J. C. Madeni
Chapter 2

FUNDAMENTAL PRINCIPLES

Brazing generally requires capillary flow of liquid filler metal through a gap between similar or dissimilar materials. As the liquid filler metal advances through the gap there are important parameters that affect the flow [3]. These parameters are,

- Capillarity
- Surface tension
- Surface roughness
- Wetting and contact angle at the solid-liquid-gas interface
- Filler material viscosity and density
- Fluid velocity
- Chemical reactions at solid-liquid interface

The joint geometry affects directly the flow of the molten filler metal in a braze joint. In order for capillary to occur the gap (height) of the joint must be much smaller than its length; typically the braze gap length is at least ten times the height. However, in this document the effect of joint geometry will not be discussed and during the experimental work, a fixed joint geometry was selected.
2.1. Capillarity

When placing a narrow tube vertically inside a container with a wetting liquid some of the liquid rises inside the tube, this phenomenon is the manifestation of capillarity [8]. The rise of the liquid occurs in air as well as in vacuum. Capillary effect is not specific to a cylindrical geometry, nor to the vertical configuration; it also applies to other settings such as a tube in different positions, a narrow channel in different positions, microchannels with varying orientations, etc. Mathematically, capillarity can be represented by the Laplace-Young [13] equation, which is derived below. Assuming that the meniscus formed in the capillary rise tube of radius \( R \) in Figure 2.1 is of spherical shape of radius \( r \), and contact angle \( \theta_E \), and the height of the liquid between points A and B is \( H \), the supporting force \( F_I \) pulling the liquid must be equal to the gravitational force \( F_g \). \( F_I \) is obtained by integrating the surface tension around the circumference and \( F_g \) is determined by integrating the pressure difference between the inside of the sphere and the outside.

![Figure 2.1. Schematic representation of a capillary tube.](image-url)
\[ F_i = 2\pi r y_{ig} \cos \theta \]  \hspace{1cm} (2.1)

\[ F_g = \pi r^2 \Delta P \]  \hspace{1cm} (2.2)

Since \( F_i = F_g \), then

\[ \Delta P = \frac{2\gamma \cos \theta}{r} \]  \hspace{1cm} (2.3)

Assuming complete wetting, where \( \theta = 0 \), then \( \cos \theta = 1 \), we obtain the Laplace-Young equation.

\[ \Delta P = \frac{2\gamma}{r} \]  \hspace{1cm} (2.4)

When the radius of the meniscus (\( r \)) is different from the radius of the capillary tube (\( R \)), the equation becomes [14]:

\[ \Delta P = \gamma \left( \frac{1}{r} + \frac{1}{R} \right) \]  \hspace{1cm} (2.5)

Manipulating equation (2.3), the height (\( h \)), also known as Jurin’s height, can be calculated [15].

\[ h \Delta \rho g = h (\rho_i - \rho_g) g = \frac{2\gamma \cos \theta}{r} \]  \hspace{1cm} (2.6)
\[ h = \frac{2\gamma \cos \theta}{r \Delta \rho g} \quad (2.7) \]

where, \( \rho_l \) is the density of the liquid, \( \rho_g \) is the density of the gas (air), and \( g \) is the gravity.

Equation (2.7) describes the law of capillary rise.

The pressure at point A in figure 2.1, right under the liquid-gas interface is given by equation (2.8)

\[ P_A = P_o - \frac{2\gamma \cos \theta}{r} \quad (2.8) \]

where, \( P_o \) is the atmospheric pressure, the negative sign indicates that the interface is subjected to an underpressure since its curvature is pointed toward the atmosphere. This pressure differential acts as a pump on the bath and causes the liquid to rise [16].

The pressure at point B is simply \( P_o \). Therefore, the pressure difference between A and B is purely hydrostatic. Thus Equation 2.8 can be rewritten as

\[ P_o - \frac{2\gamma \cos \theta}{r} = P_o - \rho gh \quad (2.9) \]
If the liquid inside the tube is in a state of overpressure, an inverted meniscus will result and the liquid would come gushing out of the tube. However, such a scenario would be incompatible with the rising liquid in a capillary tube.

2.2. Solid-liquid-gas interface

The characteristics of the solid-liquid-gas interface are described below.

2.2.1. Surface tension and surface free energy

To understand the physical origin of the surface tension let us consider the interaction of molecules, see Figure 2.2. When the molecular attraction is stronger than thermal agitation, the molecules convert from a gas phase to a phase that is more dense but still disordered that is called liquid. In the middle of the liquid the molecule has interaction in all directions with its neighbors and it is said that the molecule is in a “happy” state. However, a molecule located at the surface loses half of its interactions and becomes “unhappy” [16]. That is the fundamental reason why liquids adjust their shape in order to expose the smallest possible surface area. Nevertheless, the origin of surface tension can be explained at the molecular level, it is a macroscopic parameter. Table 1 displays the surface tension of selected solids and liquids.
Figure 2.2. Representation of a molecule at the surface missing half its attractive interactions and another molecule inside the liquid experiencing all its attractive interactions.

Table 2.1. Surface tension of selected materials at specific temperatures. [17]

<table>
<thead>
<tr>
<th>Material</th>
<th>$\gamma \text{ (ergs/cm}^2\text{)}$</th>
<th>$T \text{ (°C)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W (solid)</td>
<td>2900</td>
<td>1727</td>
</tr>
<tr>
<td>Nb (solid)</td>
<td>2100</td>
<td>2250</td>
</tr>
<tr>
<td>Au (solid)</td>
<td>1410</td>
<td>1027</td>
</tr>
<tr>
<td>Ag (solid)</td>
<td>1140</td>
<td>907</td>
</tr>
<tr>
<td>Ag (liquid)</td>
<td>879</td>
<td>1100</td>
</tr>
<tr>
<td>Fe (solid)</td>
<td>2150</td>
<td>1400</td>
</tr>
<tr>
<td>Fe (liquid)</td>
<td>1880</td>
<td>1535</td>
</tr>
<tr>
<td>Pt (solid)</td>
<td>2340</td>
<td>1311</td>
</tr>
<tr>
<td>Cu (solid)</td>
<td>1670</td>
<td>1047</td>
</tr>
<tr>
<td>Cu (liquid)</td>
<td>1300</td>
<td>1535</td>
</tr>
<tr>
<td>Ni (solid)</td>
<td>1850</td>
<td>1250</td>
</tr>
<tr>
<td>Hg (liquid)</td>
<td>487</td>
<td>16.5</td>
</tr>
<tr>
<td>NaCl (solid)</td>
<td>227</td>
<td>25</td>
</tr>
<tr>
<td>MgO (solid)</td>
<td>1200</td>
<td>25</td>
</tr>
<tr>
<td>He (liquid)</td>
<td>0.308</td>
<td>-270.5</td>
</tr>
<tr>
<td>N$_2$ (liquid)</td>
<td>9.71</td>
<td>-195</td>
</tr>
<tr>
<td>(11)Ethanol (liquid)</td>
<td>22.75</td>
<td>20</td>
</tr>
<tr>
<td>Water (liquid)</td>
<td>72.75</td>
<td>20</td>
</tr>
<tr>
<td>Benzene (liquid)</td>
<td>28.88</td>
<td>20</td>
</tr>
<tr>
<td>Cargon tetrachloride (liquid)</td>
<td>26.95</td>
<td>20</td>
</tr>
<tr>
<td>Benzaldehyde (liquid)</td>
<td>15.5</td>
<td>20</td>
</tr>
</tbody>
</table>
Surface tension can be an energy per unit area term as well as a force per unit length term [18]. In the first case, if one wants to distort a liquid to increase its surface area by an amount $dA$, the work required ($\delta W$) is proportional to the number of molecules that must be brought to the surface, which is represented by the surface tension ($\gamma$) of the liquid [19]. Mathematically this statement is represented below.

\[ \delta W = \gamma \, dA \] \hspace{1cm} (2.10)

where $\gamma$ has units of $\text{m}^{-2}$; then $\gamma$ is expressed in $\text{mJ/m}^2$.

In the second case, consider a wire frame suspending a liquid film [20]. If a force $F$ is applied to one movable side of the wire frame, and the movable side moves a distance $dx$, the work done is

\[ \delta W = F \cdot dx = 2\gamma l \, dx \] \hspace{1cm} (2.11)

where, $\gamma$ has units of $\text{m}^{-1}$, which can be expressed in units of $\text{N/m}$. The factor 2 indicates the presence of two interfaces.

Using the surface tension defined as an energy per area term, a fundamental equation for a free surface can be written
\[ dU^s = TdS - PdV + \sum_i \mu_i dn_i + \gamma dA \]  \hspace{1cm} (2.12)

The term \( dn_i \) in Equation 2.12 refers to the number of the atoms with a chemical potential \( \mu_i \) in a specified area.

If the volume is kept constant the equation becomes

\[ dU' = TdS' + \sum_i \mu_i dn_i' + \gamma dA \]  \hspace{1cm} (2.13)

Integrating this equation at constant \( T, \mu_i \), and \( \gamma \), one obtains

\[ U^s = TS' + \sum_i \mu_i n_i' + \gamma A \]  \hspace{1cm} (2.14)

\[ U^s - TS' = \sum_i \mu_i n_i' + \gamma A \]  \hspace{1cm} (2.15)

Since Gibbs free energy is given by equation 2.16,

\[ G = U - TS + PV \]  \hspace{1cm} (2.16)

If \( \Delta V = 0 \), then
\[ G = U - TS \quad (2.17) \]

therefore, we get that

\[ G^i = \sum_i \mu_i n^i_i + \gamma A \quad (2.18) \]

However, differentiating equation (2.18) with respect to a differential area as in equation (2.19), an excess quantity term is obtained. This term is determined by the number of atoms transferred in that differential area, see equation (2.20).

\[ \frac{dG'}{dA} = \sum_i \mu_i \frac{dn^i}{dA} + \gamma \frac{dA}{dA} \quad (2.19) \]

\[ \frac{dn^i}{dA} = \Gamma_i \quad (2.20) \]

Therefore, the surface free energy \( f_s \) is defined by the excess quantity term \( \mu_i \Gamma_i \) and the surface tension \( \gamma \).

\[ f_s = \frac{dG^*}{dA} = \sum_i \mu_i \Gamma_i + \gamma \quad (2.21) \]

For pure solids or liquids equation 2.20 becomes
\[ \frac{dn_i^j}{dA} = 0 \]  

(2.22)

therefore

\[ f_s = \gamma \]  

(2.23)

Thus, the use of \( f_s \) and \( \gamma \) is interchangeable for liquids [21].

2.2.2. Temperature dependence of the specific surface free energy

For one component system and most systems where surface tension measurements are carried out at low temperatures the surface tension is equal to the specific surface free energy (\( \gamma = G \)). However, as temperature increases, surface tension changes. The surface tension of most liquids decreases with temperature in a nearly linear trend [22]. Many suggestions for mathematical representation were proposed based on the near linearity of the data, as shown in Figure 2.3. One of them, attributed to Eotvos [23] is shown below,

\[ \gamma^{2/3} = k(T_e - T) \]  

(2.24)
where V is the molar volume, T_c is the critical temperature which is the temperature at which the surface tension is equal to zero, k is a constant which is about the same for most liquids and has a value of approximately 2.1 erg/K.

Figure 2.3. Surface tension (\(\gamma\)) and total surface energy (E) as a function of temperature for CCl_4. [24]

Figure 2.4. Surface tension of liquid tin as a function of temperature. [25]
The fact that the surface tension of most liquids decreases with increasing temperature indicates that the work necessary to create more surface decreases with increasing temperature. This behavior is also observed in most molten metals [25] as shown in Figure 2.4, where the surface tension of molten tin decreases as the temperature increases. Another semiempirical relationship to predict the effect of temperature on surface tension was proposed by van der Waals in 1884 but developed further by Guggenheim [26],

\[ \gamma = \gamma^0 \left( 1 - \frac{T}{T_c} \right)^n \]  

(2.25)

where \( n \) is 11/9 for many organic liquids and closer to 1 for metals, \( T_c \) is the critical temperature at which \( \gamma = 0 \), and \( \gamma^0 = \gamma \) at \( T = 0^\circ K \).

Nevertheless, there may be systems where the surface becomes more ordered with increasing temperature. Positive slopes of the \( \gamma - T \) curves have been reported by researchers that studied the temperature dependence of the surface tension of copper and zinc [27]. In contrast, the surface may become disordered faster than the corresponding bulk part; in that case, \( \gamma \) would approach zero faster than predicted by the van der Waals-Guggenheim equation. Therefore, determination of \( \gamma \) as a function of temperature provides much information about ordering at the surface.
2.2.3. Wetting and contact angle at the solid-liquid-gas interface

Wetting is the study of how a liquid in contact with a solid substrate spreads out [28-32]. This phenomenon is important in many different areas of science and industry as noted by de Gennes [5], such as:

- chemical industry (paints, ink, coloring ingredients, insecticides)
- automobile manufacturing (surface preparation prior to painting, treatment of glass to prevent water from dewetting, treatment of tires to promote adhesion on wet or icy roadways)
- glass (anti-stain and anti-frost treatment)
- food (dissolving powders such as milk or cocoa)
- soil and environmental sciences (penetration of liquids into porous soils) [33]
- construction (waterproofing of concrete, protection of monuments, treatment of greenhouse plastic)
- domestic (spreading of creams, application of mascara to eyelashes, self drying shampoos)
- life sciences (inflations of lungs at birth initiated by surfactant molecules that lower the surface energy of the lungs, wetting of the eye, rise of sap in plants, locomotion of insects on the surface of water, adhesion of parasites on wet surface) [34]
- materials science (soldering, brazing, welding, melting and casting of metals, electronics manufacturing) [3, 29, 35]

Understanding wetting is important because it enables us to control the wetting process. For some applications better liquid wettability may be needed but in other industrial applications lower wettablity may be favorable. Surface impurities removal, surface finishing modification, fluxes, application of coatings, etc. can be applied on a surface to improve wetting [36]. On the other hand, application of oils and coatings, increasing surface roughness and changing surface finishing directions, etc. can be used to delay or avoid complete wetting.

The parameter that measures the degree of wetting is called **Spreading parameter** $S$ [37]. $S$ is the measurement of the difference between the surface energy of the substrate when dry and wet. In the case of brazing, a dry substrate is when the surface is not in contact with the liquid filler metal. On the other hand, a wet surface is when the molten filler metal is spread and when solidified is adhered to the solid substrate.

$$S = (E_{subs})_{dry} - (E_{subs})_{wet}$$  \hspace{1cm} (2.26)

or
\[ S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG}) \]  

(2.27)

where \( \gamma_{SG} \) is the solid-gas surface tension, \( \gamma_{SL} \) the solid-liquid surface tension and \( \gamma_{LG} \) the liquid-gas surface tension.

When \( S > 0 \) (total wetting) the liquid spreads out completely in order to lower its surface energy. However, when \( S < 0 \) (partial wetting) the liquid drop does not spread but forms at equilibrium a spherical cap resisting to the surface with a contact angle \( \theta_e \), as seen in Figure 2.5.

If \( \theta_e \leq \pi / 2 \) the liquid is said to be mostly wetting

If \( \theta_e > \pi / 2 \) the liquid is said to be mostly non-wetting

Figure 2.5. Representation of two liquid drops falling onto a solid surface. The surface in the left promotes partial wetting, \( S < 0 \); and the surface in the right total wetting \( S > 0 \) conditions.
2.2.4. Contact angle

The contact angle at the triple point, liquid-gas-solid, is very important since it is the parameter that describes the wetting behavior. Two analyses to describe contact angle are below.

2.2.4.1. Young's equation

Nowadays the joining science field, specially the brazing and soldering fields utilizes the Young-Dupré equation [9, 38-41] to represent the contact angle at the solid-liquid-gas interface. However, this equation is based in a model that can only be applied to an atomically smooth surface because it does not consider the effects of surface roughness, which will be discussed later on this document. If a liquid bubble is in contact with a solid surface, as shown in Figure 2.6, the three phase interface defines a contact angle. This contact angle measures the degree with which the liquid wets the solid surface.

![Figure 2.6](image)

Figure 2.6. Liquid droplet on a “smooth” solid surface. \( \gamma_{sv} \) is the solid-vapor (gas) surface tension, \( \gamma_{sl} \) is the solid-liquid surface tension, \( \gamma_{lv} \) is the liquid-vapor (gas) surface tension, and \( \theta \) is the contact angle at the triple point.
Analyzing the situation in terms of simple force balance, in two dimensions, in which the surface tension forces are regarded as vectors which must be at equilibrium, the Young-Dupré equation is obtained. This equation is an equilibrium of the horizontal components of the surface tension forces.

\[ \gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta_e \]  \hspace{1cm} (2.28)

However, performing a similar force balance in the vertical direction cannot satisfy the equilibrium condition because \( \gamma_{LV} \) cannot be equal to zero in this flat rigid surface.

\[ \gamma_{LG} \sin \theta \neq 0 \]  \hspace{1cm} (2.29)

Some scientist [42] proposed that the extremely high state of local stress caused dimpling at the line of three phase contact allowing for vertical components of the \( \gamma_{SL} \) and \( \gamma_{SG} \) forces.

*Derivation of the Young-Dupré equation through a virtual variation area. [43]*

Another derivation considers a small variation in which the liquid-gas interface is displaced by a distance dN as seen in Figure 7. dN varies over the interface so that the volume of each phase remains constant. Then applying the equilibrium condition we have
\[ \gamma_{LG} dA_{LG} + \gamma_{SG} dA_{SG} + \gamma_{SL} dA_{SL} = 0 \]  

(2.30)

The variation of the solid-gas and solid-liquid are given by

\[ dA_{SL} = -dA_{SG} = \int \frac{dN}{\sin \theta} dL \]  

(2.31)

where, \( L \) is the length of the interline of three phase intersection.

