Prediction of Contact Angle for Sintered Alloy for Solid Freeform Fabrication

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ABSTRACT

The present study aimed to predict theoretically the contact angle between liquid copper drops on well-polished carbons steel. The theoretically established model was relied on standard tables for wetting parameters available in the literatures from which mathematical relations were extracted from the mutual relations existed among the parameters in the equations. The established model using Math Lab program was then used to obtain standard contact angle values for theoretical proposed standard contact geometry with impressive chemical indicators affected by the polishing processes. The contact system was the Fe-C / Cu couple which was usually fabricated by P/M route for high load self-lubricated bearings with carbon content in the range of 3-4 wt%. Resulted values for the predicted contact angle indicated a decrease of the contact angle as the temperature increased approaching zero at a high temperature of 1084 °C approximately. This will directly reflected on the degree of wetting of molten copper with iron, with an associated increase in rate of copper diffusion at the carbon steel surface, which was considered as indicators for surface chemistry interfere with the polishing process.

INTRODUCTION

Wetting has received increased interest from both fundamental and applied points of view. It plays an important role in many industrial processes, such as oil recovery, lubrication, liquid coating, printing, and spray quenching [1]. In recent years, there has been an increasing interest in the study of super hydrophobic surfaces, due to their potential applications in, for example, self-cleaning, Nano-fluidics, and electro wetting [2]. Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. Small contact angles (<90°) correspond to high wettability, while large contact angles (>90°) correspond to low wettability as shown in table 1. Most of wetting techniques can be classified into two main groups: the direct optical method and the indirect force method. Calculations based on measured contact angle values yield an important parameter—the solid surface tension, which quantifies the wetting characteristics of a solid material.

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Table 1. Types of contact angles and wetting degree

<table>
<thead>
<tr>
<th>Contact angle</th>
<th>Degree of wetting</th>
<th>Strength of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Solid/liquid interactions</td>
</tr>
<tr>
<td>θ = 0</td>
<td>Perfect wetting</td>
<td>strong</td>
</tr>
<tr>
<td>0 &lt; θ &lt; 90°</td>
<td>high wettability</td>
<td>strong</td>
</tr>
<tr>
<td></td>
<td></td>
<td>weak</td>
</tr>
<tr>
<td>90° ≤ θ &lt; 180°</td>
<td>low wettability</td>
<td>weak</td>
</tr>
<tr>
<td>θ = 180°</td>
<td>perfectly non-wetting</td>
<td>weak</td>
</tr>
</tbody>
</table>

Theoretical Background

Consider a liquid drop resting on a flat, horizontal solid surface (Fig. 1). The contact angle is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface (geometrically acquired by applying a tangent line from the contact point along the liquid-vapor interface in the droplet profile). The interface where solid, liquid, and vapor co-exist is referred to as the “three-phase contact line”. Figure 1 shows that a small contact angle is observed when the liquid spreads on the surface, while a large contact angle is observed when the liquid beads on the surface. More specifically, the liquid contact angle less than 90° indicates that wetting of the surface is favorable, and the fluid will spread over a large area on the surface; while contact angles greater than 90° generally means that wetting of the surface is unfavorable so the fluid will minimize its contact with the surface and form a compact liquid droplet. For example, complete wetting occurs when the contact angle is 0°, as the droplet turns into a flat puddle. For super-hydrophobic surfaces, water contact angles are usually greater than 150°, showing almost no contact between the liquid drop and the surface, which can rationalize the “lotus effect” [3].

![Figure 1: Contact Angle Diagram](image-url)
Furthermore, contact angles are not limited to the liquid-vapor interface on a solid; they are also applicable to the liquid-liquid interface on a solid. Ideally, the shape of a liquid droplet is determined by the surface tension of the liquid. In a pure liquid, each molecule in the bulk is pulled equally in every direction by neighboring liquid molecules, resulting in a net force of zero. However, the molecules exposed at the surface do not have neighboring molecules in all directions to provide a balanced net force. Instead, they are pulled inward by the neighboring molecules (Fig. 2), creating an internal pressure. As a result, the liquid voluntarily contracts its surface area to maintain the lowest surface free energy. From everyday life, we know that small droplets and bubbles are spherical, which gives the minimum surface area for a fixed volume. This intermolecular force to contract the surface is called the surface tension, and it is responsible for the shape of liquid droplets. In practice, external forces such as gravity deform the droplet; consequently, the contact angle is determined by a combination of surface tension and external forces (usually gravity).

