Determination of Macro-Contact Angle and Line Tension at High Temperatures for Au/Al₂O₃ System at 1373 K Using a Micro-Scale Wetting Method

Joonho Lee¹, Kazuki Morita² and Toshihiro Tanaka¹

¹Department of Materials Engineering and Processing, Osaka University, Suita 565-0871, Japan
²Department of Materials Engineering, the University of Tokyo, Tokyo 113-8656, Japan

The size effect of a drop on the contact angle was discussed for the Au/Al₂O₃ system. As the size of the drop decreases, the shape of the drop closes to a sphere and the contact angle is obtained by the equation \[ \theta = \cos^{-1}\left(1 - h/R_{\text{Max}}\right) \], where \( \theta \) is the contact angle between the drop and substrates, \( h \) is the height of the drop and \( R_{\text{Max}} \) is the maximum radius of the drop. The contact angle between liquid gold and alumina polycrystalline substrates having the roughness of 0.141 \( \mu \)m is obtained by eq. (1), which is determined by Young’s equation as described by eq. (2). Therefore, we usually observe that the preceding and receding contact angles are different. In addition, when some reactions are accompanied by mass transfer at the liquid/solid interface, the contact angle generally decreases, establishing a mechanical equilibrium contact angle. In the situation of the mechanical equilibrium, the line tension is related to stretching energy and may have both positive and negative values.

Fig. 1 The equilibrium contact angle between a sessile drop and a solid substrate. \( \sigma_L \) and \( \sigma_S \) denote the surface tension of liquid and solid, respectively. \( \kappa \) and \( r \) are the line tension and the radius of the liquid drop. Equation (2) becomes small enough to be ignored, yielding the classical Young’s eq. (1). Thermodynamically, the line tension is defined as the work of formation per unit length of a new line, so that it should have a positive value. Experimentally, however, the thermodynamic equilibrium contact angle is difficult to obtain, because of the absence of diffusional equilibrium for solids where the chemical potential gradients near the surface are at equilibrium.

1. Introduction

A non-reactive liquid metal drop resting on a solid ceramic substrate exhibits a contact angle \( \theta \) (generally higher than 90°), which is determined by Young’s equation as described by eq. (1).

\[ \sigma_L \cos \theta = \sigma_S - \sigma_L \] (1)

where \( \sigma_L \), \( \sigma_S \), \( \sigma_I \) and \( \theta \) are the surface tension of solid, the interfacial tension between solid and liquid, the surface tension of liquid and the contact angle, respectively. \( S, V \) and \( L \) refer to solid, vapor and liquid, respectively.) Equation (1) has been generally accepted to be valid for a macro-scale liquid drop. However, precisely, eq. (1) should be re-written by eq. (2) because solid, vapor and liquid phases are divided not only by faces but a line as shown in Fig. 1.

\[ \sigma_L \cos \theta = \sigma_S - \sigma_L - \kappa/r \] (2)

where \( \kappa \) and \( r \) are the line tension and the radius of the liquid drop. Equation (2) is obtained for a horizontal solid surface by assuming that the dependence of the line tension on curvature is negligible. For a large drop (having a large curvature radius of the triple line), the line tension term in eq. (2) becomes small enough to be ignored, yielding the classical Young’s eq. (1). Thermodynamically, the line tension is defined as the work of formation per unit length of a new line, so that it should have a positive value. Experimentally, however, the thermodynamic equilibrium contact angle is difficult to obtain, because of the absence of diffusional equilibrium for solids where the chemical potential gradients near the surface are at equilibrium.

Therefore, we usually observe that the preceding and receding contact angles are different. In addition, when some reactions are accompanied by mass transfer at the liquid/solid interface, the contact angle generally decreases, establishing a mechanical equilibrium contact angle. In the situation of the mechanical equilibrium, the line tension is related to stretching energy and may have both positive and negative values.

There have been several reports on the line tension at room temperature (8) (or slightly higher temperatures up to \text{616 K}^{2}), but no researchers except Ueda et al. (9) have reported on the line tension at much higher temperatures. Ueda et al., however, chose a reactive system (Fe/Al₂O₃ at 1873 K in the atmosphere of various oxygen partial pressure), obtaining very high negative values as the line tension. It is believed that the measured values by Ueda et al. (10) in the Au-O/Al₂O₃ system in Ar-5%H₂ atmosphere with Ti getter) are the mechanical line tension, which may not equal to the thermodynamic line tension, and could have negative values as explained above.

In the present work, a micro-scale non-reactive liquid metal drop (gold) resting on a solid ceramic substrate (alumina) was investigated to determine the macro-scale contact angle and the line tension at high temperatures simultaneously.