Figure 2.7. Representation of a virtual variation in area of the three phase contact for the derivation of Young-Dupré equation. [43]

The variation in \( A_{LG} \) has two components, one due to translation of the surface and the other due to the change in curvature.
\[ dA_{LG} = \int \frac{dN}{\tan \theta} \, dL + \int_{A_{LG}} dN (c_1 + c_2) dA_{LG} \quad (2.32) \]

Figure 2.8. Representation of the variation in volume of the liquid phase on translation of the liquid-gas interface. [43]

Similarly, the volume change of the liquid phase \( dV_L = -dV_G \) may be written as the sum of two terms, one due to translation of the surface and one due to expansion of the surface, as seen in Figure 2.8.

\[ dV_L = \int_{A_{LG}} dNdA_{LG} + \frac{1}{2} \int \frac{(dN)^2}{\tan \theta} \, dL \quad (2.33) \]

Since \( dN \) is very small, \((dN)^2\) is even smaller, the second integral in Equation (2.33) is negligible. Also, since the volume of each phase was to remain constant during this virtual variation, i.e. \( dV_L = 0 \), the first integral in Equation (2.33) and by comparison the second integral in equation (2.32) are also of order \((dN)^2\) they are negligible. Then,
\[ dA_{LG} = \int \frac{dN}{\tan \theta} dL \]  \hspace{1cm} (2.34)

substituting Equations (2.31) and (2.34) in (2.30) yields

\[ \gamma_{LG} \int \frac{dN}{\tan \theta} dL + (\gamma_{SL} - \gamma_{SG}) \int \frac{dN}{\sin \theta} dL = 0 \]  \hspace{1cm} (2.35)

Since \( \theta \) is only a function of the interfacial tensions and not of position, it can be removed from the integral,

\[ \left( \frac{\gamma_{LG}}{\tan \theta} + \frac{\gamma_{SL} - \gamma_{SG}}{\sin \theta} \right) \int dN dL = 0 \]  \hspace{1cm} (2.36)

or

\[ \gamma_{LG} \cos \theta = \gamma_{SG} - \gamma_{SL} \]  \hspace{1cm} (2.37)

which is the Young-Dupré equation.

2.2.4.2. Wenzel's equation

In order to obtain a more realistic expression for the contact angle, several models were developed. One of the first attempts on understanding the influence of roughness on
wetting is due to Wenzel (1936). Wenzel [44-46] introduced the idea of the roughness factor $r$, which is defined as

$$r = \frac{\text{actual surface}}{\text{geometric surface}}$$  \hspace{1cm} (2.38)

![Figure 2.9. Representation of the edge of a drop placed on a rough surface, for the development of Wenzel's model [44].](image)

The numerator in Equation (2.38) is the surface considering the changes in the texture of the surface, this means the valleys and hills and other defects present on it. On the other hand, the denominator in the same equation indicates the linear dimension of the surface without considering any of the surface texture.

In a real solid, the actual surface will be greater than the geometric surface. Assuming that the local contact angle $\theta_E$ is given by the Young-Dupré equation, the apparent angle on a rough but chemically homogenous surface is $\theta^*$. A final assumption
is that the roughness scale is very much smaller than the size of the liquid drop. The apparent angle $\theta^*$ can be evaluated by considering a small displacement $dx$ of the line of contact in a direction parallel to the surface and to the fluid displacement as shown in Figure 2.9. Under this circumstance the surface energies change by an amount $dE$

\[ dE = r(g_{SC} - g_{SG})dx + g_{LG}dx \cos \theta^* \]  \hspace{1cm} (2.39)

When $r=1$ the Young-Dupré relation is recovered which implies in a smooth surface. When $r>1$, i.e. a rough surface, the equilibrium condition leads to Wenzel’s relation.

\[ \cos \theta^* = r \cos \theta_e \]  \hspace{1cm} (2.40)

2.2.5. Contact angle hysteresis

Everet [45] eveloped a criterion to observe the hysteresis phenomenon. Figure 2.10 is a schematic of a plate mounted vertically in a liquid, where the force on the plate is continually measured upwards and downwards.
Figure 2.10. A thin plate immersed in a liquid being pulled upwards by the force $W$, and forming a contact angle $\theta$ [45].

When the edge of the plate just touches the liquid, a meniscus forms and the force on the plate increases by an amount equal to the weight of the liquid in the meniscus [47]. As the plate is immersed, the force decreases because of buoyancy. If there is no contact angle hysteresis, the relationship between the depth of immersion versus force is linear, as shown in Figure 2.11(a). If there is hysteresis the relationship is represented by the hysteresis loop displayed in Figure 2.11(b). As the plate is immersed the contact angle builds up to $\theta_s$ with a corresponding decrease in force. When $\theta$ reaches $\theta_s$, the angle remains constant and the depth of immersion versus force curve becomes a straight line with a slope due to buoyancy. As the direction of travel is reversed, the contact angle changes from $\theta_s$ to $\theta_r$. When $\theta$ reaches $\theta_r$, the receding angle side of the curve becomes straight, again having the buoyancy slope. The dashed lines in Figure 2.11(b), are formed by changing from immersion to emersion at different depths.
Figure 2.11. Force-depth of immersion relationships (a) without hysteresis, and (b) with hysteresis, for the experiment in Figure 2.10 [48].

Observation of variations in contact angles which do not fit the above criteria are represented in Figure 2.12. Changes in any or all of $\gamma_{so}$, $\gamma_{sl}$, and $\gamma_{ls}$ during measurement can change $\theta$. In Figure 2.12, the interaction of the liquid with the solid surface causes the loop to be shifted to lower angles. When this occurs, the slopes of the curve deviate from the buoyancy slope, because certain portions of the slide have been in contact with the liquid for longer times than others, which is a kinetic effect.
Figure 2.12. Hysteresis loop produced by the solid-liquid interaction [49].

In another experiment Johnson and Dettre [50-55] have identified that in real solid surfaces, for a given solid-liquid system, a number of stable angles can be measured. Two reproducible angles are the largest and the smallest. These are called the advancing angle, $\theta_a$, and the receding angle, $\theta_r$, respectively. The advancing angle is measured by advancing the periphery of a drop over a surface and the receding angle is measured by pulling it back. The difference, $\theta_a - \theta_r$, produces the phenomena called contact angle hysteresis.

The origins of hysteresis on a rough surface can be illustrated by a drop on a tilted rough plate, as shown in Figure 2.13(a). The front and rear edges both meet the solid
with the same intrinsic angle $\theta_0$. However the macroscopic angles at front and rear measured with respect to the tilt plane are clearly different. If the plate is tilted more, the periphery will adjust itself, always maintaining the microscopic angle $\theta_m$, and adjusting the $\theta_a$ and $\theta_r$ angles. When $\theta_a$ and $\theta_r$ become the advancing and receding angles respectively, i.e. the largest and smallest as defined earlier, the drop will no longer be able to adjust itself and will roll off the plate. If there was no hysteresis the drop would roll off at the slightest tilt of the plate.

![Diagram](image)

Figure 2.13. (a) Representation of a liquid drop on an inclined plane [56]. (b). Contact angle hysteresis measured by Johnson and Dettre [57].

If the forces on the drop are balanced, Equation 2.41 is obtained. The left side is the force on the drop due to gravity, and the right side is a term that includes the surface forces around the periphery.
\[ mg \sin \alpha = w \gamma_{LG} (\cos \theta_r - \cos \theta_a) \]  

(2.41)

where, \( m \) is the mass of the drop, \( \alpha \) is the tilt angle, \( w \) is the width of the drop, \( \theta_a \) is the contact angle at the leading edge and \( \theta_r \) the angle at the rear.

The \( \theta_a \) and \( \theta_r \) angles as a function of the roughness factor "r" measured by Johnson and Dettre are shown in Figure 213 (b). Since the parameter "r" was not measured rigorously, the abscissa increasing roughness is qualitative only.

2.3. Surfaces of solids

The surfaces of solids can have various characteristics that are important to be analyzed. This section intends to provide information for the characterization of solid surfaces.

2.3.1. Nature of surfaces

Solid surfaces, or more exactly a solid-gas or solid-liquid interface, have complex structures and complex properties, which depend upon the nature of the solid, the method
of surface preparation, and the interaction between the surface and the environment [58-61]. Therefore, the properties of solid surfaces are very important to surface interaction because they affect the real area of contact, wetting, friction, wear, and lubrication. These properties are also important in optical, electrical, thermal performance, painting and aesthetic applications [58].

As seen later in the next section, solid surfaces irrespective of the method of formation contain irregularities or deviations from the intended form [59]. No machining method exists that will produce a molecularly flat surface on materials. Even those apparently smoothest surfaces contain irregularities in the scale of atomic distances. Besides the physical surface irregularities, the solid surface consists of zones with different physicochemical properties [60], which will also be discussed later in the text.

2.3.2. Surface roughness

Again, it is important to start this section by saying that a completely flat surface does not exist in solids; unless we are talking about an atomically smooth surface. Solid surfaces are at least atomically rough if not microscopically or macroscopically rough, see Figure 2.14(a). Crystalline solids have potentially an essentially infinite number of distinguishable different crystallographic surfaces, which can be defined by appropriate Miller indices. Therefore the surface of a crystalline solid is comprised of different types
of surface each possessing its own value of surface tension $\gamma_i$. A realistic model, known as the TLK model [61] is displayed in Figure 2.14(b), in which ledges, terraces, kinks, vacancies and adatoms can be observed. Clearly, surface tension $\gamma_i$ is a function of interface orientation.

A convenient method of representing the variation of $\gamma$ with surface orientation in three dimensions is to construct a surface about an origin such that the free energy of any plane is equal to the distance between the surface and the origin when measured along the normal to the plane in question. This type of representation is known as $\gamma$-plot, an example is shown in figure 2.15.

![Diagram](image)

(a) (b)

Figure 2.14. (a) Solid-liquid interface, atomically smooth and real surfaces. (b) TLK-model, a realistic representation of a solid surface [61].
Figure 2.15. A possible (110) section through the γ-plot of an fcc crystal [61].

Macroscopically rough surfaces can be analyzed in a different manner for manufacturing purposes [62]. The terms surface finish and surface roughness are widely used to quantify the smoothness of a surface. In this context, roughness consists of the finer irregularities of the surface texture, including those irregularities that result from the inherent action of the production process. Waviness includes all irregularities whose spacing is greater than the roughness sampling length and less than the waviness sampling length. Flaws are unintentional surface defects. All these terms will be addressed later in the text. Figure 2.16 shows a representation of surface roughness and waviness.
Figure 2.16. Schematic representation of a rough oriented surface [62].

2.3.3. Physicochemical characteristics of solid surfaces

As mentioned before, besides physical roughness, surfaces consist of zones with unique physico-chemical properties [58] as seen in Figure 2.17. These zones are the base material, light and heavy deformed layers, Beilby layer, chemically reacted layer, chemisorbed layer and physisorbed layer which is the contact surface. However, in the case of most metals, alloys and many non-metals, they form surface oxide layers when in contact with air. If these materials are in contact with other environments they are likely to form other layers, such as nitrides, sulfides, and chlorides.
Figure 2.17. Representation of the zones of a solid surface in a transverse cross section of the surface, which have different physicochemical properties [58].

The base material is generally not affected by the environment in contact; therefore, its properties are that of the bulk material. The deformed layer results from the forming process by which the material surface was prepared. For example in grinding, lapping, machining or polishing, the surface layers are plastically deformed and become highly strained. This strained layer is called deformed or work hardened layer an is an integral part of the material itself [58-59]. The amount of deformed material and degree of deformation depends on the amount of energy put into the deformation process, and the nature of the material. Typical ranges of the lightly and heavily deformed layers are 1 to 10 and 10 to 100 \( \mu m \), respectively. Deformed layers are also present in ceramics and polymers. The Beilby layer in metals and alloys is produced by melting and surface flow
during machining of layers that are then hardened by quenching as they are deposited on the cool underlying material. Beilby layers typically range from 1 to 100 nm.

The *chemically reacting layer*, ranging from 10 to 100 nm, is the metal layer that reacts with oxygen and forms oxide layers when in contact with air. In other environments, they may form nitrides, sulfides and chlorides [63-64]. Thickness of this layer depends on the reactivity of the material to the environment, reaction temperature and time. Polymers generally do not form an oxide layer. Ceramic materials, such as Al2O3, have oxygen as an integral part of the structure, so an oxide layer is not expected.

The *physisorbed layer* [64] is the layer which admits inert gases, such as argon or krypton to the surface and can produce the physical adsorption of the gas molecules to the clean surface. Most common adsorbed molecules are water vapor, oxygen, and hydrocarbons. Van der Waals forces are typically involved in physisorption with no exchange of electrons taking place in this layer. The thickness of this layer can be monomolecular or polymolecular (0.3 to 3 nm). Finally the *chemisorbed layer* [64] is the layer where sharing of electrons, or electron interchange occurs between the chemisorbed species and the solid surface, resulting in covalent bonding. However, the chemisorbed species retain their own individual identity allowing their recovery by appropriate treatment of the surface. The chemisorbed layer is limited to a monolayer.
2.3.4. Methods of surface layers characterization

There are various surface analytical techniques that can be used for specific surface layer characterization [65]. The metallurgical properties of a deformed layer, such as grain size and microstructure, can be analyzed by optical microscopy or scanning electron microscopy (SEM). Microcrystalline structure, dislocation density and residual stresses can be analyzed with a transmission electron microscope (TEM). In both cases, appropriate sample preparation is required. The crystalline structure of a surface layer can be examined by X-ray, high energy or low energy electron diffraction techniques. X-ray energy dispersive analyzer (X-REDA), Auger electron spectroscope (AES), electron probe microanalyzer (EPMA), ion-scattering spectrometer (ISS), Rutherford backscattering spectrometer (RBS), and X-ray fluorescence (XRF) can be used for an elemental analysis of a surface layer.

X-ray photoelectron spectroscopy (XPS), energy dispersive spectrometer (EDS) and secondary ion mass spectrometry (SIMS) can be used to perform chemical analysis of a surface layer. The thickness of the layers can be measured by depth-profiling a surface, while conducting a surface analysis. For the chemical analysis of the adsorbed organic layers, mass spectrometry, Fourier transform infrared spectroscopy (FTIR), Raman scattering, nuclear magnetic resonance (NMR) and XPS tools can be used.
2.3.5. Surface roughness analysis

As mentioned earlier in the document, surface texture includes various characteristics of solid surfaces [58, 62, 66-68], which are shown in Figure 2.18, these are the following:

- roughness, including nano and micro roughness
- waviness, which is macroroughness
- lay, and
- flaws

Nano and microroughness

This type of roughness is formed by fluctuations in the surface of very short wavelengths. It is characterized by hills or asperities and valleys of varying amplitudes and spacings, which are large compared to molecular dimensions. The third magnification in Figure 2.18 displays the peaks (asperities) and valleys of the nanomicrohardness.

Waviness

Waviness is the surface irregularity of longer wavelengths and is also called macroroughness. It includes all irregularities whose spacing is greater than the roughness sampling length and less than the waviness sampling length. It is defined by its width or
spacing and height. Waviness may result from factors such as machine or workpiece deflections, vibration, heat treatment, or warping strains. The second magnified surface representation in Figure 2.18 shows the waviness.

Lay

Lay is the principal direction of the predominant surface pattern, which is often determined by the production method. In this work lay is also referred as "surface finishing direction" because the surface was purposely produced with a specific finishing direction and grade. Lay is indicated in the top surface sketch in Figure 2.18.

Flaws

Flaws are unintentional, unexpected and unwanted interruptions in the topography of that specific surface. If the surface contains gross deviations from nominal shape of very long wavelengths, they are known as error of form, and are not considered as part of the surface texture. Flaws are represented in Figure 2.18 in the top sketch.

Most engineering surfaces are random and can be isotropic or anisotropic, and Gaussian or non-Gaussian, depending on the surface processing method. Grinding and milling generally lead to anisotropic and non-Gaussian surfaces [58].
Figure 2.18. Representation of surface texture displaying various surface characteristics [58].
2.3.6. Roughness parameters

Surface roughness is commonly referred as the height variations of the topography relative to a reference plane. It is characterized by two statistical height parameters, these are the following:

- $R_a$, CLA (center-line average), or AA (arithmetic average)
- Standard deviation or variance ($\sigma$), or $R_q$ or root mean square (RMS).

For stating the mathematical formulas of the surface roughness parameters consider the surface profile in Figure 2.19. In this surface profile, the heights are measured from a reference line. The mean line is defined as the line such that the areas between the profile and the mean line, above and below, are equal.

![Figure 2.19. Schematic representation of a surface profile [58].](image)

Roughness average ($Ra$) is the arithmetic mean roughness value
\[ R_a = \frac{1}{L} \int_0^L |Y(x)| \, dx \]  

(2.42)

where, \( R_a \) is the arithmetic average deviation from the mean line, \( L \) is the sampling length and \( y \) is the ordinate of the profile curve.

Root mean square roughness (\( R_q \)) is the root mean square (rms) parameter corresponding to \( R_a \). It is represented mathematically by the equation

\[ R_q = \sqrt{\frac{1}{L} \int_0^L (Y(x))^2 \, dx} \]  

(2.43)

Other statistical height descriptors, rarely used, are skewness (Sk) and kurtosis (K). Also, \( R_n \), which measures the maximum peak to valley height, is a surface measurement parameter. Other parameters which have limited use are:

- \( R_p \), maximum peak height, maximum peak to mean height.
- \( R_v \), maximum valley depth or mean lo lowest valley height.
- \( R_z \), average peak to valley height, and
- \( R_t \), vertical distance between the highest and lowest points.

Definitions for each of the parameters mentioned, their mathematical formula and use is shown in Table 2.2.
Table 2.2. Definitions for the surface analysis parameters, their mathematical formula and use.

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
<th>Calculation</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p$</td>
<td>Maximum profile peak height. It is the distance from the mean surface to the highest point in the evaluation area.</td>
<td>Measured</td>
<td>Peak height provides information about friction and wear on a surface.</td>
</tr>
<tr>
<td>$R_v$</td>
<td>Maximum profile valley depth. It is the distance from the mean surface to the lowest point in the evaluation area.</td>
<td>Measured</td>
<td>Valley depth provides information about how a surface may retain lubricant</td>
</tr>
<tr>
<td>$R_z$</td>
<td>The average maximum profile of the ten greatest peak-to-valley separations in the evaluation area.</td>
<td>$R_z = \frac{1}{10} \left[ \sum_{i=1}^{10} H_i - \sum_{j=1}^{10} L_j \right]$</td>
<td>It is useful for evaluating surface texture on limited access surfaces, such as small valve seats and the floors and the walls of grooves, particularly when the presence of high peaks and deep valleys is of functional significance.</td>
</tr>
<tr>
<td>$R_t$</td>
<td>Maximum height is the vertical distance between the highest and lowest points in the evaluation area.</td>
<td>$R_t = R_v + R_p$</td>
<td>Maximum height describes the overall roughness of a surface.</td>
</tr>
</tbody>
</table>
2.3.7. Hydrophilic surfaces

An attempt to incorporate the surface heterogeneity was the **Cassie-Baxter model** [69]. In this case the surface is planar but is chemically heterogeneous. Assuming that the surface is made of two species, one being the darker surface and the other the gray surface in Figure 2.20, each characterized by its contact angle $\theta_1$ and $\theta_2$, respectively.