Theoretically, the contact angle is expected to be characteristic for a given solid-liquid system in a specific environment [4]. As first described by Thomas Young, the contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions (Fig. 1):

\[ \gamma_{lv} \cos \theta_Y = \gamma_{sv} - \gamma_{sl} \]  

Where: \( \gamma_{lv}, \gamma_{sv}, \) and \( \gamma_{sl} \) represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and \( \theta_Y \) is the contact angle. Equation (1) is usually referred to as Young’s equation, and \( \theta_Y \) is Young’s contact angle (see table 1).

Previous Works
Wetting have been extensively investigated and well understood at the macro-scale (millimeters); while the wetting behavior at the micro- or Nano-scale (micro- or nanometers) has yet to be thoroughly studied, and many issues remain unresolved. The study of ultra-small droplets on solid surfaces allows wetting theories to be tested down to the Nano-scale, where the wetting behavior is significantly influenced by line tension and liquid evaporation (both are usually negligible in macro-scale studies). These studies have relevance to many industrial applications, such as friction in micro electro-mechanical systems (MEMS) devices [5], flotation in mineral recovery [6], and wastewater treatment [7].

At the micro- or Nano-scale, it is possible to take advantage of the fact that the influence of gravity is negligible compared to the influence of surface tension; consequently, the droplet can be approximated as part of a sphere [8], [9]. There are, however, complications due to the small size. As the drop becomes smaller, the effect of the line tension at the three-phase contact line becomes larger compared to the effect of surface tension [10],[11]. For micro- or even nanometer-sized droplets, the line tension can significantly affect the measured contact angle [12]. Thus, at micro- and Nano-scales, the classical Young’s equation must be modified, which is usually done by adding a second term to take the line tension effect into account [13]:

\[
\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \\
\cos \theta R = \cos \theta - \frac{\sigma \gamma_{lv}}{R}
\]

for the droplet. The quantity \( \gamma \) is the surface tension, \( \sigma \) is the line tension of the three-phase system, and \( R \) is the radius of the drop at the surface. The subscripts \( s \), \( l \), and \( v \) indicate the solid, liquid, and vapor phases, respectively.

Another problem associated with small droplets is the effect of evaporation, which is especially problematic when working with atomic force microscopy (AFM), because AFM requires at least 15–30 min to produce a stable image.

Picknett and Bexon [14] studied the changes of droplet profile during evaporation. They found that there exist two stages: a first “constant contact area” phase dominates until the contact angle decreases to certain value, at which point a second “constant contact angle” phase dominates thereafter. This model has been supported by Soolaman and Yu [15], who reported that the evaporation of water micro-droplets progresses from the start stage (decreasing contact angle, constant contact area) to the shrinking stage (constant contact angle, decreasing contact area). Therefore, the evaporation effect must be taken into consideration when interpreting micro and Nano-droplets profiles.

**Methods of Measuring Contact Angle**

Several methods for measuring the contact angles of ultra-small droplets have been reported thanks to the availability of advanced imaging techniques such as interference microscopy, confocal microscopy, environmental scanning electron microscopy (ESEM), and AFM to establish the droplet profiles [16].

Although the study was to compare the theory with a grant mention the practical side,. Interference microscopy method utilizes the fringe patterns formed by the interfering beams reflected from the solid-liquid and the liquid-vapor interfaces to calculate the contact angle value. It is best suited for droplets with low contact angles (less than 30°),in
which case individual interference fringes are readily resolved. Jameson and DelCerro [17] used this technique for cases in which the underlying phase is transparent.