2. Experimental

2.1 Materials and procedure

In the present work, in order to avoid any reactions which may affect the contact angle, gold and alumina were chosen as the liquid metal and the solid substrate, respectively. Chatain et al. (10) presented that in the Au-O/Al₂O₃ system the surface tension and contact angle in macro-scale are constant.
(131 ± 3°) over the oxygen pressure ranging from 10⁻¹⁵ to 5 × 10⁴ Pa at 1363 K. Noting that the surface tension and contact angle for liquid metal decrease with increasing oxygen activity due to oxygen adsorption at the surface of the metal and the interface between the metal and the substrate, it is expected that we can measure the accurate contact angle between liquid and solid without oxygen contamination using the Au/Al₂O₃ system. (∂Gₗ = ∂Gₚ term is constant in eq. (2).)

In the present investigation, the contact angle between liquid gold and alumina substrates was measured at 1373 K (practically in the temperature range between 1363 ~ 1376 K) in a purified argon gas atmosphere. A piece of gold chip weighing 0.0020 ~ 0.0125 g cut from a high purity gold wire (99.99%) was placed on the high purity alumina (99.6%) substrates. The roughness of the surface of the alumina substrates was measured with an atomic force microscopy analyzer before experiments, yielding 0.141 μm in the RA number. Experiments for size dependence were conducted with alumina polycrystalline, and additional experiments with (0001) and (1120) alumina single crystals faces were done to understand the effect of heterogeneity of polycrystalline substrates. The apparatus and experimental techniques are the same as described in our previous contribution.¹¹)

### 2.2 Novel method determining micro-scale contact angle for a non-wetting system

#### 2.2.1 Geometry of micro-scale drop

The contact angle of a micro-scale drop could be obtained by the height-width method using eq. (3) with information such as the height of a liquid drop (h) and the radius of the interface between liquid and solid (r).⁸,¹²)

\[ \theta = 2 \tan^{-1} \left( \frac{h}{r} \right) \]  

(3)

However, from a vertical direction in a non-wetting system (90° < θ < 180°), the contact angle cannot be determined, because r cannot be measured. (Usually, the micro-scale contact angle is determined from the vertical direction.¹¹,¹²). Although we could investigate a liquid drop from a horizontal direction, it is very difficult to determine the position of the triple line (or the length of r) in thresholding a captured image.

In order to determine the contact angle of a micro-scale drop in a non-wetting system, we suggest a new equation from geometric relation of a micro-drop as below. Here, due to such reasons described above, it is preferred to obtain the contact angle only with available and reliable data such as height (h) and the maximum radius (R_max.) in Fig. 2. Since (L_OCB+L_CBO) and (L_CBO+L_DBB′) equal to 90°, L_CBO equals to L_DBB′ (≈ 180° - θ). Accordingly,

\[ \cos \theta = -\cos(180° - \theta) = 1 - \frac{h}{R_{\text{Max.}}} \]  

(4)

Equation (4) can be re-expressed by eq. (5).

\[ \theta = \cos^{-1} \left( 1 - \frac{h}{R_{\text{Max.}}} \right) \]  

(5)

#### 2.2.2 Application limit of new method

From a simulation study on the size effect of liquid gold on the spherical geometry, we can obtain the application limit of eq. (5). The profile of a drop is drawn from Laplace equation described as eq. (6).

\[ \frac{1}{R_1} + \frac{\sin \phi}{x} = \frac{2}{R_o} + \frac{z \Delta \rho g}{\sigma} \]  

(6)

where \( R_1, R_o, \phi, \sigma \) are the curvature radius at a point of interest, the curvature radius at the apex, the turning angle, the horizontal position of interest, the vertical position of interest, the difference in densities between the drop and the surrounding phase, the gravitational constant and the surface (or interface) tension. Details are shown in literatures.¹³⁻¹⁵

The solid curves in Figs. 3(a)~(d), respectively, show the profiles of the drops of liquid gold for \( R_o = 0.5, 0.05, 0.02 \) and 0.005 cm. The contact angle for those profiles was set as 130°. The values of the density and the surface tension of liquid gold are quoted from the literatures: 17.36 g/cm³ and 1160 mN/m respectively at 1373 K.¹⁶) The dotted curves in Fig. 3 indicate the circle profile obtained by adjusting center position of the circle to have the curvature radius at the apex. As can be seen from Fig. 3, the shape of the liquid gold approaches a complete circle with a decrease in the drop size, yielding no difference between the two angles. In the present work, as a shape parameter (η) of a liquid drop, the difference between the curvature radius at the apex and the maximum radius of a sessile drop was defined.

\[ \eta = \frac{R_o - R_{\text{Max.}}}{R_o} \times 100 \% \]  

(7)