Figure 2.20. Representation of the edge of a drop placed on a chemically composite surface [70]

$f_1$ and $f_2$ are the fractional surface areas occupied by each of these species. Here, the energy variation associated with a small displacement $dx$ is

$$dE = f_1 (\gamma_{SL} - \gamma_{SG})_1 dx + f_2 (\gamma_{SL} - \gamma_{SG})_2 dx + \gamma_{LG} dx \cos \theta'$$

(2.44)

Minimization of $E$ using the Young-Dupre equation leads to the Cassie-Baxter relation:
\[
\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2
\]  

(2.45)

In the case of composite rough surfaces that are hydrophilic [70], some of the liquid escapes from the drop and penetrates into the nooks and crevices of the solid. The volume of the liquid film captured in these surface defects is insignificant compared to the total volume of the liquid; therefore, it is considered negligible. Then, the drop finds itself on a wet substrate viewed as a patchwork of solid and liquid. Figure 2.21 shows a surface representation consisting of a solid surface, dark colored, and an array of empty grooves with shapes of wells, gray colored. Using this surface representation, the objective is to calculate the apparent angle \( \theta^a \) of a drop in contact with such a surface. The relative fractions of the solid and liquid phases underneath the drop are represented by \( \Phi_s \) and \( (1-\Phi_s) \) respectively. Applying the Cassie-Baxter equation to the surface, with contact angles \( \theta_s \) and 0, we then obtain:

\[
\cos \theta^* = 1 - \Phi_s + \Phi_s \cos \theta_s
\]  

(2.46)

Figure 2.21. Representation of a hydrophilic porous surface. The dark area is solid and the gray areas are empty wells that become filled with liquid before the bulk liquid wets the surface [70].
2.3.8. Hydrophobic surfaces

When a surface is hydrophobic, the surface energy of the dry solid is less than that of the wet solid, which is consistent with the Young’s relation where $\theta_E > 90^\circ$ is equivalent to $\gamma_{SG} < \gamma_{SL}$. Then, in hydrophobic [70] rough surfaces, air can actually remain trapped under the drop only if Young’s relation applies wherever contact lines appear. Then the drop rests on a composite surface made of solid and air.

![Diagram](image)

Figure 2.22. Representation of a hydrophobic porous surface [70].

Using the representation in Figure 22, where the dark blocks are solid and the white areas is an array of holes in a solid surface, the conditions for such air pockets to appear and the macroscopic contact angle $\theta^*$ can be determined. The contact angles for the solid part and the empty wells are $\theta_E$ and $\pi$ respectively. Since the surface is mixed, the Cassie-Baxter model can be applied, then

$$\cos \theta^* = -1 + \Phi_1 (\cos \theta_E + 1)$$

(2.47)
A possible mechanism for air trapping \cite{71} in surfaces that assume sinusoidal roughness is suggested in Figure 2.23.

![Figure 2.23. Representation of the edge of a drop on a rough (sinusoidal) surface \cite{71}.](image)

In situations when the contact angle is large and the surface sufficiently rough, the liquid may trap air as it flows over the surface. If it is assumed that the local or true angle $\theta_i$ remains invariant as the liquid advances over a roughness asperity, then if $\theta_i$ is large, the liquid surface can be so reentrant that it intercepts the next asperity and traps air between the two. In this case, the Cassie-Baxter relation becomes:

$$\cos \theta' = r f_1 \cos \theta_i - f_2$$  \hspace{1cm} (2.48)

2.4. Filler metal viscosity

The viscosity of the liquid in a capillary tube plays an important role in the velocity of the liquid rising up inside the tube. In the case of brazing, since the filler
metal is in its molten state, which is by definition, at a temperature greater than 450°C, viscosity of this filler material as a function of temperature and composition must be understood.

The temperature dependence of viscosity follows the Arrhenius behavior of fluidity [72], as described by the equation below:

\[ \eta(T) = \eta_0 \exp \left( \frac{E}{RT} \right) \]  \hspace{1cm} (2.49)

where, \( E \) is the activation energy for viscous flow, \( \eta_0 \) the pre-exponential viscosity and \( R \) the universal gas constant. This equation seems adequate to fit the data for the liquid alloys above the equilibrium melting point.

Many other multiparameter formulae have been proposed for viscosity. One recent was formulated by Andrade [73]. This relationship is of the form

\[ \eta(T) = \frac{C_1}{\nu^{1/3}} \exp \left( \frac{C_2}{\nu T} \right) \]  \hspace{1cm} (2.50)

where, \( C_1 \) and \( C_2 \) are constants and \( \nu \) the specific volume.
In the case of the composition-dependence viscosity, Gerhardt and Kostlin [74] first related the viscosity of alloys to phase diagram features. Their conclusions, which are based on extensive experimental data, are summarized in Figure 2.24. In systems showing complete miscibility in solid and liquid states, the viscosity approximates to the weighted average viscosity of the two elements, see Figure 2.24(a). Simple eutectic systems show a negative deviation from this behavior, as shown in Figure 2.24(b). More complicated systems, with the formation of intermetallic compounds, show more complex behavior, with maxima of viscosity in the liquid state at compositions corresponding to those of crystalline compounds, see Figure 2.24(c).

Figure 2.24. The composition dependence of isothermal liquid viscosity in three types of binary alloys [74].
A mathematical formulation of the composition dependence of viscosity was proposed by Moelwyn-Hughes [75]. This formulation was based on the interdiffusion coefficient using the Stokes-Einstein relation and is of the form

$$\eta = (x_A \eta_A + x_B \eta_B \left(1 - 2x_A x_B \frac{\Omega}{RT}\right))$$  \hspace{1cm} (2.51)$$

where, $\eta_A$ and $\eta_B$ are the viscosities of the elements, $x_A$ and $x_B$ are the mole fractions and $\Omega$ the regular solution interaction parameter.

The most successful correlation of the melting point viscosity was proposed by Andrade [74]. He stated that the near-equality of the specific heats of solid and liquid at the melting point suggest similar atomic vibration in each. His mathematical formula is the following:

$$\eta(T_m) = C_A \frac{\sqrt{A T_m}}{V^{2/3}}$$  \hspace{1cm} (2.52)$$

where, $A$ is the atomic weight, $T_m$ is the melting temperature, and $V$ is the molar volume at $T_m$. Andrade showed that $C_A$ was roughly constant for pure metal melts and for liquefied diatomic gases. Its value was estimated to be $1.655 \times 10^{-7} \ (J/K \ mol^{1/3})^{1/2}$. 
2.5. Fluid velocity

The fluid velocity in a capillary tube has been studied extensively in the fields of capillary flow in microgravity and in colloidal science. In the case of brazing, specifically joining a vertical bar to a horizontal bar as shown in Figure 2.25, a basic equation for fluid velocity ($V$) was offered by Lugscheider [76].

![Figure 2.25. Schematic representation of a butt joint with vertical capillary flow.](image)

\[
V = \frac{\gamma_{Lg} D \cos \theta}{4 \eta H}
\]  

(2.53)

where, $\gamma_{Lg}$ is the liquid-gas surface tension, $D$ is the plate separation, $\theta$ is the contact angle, $\eta$ is the liquid viscosity and $H$ the height to which the molten filler metal has risen.
Another velocity relationship obtained by Hosking [77] from the analysis by Milner [78] was based in a horizontal braze joint as displayed in Figure 2.26. The velocity relationship is shown below:

\[ V = \frac{P(0.25D^2 - y^2)}{4\eta x} \]  \hspace{1cm} (2.54)

where, \( P \) is the fluid pressure, \( D \) is the gap height, \( x \) and \( y \) are the horizontal and vertical position of the meniscus respectively, and \( \eta \) is the liquid viscosity.

Another attempt to develop a velocity relationship for horizontal capillary flow as shown in Figure 2.27, was made by de Gennes [79]. Neglecting the chemical reaction at the solid-liquid interface, the mathematical relationship is written below.
Figure 2.27. Column of a reactive fluid inside a capillary tube [79].

\[ V = \left( \frac{\gamma_1 d}{8 \eta \tau} \right)^{1/2} \]  \hspace{1cm} (2.55)

where, \( \gamma_1 \) is a coefficient characterizing the reduction in wettability, \( d \) is the gap height, \( \eta \) is the viscosity of the liquid and \( \tau \) is a time constant, \( \tau = (k \epsilon)^{-1} \). This expression of \( \tau \), was developed for a reactive fluid inside a capillary tube, where \( k \) is a kinetic constant and \( \epsilon \) is the concentration of the reagent in the liquid.

While each of these equations describe fluid flow in a capillarity, as a function of viscosity and joint gap parameters, none of these equations really considered the surface roughness effect on the velocity of the capillary flow.
2.6. Chemical reactions at the solid-liquid interface

Reactions may occur at the base metal/liquid interface [80-86]. The most important ones are the base metal dissolution and intermetallic formation.

It is known that as the molten filler metal flows in a braze joint the chemical composition at the solid-liquid interface changes because of base metal dissolution among other reasons. Since capillary flow occurs in a very short time (typically less than a second) this chemical reaction is small. In this research, it is being assumed that this phenomenon is negligible in order to simplify the fluid flow analysis.

The formation of intermetallic compounds is another chemical reaction that occurs at the solid-liquid interface. Intermetallic formation is necessary to promote good adhesion. However, in excessive amounts it may be a cause of joint failure. The intermetallic formation is more easily seen in solder joints because its formation require enough time for the reaction to occur [87], since in soldering the molten metal flows at much lower rates than in the case of brazing (capillary flow).

Assuming that the solid surface is not completely smooth, uneven surfaces will allow more internal flow of the molten solder, which might affect the substrate dissolution and the formation of intermetallic compounds. The mechanisms of solder to
substrate interaction: volume diffusion, chemical reactions and substrate dissolution, reduce the free energy of the system and affect the dynamic phenomenon within the system.

The amount of substrate dissolution is related to its solubility in the specific solder. On the other hand, the amount of IMC formation depends more on the solubility of the active element in the base metal. Both mechanisms depend on the time that the solder resides at temperatures greater than the liquidus temperature. Figure 2.28 is a schematic of the mechanism of intermetallic formation discussed above.

![Diagram](image)

Figure 2.28. Schematic of the intermetallic formation at the copper-solder interface when the solder is rich in tin [88].
There are thermodynamic models that attempt to predict the wetting/non-wetting behavior and wetting angles by accounting for all the free energy changes in the system. The first model was developed by Laurent [89] and Kristalis [90], they predicted the final contact angle based on the initial contact angle before the reaction, the substrate/liquid interfacial tensions before and after the reaction, and the free energy of the reaction. The shortcoming of this model is that it is experimentally difficult to evaluate due to the uncertainty in the oxygen activity calculations and problems with measuring the substrate/liquid interfacial tensions. The model is represented by the equation below:

\[
\cos \theta = \cos \theta^0 + \frac{\sigma_{sl} - \sigma_{sl}^0}{\sigma_{ls}} \frac{\Delta F_r}{\sigma_{ls}}
\]  

(2.56)

where, \( \sigma_{sl} \) is the interfacial tension before the reaction, \( \sigma_{sl} \) is the interfacial tension after the reaction, \( \theta^0 \) is the contact angle before the reaction, and \( \Delta F_r \) is the free energy of the reaction.

The second model in Equation (2.57), developed by Lochman [91], was a correction to Young’s equation to include the substrate/liquid chemical reaction. The triple point in a sessile drop in a reactive system is shown in Figure 2.29.
Figure 2.29. Sessile drop configuration in a reactive substrate/liquid system.

\[ \gamma_{sg} - \gamma_{sl} - \gamma_{ss} + A \Delta G = \gamma_{lg} \cos \theta \]  

(2.57)

where, \( A \) is a constant related to the models of product formed per unit extension of the drop on the surface, \( \Delta G \) is the Gibb’s free energy for the reaction, \( \gamma_{ss}, \gamma_{sl}, \gamma_{lg} \) and \( \gamma_{sg} \) are the solid-solid, solid-liquid, liquid-gas, and solid-gas surface tensions.

Kang [92] developed a third model based on free energy change contributions due to the substrate/liquid reactions and contributions due to surface energy changes. Mathematically, this model is represented by the driving force for wetting (dE/dr) in Equation (2.58).

\[ \frac{1}{2m} \frac{dE}{dr} = \sigma + \Gamma(\theta) \]  

(2.58)
where, \[ \Gamma(\theta) = \gamma(\cos \theta - \cos \theta_c) \]

\[ \cos \theta_v = \frac{\gamma_a - \gamma_{AC} - \gamma_{BC}}{\gamma_b} \]

\[ \sigma = \frac{\rho A \Delta G_f}{x M_A} \]

also, \( \rho_A \) is the density of A, \( t_A \) is the thickness of A that reacts to form \( A_x B_y \), \( M_A \) is the atomic mass of A, \( x \) is the number of A atoms in \( A_x B_y \), and \( \Delta G_f \) is the Gibb’s free energy of formation of compound \( A_x B_y \).

Chapter II described the fundamental principles that affect the molten filler metal flow in braze joints. It is necessary to recall that the main purpose of this work is to characterize the flow of filler metals in a parallel braze gap, which is driven by capillarity and the dynamic liquid-solid interaction.
Chapter 3

EXPERIMENTAL PROGRAM

The task to be accomplished in the experimental part was to be able to observe an actual furnace brazing experiment, so filler metal flow data can be obtained. The main objective of these experiments was to produce reliable data for a fundamental study of how filler metals flow in the joint gap. In order to accomplish that, an experimental set up and procedure were developed. This experimental set up consisted of a furnace, data acquisition system and a high speed video system. The experimental procedure involved three main tasks. First, the base metal surface analysis; second, base metal surface preparation; and third, production of joints and image capturing. Braze specimens were designed and their geometry and dimensions were maintained constant for all the experiments. Also, a convenient experimental matrix was designed using materials such as 304 stainless steel, copper and nickel. Below is a detailed description of the complete experimental process.

3.1. Experimental setup.

The experimental setup, in Figure 3.1, consists of three main parts.
Center: The experimental sample is placed in the center of a ceramic tube inside the furnace. It is important to have complete control of the temperature inside the furnace because it is essential to know the exact temperature at which the filler metal melts and flows through the braze gap. Therefore, the furnace temperature was characterized and the data is shown below in Figures 3.2 to 3.4.

Right side: Thermocouples are attached to the specimen and the temperature data are acquired using a LabView-based data acquisition system (DAS). In addition, by flowing the desired inert gas, the environment inside the furnace can be controlled to avoid sample and filler metal surface oxidation.

Left side: A high speed video system consists of a video camera, a 500 mm telescopic lens, and a high speed video recorder (Kodak Ekta Pro 1000) was used. This video camera is capable of taking up to 1000 fps (frames per second). Also, a light source directed to the specimen inside the furnace is placed in the left side of the furnace.
Figure 3.1. Experimental setup for the investigation of filler metal flow mechanics in braze joints.
The furnace temperature was measured as a function of time to find the time to heat up to the desired temperature. In the example below the desired temperature was 1000°C, which was reached in 170 minutes. The heating rate, determined by the slope of the curve at specific times, was very fast at the beginning but very slow near the desired temperature as shown in Figure 3.2.

![Temperature vs Time Graph](image)

Figure 3.2. Temperature as a function of time upon heating the furnace up to 1000°C.

Temperature measurements from the center towards the back end of the furnace were acquired. These measurements were made to find the change in temperature along the heated ceramic tube inside the furnace. It was found that for the temperature of 1000°C there is a stable region of 4 inches in the middle of the furnace, which is the location of the heating elements. Then, the temperature gradient along the ceramic tube
restricts the location of the specimen, with a section of 4 inches, \( \pm 2 \) from the center. The temperature drops down to 700\(^\circ\)C at the ends of the ceramic tube as shown in Figure 3.3.

![Graph showing temperature variation](image)

**Figure 3.3.** Temperature as a function of distance from the center of the furnace towards the back end.

Also, the temperature was measured \((T=1003^\circ)\) at the cross section of the tube exactly at the center of the tube, where the braze specimen would be located. The radial variation of temperature is very small. As it is shown in Figure 3.4, it was found that the temperature is mostly constant in the cross sectional area of the tube \((T=1003^\circ)\), except at the walls of the ceramic tube where the temperature was 1000\(^\circ\).
During the experiments, the actual temperature at which pure copper melts was measured using thermocouples located three millimeters below the bottom surface in the braze specimen and a LabView based data acquisition system. The average measured temperature was 1094°C, which was constant for all the experiments, see Figure 3.5. The literature reports that pure copper melts at 1083.8°C; however, the measured melting temperature is approximately 10°C higher; this is considered to be the superheat temperature.
3.2. Specimen geometry and dimensions.

To visualize molten filler metal flow a specially designed specimen was used. A front view drawing of the experimental specimen is displayed in Figure 3.6, this is actually the view that the video camera sees. Small pieces of the solid filler metal are placed at the left compartment of the specimen in Figure 3.6, once these pieces melt, fill the compartment and flow to the right side through the microchannel or braze gap. A fillet is formed at the end of the flow in the right compartment of the specimen. This specimens were fabricated according to the geometry and dimensions displayed in Figure 3.7. This specimen is somewhat similar to those used in experiments at Sandia National Laboratories [93]. However, the difference is that these specimens are composed of two
parts: the top and bottom parts. The bottom part enables the variation of surface roughness and also the use of dissimilar materials between the top and bottom parts. Data obtained in this work can be compared with those collected by Hosking [93] using a gleeble thermomechanical simulator at Sandia National Laboratories.

Figure 3.6. Front view of the specimen used in the study of filler metal fluid mechanics in a parallel braze gap. (Not drawn to scale)
Figure 3.7. Geometry and dimensions for the fabrication of the experimental specimen for the study of filler metal flow in a braze gap.
3.3. Experimental matrix.

In order to use classical physicochemical principles and basic fluid mechanics to carry out this study, the experimental matrix was designed using materials that can minimize the complications of the effects of chemical interaction and alloying between the base metal (BM) and filler metal (FM). Pure copper (melting temperature = 1083.8°C) was used as the filler metal and the two base metals were 304SS and pure nickel. The furnace environment was kept constant using ultra high purity (UHP) argon gas. The bottom base metal surface roughness was varied to study its effect on filler metal fluid mechanics on parallel braze gaps. The experimental matrix is shown in Table 3.1.
Table 3.1. Base material, filler metal and surface finishing of the specimens prepared according to the indicated finishing direction.

<table>
<thead>
<tr>
<th>Base Material</th>
<th>Filler Metal</th>
<th>Gas 1</th>
<th>Surface Finish</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Long. Dir</td>
</tr>
<tr>
<td>304 SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dir</td>
</tr>
<tr>
<td>304 SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Long. Dir</td>
</tr>
<tr>
<td>304 SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dir</td>
</tr>
<tr>
<td>304 SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Polished</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Long. Dir</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dir</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Long. Dir</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dir</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Polished</td>
</tr>
</tbody>
</table>
3.4. Experimental procedure.

Prior to the experiment, three tasks were performed: Production of BM with desired surface finishing conditions, BM surface analysis, and cleaning of the BM and FM surface.