Fischer and Ovryn improved the technique by developing a geometrical optics-based model to interpret the optical path length through a thick refractive specimen. Confocal microscopy, on the other hand, is best suited for droplets with higher contact angles (30–90°) since such droplets have greater heights, thus allowing the collection of a larger number of image slices from which the drop profile can be reconstructed. Sundberg et al. [18] recently used a combination of interference microscopy and confocal fluorescence microscopy to study the contact angles of micrometer-sized nucleated water droplets. The method was designed for measuring both low (<30°) and high (30–90°) contact angles. For droplets displaying low contact angles, the profiles can be reconstructed from the interference patterns, whereas for contact angles too high to allow resolution of interference fringes, a low concentration of fluorescent dye was mixed with water to allow the recording and analysis of 3D image stacks. The results were compared with contact angles of macroscopic (millimeter scale) droplets, and a dependence of contact angle on droplet sizes was found. At small radii (below 10μm), the contact angles obtained are larger than the macroscopic contact angles, indicating a positive line tension effect. When the radii of the droplets are more than 10μm, the average contact angles on microscopic droplets are largely the same as their macroscopic counterparts. In general, interference and confocal methods can measure droplets with diameters of about 10 to 100μm. New techniques with higher resolution are needed for Nano scale measurements.

A number of methods have been developed to deposit micro- and Nano scale liquid droplets on surfaces. The simplest way is to use an air sprayer [19], which generates ultra-small droplets by mixing macro-scale droplets with a jet of compressed air.

**Contact Angle Determination Procedures:**

Determination of contact angle \( \theta_c \) could be accomplished via two possibilities:

**Theoretical methods for the determination of the contact angle from the available wetting data tables**

This route was the major method used in this study for the determination of wetting contact angle \( \theta_c \) depending on Young’s Equation, which in modified form will be:

\[
\theta_c = \cos^{-1} \left[ \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \right]
\]

... (4)

**Experimental methods using laboratory prepared samples**

This method although seemed interesting, for contact angle determination, but most of the required equipment and facilities were not available for the time being. For the sake of benefits, some of the main steps were listed below:

- Preparation of powdered samples of (Fe-C/Cu) at different percentages and forming pellets by pressing and sintering it in the range 1120-1150°C.
- Metallurgical preparation to mirror finished surface.

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Use of special graphite furnace which allow inert and vacuum environments for the determination of contact angle.

Results and Conclusions:
Contact angle $\theta_c$ were calculated and predicted using literature’s available data tables for wetting parameters and Math Lab computer programs, and the values were listed in table 2, as a function of temperature. [20]

Table (2): Values of contact angles and interfacial tensions at different temperatures

<table>
<thead>
<tr>
<th>No</th>
<th>Temperature (°C)</th>
<th>$\gamma_{sv}$ (ml/m$^2$)</th>
<th>$\gamma_{sl}$ (ml/m$^2$)</th>
<th>$\gamma_{lv}$ (ml/m$^2$)</th>
<th>$\theta_c$°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1085</td>
<td>1461</td>
<td>332</td>
<td>1295</td>
<td>29.4</td>
</tr>
<tr>
<td>2</td>
<td>1100</td>
<td>1522</td>
<td>387</td>
<td>1292</td>
<td>28.5</td>
</tr>
<tr>
<td>3</td>
<td>1120</td>
<td>1567</td>
<td>421</td>
<td>1289</td>
<td>27.2</td>
</tr>
<tr>
<td>4</td>
<td>1130</td>
<td>1610</td>
<td>444</td>
<td>1284</td>
<td>24.7</td>
</tr>
<tr>
<td>5</td>
<td>1150</td>
<td>1752</td>
<td>493</td>
<td>1274</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Figure (3): Show the variation of contact angle with temperature for (Fe-C/Cu) system

From the above results, it was clear that the contact angle decreased as the temperature increased and having a value of zero at 1150°C. This will lead to the conclusion that; as the temperature increased the wettability and diffusion of Cu with iron also enhanced, since higher wettability gives stronger interaction between metallic liquid and the solid substrate resulting in more Cu penetration into the Fe inter-particle and grain boundaries. Taking into consideration the effect of carbon in Fe-C-Cu system it was expected to hindered penetration of liquid Cu, which results in lower initial diffusion distances. At
sufficient soaking temperature and time a homogenization level of Cu in Fe-C will be achieved because as the temperature increased the contact angle decreased and Cu will spread more and more on the surfaces which in direct contact with it. Such studies will assist in applications related to the fabrication of various composited sintered alloys by powder metallurgy route for homogeneous and difficult to cast alloys [21].

REFERENCES