3.4.1. Production of BM with desired surface finishing conditions.

The bottom part of the joint specimen (shown in Figure 3.6) was finished to different surface conditions. Grinding paper of different grades, 240, 600, and 6 μm grit, were used as abrasives for conditioning the surface texture of the specimen in a controlled manner. The surfaces were produced with parallel grooves so the fluid may flow along the finishing directions or transverse to them.

3.4.2. BM surface analysis procedure.

After grinding the surface of the bottom base metal to the desired level, it was cleaned by rinsing with water, ethanol and immediately dried with air. If the surface is not dried appropriately, corrosion occurs and alters the surface finish conditions. The dried surface is then analyzed using an optical profilometer shown in Figure 3.8. An area
of 10 mm$^2$, i.e. 5 mm along the braze gap and 2 mm transverse to the braze gap, were scanned on each specimen.

The profilometer is a non-contact, optical tool to analyze surfaces, and contains an interference microscope in it, shown in Figure 3.9. Vertical scanning-interferometry (VSI) was the technique used for the surface analysis [94]. A white light beam that is not filtered passes through a microscope objective lens to the sample surface. A beam splitter reflects half of the incident beam to the reference surface. The beams reflected from the sample and the reference sample recombine at the beam splitter to form interference fringes. The system measures the degree of fringe modulation or coherence. This measurement is performed as the reference arm containing the interferometric objective moves vertically to scan the surface at varying heights.

Figure 3.8. Wyko profilometer system.
Figure 3.9. Interference microscope to analyze solid surfaces [94].

Important surface analysis parameters obtained are Ra, Rq, Rz, and Rt. Ra is the roughness average, Rq the root mean square average between the height deviations and the mean/line surface. Rz is the average maximum profile of the ten greatest peak-to-valley separations, and Rt is the vertical distance between the highest and lowest points. The mathematical relations and uses of these parameters were summarized in Table 2.2 in
chapter II. Also, surface data obtained from profilometry can be represented in several forms. The most commonly used forms are the histogram, and bearing ratio.

The **histogram plot**, shown in Figure 3.10, is a distribution plot which shows the distribution of individual surface height values in histogram form. The horizontal axis indicates the individual height values, and the vertical axis the number of data points contained within equally spaced intervals. This histogram plots also include a Gaussian curve drawn over the histogram, which is based on the rms, the number of points in the data set and the bin size. The bin size can be from 10 to 5,000 and is set by the user of the equipment. Both of these curves allow the comparison of a normal distribution to the actual distribution of the data set.

![Histogram of near-Gaussian surface](image)

Figure 3.10. Histogram of near-Gaussian surface [94].
The bearing ratio $t_p$, also known as the material ratio, is the ratio of the bearing length to the assessment length $L$. Bearing length is the length of the bearing surface at a length $p$ below the highest peak, or a selected distance above or below the mean line, and the bearing area is the area of the surface cut by a plane at this specific depth. In order to use the bearing ratio, a graphical representation of the bearing ratio $t_p$ in relation to the profile level must be developed; so it shows how the profile bearing ratio varies with level. This curve is known as bearing ratio curve or material ratio curve and is displayed in Figure 3.11. The bearing ratio curve is the curve generated by running a plane, extending parallel to the mean surface plane, down through the surface profile, and is defined as the percentage of the plane that intercepts the material versus the depth of the plane into the surface. Parameters of the bearing ratio curve are important for specific calculations.

![Diagram of bearing ratio curve and corresponding surface profile](image)

Figure 3.11. Bearing ratio curve (right) and corresponding surface profile (left) [94].
3.4.3. Base metal and filler metal surface preparation prior to brazing.

The horizontal surfaces (top and bottom) of the base metal and the surface of the filler metal were cleaned for oxide removal right before the initiation of the experiment. A 2% hydrochloric acid aqueous solution and ethanol were used in the cases of the 304SS and nickel surfaces. In the case of the copper surface, water-based solution of ammonium hydroxide, trisodium phosphate and sodium tetraborate pentahydrate was used to clean the copper surface. After letting the copper surface dry for a few seconds, a solution of water-based phosphoric acid was applied. This cleaning process was followed by the flow of constant ultra high purity (UHP) argon in the furnace, which minimized the oxide formation while the specimens were inside the furnace during the experiment.

3.4.4. Production of joints and image capturing.

After the surface cleaning operation detailed above, the specimen was mounted in between two clamps located at the left and right ends, as shown in Figure 3.12. A coating of microbraz green stop-off was applied to the face of the specimen with the purpose of minimizing the reflection of the BM materials at high temperatures. When the BM reflection from the furnace is high, the braze gap is not observed in the video images. Therefore, the microbraz coating is very necessary and the results are video images with
good resolution, capturing the filler metal flow in the braze gap. Front light (optical fiber light) directed to the specimen helps observe the specimen during furnace heating.

Temperature data is acquired by using a thermocouple attached to the sample and to a LabView-based data acquisition system (DAS) in a computer [95]. The DAS was calibrated to capture temperature data with ±0.1°C of accuracy using K-type calibrated thermocouples.

Video images are captured using a Kodak Ektar Pro 1000 high-speed video camera equipped with a 10 cm extender between the camera and the lens and a 500 mm telescopic lens. The video recording of the experiment is taken at 250 fps. It is possible to increase the recording rate but it would decrease the resolution of the images and more front light would be needed.

Figure 3.12. Specimen mounting and face coating.
3.5. Image analysis procedure.

The image analysis procedure consisted in three steps, which are explained below.

*Film analysis using the Kodak EktaPro motion analyzer.*

Once an experiment was recorded with the Kodak EktaPro high-speed video camera, it was analyzed using the motion analyzer in the same high-speed video system since it used cassettes that could only be used with this video system. The filler metal motion analysis was carried out by analyzing all the recorded images individually frame by frame. In each image the distance of fluid front was measured with respect to the origin, as shown in Figure 3.13.

*Analog images capturing and conversion to digital images.*

The experiment film being analyzed (frame by frame), was copied to a VHS system which was then converted to digital images using an interface software package. Also, the experiment films were recorded on DVDs to obtain better quality images, but these were not frame by frame.

*Image analysis using graphics software packages.*

The digital images were analyzed using Adobe Photoshop software to measure the contact angle in the individual frames. To obtain good images of the triple contact
point (solid-liquid-gas), the contrast was increased in each picture; then, the picture was converted to the film mode available in the software, in which the contact angle measurements were carried out.

Finally, the joined specimens were cut longitudinally and transversely to the direction of fluid flow. The cut samples were mounted, ground and polished for microscopic analysis. Optical microscopy and SEM were used.

Figure 3.13. Method for the measurement of the advance of the filler metal flow front.
Chapter 4

RESULTS AND DISCUSSIONS

This section presents discussions of the experimental observations in this research. First, a detailed analysis of the surface texture of the base metal is presented. This surface texture is later correlated with the surface tension and filler metal velocity. Second, filler metal velocity is determined from the film acquired with the high-speed video system. Third, using the same data as for the fluid velocity, the contact angle is measured and related to the fluid velocity and surface roughness. Fourth, a discussion of the effects of velocity and contact angle is presented. In many situations it is necessary to refer to previous Figures to follow the discussions introduced in this chapter. Also, there are some terms that are constantly used such as SFC meaning surface finishing conditions and $\theta$ that is always the measured wetting or contact angle defined by Young-Dupréé. Modifications of these terms are discussed in their respective sections.

4.1. Base metal surface analysis.

It is important to be able to accurately characterize the surface texture of the specimens used in this research. It is the basic premise of the work that surface texture is a major factor affecting the molten filler metals flow in brazing. Therefore, surface
roughness measurements can also be a factor to predict flow and wetting of filler metals in braze joints.

The raw surface analysis data obtained is very important; however, in order to get more significant data for a specific surface finishing condition, it was necessary to filter it to obtain an average surface representation. Therefore, analyzing the surface texture data had the following sequence.

- Obtain raw data
- Compare the data with a Gaussian distribution
- Obtain a bearing curve to determine the amount of surface area in the valleys throughout the surface profile. This number is obtained by comparing the surface of the peaks that would be smeared by friction with other metal, with the surface area of the valleys that would trap the lubricant applied in such operation. Therefore, the only use of the bearing ratio in this work is to compare among the different finishing conditions, which surface would have more valleys surface area to trap liquid.
- Handle the surface data as a linear function. Then, apply the Fourier transform method using the inverse Fourier transform [96] to obtain representative data.

From a strictly mathematical point of view, the Fourier transform evolves naturally from a Fourier series when the interval of convergence is allowed to approach
infinity. Instead of using sines and cosines, as in a Fourier series, the Fourier transform uses exponentials and complex numbers. For a signal function \( f(t) \), the Fourier transform in Equation (4.1), and the inverse Fourier transforms, in Equation (4.2), are defined:

\[
F(\sigma) = \int_{-\infty}^{\infty} f(t)e^{-j\sigma t} \, dt \quad (4.1)
\]

\[
f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\sigma)e^{j\sigma t} \, d\sigma \quad (4.2)
\]

where, \( j \) is the imaginary unit number "i"; and \( \omega \) is the range of angular frequencies associated with the signal, i.e. the frequency content of the signal.

The Fourier transform is used for analyzing the frequency content of continuous signals, as in the case of the surface texture data. The inverse Fourier transform method described by Equation (4.2) is used for surface data analysis [89].

Surface analysis was performed in all the experimental specimens. However, for analytical purposes, a representative surface of each finishing condition will be discussed in this document. Also, 304 stainless steel and nickel surfaces that have been finished to the same condition have similar degree of surface texture. Therefore, these surfaces will be analyzed independent of the material; and the surface parameters for individual
finishing conditions will be valid for both materials. The term SFC, meaning surface
finishing conditions, will be used throughout this document.

Surface finished with 240 grit SiC grinding paper

Surface of the base metal, finished with 240 grit SiC grinding paper, was
analyzed. The graphical 2-D representation is shown in Figure 4.1, and the statistical
parameters Ra, Rq, Rz, and Rt, that describe the surface texture are 396.95 nm, 542.72
nm, 8.05 µm and 9.17 µm respectively. At the right side of the contour plot, the scale
clearly indicates the highest point (7.22 µm) and the lowest point (-1.96 µm); making the
peak-valley difference 9.18 µm. In Figure 4.2, a 3-dimensional graphic representation is
shown. Visibly the linear marks of the surface finishing direction are noted and the
roughness and pseudo waviness of the surface are observed. Surface analysis data can
also be represented by a histogram, which describes a frequency distribution of the data
resulting from the surface texture. Figure 4.3 evidences that the surface analysis data is
similar to a broad normal Gaussian distribution, which indicates that the surface
roughness of the material is randomly distributed. The mean, \( \mu_1 \), and standard deviation,
\( \sigma_1 \), are 45 nm, 0.4 µm, respectively. The corresponding bearing ratio curve is presented
in Figure 4.4 from which \( V_2 \) is obtained. \( V_2 \), in this case equal to 31.46 nm is a measure
of the valley areas in the profile, which would promote void formation during filler metal
wetting as it will be discussed later in this document.
Figure 4.1. Contour plot of the surface texture and surface statistics summary shown in the box at the left. Sample with SFC = 240 grit SiC paper.

Figure 4.2. 3-dimensional surface representation. Sample with SFC=240 grit SiC paper.
Figure 4.3. Histogram of the surface roughness data. The plot also shows the Gaussian curve indicating normal distribution. Sample with SFC=240 grit SiC paper.

Figure 4.4. Bearing ratio curve. Sample with SFC=240 grit SiC paper.
In Figure 4.5 (a), the x and y profiles of the surface are shown. As it can be seen, the x-profile shows finer roughness, the peak-to-valley difference is approximately 1.40 μm. However, the y-profile has approximately 3.0 μm difference. Not only that, but the y-profile has smaller period compared to that of the x-profile. Using the inverse Fourier transform for analyzing the data, one can obtain the plot in Figure 4.5 (b). It is seen that the x-profile data is not completely random, it has some dominant periodic features in the negative side of the average roughness. This implies that this specific surface texture is more in the valleys regime than in the peaks regime. The plots in Figure 4.5(b) also show the representative waviness of the surface texture in the x and y directions. In the y-direction the period of the waviness is large compared to the one in the x-direction. Therefore, the y-profile exhibits much more dominant periodic features.
Figure 4.5. Two dimensional results showing the x and y surface profiles (a) original data, and (b) curve obtained after Fourier transform was applied. Sample with SFC=240 grit SiC paper.
Surface finished with 600 grit SiC grinding paper

Similarly, for the surface finished with 600 grit SiC grinding paper, the data is analyzed in Figures 4.6 to 4.10. Figure 4.6 shows the 2-D graphic representation of the surface and the respective statistical parameters are $R_a = 97.35$ nm, $R_q = 127.71$ nm, $R_z = 1.50$ μm, and $R_t = 1.96$ μm. The scale in the picture clearly indicates the highest point (1.10 μm) and the lowest point (-0.86 μm), with a 1.96 μm difference. The corresponding 3-dimensional graphic representation is shown in Figure 4.7. Again, as in the previous case, the orientation of the finishing direction can be observed. Surface roughness and waviness have also decreased in magnitude with respect to the 240 grit SFC sample. The histogram for this sample in Figure 4.8, shows a curve slightly shifted to the left from a Gaussian distribution but it maintains the normal distribution probability shape. Importantly, it should be noted that the mean and standard deviation have reduced significantly ($\mu_1 = -32$ nm and $\sigma_1 = 0.26$ μm). The $V_2$ value of the bearing curve (15.86nm) in Figure 4.9 decreased much indicating that the area in the profile that may cause void formation has gotten smaller with respect to the previous sample. X and y profiles in Figure 4.10 (a) indicate major difference in roughness and in waviness. The y-profile is rougher than the x-profile and the peak-to-valley difference is 0.8 μm. For the x-profile that difference is 1.40 μm. The plots in Figure 4.10 (b) showing the inverse Fourier transform for the data in Figure 4.10 (a), can be interpreted like the data in Figure 4.5 that y-profile was rougher than the x-profile. In addition, it shows that the waviness
varies significantly. x-profiles with shorter wavelength and the y-profile with larger wavelengths.

Figure 4.6. Contour plot of the surface texture and surface statistics summary shown in the box at the left. Sample with SFC = 600 grit SiC paper.

Figure 4.7. 3-dimensional surface representation. Sample with SFC = 600 grit SiC paper.
Figure 4.8. Histogram of the surface roughness data. The plot also shows the Gaussian curve indicating normal distribution. Sample with SFC = 600 grit SiC paper.

Figure 4.9. Bearing ratio curve. Sample with SFC = 600 grit SiC paper.
Figure 4.10. Two dimensional results showing the x and y surface profiles (a) original data, and (b) curve obtained after Fourier transform was applied. Sample with SFC=600 grit SiC paper.
Surface finished by polishing with 6 μm diamond slurry.

Following the same approach, the base metal surface polished down to 6 μm with diamond slurry was analyzed. The 2-D graphic representation of the surface is displayed in Figure 4.11 and shows a very uniform surface with the exception of two large flaws. It is obvious that this surface is much smoother than the two previously presented, which can also be distinguished by the scale in the picture showing a peak-to-valley difference of approximately 1.45 μm. The surface statistical parameters are Ra = 30.40 nm, Rq = 41.73 nm, Rz = 1.14 μm, and Rt = 1.45 μm. Figure 4.12 shows the 3-dimensional graphic representation of the surface texture, which does not exhibit pronounced finishing directions, normal for a roughly polished surface. The histogram for this sample in Figure 4.13 shows a very narrow and near Gaussian probability curve meaning that the surface texture is more regular and has a narrower probability range for roughness. In fact, the mean and standard deviation have reduced significantly (μ3 = 2 nm and σ3 = 40 nm) compared to the previous two cases. In addition, the bearing curve in Figure 4.14 indicates also that the area in the profile that may cause void formation is insignificant, in fact, V2 is only 2.54 nm. Both, the x and y profiles in Figure 4.15 (a) also confirm the very fine roughness but the x profile exhibits more pronounced waviness. The peak-to-valley difference is 0.35 μm and 0.22 μm for the x and y profiles, respectively. The x and y data profiles processed with the inverse Fourier transform also indicate a very fine
roughness, but the correlation in the x-direction confirms greater waviness than in the y direction, as shown in Figure 4.15 (b).

Figure 4.11. Contour plot of the surface texture and surface statistics summary shown in the box at the left. Sample polished to 6 μm.

Figure 4.12. 3-dimensional surface representation. Sample polished to 6 μm.
Figure 4.13. Histogram of the surface roughness data. The plot also shows the Gaussian curve indicating normal distribution. Sample polished to 6 μm.

Figure 4.14. Bearing ratio curve. Sample polished to 6 μm.
Figure 4.15. Two dimensional results showing the x and y surface profiles (a) original data, and (b) curve obtained after Fourier transform was applied. Sample polished to 6 \( \mu \text{m} \).
From the analysis in the previous pages, the differences in surface texture among the three samples can be compared. Evaluating the bearing ratio curves for the three surface conditions, in Figure 4.16, one can easily observe that rougher surfaces have potential sites to promote void formation; on the other hand, finer surfaces in the order of 6 μm will have reduced number of those sites. This trend is also shown by the V₂ values, which range from 2.54 nm, 25.86 nm and 31.46 nm for the 6 μm, 600 and 240 grit finishing conditions respectively. Therefore, as the surface roughness increases the V₂ values obtained from the bearing ratio curves also increase, meaning that rougher surfaces will have more valleys surfaces to retain liquids. The overall data for the surface analysis is summarized in Table 4.1.

![Figure 4.16. Comparison of the bearing ratio curves for surfaces with 240 grit, 600 grit and 6 μm surface finishing conditions.](image-url)
Table 4.1. Surface parameters summary for the three surface finishing conditions 240 grit, 600 grit and 6 μm polishing.

<table>
<thead>
<tr>
<th>SFC</th>
<th>Ra (nm)</th>
<th>Rq (nm)</th>
<th>Rz (μm)</th>
<th>Rt (μm)</th>
<th>λx (μm)</th>
<th>λy (μm)</th>
<th>Sf</th>
<th>V2 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>240 SiC paper</td>
<td>396.95</td>
<td>542.72</td>
<td>8.05</td>
<td>9.17</td>
<td>21.9</td>
<td>8.3</td>
<td>1.0200</td>
<td>31.46</td>
</tr>
<tr>
<td>600 SiC paper</td>
<td>194.14</td>
<td>260.54</td>
<td>3.17</td>
<td>3.43</td>
<td>26.2</td>
<td>6.7</td>
<td>1.0067</td>
<td>15.86</td>
</tr>
<tr>
<td>6 μm polish</td>
<td>30.40</td>
<td>41.73</td>
<td>1.14</td>
<td>1.45</td>
<td>10.62</td>
<td>7.4</td>
<td>1.0006</td>
<td>2.54</td>
</tr>
</tbody>
</table>

4.2. Determination of fluid velocity

Molten filler metal velocity was determined by obtaining distance-time measurements from individual frames of the recorded experiments with the high-speed video system. These measurements were performed using a sequence of still images. As an example, Figure 4.17 displays such a sequence for the experiment performed with BM = 304SS, FM = Cu, furnace environment = UHP argon gas, SFC = 240 grit, and flow direction perpendicular to the surface finishing direction.

Generally, the fluid flow behavior in each system had similar smooth “inclined S” shape, but with small variations which were the effect of the base metal surface roughness. Nevertheless, since the fluid behavior depicted by the distance-time curves were similar, each curve can be characterized by identifying several points of interest.
Figure 4.17. Sequence of molten filler metal flow through a brazing gap, from which fluid front advancement as a function of time plots were obtained.
Points of interest during filler metal flow

Several points of interest during filler metal flow were identified as shown in Figure 4.18 (a) and (b). These are the following:

- initiation of flow zone
- fast flow zone
- transient arrest point
- residence zone
- fillet formation zone, and
- fillet maximum extension point

See caption in next page.
Figure 4.18. Points of interest during filler metal flow (a) in the video image, and (b) in the distance-time curve.

The initiation of flow zone is the region where the brazing gap begins at the left side of the sample. It was identified because the fluid velocity is very slow, the wetting angle decreases drastically; therefore, the liquid-gas surface energy decreases. Possible reasons of this happening are the effect of filler metal melting, wetting in both the bottom and top solid surfaces, and the change in capillary pressure. The fast flow zone is the region where flow velocity is the fastest. In this study, the average flow velocity values presented, designated by $V_{avg}$, are those of this region. Here, the wetting angle generally does not have very drastic changes. This flow occurs until it reaches a transient arrest point, which is the point at the location where the fluid velocity decreases drastically. From here on, the residence zone starts. The fluid seems to reside but it is actually
moving very slowly, almost as in the case of the initiation of flow zone. Possible mechanisms for the drastic reduction of the fluid velocity are the increase in $\gamma_{LG}$, rough surface, high contact angle, and the decrease in the pressure difference that drives capillary flow. Once the fluid reaches the right end of the brazing gap the fillet formation zone is identified. Here, the molten filler metal exits the capillary to wet the vertical member as well continuing in the x-direction. Nevertheless, fillet formation mechanism need to be studied in detail, they are not addressed in this document. Finally, the fillet maximum extension point is determined as the end point where the molten filler wets. This point is also observed after solidification of the fluid occurs, meaning when the joint is at room temperature outside the furnace.

From the distance-time plots, one can obtain the average velocity, $V_{avg}$, of the fluid in the microchannel. As mentioned before, it is actually the velocity in the fast flow zone. This average velocity $V_{avg}$ is taken because it covers about 96% of the microchannel length, depending on each specific experiment. Since, braze joint strength is a direct function of the wetting area, the way that the molten filler flow over that area and wetting are critical and can be expressed as the average filler metal velocity. Also, the average velocity is taken in the region where the capillary forces are more stable [96], which does not occur at the beginning or at the end of the microchannel.
To exemplify the analysis the data obtained using this experimental technique, several distance-time plots are presented below. Figures 4.19 - 4.22, are some of the results obtained for the joint system BM = 304SS, FM = Cu. In Figures 4.19 and 4.20, the average velocity determination plots are displayed for experiments carried out using the specimens having 240 grit SFC in the longitudinal and in the transverse directions, respectively. Figure 4.19 exhibits a smooth initiation of flow, as soon as the molten metal reaches the fast flow zone the localized velocity ($V_{loc}$) increases dramatically. At almost 2 mm from the origin of flow the slope of the curve decreases slightly, indicating a slight decrease in the $V_{loc}$. However, the average velocity, $V_{avg}$, is not dramatically affected by the two local velocities; therefore, it is determined to be 265 mm/s. Figure 4.20 corresponds to the sample with transverse finishing direction. In this specimen, the observations are very different from the previous. The local velocity $V_{loc}$ at the initiation of flow zone is slower. In addition, the fast flow zone displays a curve significantly wavy, showing three peaks along the curve. Comparing the wavy curve with the y-profile of the surface texture data in Figure 4.5, it can be concluded that the fluid velocity was affected by the roughness and waviness of the surface. However, the inverse transform of the y surface profile in Figure 4.5(b) indicates the presence of three peaks that can very well relate to the perturbation in the filler metal flow in Figure 4.20. As a whole, the average velocity for this experiment is equal to 249 mm/s.
Figure 4.19. Distance versus time plot for the determination of the average fluid velocity for the sample with 240 grit SFC. Fluid flow is along the finishing direction.

Figure 4.20. Distance versus time plot for the determination of the average fluid velocity for the sample with 240 grit SFC. Fluid flow is transverse to the finishing direction.
Figure 4.21 displays the distance versus time curve for the surface prepared with 600 grit SiC paper; the fluid flow is transverse to surface finishing direction. In this Figure, it is very well observed that the curve is smoother than in the previous case. Basically, there are no significant disturbances during fluid flow as with the previous sample. The determined average velocity is 282 mm/s. In Figure 4.22, the flow is on the 6μm SFC, the average fluid velocity is determined from the distance-time curve. The most important observation in this data is the obvious definition of the identified zones during flow. The transition of the fluid flow to the next zone also occurred in a sharp manner. The average velocity increased significantly to 316 mm/s.

Figure 4.21. Distance versus time plot for the determination of the average fluid velocity for the sample with 600 grit SFC. Fluid flow is transverse to the finishing direction.
Figure 4.22. Distance versus time plot for the determination of the average fluid velocity for the sample finished with 6 μm diamond slurry.

When the base metal is nickel, the distance versus time plots are presented in Figures 4.23-4.26. In Figure 4.23, the distance-time curve exhibits a smooth behavior in the fast flow region; this is due to the filler metal flowing longitudinally to the direction of the surface finish. Even though the surface finishing condition is 240 grit, there was a smooth continuous flow of filler metal without major turmoil. The average velocity for this specific experiment resulted in 336 mm/s. In the case of the flow direction being transverse to the surface finishing orientation, for similar surface grade, the curve in Figure 4.24 displays some humping; which again is presumed to be the effect of the waviness of the surface. The determined average velocity is 326 mm/s.
Figure 4.23. Distance versus time plot for the determination of the average fluid velocity for the sample with 240grit SFC. Fluid flow is along the finishing direction, BM = Ni.

Figure 4.24. Distance versus time plot for the determination of the average fluid velocity for the sample with 240grit SFC. Fluid flow is transverse to the finishing direction, BM=Ni.
When the surface finishing conditions are smoother than in the previous case, such as surface finished to 600 grit and 6 μm, the distance-time curves are quite different from the experiments on surfaces finished with 240 grit. Figure 4.25 corresponds to the flow of the filler metal, transverse to the surface finish direction, on the nickel surface finished to 600 grit SiC paper. The curve (fluid behavior) in the fast flow zone of the specimen exhibited some humping. These humps are the effect of the transverse grooving on the surface created by grinding it in that direction. Going back to the surface analysis in section 4.1, it was seen that the roughness characterized by $R_t$ is 3.5 μm and the waviness characterized by $\lambda$ is equal to 7 μm, which is enough to alter the smooth flow of the filler metal. The average fluid velocity for this specimen resulting in 339 mm/s was determined in the same manner as in the previous cases.

In the case when the filler metal flow is on a nickel surface finished to the 6 μm polish grade, the curve on the distance-time plot is very smooth with no perturbations. For this specific experiment, the determined fluid average velocity is 346 mm/s. Summary of results of the average velocity determination for the experiments carried out with both, the 304 stainless steel and nickel base metals, and copper filler metal are displayed in Table 4.2.
Figure 4.25. Distance versus time plot for the determination of the average fluid velocity for the sample with 600 grit SFC. Fluid flow is transverse to the finishing direction, BM = Ni.

Figure 4.26. Distance versus time plot for the determination of the average fluid velocity for the sample with 6 µm SFC, BM = Ni.
Effect of surface roughness, finishing direction and material composition on the filler metal average velocity.

The effect of surface roughness on the filler metal average velocity has been analyzed in Figures 4.27 and 4.28. In the case of the joint system with BB=304 stainless steel and FM=copper, as the surface roughness decreases the filler metal average velocity increases, as shown in Figure 4.27(a) and (b) [97-99]. In addition, in both, the transverse and longitudinal flow direction with respect to the surface finishing direction, Figures 4.27(a) and (b) respectively, the average velocity increase occurs almost following a quadratic equation. Considering the scattering of the data, the average velocity will be in the range limited by the dashed lines in both plots. The reason for this behavior of the average molten filler velocity can be attributed to the rough surface of a material with heterogeneous composition [100], such is the case of 304 stainless steel. Since this material is composed by several chemical elements (C=0.08, Mn=2.00, Si=1.00, Cr=18.0-20.0, Ni=8.0-10.5, P=0.045, S=0.03, and Fe=remainder, all amounts in weight percent), their effect on the velocity when the surface is rougher is more significant. This is because surfaces that contain various chemical elements are more difficult to wet than pure materials.

Results for the joint system BM=nickel and FM=copper, are depicted in Figure 4.28. As with the previous system, the filler metal average velocity increases as the
Figure 4.27. Effect of surface roughness on the filler metal average velocity when the filler metal flow is in the (a) transverse, and (b) longitudinal direction with respect to the surface finishing direction. Joint system BM = 304 stainless steel and FM = copper.
Figure 4.28. Effect of surface roughness on the filler metal average velocity when the filler metal flow is in the (a) transverse, and (b) longitudinal direction with respect to the surface finishing direction. Joint system BM = Nickel and FM = Copper.
surface roughness decreases. This is true in both cases, the transverse, in Figure 4.28(a) and longitudinal, Figure 4.28(b), flow direction with respect to the surface finish direction. In this braze system, the molten filler velocity increases almost linearly as indicated by the dashed boundary lines in Figures 4.28 (a) and (b). This may be due to the effect of the homogeneous surface, such as pure nickel. It is known that pure materials are more wettable than alloys [100-102]. When the surface finishing direction is transverse to the fluid direction, Figure 4.28(a) the velocity data is more scattered for rougher surfaces. On the opposite, as the surface gets smoother the range of the data distribution also decreases, meaning that the average velocities obtained are more accurate. In the case when the surface finishing direction is longitudinal to the fluid flow, see Figure 4.28(b), the range of distribution of the data is constant.

Table 4.2. Summary of the determination of the average flow velocity and the effect of surface finish on the fillet metal fluid flow.

<table>
<thead>
<tr>
<th>BM</th>
<th>FM</th>
<th>Gas</th>
<th>Surface Finish Condition</th>
<th>Individual (V_{avg}) (mm/s)</th>
<th>Overall (V_{avg}) (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dr. 240 grit SiC paper</td>
<td>249 247 255</td>
<td>250</td>
</tr>
<tr>
<td>304SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Long. Dr. 240 grit SiC paper</td>
<td>282 277 265</td>
<td>275</td>
</tr>
<tr>
<td>304SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dr. 600 grit SiC paper</td>
<td>298 292 299</td>
<td>296</td>
</tr>
<tr>
<td>304SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Long. Dr. 600 grit SiC paper</td>
<td>303 335 315</td>
<td>318</td>
</tr>
<tr>
<td>304SS</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Polished 6 mm diamond slurry</td>
<td>316 341 307</td>
<td>321</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dr. 240 grit SiC paper</td>
<td>285 326 305</td>
<td>305</td>
</tr>
<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Long. Dr. 240 grit SiC paper</td>
<td>336 312 325</td>
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<tr>
<td>Nickel</td>
<td>Cu</td>
<td>UHP Ar</td>
<td>Trans. Dr. 600 grit SiC paper</td>
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<tr>
<td>Nickel</td>
<td>Cu</td>
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<td>Long. Dr. 600 grit SiC paper</td>
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<tr>
<td>Nickel</td>
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<td>UHP Ar</td>
<td>Polished 6 mm diamond slurry</td>
<td>346 360 345</td>
<td>350</td>
</tr>
</tbody>
</table>
4.3. Capillary flow, wetting angle (θ) measurement.

It is known that the molten filler metal flows through a braze gap driven by capillary action. Studies on capillary flow, especially in vertical tubes, can be found in the literature [2-4, 103-108]. For the analysis of capillary flow in horizontal braze gaps the conditions are different. In a horizontal gap only two walls, top and bottom, exist; however, in the vertical tube, the wall is circular.

The capillary meniscus, having a “C” shape, of the advancing fluid front observed in the video enables the measurement of the wetting angles along the braze joint in the base metal-liquid-gas interface. Measurements of the wetting angle (θ) [109-115] was performed along the horizontal gap in the controlled surface, which is the surface with different finishing conditions, as shown in Figure 4.29. The method depicted in Figure 4.29, consists in first setting the images of the sequenced frames in a picture development mode, which reveals clearly the “C” shape of the advancing liquid front. Then, the base metal surface-molten filler metal interface is determined, meaning drawing a horizontal line at this interface, which becomes a reference line. Then, draw a line tangent to the curve of the liquid-gas interface, near the triple point, the contact angle is the angle measured between these two lines. This procedure was repeated consistently in all the image frames for all the experiments. As an example, the measured contact or wetting angle as a function of time is presented in Figures 4.30 and 4.31.
Figure 4.29. Determination of the wetting angle $\theta$.

The plot in Figure 4.30 displays the wetting angle as a function of time for the brazing experiment performed in the joint system, BM=304 stainless steel, FM=copper, furnace environment=UHP Argon gas and SFC=240 grit SiC paper, the filler metal flow was in the direction of the surface finishing marks. As can be observed in the figure, the curve exhibits drastic changes along the braze gap. These changes are related to the zones of interest during filler metal flow. For example, it is observed that in the initiation of flow zone, the wetting angle $\theta$ decreases drastically from $90^\circ$ to $12^\circ$. Entering the fast flow zone, $\theta$ increases slightly along the microchannel until it reaches $22^\circ$, which is identified as the transient point. In the residence zone the contact angle increases drastically up to $36^\circ$ and in the filler metal extension zone the wetting angle drastically decreases down to $10^\circ$. Correlating the average velocity data and the wetting angle data,
it is observed that for high velocities the wetting angle is low. In contrast, for slower fluid velocities the corresponding wetting angle is high.

Most of the changes in wetting angle occur at the beginning of filler metal flow and at the end of the channel. The change in wetting angle at the beginning of the microchannel occurs right after the filler metal melts. Starting when the filler material melts in the left compartment of the braze specimen, the molten filler starts to wet the bottom surface of the microchannel, reducing the contact angle. Right after the wetting angle at the bottom surface is lowered, the molten filler begins to wet the top surface of the braze gap also reducing the wetting angle. This process takes some time and provides the conditions for capillarity to control the fluid flow in the braze joint. The change in wetting angle at the beginning of the microchannel does not drive the filler metal flow in the majority of the joint but certainly affect the way the flow starts to happen. In the same manner, the change in wetting angle at the end of the microchannel has an important role in fillet formation. As the molten filler metal fills the right end of the braze gap, the wetting angle (θ) increases slightly to form a fillet. Right at the end of the gap the contact angle increases drastically to approximately 34° because the liquid wets slightly the vertical wall of the right compartment; then, the contact angle (θ) decreases drastically to its final value in the fillet. If there is not enough capillary pressure, meaning not low enough liquid-gas surface tension, the fillet wetting angle will be high;
if the opposite occurs one can expect lower fillet wetting angles, which are desirable [116,117].

![Graph showing wetting angle measurements over time](image)

Figure 4.30. Wetting angle measurements as a function of filler metal flow time along the braze channel. Filler metal flow was along the surface finishing marks of 240 grit SFC.

In the case when the SFC for the same joint system is transverse to the direction of flow, see Figure 4.31, the wetting angle $\theta$ has slightly similar behavior as in the previous case. This specific analysis corresponds to the data of the braze experiment explained in Figure 4.20. However, during the development of the wetting angle along the microchannel, a large hump is observed at the end of the flow, right before the fillet formation. This hump occurs because of the sudden lose in capillary pressure. Also, since it is known that the fluid front is advancing transversely to the grooves developed
by the surface finishing conditions at this coarse level (240 grit), it is expected to see a major effect on the wetting angles. Effect of surface roughness will be discussed in detail in section 4.5.

Figure 4.31. Wetting angle measurements as a function of filler metal flow time along the braze channel. Filler metal flow was perpendicular to the surface finishing marks in 240 grit SFC.

4.4. Determination of surface tension ($\gamma_{LG}$) and total surface energy ($E'$).

The determination of the liquid-gas surface tension ($\gamma_{LG}$), is based on the measured wetting angles. As discussed in Chapter II, using the Young-Dupré relation
stated in Equation (2.28) [9-11], the liquid-gas surface energy ($\gamma_{LG}$) can be determined along the horizontal braze channel,

$$\gamma_{LG} = \frac{\gamma_{SG} - \gamma_{SL}}{\cos \theta}$$

where, $\gamma_{LG}$ is the liquid-gas surface energy, $\gamma_{SG}$ is the solid-gas surface energy, $\gamma_{SL}$ is the solid-liquid surface energy, and $\theta$ is the wetting angle.

In addition, based on thermodynamic analysis at the flow front by Adamson [116], the total surface energy ($E^T$) can be calculated.

$$dG = \gamma dA$$

$$G' = \gamma = \left( \frac{\partial G}{\partial A} \right)_{T,P}$$

$$dq = TdS = TS^s dA$$

$$\left( \frac{\partial G^s}{\partial A} \right)_P = -S^s$$
\[ \frac{d\gamma}{dT} = -S' \]  \hspace{1cm} (4.5)

\[ H' = E' = G' + TS' \]  \hspace{1cm} (4.6)

\[ E' = \gamma - \frac{T d\gamma}{dT} \]  \hspace{1cm} (4.7)

where, \( E' \) is the total energy of the fluid advancing front, and \( d\gamma/dT = -0.176 \) [96].

These parameters, wetting angle (\( \theta \)), liquid-gas surface energy (\( \gamma_{lg} \)) and total energy of the fluid advancing front (\( E' \)) can be used in mathematical and computational models to predict the fluid characteristics of filler metal flow in horizontal braze gaps. Figure 4.32 displays the (a) liquid-gas surface energy (\( \gamma_{lg} \)), and the (b) total energy (\( E' \)) as a function of time plots for the joint system BM=304SS and FM=Cu. Both plots are based on the measured wetting angles, showed in Figure 4.31, when the molten filler metal flow is in the direction perpendicular to the surface finishing marks in 240 grit SFC.
Figure 4.32. (a) Liquid-gas surface energy ($\gamma_{LG}$), and (b) total energy ($E^t$) as a function of time plots for the joint system BM=304SS and FM=Cu. Filler flow is in the direction perpendicular to the surface finishing grooves in 240 grit SFC.
Figure 4.33. (a) Liquid-gas surface energy ($\gamma_{LG}$), and (b) total energy ($E^t$) as a function of time plots for the joint system BM=Nickel and FM=Cooper. Filler metal flow is in the direction longitudinal to the surface finishing grooves in 240 grit SFC.
The change of the liquid-gas surface tension ($\gamma_{LG}$) as a function of time plotted in Figure 4.32 (a) reveals that the humps observed on the wetting angle-time curves are diminished. Again, the shape of this curve is general for all the other brazing experiments performed in this study. The magnitude of the liquid-gas surface tension ($\gamma_{LG}$), changes in the different zones during flow. It decreases in the initiations of flow zone, levels out in the fast flow zone, increases slightly at the fillet formation, and decreases drastically on the fillet. The values of $\gamma_{LG}$ in the fast flow zone when the surface roughness is 240 grit grinding in the transverse direction, are approximately 1200 erg/cm$^2$. In the case when the surface roughness is 240 grit grinding in the longitudinal direction $\gamma_{LG}$ is approximately 1150 erg/cm$^2$, indicating that the direction of surface finishing has an effect on the liquid-gas surface tension $\gamma_{LG}$. This effect is due to the variation in wetting angle in both transverse and longitudinal flow directions with respect to the surface finishing orientation. In the case of the transverse flow direction, the interaction between the liquid advancing front and the surface roughness produces a significant dynamic effect on the liquid-gas surface tension, $\gamma_{LG}$, which increases the $\gamma_{LG}$ value. Since the contact angle changes, the liquid-gas surface tension $\gamma_{LG}$ changes in a localized scale [117-119], because the liquid in contact with the surface may find a hydrophobic or hydrophilic surface, which will be discussed in sections 4.5.2 and 4.5.3. When the flow direction is longitudinal to the surface finishing direction, the dynamic
effect is smaller because the liquid-solid interaction is smoother; so, the $\gamma_{LG}$ values decrease.

The total surface energy of fluid front ($E^s$) as a function of time curve displayed in Figure 4.32 (b) has similar shape as in the case of $\gamma_{LG}$ as a function of time. The only difference is that in the later case the magnitude of $E^s$ is higher all along the parallel gap. For instance when the surface roughness is 240 grit SFC, $E^s$ is approximately 1400 erg/cm$^2$. According to theory, this increase is because $E^s$ considers not only the atoms at the surface of the liquid but it considers as much as four atomic layers inside the liquid surface [116]. This type of datum $E^s$, is used in molecular-dynamics based fluid flow simulations.

Figure 4.33, displays similar sequence; however, these data is for the case when the filler metal flow was in the direction transverse to the surface finishing lines in the BM=nickel and FM=copper. In Figure 4.33 (a) the surface energy as a function of time is plotted, it exhibits a significant $\gamma_{LG}$ decrease at the initiation of flow but levels out to $\gamma_{LG}$=800 erg/cm$^2$ along the parallel braze gap. At the end of the microchannel $\gamma_{LG}$ increases slightly at the fillet formation site and then it decreases in the filler. In general, $\gamma_{LG}$ does not have significant changes along the braze gap because there is no This is because the direction of flow is longitudinal to the direction of surface finish. In this
situation there is no significant dynamic fluid-to-solid interaction so there is less surface features to increase the surface tension. In Figure 4.33 (b) the corresponding total surface energy is plotted as a function of time. The shape of the curve is exactly similar as in the case of the liquid-gas surface tension ($\gamma_{LG}$) as a function of time. Importantly, the total surface energy increases in magnitude along the microchannel, specifically up to about 1000 erg/cm$^2$ in the fast flow region.

4.5. Effect of surface roughness on wetting angle ($\theta$), liquid-gas surface tension ($\gamma_{LG}$) and average velocity ($V_{avg}$).

It has been observed that surface texture has a significant effect on the wetting angle [118-121], specially in surfaces finished with coarser abrasive SiC paper. Most of the filler metal flow experiments carried out on the 240 grit SFC exhibit perturbations on the fluid flow; those observations are evident in form of humps in the distance-time and wetting angle-time plots previously discussed.

4.5.1. Effect of surface roughness stated by Wenzel’s theory

According to the model proposed by Wenzel and discussed in Chapter II, section 2.2.4.2
\[ \cos \theta^* = r \cos \theta \quad (2.40) \]

where, \( \theta^* \) is the localized contact angle that depends on surface roughness, \( r \) is the real surface-to-geometric surface ratio, and \( \theta \) is the measured wetting angle.

In all surfaces, the real surface area is always larger than the geometrical area, this ratio "\( r \)" affects the determination of the wetting angle. From the surface analysis discussed at the beginning of this chapter, the \( r \) values for the analyzed surfaces were obtained, these are \( r_{240} = 1.020 \), \( r_{600} = 1.008 \) and \( r_{6\mu m} = 1.0006 \). Considering the model proposed by Wenzel, the localized wetting angle \( \theta' \) can be calculated. Figure 4.34 shows a comparison between Wenzel’s wetting angle, Figure (a), and the measured angle, Figure (b), as a function of time. This experiment corresponds to the sample with fluid flow transverse to the finishing marks in the 240 grit SFC samples. In Figure 4.34 (b) Wenzel’s wetting angle as a function of time curve demonstrates that the angle is reduced. For angles higher than 20 degrees, Wenzel’s and measured angles are the same; however, when the angles are less than 20 degrees, Wenzel’s angle decreases. Overall the calculated angles have similar behavior as the measured angles, meaning same shape of the curves.
Figure 4.34. Effect of surface roughness in wetting angle. (a) measured Young-Dupré’s angle as a function of filler metal flow time; and (b) calculated Wenzel’s angle as a function of fluid flow time. Both plots correspond to the same brazing experiment.

Considering a rough surface as in Figure 4.35, when the fluid front faces a hump the contact angle increases, as shown in the schematic below, then this angle is not affected by the surface roughness because the liquid front thinks that there is a change in the direction of flow. However, as the liquid front finds a downhill slope, the contact angle drastically decreases, when the surface becomes flat the angle will still maintain its low contact angle until it finds another surface hump. These are the cases in which Wenzel’s theory affects the most. Therefore, surfaces that exhibit rough textures will be more affected by Wenzel’s theory, but finer surfaces will not.
Figure 4.35. Schematic of fluid flow over a rough surface illustrating the mechanism of the change in Wenzel’s wetting angle $\theta^*$ on rough surfaces; in this case, surfaces with transverse grinding directions.

It can be concluded that when the measured angle is less than 20 degrees the roughness of the surface has had larger effect on the wetting angle. Since the lower wetting angles decrease the $\gamma_{LG}$, it increases the velocity of the fluid. When the contact angle is greater than 20, the measured and calculated wetting angles are the same. At this level, the surface roughness has no effect on the wetting angle $\theta$, liquid-gas surface tension ($\gamma_{LG}$) and average filler metal velocity ($V_{avg}$).

4.5.2. Filler metal flow on hydrophilic surfaces

Another theory indicates that within a microchannel there can be surfaces that are hydrophilic. Specimens with very fine surface finish conditions perpendicular to the
fluid flow are considered to be “hydrophilic surfaces”. Note that even though the fluid is not water, the term “hydro” will be used. This type of surfaces has an affinity for wetting. Some of the liquid escapes from the fluid front and penetrates into the nooks and crevices. Then the liquid layer finds itself on an already wet (prewet) substrate. This phenomenon of hydrophilic surfaces was stated by de Gennes [9], based on the Cassie-Baxter theorem [122] presented in Chapter II, section 2.3.7. In the schematic illustration of a hydrophilic surface in Figure 2.21, it is observed that the surface contains wells that are already wetted. Evidence of this theory was found in the specimens with a fine surface such as the 6 μm SFC, as shown in Figure 4.36. In this case the crevice acts as a vertical tube having the fluid on top. As soon as the opening of the crevice sees the fluid, it rapidly develops capillary phenomenon and the fluid flows downwards. This downward flow is confirmed by the “C” shape of the fluid front inside the crevice. Then, this region is already wet (prewet) when the bulk fluid front comes in contact. In this case, if a surface has many of these crevices, they will decrease the wetting angle and liquid-gas surface tension (γ_{LG}) resulting in higher average filler metal fluid velocity (V_{avg}).
Figure 2.21. Representation of a hydrophilic surface [9].

Figure 4.36. Evidence of crannies present in very fine surfaces (6 μm) developing capillary phenomena in the vertical direction, which affect the wetting angle.

One negative aspect of these hydrophilic surfaces is that the unfilled or partially filled crannies on the surface may act as stress concentrators within the joint. For example cracks may nucleate at the tip of these sites, which will affect the reliability and life of the joint itself.
More specifically, in the case of prewetting, two types of situations may occur. One, if the film penetrating the notches on the surface does not have enough time to dissolve the base metal or react with it to produce intermetallic materials. Two, if the materials in the joint system are reactive, as indicated by the models described in pages 57 to 59 in Chapter II.

In the first case, prewetting can actually increase the filler metal velocity. The mechanism of increasing the velocity is that as soon as the liquid/gas interface touches the prewetted surface (nooks and notches filled with liquid metal) will rapidly advance by the length of the prewetted area, molten Cu sees molten Cu, then the localized contact angle, θ, is reduced as well as the liquid/gas surface tension, γ_{LG}, and the fluid velocity increases. As soon as the liquid/gas interface reaches the dry solid area, molten Cu sees 304SS; then, the liquid/gas surface tension, γ_{LG}, resumes, the contact angle, θ, increases, the liquid wets that surface slower than in the previous wetted area, and the fluid velocity decreases. The extent of prewetting is important because if the liquid film is prewetting much of the surface area, then there is less dry surface area where the liquid-gas interface movement will be slowing down. The total effect will be an increase of filler metal velocity.

In the second case, prewetting may actually interfere the filler metal flow in a more active manner. If all the nooks, notches in the surface are prewetted, and that
prewetting liquid reacts with the substrate by dissolving it or forming intermetallics, the fluid velocity will be altered. When the liquid/gas interface touches the dry solid surface, the contact angle, $\theta$, and liquid/gas surface tension, $\gamma_{L,G}$, increase and the flow is altered. When the liquid/gas front touches a notch filled with an intermetallic material, again the liquid/gas surface tension changes and the contact angle changes, this surface interaction may also reduce the velocity of the fluid. If the film of liquid prewetting the notches in the surface dissolves some of the base material, the density and viscosity of the liquid film filling the notch is altered depending on the extent of the dissolution occurring. Then, the copper liquid/gas front sees an intermetallic or an alloy (304 stainless steel dissolved in copper); therefore, the liquid/gas surface tension, $\gamma_{L,G}$, and the contact angle, $\theta$, are altered, which may affect the filler metal flow.

Sometimes, rough surfaces can also be hydrophilic, however, their effect in a braze joint is negative. When the filler metal average velocity ($V_{avg}$) is sufficiently high, the filler metal wets both surfaces of the braze gap, top and bottom, creating large pores in the middle of the braze gap. As we can see in Figure 4.37 (a), the molten metal wets the bottom and top surfaces producing air pocket in the middle of the sample. This phenomenon was observed on 304SS samples with 240 grit finishing condition. Eventually, after about 10 minutes of brazing time, the braze gap, meaning all those air pockets, fill themselves with the molten metal, as in Figure 4.37 (b). In some cases the air pockets in the brazing gap remain unfilled even after the complete brazing cycle. The
evidence of this phenomenon is shown in a sample after it is solidified, in Figure 4.38 (a). This specific case was for the 304SS specimens with 240 grit surface finishing conditions and the filler metal flow in the direction transverse to the grinding lines, see Figure 4.38 (b).

Figure 4.37. (a) Experimental observation of the formation of an air pocket inside the braze gap as a result of the top and bottom surfaces being hydrophilic. (b) Filled gap after 10-15 minutes of the initiation of flow.
Figure 4.38. (a) Solidified braze joint as evidence of the wetting of the top and bottom surfaces creating air packets between them. (b) Surface roughness of the respective 304SS sample.

Many times during braze integrity assessment, the observation of porosity and air pockets such as those in Figure 4.38 (a), are considered solidification shrinkage because of their appearance. Nevertheless, the experimental results shown in Figure 4.37 (a) and (b) are clear evidence that void formation is the effect of high fluid velocities over rough hydrophilic surfaces. The picture frames captured during liquid metal flow, in Figure 4.37 (a), shows the voids at the center of the braze gap. The reason why these voids do not fill in even after the completion of the brazing cycle is because of the high pressure trapped inside of them and mathematically explained by the Laplace Equation (Equation 2.4) in Chapter II. Low magnification observation of these pores or voids may lead to conclude that they are because of solidification shrinkage, more careful microscopic evaluation demonstrates that it is because of the molten filler metal wetting and rapid flow on the opposite surfaces.
4.5.3. Filler metal flow on hydrophobic surfaces

Hydrophobicity in rough surfaces means that the surface energy of the dry solid is less than that of the wet solid [9], consistent with Young’s relation (in which $\theta > 90$ is equivalent to $\gamma_{SG} < \gamma_{SL}$). Under these conditions, it is not necessary expected that the solid/liquid interface would conform to the topographical features of the solid surface. Air can remain trapped under the liquid, at least as long as Young’s relation remains satisfied at the contact line. Then the liquid rests on a composite surface made of solid and air as shown in Figure 2.22. This theoretical analysis was first stated by Cassie and Baxter and was introduced in Chapter II, section 2.3.8. of this document.

Surfaces that are coarse enough having relatively large defects such as notches and nooks besides the fine roughness, can develop into a hydrophobic surface. This theory was verified in the fluid flow experiments on the nickel 600 grit SFC specimens having the fluid flow in the direction transverse to the surface grooves. This surface texture is not very rough compared to the 240 grit SFC but it contains certain amount of large grooves such as the one in Figure 4.39. In this specific case, this notch in the sample was found in the middle of the fast flow zone during filler metal flow. Therefore, the conditions were low wetting angles ($\theta = 16^\circ$), low liquid-gas surface tension ($\gamma_{LG} = 800$ erg/cm$^2$) and high average filler metal velocity ($V_{avg} = 326$ mm/s). As the fluid advances with a low contact angle, it finds a hump, as soon as the fluid front reaches top of the
hump the velocity of the fluid takes control for a moment and makes the fluid front intercept the next hump leaving air trapped between the two in the bottom of the groove or notch. If the grooves in the surface are wide enough such effect does not occur. This evidence can be observed in Figure 4.39 (b) indicated by the arrows. Therefore, there is a range of the wetting angle where this phenomenon occurs. Efforts were made to represent this phenomenon with empirical formulas, such as the one proposed by Johnson and Dettre [123], which is stated below.

\[
\cos \theta_c = f_1 \cos \theta - f_2
\]  

(4.8)

where, \( f_1 \) is the unwetted surface, \( f_2 \) the wetted surface, \( \theta \) the measured wetting angle, and \( \theta_c \) the localized angle.

Another factor for the formation of voids in Figures 4.39 (a) and (b), may be the capillary pressure trapped in the bottom of the notch, if the notch is localized. Assuming constant temperature and volume, and instantaneous equilibrium, as the liquid enters the notch, see Figure 4.39 (a), it may trap pressure which may promote the formation of a bubble, as indicated by Equation 2.4. The combination of the three, the capillary pressure trapped, the dynamics of the contact angle and the geometry of the notch may be responsible for the void formation.
Figure 4.39. (a) Air pocket trapped in the bottom of the v-groove. (b) Same picture as in (a) but at lower magnification. It shows the narrow v-groove in the left, trapping air, and the wider v-groove filled with the molten metal.

Coarse surfaces with aligned grooves or randomly oriented grooves can produce hydrophobic surfaces. The schematic in Figure 4.40 indicates that if the contact angle is large and surface sufficiently rough, the liquid may trap air. Assuming that the true angle \( \theta_i \) remains invariant as the liquid advances over a rough surface of the shape showed in the schematic, then if \( \theta_i \) is large the liquid can be so reentrant that intercepts the next hill leaving air trapped in between the two [71]. In the schematic, \( f_1 \) is the unwetted surface, \( f_2 \) is the wetted surface, \( \theta_i \) is the contact angle with respect to a horizontal plane and is measured from the liquid advancing direction.
Figure 4.40. Schematic of an edge of a liquid front flowing towards the right side creating air pockets in the bottom of the grooves of the base surface [71].

Other factors that may affect the formation of voids at the bottom of the notches in rough surfaces, is the hysteresis occurring with the angles. When liquids flow on rough surfaces, as shown in Figure 2.13(a), the contact angles can be in advancing or receding situations. Advancing position is when the liquid/gas interface touches the downhill of a surface peak; and the receding position is when the liquid/gas interface touches the uphill of a surface peak. Advancing angles (>110°) are usually higher than receding angles and they increase as surface roughness increases, as shown in the plot in Figure 2.13(b). Therefore, if these high advancing angles are in contact with a rough surface such as when the molten filler metal flows transversely to the 240 grit surface finishing direction, they may increase the formation of voids at the bottom of the deep valleys.
Using the same specimen geometry as in Figures 3.5 and 3.6, experiments were carried out with alumina (Al$_2$O$_3$) base material coated with titanium, in the bottom surface, and nickel in the top surface. Copper was used as a filler metal. The surface analysis of the sample clearly show a very coarse surface with randomly oriented groves, as displayed in Figure 4.41 (a). The surface parameters for the titanium coating are the following Ra = 1.96 μm, Rq = 2.64 μm, Rz = 21.86 μm, Rt = 24.71 μm. As in the previous experiments, Rt is the parameter used to characterize the surface roughness. An Rt of 24.71 μm is at least 22 % of the 113 μm braze gap vertical distance. Experimental results indicate that the titanium coating surface did not wet at all. Roughness of this scale significantly affects the wetting angle, liquid-gas surface energy, and average velocity, dewetting the surface instead of promoting wetting. As copper melted it started to form a meniscus at the entrance to the braze gap. However, the titanium surface dewetted forcing the molten copper to wet the walls of the left compartment of the specimen which was nickel. Even though the sample was in an inclined surface with a 45° angle, the copper molten metal did not wet the titanium surface, as shown in Figure 4.41 (b). The dynamic characteristics of the molten metal play an important role because in this experiment some dynamic wetting on the titanium characterized by the contact angle was observed.
Figure 4.41. (a) Surface roughness of an Al$_2$O$_3$ base material coated with Ti. (b) Specimen displaying the formation of a meniscus in the Ni base metal in the left compartment after dewetting from the Ti surface.

**Wetting and air trapping**

Surface roughness always expands the possibilities of wetting and non wetting situations. The first prediction of wetting to non-wetting transition can be achieved by a threshold “$r$” value obtained from Wenzel’s equation (Equation 2.40). If $\theta = 0$, then $\cos(0) = 1$, thus,

$$r^* = \frac{1}{\cos \theta_e}$$  \hspace{1cm} (4.9)

where, $r^*$ is the wetting to nonwetting transition value, and $\theta_e$ is the measured angle.

Figure 4.42 displays the corresponding $r^*$ value for angles between 0 and 180 degrees. The graph also shows that angles ranging from 0 to approximately 90 degrees
fall in the wetting regime and angles from approximately 90 to 180 degrees in the non-wetting regime; also, positive $r^*$ values indicate good wetting properties as opposed to negative $r^*$ values.

![Wenzel roughness factor](image)

Figure 4.42. Wenzel roughness factor, $r^*$, as a function of wetting angle, indicating the transition from non-wetting to wetting regimes.

In the case of hydrophilic surfaces, because of the presence of notches, there cannot be total wetting ($\theta^*=0$), since the liquid flows on a partially wetted surface ($\theta_e \neq 0$). Assuming that the surface is an array of solid and liquid “cells” of dimension $dx$, and considering that the wetting film advances by a distance $dx$ on that surface, the
wet surface is \( r \text{dx} \), but this movement also leaves a solid surface area \( \phi_s \text{dx} \). Then, the energy change is given by:

\[
dE = (r - \Phi_s)(\gamma_{SL} - \gamma_{SG}) \text{dx} + (1 - \Phi)\gamma_{LG}\text{dx}
\]  

(4.10)

where, \( r \) is the roughness factor, \( \phi_s \) is the fraction of the solid surface area, \((1 - \phi_s)\) is the fraction of the liquid (prewetted) surface area, \( \gamma_{SL} \), \( \gamma_{SG} \) and \( \gamma_{LG} \) are the solid-liquid, solid-gas and liquid-gas surface tensions.

The movement of the liquid/gas front line will be energetically favorable (\( \text{dE}<0 \)) if the cosine of Young’s angle verifies the inequality:

\[
\cos\theta_c > \frac{1 - \Phi_s}{r - \Phi_s}
\]  

(4.11)

This equation defines an angle \( \theta_c \) that can have values between 0 to 90 degrees, such that when \( \theta_l < \theta_c \) a liquid film will prewet the notches and nooks in the surface.

In the case of hydrophobic surfaces, Wenzel’s model applies; however, de Gennes [79] shows that it is favorable for the liquid/gas front to follow the roughness of the surface if the contact angle \( \theta_l \) is between 90 degrees and a certain angle \( \theta_c \) given by:
\[
\cos \theta_c = \frac{(\Phi_s - 1)}{(r - \Phi_s)}
\] (4.12)

Nevertheless, experiments have shown [79] that even in this regime air can still be trapped in the notches of the surface. Therefore, this regime can only be considered metastable.

**Mechanisms for air trapping**

Figure 4.43 assumes a sinusoidal shape solid surface. Both surfaces have different amplitudes but equal wavelengths. Assuming the contact angle \( \theta \) slightly more than 90 degrees, from the graphic representation it can be deduced that the finer surface is wetted by the liquid, but the rougher surface can trap air.

![Diagram](image)

Figure 4.43. Graphic representation of sinusoidal surfaces, (a) surface with similar wavelength but smaller amplitude, and (b) surface with same wavelength but larger amplitude.
If the surface profile is represented by \( z = a \cos(kx) \), the air pocket formation threshold can be determined. The maximum slope of the profile is \(|ak|\), and the condition for air trapping (when the liquid/gas front is horizontal), for a given \( \theta_E \) is:

\[
a > \frac{\lambda \tan \theta_E}{2\pi}
\]  

(4.13)

where, \( \lambda \) is the wavelength of the surface profile, and \( \theta_E \) is the contact angle.

Ploting \( \frac{\lambda \tan \theta_E}{2\pi} \) as a function of the contact angle \( \theta_E \), the condition for air trapping is that the corresponding values in the y-axis, for each angle, must be larger than the y-values.

![Graph showing threshold value for air trapping as a function of contact angle.](image)

Figure 4.44. Threshold value for air trapping as a function of contact angle.
Considering the limit of $|ak|<<1$, the roughness is given by the relation:

$$r = 1 + \frac{(ka)^2}{4}$$  \hspace{1cm} (4.14)

Combining equations (4.13) and (4.14), a final threshold "r" for air trapping is obtained.

$$r^* = 1 + \frac{\tan^2 \theta_E}{4}$$  \hspace{1cm} (4.15)

![Graph showing threshold $r^*$ as a function of contact angle $\theta_E$](image)

Figure 4.45. Threshold, $r^*$, for air trapping as a function of contact angle.

A summary, according to de Gennes [79], of surfaces that promote air trapping is provided by Figure (4.46). This plot indicates that for an apparent contact angle $\theta^*$, there is a Young's contact angle $\theta_E$. If $\cos \theta_E$ is negative ($\theta_E>90$), then the liquid is flowing
over a hydrophobic surface as long as the $\cos \theta^*$ reaches the $\phi$-1 value. On the other hand, if $\cos \theta_E$ is positive ($\theta_E < 90$), then the liquid is flowing over a hydrophilic surface as long as $\cos \theta_E$ is limited by the positive $\cos \theta^*$, bounded below the lines a, b, c. This diagram indicates that the equation for hydrophobic surfaces stated in Equation (2.47) describes the hydrophobic regime, whereas the hydrophilic regime can be described by two equations, Wenzel model represented by Equations (2.40) and the equation for hydrophilic surfaces in contact with liquids, stated in Equation (2.46), depending on the value of the contact angle.

![Diagram](image)

Figure 4.46. Summary of the apparent contact angle as a function of Young’s contact angle, described by their cosines, for a liquid on a textured surface. [79]
From the analysis of all the experiments carried out in this study, it is necessary to summarize the effects of surface roughness on the dynamic variables measured along the brazing parallel gap. In order to obtain a correlation of the contact angle $\theta$, an average wetting angle was obtained in the fast flow region of the microchannel. It is not the intention to ignore the initiation of flow, residence zone and the other smaller zones during flow. However, the region that is completely driven by capillary action is the fast flow zone. Therefore, taking this average wetting angle provides a general idea of the effect of roughness.

Figures 4.47 and 4.48 represent the relationship between the average wetting angle in the fast flow zone and the surface roughness represented by the three abrasive numbers of the surface finishing used during experimentation. It should be noted that the 6 $\mu$m SFC is equivalent to the 1200 grit SiC paper, this abrasive number is being used instead of the 6 $\mu$m only for representing in the Figure, the actual surfaces were polished with 6 $\mu$m. The analysis in Figure 4.47 is for the experiments carried out on the 304 stainless steel surfaces. From this plot the general conclusion is that the average wetting angle decreases as the surface roughness becomes finer, this is represented by the two dashed lines that serve as an envelope of how the average wetting angle changes. In the case of 240 grit SFC, large scatter in $\theta_{avg}$, is observed, due to the large peaks and valleys that the fluid front finds in its way. Conversely, for the 6 $\mu$m SFC the $\theta_{avg}$ data is more
concentrated. The finer surface reduces the liquid-gas surface tension and allows the liquid front flow easily.

Similar behavior is observed for the case when the base metal surface is nickel. The major difference, exhibited in Figure 4.48 is that the envelope by the dashed lines gets slightly thinner, meaning that the $\theta_{\text{avg}}$ is less scattered on the nickel surfaces. Again, the average wetting angle decreases as the abrasive number increases, in other words, the surface becomes finer.

In the case of the effect of surface roughness in the average filler metal velocity, the relationship between the two are represented in Figures 4.49 and 4.50. The general conclusion from both Figures is that as the surface becomes finer the average filler metal velocity increases. Figure 4.49 is the relationship for the experiments performed in the 304 stainless steel. Here, it is observed that the data is somewhat scattered but also it has a range delimited by the two dashed curves that provides an idea of how much the velocity increases in each abrasive number. The average velocity reduces drastically in the rougher surface because of the more significant dynamic factors affecting the filler metal flow, and also because of the heterogeneous 304 stainless steel surface. When the base metal surface is nickel, see Figure 4.50, it is observed that the average contact angle measurements are more scattered at the 240 grit level. However, in
the case of higher abrasive number (finer surfaces) the average contact angle data is more clustered, meaning that the measurements made in those fine surfaces are more repetitive.

Figure 4.47 Average wetting angle as a function of surface roughness for the experiments carried out on the 304 stainless steel surfaces.

Figure 4.48 Average wetting angle as a function of surface roughness for the experiments carried out on the nickel surfaces.
Figure 4.49. Effect of surface roughness on the filler metal average velocity in the experiments performed on 304 stainless steel surfaces.

Figure 4.50. Effect of surface roughness on the filler metal average velocity in the experiments performed nickel surfaces.
Chapter 5

MATHEMATICAL MODELING OF FLUID FLOW

Brazing technology plays an important role in the current joining field. However, this technology has evolved as a result of a practical approach. It is important to recognize the empirical work as it is perhaps more important to address the engineering and scientific issues that control the brazing process. It is in that sense that this section of the document proposes a mathematical model for filler metal fluid flow based on Order of Magnitude Scaling (OMS) [124-131]. This mathematical modeling method has been reinstated in the recent years and is becoming more applied in the scientific field.

The most important feature of the proposed model is that it considers the roughness of the base metal surface where the molten filler metal flows. Currently available mathematical expressions were proposed by Milner [78], Lugscheider [76], Hosking [77], and de Gennes [79]. However, until now, no mathematical model is able to incorporate roughness as part of the brazing process. There are two variables in the model that provide the relationship with the base metal surface, these are $\theta_1$ and $\theta_2$ the contact angles with the bottom and top walls of the microchannel respectively. These two contact angles can be either the measured angles or the calculated ones using the
Wenzel, Cassie-Baxter or Johnson-Dettre models, depending on the needs and applications.

The problem in question is the molten filler metal flow process in a parallel brazing gap. It is known that the controlling phenomenon in these types of problems is capillarity, but the dynamic interaction of the flow with the base metal is also very important. However, it is necessary to apply fluid flow theory [132-135] to obtain an important parameter that is the average velocity $V_{\text{avg}}$ of the molten filler metal. This parameter $V_{\text{avg}}$ is of engineering importance since most people in the brazing industry would like to know in order to predict brazing time, wetting time, etc for a specific joint.

5.1. Factors to consider in a mathematical model.

Several factors that affect the filler metal flow need to be considered. The most important factors are filler metal viscosity, density, temperature, capillary pressure, surface tensions (solid-liquid, solid-gas and liquid-gas), contact angles (dynamic and static) [136-137], base/filler metal chemical interaction, surface roughness and geometry and dimensions of the brazing parallel gap.

Since the filler metal flow theory is not well developed yet, initial models may have to examine selected variables, making small steps at a time. For example, the base
metal/filler metal chemical reactions at the interface during filler metal flow [138] cannot be experimentally quantified and incorporated in these models. Figure 5.1 displays the several level at which the filler metal fluid front interacts with the solid surface. These levels are macroscopic (several hundreds of microns), in which the contact angles can be measured; submicroscopic (30 – 1000 Å), in which the contact angles can be calculated; and the molecular scale at which quantification in a dynamic experiment would be difficult. This molecular scale is at which many chemical and electrochemical reactions occur in liquids at or near room temperature. Interest has increased in using the molecular dynamics modeling tools available. However, to incorporate the diffusion and thermodynamics into the problem at this point will just make the analysis complicated.

Figure 5.1. Three-phase juncture in dynamic wetting. (a-c) macroscopic scale – several tens of microns. (d, e) submicroscopic scale – 30-1000Å. (f) molecular scale [138].
5.2. Model development.

This section describes the development of the mathematical model, beginning with the definition of Order of Magnitude Scaling, the fluid theory, the governing equations and boundary conditions, scaling and determination of the mathematical relation for molten filler metal velocity.

5.2.1. Order of magnitude scaling methodology.

Order of magnitude scaling introduces a modeling methodology that brings the fields of dimensional analysis and asymptotic considerations [124-131]. It consists on transforming the governing differential equations into a set of algebraic equations that are much easier to handle and simpler to solve. Nevertheless, prior understanding of the physical problem is necessary in order to perform the adequate normalization and asymptotic considerations. It must be stated that the results obtained using OMS are estimations of the characteristic values of the unknown functions [124].

5.2.2. Fluid flow theory

From experimentation described in the previous chapters, it is known that the fluid flows with different rates in each of the zones defined in Chapter IV. In the linear
region of flow called “fast flow zone”, as indicated in Figure 4.18, the flow is laminar as defined by the Reynolds number (Re) [132] in equation (5.1).

\[
Re = \frac{\rho u h}{\eta}
\]  

(5.1)

where, \(\rho\) is the liquid density, \(u\) the liquid velocity, \(h\) the characteristic length, and \(\eta\) the fluid viscosity.

The values of the Reynolds Number for the experimentally determined highest and lowest average velocities (\(u = 0.35 \text{ m/s}\) and \(u = 0.25 \text{ m/s}\)) are \(Re = 82.1\) and \(Re = 58.6\), respectively. By definition laminar flow is characterized by \(Re < 2000\). Since the experimentally measured Re values are less than 2000; then, the flow regime in the “fast flow zone” is laminar. The \(\rho, u, h, \eta\) values were taken from Table 5.1.

Table 5.1. Properties of the filler metal (copper), gravity constant, and geometric parameters. [139]

<table>
<thead>
<tr>
<th>Density [(\text{kg/m}^3)]</th>
<th>Viscosity [Pa.s]</th>
<th>Surface Tension at Melting Point [N/m]</th>
<th>Gravity [m/s(^2)]</th>
<th>h [m]</th>
<th>H [m]</th>
<th>L [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7900</td>
<td>4.377x10(^{-3})</td>
<td>1.32</td>
<td>9.81</td>
<td>0.13x10(^{-3})</td>
<td>2.735x10(^{-3})</td>
<td>5x10(^{-3})</td>
</tr>
</tbody>
</table>
Also, it is necessary to evaluate the fluid flow to determine if the viscous or surface tension forces are more significant. The capillary number $Ca$ [133] is a dimensionless parameter that provides that relationship,

$$Ca = \frac{\eta u}{\gamma_{LG}}$$  \hspace{1cm} (5.2)

where, $\eta$ is the viscosity of the liquid, $u$ the velocity of the liquid and $\gamma_{LG}$ is the surface tension of the liquid.

The capillary number values are $8.3 \times 10^{-4}$ and $1.2 \times 10^{-3}$ for $u = 0.25$ m/s and $u = 0.3$ m/s, respectively. Since both are less than one, they indicate that the surface tension forces are more significant over the viscous forces during filler metal flow.

5.2.2.1. Governing equations and boundary conditions

In order to find the solution for this problem it is necessary to make several assumptions, which are the following:

- the fluid is Newtonian, with constant density and viscosity,
- the fluid is incompressible and isothermal, and no external pressure gradients are applied (constant $P$)
• the flow is steady and two dimensional in the x-y plane,
• there is no slip on the walls of the microchannel,
• the body forces are negligible,

A schematic of the fast flow zone is presented in Figure 5.2. In this schematic, the flow is towards the right side, the origin of the x and y axis is set to the center of the height of the two parallel plates at the left end. The notation for Figure 5.2 is the following:

\( \theta_1 \) and \( \theta_2 \) are the liquid-solid-gas contact angles.

L is the length of the channel,

h is the separation between the top and bottom plates, and

\( x_c \) is the characteristic horizontal distance from the origin to the center of the fluid front.
Figure 5.2. Schematic representation of the parallel plates where laminar flow occurs and its dimensions.

**Governing equations**

The filler metal flow is governed by two types of equations, the conservation of momentum equation defined by the Navier-Stokes equation; and the mass balance equation [132]. These equations will assist in determining if inertial or viscous effects dominate the flow.

\[
\rho \frac{D u}{D t} = -\nabla P + \eta \nabla^2 u + \rho g \quad \text{General Navier-Stokes} \tag{5.3}
\]

Then, the equation of motion (Navier-Stokes) in rectangular coordinates \((x, y, z)\) is:
x-component

\[ \rho \left( \frac{\partial u_x}{\partial t} + u_x \frac{\partial u_x}{\partial x} + u_y \frac{\partial u_x}{\partial y} + u_z \frac{\partial u_x}{\partial z} \right) = -\frac{\partial P}{\partial x} + \eta \left( \frac{\partial^2 u_x}{\partial x^2} + \frac{\partial^2 u_x}{\partial y^2} + \frac{\partial^2 u_x}{\partial z^2} \right) + \rho g_x \]  \hspace{1cm} (5.4)

y-component

\[ \rho \left( \frac{\partial u_y}{\partial t} + u_x \frac{\partial u_y}{\partial x} + u_y \frac{\partial u_y}{\partial y} + u_z \frac{\partial u_y}{\partial z} \right) = -\frac{\partial P}{\partial y} + \eta \left( \frac{\partial^2 u_y}{\partial x^2} + \frac{\partial^2 u_y}{\partial y^2} + \frac{\partial^2 u_y}{\partial z^2} \right) + \rho g_y \]  \hspace{1cm} (5.5)

z-component

\[ \rho \left( \frac{\partial u_z}{\partial t} + u_x \frac{\partial u_z}{\partial x} + u_y \frac{\partial u_z}{\partial y} + u_z \frac{\partial u_z}{\partial z} \right) = -\frac{\partial P}{\partial z} + \eta \left( \frac{\partial^2 u_z}{\partial x^2} + \frac{\partial^2 u_z}{\partial y^2} + \frac{\partial^2 u_z}{\partial z^2} \right) + \rho g_z \]  \hspace{1cm} (5.6)

However, since there is no flow in the z direction, the z component of the equation is ignored. Also, the body force term in the x-direction is neglected since it is equal to zero \((\rho g_x = 0)\) because gravity does not affect in this direction. From this point on, the notation will be \(u\) for the velocity term in the x-direction, and \(v\) for the velocity term in the y-direction. Then we have:

\[ \text{N-S x} \hspace{1cm} \rho \left( \frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + u \frac{\partial u}{\partial y} \right) = -\frac{\partial P}{\partial x} + \eta \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \]  \hspace{1cm} (5.7)
N-S \[ y \]
\[
\rho \left( \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = - \frac{\partial P}{\partial y} + \eta \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) + \rho g_y, \quad (5.8)
\]

Mass balance \[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad (5.9)
\]

In these sets of equations there are two independent variables, these are \( x \) and \( y \), defined for an infinite domain. To proceed with the model a finite domain must be defined for the scaling. A finite domain \( L \) is defined in the \( x \)-direction, the domain in the \( y \)-direction will be limited by \( h/2 \).

**Boundary conditions**

No slip boundary conditions apply at the surfaces of the two walls (plates), top and bottom. Therefore, the velocity of the fluid is equal to the velocity of the fluid at the wall.

\[
P(0,0,t) = \rho g H - \frac{1}{2} \rho v^2(0,0,t)
\]

\[
P(0,x, t) = -P_i
\]

\[
u(x, y, 0) = 0
\]

\[
u(x, y, 0) = 0 \quad (5.10)
\]

\[
u \left( x, \pm \frac{h}{2} \right) = 0
\]
\[ \nu \left( x \pm \frac{h}{2} \right) = 0 \]

A set of parameters and units are these parameters that completely determine the problem. It is obtained by inspecting the governing equations and boundary conditions. Therefore, the set of parameters \( \{P\} \) for this problem is the following:

\[ \{P\} = \{\rho, \eta, \gamma, g, P, h, H, x_c\} \]

Selecting the SI units system for this problem, the set of reference units \( \{R\} \) is obtained. This is done by expressing the units of each element of \( \{P\} \) in the SI system. Thus,

\[ \{R\} = \{m, \text{kg}, \text{s}\} \]

**Reduce governing equations**

Using the parallel flow concept [133], equations (5.11) can be stated.

\[ \nu = 0 \quad \Rightarrow \quad \frac{\partial u}{\partial x} = 0 \quad \Rightarrow \quad u(y, t) \quad (5.11) \]
Then, governing equations can be reduced to two equations (5.12) and (5.13), which are:

\[
\rho \left( \frac{\partial u}{\partial t} \right) = -\frac{\partial P}{\partial x} + \eta \left( \frac{\partial^2 u}{\partial y^2} \right) \tag{5.12}
\]

\[
0 = -\frac{\partial P}{\partial y} + \rho g y \tag{5.13}
\]

5.2.2.2. Scaling

Scaling of variables

Equations (5.14) introduce the dimensionless velocity and positions variables. Essentially the variables are normalized so their values can only be from 0 to 1; these quantities will be identified by an asterisk.

\[
t = t \, t^*
\]

\[
x = x \, x^*
\]

\[
y = \frac{h}{2} \, y^*
\]

\[
u(x, y, t) = u_c \, u^* (x^*, y^*, t^*)
\]

\[
P(x, t) = -P + \left( P_e - \frac{1}{2} \rho u_c^2 \right) P^* (x^*, t^*)
\]

(5.14)
where \( P_c = \rho g H + P_1 \) \hspace{1cm} (5.15)

**Scaling of differential expressions**

The differential expressions from equations (5.12) and (5.13) are then scaled. The notation OM in equations (5.17) to (5.20) means “order of magnitude”.

\[
\frac{u}{x} = \text{const} \hspace{1cm}  \left( \frac{\partial u}{\partial x} \right)^* = 0 \hspace{1cm} (5.16)
\]

\[
\frac{\partial u}{\partial t} = u_c \left( \frac{\partial u}{\partial t} \right)^* \hspace{1cm} \text{OM} \hspace{0.5cm} \left( \frac{\partial u}{\partial t} \right)^* = 1 \hspace{1cm} (5.17)
\]

\[
\frac{\partial P}{\partial x} = \frac{P_c}{x_c} - \frac{1}{2} \frac{\rho u_c^2}{x_c} \left( \frac{\partial P}{\partial x} \right)^* \hspace{1cm} \text{OM} \hspace{0.5cm} \left( \frac{\partial P}{\partial x} \right)^* = 1 \hspace{1cm} (5.18)
\]

\[
\frac{\partial^2 u}{\partial y^2} \approx \frac{2}{(h/2)^2} u_c \left( \frac{\partial^2 u}{\partial y^2} \right)^* \hspace{1cm} \text{OM} \hspace{0.5cm} \left( \frac{\partial^2 u}{\partial y^2} \right)^* = 1 \hspace{1cm} (5.19)
\]

\[
\frac{\partial P}{\partial y} = \left( \frac{P}{y} \right)_c \left( \frac{\partial P}{\partial y} \right)^* \hspace{1cm} \text{OM} \hspace{0.5cm} \left( \frac{\partial P}{\partial y} \right)^* = 1 \hspace{1cm} (5.20)
\]

**Replace scaled variables into governing equations:**

\[
\rho u_c \left( \frac{\partial u}{\partial t} \right)^* = -\frac{P}{x_c} \left( \frac{\partial P}{\partial x} \right)^* + \frac{\rho u_c^2}{2x_c} \left( \frac{\partial P}{\partial x} \right)^* + \eta \frac{8u_c}{h^2} \left( \frac{\partial^2 u}{\partial y^2} \right)^* \hspace{1cm} (5.21)
\]
\[
0 = -\left( \frac{\partial P}{\partial y} \right)_c \left( \frac{\partial P}{\partial y} \right)_e^* - \rho g
\]  
(5.22)

Based on the scaling relationships defined above, a set of estimations \( \{ S \} \) is obtained:
\[
\{ S \} = \left\{ u, u_c, \left( \frac{\partial P}{\partial y} \right)_e \right\}
\]

### 5.2.2.3. Determination of velocity

From the reduced governing equations (5.7) to (5.9), capillary flow can be inertial or viscous dominated flow.

From equation (5.22), we obtain,
\[
0 = -\left( \frac{\partial P}{\partial y} \right)_c \left( \frac{\partial P}{\partial y} \right)_e^* - \rho g
\]  
(5.23)

Also, from equation (5.21), equating terms 2 and 4, the pressure term and viscosity term, respectively; we obtain,

\[
\frac{P_c}{x_c} = \eta \frac{8u_c}{h^2}
\]  
(5.24)

then, the velocity equation is:
\[ u_c = \frac{P_c h^2}{8x_c \eta} \tag{5.25} \]

**Determination of pressure at the meniscus**

The total pressure is given by equation (5.15); however, since the term \( \rho gh \) is significantly small compared to \( P_I \), can be neglected. Then, \( \rho gh = 0 \). In addition, the effect of the pressure, \( \rho g H \), can be considered insignificant during experimentation because only small quantities of the filler metal are placed in the left compartment. As it melts it does not usually fill the whole compartment, which in this case is defined by the height \( H \), it only fills the compartment partially.

Using the schematic in Figure 5.5, \( P_1 \) is obtained by force balance in the \( x \)-direction. Then, \( P_1 \) becomes:

\[ P_1 = \frac{\gamma_{LG}}{h} (\cos \theta_1 + \cos \theta_2) \tag{5.26} \]

In Figure 5.3, and in equation (5.26), the angles \( \theta_1 \) and \( \theta_2 \) are the contact or wetting angles in the bottom and top walls of the braze microchannel. \( \gamma_{LG} \) is the liquid-gas surface tension.
Figure 5.3. Schematic representation of the contact angles on the top and bottom walls, and the liquid-gas surface tension ($\gamma_{LG}$) in the braze gap.

Then, replacing the value of $P_1$ for $P_c$ in equation (5.24), the final equation for the filler metal velocity is obtained.

$$u_c = \frac{\gamma_{LG} h (\cos \theta_1 + \cos \theta_2)}{8x_c \eta} \quad (5.27)$$

where, $\gamma_{LG}$ is the liquid-gas surface tension, $h$ is the height of the braze gap, $\theta_1$ and $\theta_2$ are the contact or wetting angles in the bottom and top walls of the braze microchannel, respectively, $x_c$ is the horizontal distance in the braze joint, and $\eta$ is the viscosity of the molten filler metal.
The values of $\theta_1$ and $\theta_2$ determine the relationship with the base metal surface roughness. That means these can be the contact angles measured during an experiment or they can be determined angles based on the different theories available, such as the Wenzel, Cassie-Baxter, and Johnson-Dettre mathematical relationships for wetting angle.

5.3. Validation of the model

Several other equations have been developed over the years to calculate the velocity of a fluid through a system driven by capillary phenomenon. Those equations are summarized below and were used to compare the values obtained with the mathematical expression obtained in this work. It should be mentioned that the work by Lugscheider [76] was developed for vertical braze joints. In the case of the expressions by Milner [78] and Hosking [77], the equations were developed for horizontal braze joints, as in this work. De Gennes [79] work on the other hand was carried out in glass tubes oriented horizontally, and for liquids at room temperature.

\[
\text{Lugscheider (vertical joint)} \quad u = \frac{\gamma L \cos \theta}{4\eta L} \quad (5.28)
\]

\[
\text{Hosking (horizontal plates)} \quad u = \frac{P(0.25h^2 - y^2)}{2\eta x} \quad (5.29)
\]
De Gennes (horizontal tube)  
\[ u = \left( \frac{\gamma_{lg} h}{\eta 8\pi} \right)^{1/2} \]  
(5.30)

De Gennes (horizontal tube)  
\[ u = \frac{\Delta \gamma h}{8L \eta} \]  
(5.31)

Milner (horizontal plates)  
\[ u = \frac{\gamma_{lg} h \cos \theta}{6\eta L} \]  
(5.32)

In these equations, \( \gamma_{lg} \) is the liquid-gas surface tension, \( \eta \) is the viscosity of the liquid, \( \rho \) is the density of the liquid, \( \theta \) is the contact angle, \( h \) is the height of the capillary gap, \( L \) is the length of the tube or microchannel, \( P \) is the pressure, \( x \) is the position along the \( x \)-direction, \( y \) is the position along the \( y \)-direction, \( \tau \) is a time constant [79] which is a few minutes at least.

The validation of the proposed mathematical expression comes from comparing the results with those obtained with Lugscheider, Milner, and De Gennes work. In Figures 5.4 (a), (b), (c) and (d), velocity of the filler metal as a function of distance from the origin in the \( x \)-direction is plotted.
In Figure 5.4, two of the curves, using Lugscheider and Milner Equations, were calculated using the contact angle $\theta_1$, which are the measured angles in contact with the bottom base metal surface. Since the equation after de Gennes does not have an angle as variable, it only took into account the variation of the length of the braze joint. For the curve calculated using the equation developed in this work, two contact angles, $\theta_1$ and $\theta_2$, for the bottom and top, respectively were used. $\theta_1$ is the angle obtained experimentally, and $\theta_2$ is assumed twice the value of $\theta_1$ in the fast flow and residence zones. The first plot, Figure 5.4 (a), displays the velocity-distance plot from the origin to the end of the braze microchannel (0 – 5 mm). It is evident that the velocity increases rapidly up to about 240 m/s; then, it reduces dramatically. Since the lines are not very clear, the scale in x is reduced to observe the three important parts of the flow: the beginning of flow, the fast flow zone and the residence zone, which is extended to the fillet formation zone. In Figure 5.4 (b), the velocity calculated by Lugscheider and Madeni increases quickly to 236 m/s followed by the curves after de Gennes and Milner. At the end of the initiation of flow zone, the velocities reached from 24.8 m/s to 13.6 m/s. In the fast flow region, Figure 5.4 (c), the velocities decrease more, leveling out at 2 m/s, the maximum values are obtained by Madeni and Lugscheider curves. The residence zone starts with fluid velocities of 2 m/s which reduces 1.5 m/s in the fillet formation zone, at the end of the fillet formation, the velocity also increases slightly. The highest velocity values were achieved with Lugscheider equation, followed by Madeni, Milner and de Gennes.
In general, the four equations provide velocities following the same behavior, they increase in the initiation of flow region; then, they decrease drastically entering the fast flow zone, after that they keep decreasing at very slow rate, near constant velocity. The highest average fluid velocity obtained experimentally is 0.35 m/s, which is much lower than the 3.5 m/s values obtained for the fast flow regime, with the equations.

Plotting the velocity as a function only to the contact angle and not to the position of the meniscus as the liquid advances in the joint gap, the results are much different, see Figure 5.5. At the initiation of flow the velocity increases rapidly and levels out completely in the fast flow region. The highest velocity value of 1.9 m/s was achieved by the curve after Lugscheider, followed by the curve after Madeni, \( u = 1.8 \) m/s, then followed by Miler with \( u = 1.3 \) m/s, and finally by de Gennes with \( u = 0.98 \) m/s. In the residence zone the fluid velocity decreases slightly, about 0.4 m/s. However, since de Gennes equation does not depend on the contact angle, the velocity results are constant, \( u = 0.98 \) m/s. This value is three times more than the values obtained experimentally.
Figure 5.4. Velocity of the filler metal as a function of distance, calculated using the four velocity equations. The curve for calculated with the mathematical expression developed in this work, considers different contact angles $\theta_1$ and $\theta_2$, $\theta_2 > \theta_1$. (a) Velocity over the complete braze length, (b) velocity in the initiation of flow region, (c) velocity in the fast flow region, and (d) velocity in the residence zone and fillet maximum extension point.
Figure 5.5. Velocity of the filler metal as a function of distance, calculated by using the model after Lugscheider, Milner, de Gennes and Madeni.

The mathematical relation obtained in this work accounts for instantaneous changes in the wetting characteristics. Results, indicate that the velocity values obtained fall within the predictions made by previous models. The developed equation allows to obtain instantaneous velocities at specific position along the braze gap, taking into account the interaction with the top and bottom surfaces by their respective contact angles. These instantaneous velocities are dynamic since they are based on the instantaneous change in contact angles at different positions along the joint.
Chapter 6

CONCLUSIONS

Research of filler metal flow in braze joints is in general still in its infancy. In that sense, the present research study covered important issues regarding the evaluation and characterization of the flow of braze filler metals at high temperatures, through a braze gap. This investigation also brought additional understanding of the dynamic nature of molten metal flow in a microchannel, including the dependency of surface tension and wetting angle on flow velocity.

The first issue was the development of an experimental technique able to study in situ filler metal flow in a dynamic setting rather than static or after the completion of the joining procedure. Second, in order to focus the research on the factors that affect the filler metal flow characteristics, two braze systems were studied: 304 stainless steel base metal with copper filler metal and nickel base metal with copper filler metal. Third, the effect of base metal surface roughness on filler metal flow was meticulously determined. Additional experiments that support the theories stated in this document using coated base metals were conducted. Fourth, a mathematical model based on the “order of magnitude scaling” was developed to predict the velocity of the filler metal as a function of the base metal surface roughness. Finally, the mathematical expression developed was
compared with previously developed equations to demonstrate the application of this
model and its use in the braze industry.

Based on the analysis performed and results presented in the previous chapters,
the following conclusions can be drawn.

- Filler metal flow in a parallel braze gap can be divided into several zones during
  flow; these are the initiation of flow, fast flow, residence, and fillet formation
  zones. The initiation of flow zone is characterized by slow fluid velocity and
  small distance traveled at the order of 0.2 mm. The fast flow zone is
  characterized by the fast velocity of the fluid, at the order of $10^2$ mm/s and the
  distance that this zone covers is several millimeters. The residence zone is a field
  at the end of the braze joint where the velocity is slow and before fillet formation.
  The length of this zone is at the order of fractions of a millimeter. The fillet
  formation zone is characterized by reduced velocity, which reaches zero at the
  formation of the fillet.

- When the flow is parallel to the surface finishing direction, molten copper on 304
  stainless steel base metal flowed at an average velocity of 275 mm/s (SFC=240
  grit), and 318 mm/s (SFC=600 grit), which are slower than in nickel base metal,
  324 mm/s (SFC=240 grit) and 341 mm/s (SFC=600grit).

- When the flow is transverse to the surface finishing direction, molten copper on
  304 stainless steel base metal flowed at an average velocity of 250 mm/s
(SFC=240 grit), and 296 mm/s (SFC=600 grit), which are slower than in nickel base metal, 305 mm/s (SFC=240 grit) and 327 mm/s (SFC=600 grit).

- When the surface is polished with 6 μm diamond slurry, molten copper on 304 stainless steel base metal flowed at an average velocity of 321 mm/s, which is slower than in nickel base metal, 350 mm/s.

- Defects present in finer surfaces (6 μm polishing quality) such as thin nooks and crevices behave like individual capillary tubes in the base metal surface, where liquid penetrates by capillary action but does not fill all the way this surface defects, promoting fine void formation. These type of surfaces are referred to as hydrophobic surfaces.

- Large voids are promoted in the middle of the vertical direction along the braze joint when the filler metal flows in rougher surfaces such as a surface finished with a 240 grit size SiC grinding paper letting the fluid flow perpendicular to the finishing direction.

- Large voids are promoted at the bottom of the surface valleys in rough surfaces finished with 240 grit size SiC paper, making the surface hydrophobic.

- A mathematical model based in order of magnitude scaling was developed. The filler metal velocity in braze gaps can be predicted as a function of the surface tension of the fluid, the contact angle forming at the liquid-gas-solid interfaces at the top and bottom surfaces, surface roughness and the viscosity of the fluid.
Chapter 7

FUTURE WORK

There is still much to investigate about the flow of molten filler metals in brazing, especially because of the desire to increase the efficiency in the production of braze joints. It has been shown that wettability, spreading, porosity, void formation, poor fillet formation are the major problems during brazing. The localized interaction of the molten filler metal with the surface needs to be systematically studied in different systems. That information would provide answers to many questions, which can help minimize the problems. Some of the topics of future work are:

- Investigate the phenomena of capillarity at the initiation of flow, and at the end of filler metal flow.
- Study the geometric and surface condition factors and physical aspects affecting the velocity at the initiation of flow and at the fillet formation.
- Braze joint fillet formation characteristics (fillet size, shape, surface, wetting angle)
- Study effect of solidification on braze shrinkage.
- Investigate the effect of filler velocity on the formation of voids in different surfaces.
- Evaluate different joint geometries and orientations.
- Determine the effect of change in the direction of the microchannel in the base metal on wetting, filler metal velocity, etc.
- Study the effects of surface coating to increase or decrease the filler metal flow rate.
- Study the effect of surfaces of dissimilar materials on the flow of the filler metals.
- Measure the extent of prewetting in rough surfaces.
- Determine the joint mechanical properties as a function of joints produced using hydrophobic and hydrophilic surfaces.
- Evaluate base metal dissolution, diffusion and liquid-solid chemical reaction effects on filler metal flow characteristics.
- Measure parameters such as viscosity, \( \eta \) and density, \( \rho \) at specific temperatures to obtain data that can be applied to fluid flow models.
- Measure hysteresis and its effects on wetting.
- Study wetting and filler metal flow over surfaces composed by different bulk materials each with different surface roughness.
- Develop models that can incorporate the liquid-solid chemical interaction.
REFERENCES


[87] J. C. Madeni, S. Liu, and T. Siewert, *Intermetallic Formation and Growth at the Tin-based Solder Alloys (Sn-3.5Ag, Sn-0.7Cu, Sn-3.2Ag-0.8Cu AND Sn-9Zn) and Copper Substrates*, 2nd International Brazing and Soldering Conference February 17-19, 2003, San Diego, California.