From Fig. 3(c), we can conclude that the application limit of eq. (5) is when the shape parameter η is less than 0.1%. In other words, if a micro-scale liquid gold drop (less than about 400 μm in diameter) is investigated, the shape is almost close to a sphere, and the contact angle can be determined by eq. (5).
3. Results and Discussion

3.1 Effect of size on contact angle

Equation (2) may be rewritten as eq. (8).

$$\cos \theta = \cos \theta_{\infty} - \left( \frac{\kappa}{\sigma_{LV}} \right) \frac{1}{R_{\text{Max.}}}$$ (8)

where $\theta_{\infty}$ is the contact angle when $R_{\text{Max.}} \rightarrow \infty$. Then, if we plot $\cos \theta$ versus $1/R_{\text{Max.}}$, we can obtain a linear relationship, yielding the macro-scale contact angle and the line tension from the intercept with the vertical axis and the slope, respectively. Figure 4 shows the measurements of $\cos \theta$ with respect to the reciprocal value of the maximum radii of liquid gold. Using a linear regression analysis, we obtained $134^\circ$ and $3.50 \times 10^{-7}$ N for the macro contact angle and the line tension, respectively. The macro-scale contact angle of the present work shows reasonable accordance with the previous

Fig. 3 Calculated shape of a pure gold sessile drop on an alumina substrate at 1373 K, where the surface tension is 1160 mN/m, the density is 17.36 g/cm$^3$ and the contact angle is $130^\circ$. $R_o$ are 0.5, 0.05, 0.02 and 0.005 cm in Figs. (a), (b), (c) and (d), respectively.

Fig. 4 Effect of maximum radius of the liquid gold drop on alumina substrates on contact angle at 1360 ~ 1373 K.
measurements (131 ~ 140°). The obtained line tension is considerably reasonable, because usually the line tension is reported not to depend strongly on materials, having a value between 10^{-12} and 10^{-6} N. The line tension obtained in the present work is very small compared with the surface or interfacial tension. Hence, we may expect that the interfacial tension obtained from Young’s equation in macro scale is applicable to nucleations or nano-particle modeling. Recent reports by Tanaka et al. and Lee et al. employed the surface and interfacial tensions obtained from Young’s equation in macro-scale for nano-particles larger than 10 nm in diameter, which are considered reasonable based on the present results.

In Fig. 4, some results of micro-scale contact angle with (0001) and (1120) alumina single crystal faces are plotted for comparison. Even though measured values show large scattering, it is noteworthy that the contact angle on (0001) face is lower than that on (1120). Thus, we may expect that the heterogeneity of the surface energy of alumina polycrystalline may affect the measurements of the contact angle. It is also well recognized that a large axisymmetric shape could be obtained with smaller liquid drop, and micro-scale liquid drop is more likely to form an axisymmetric drop. Accordingly, the macro-scale drop may lose the axisymmetric shape. In the present work, the macro-scale gold drop weighing 0.1438 g on an alumina polycrystalline substrate was investigated, resulting a non-axisymmetric shape of liquid gold drop. (Right (141°) and left (135°) contact angles in a direct observation slightly differ with each other.) Using Young-Laplace fitting method, we obtain the contact angle 143°, which is slightly higher than the present result (134°). Accordingly, the difference in the measured values by micro- and macro-scale is considered caused by the non-axisymmetric shape of liquid drop in macro-scale.

3.2 Effect of capillary constant on shape parameter

Equation (5) is valid for a spherical liquid drop, so that it is important to know the limit of the available drop size. Recently, Lee et al. have shown that as the capillary constant (C.C. = Δ/σ in eq. (6)) increases, the profile of liquid metal drop is more affected by gravitational force at a constant size, and the errors in surface tension measurements decreases. Accordingly, the capillary constant is considered to determine the shape of liquid drop. Figure 5 shows the simulated results of the shape parameter as a function of the curvature radius at the apex (Ro). In the simulation, Bi, Sn, Cu and Co was used, having different capillary constants. (Table 1) It is considerable that the shape parameter (η) and the curvature radius at the apex (Ro) have a linear relationship in logarithmic scale with a constant slope regardless of metal species when Ro is less than 0.1 cm. Therefore, we may consider that the limit of the available drop size could be expressed only by the capillary constant. In Fig. 6, the curvature radius in logarithmic scale at a constant shape parameter (limit of application of eq. (5), η = 0.1) is shown as a function of the capillary constant in logarithmic scale. The linear regression yields

\[ \log R_o (\eta = 0.1) = -2.608 - 0.4934 \log \text{(C.C.)} \] (9)

From this relationship, if we know the capillary constant of metal or alloy, we can estimate the size of drop to form a spherical shape.

4. Conclusions

In this paper, the size effect of drop on the contact angle between liquid gold and alumina substrates was discussed by

![Fig. 5 Relationship between the shape parameter of the liquid metal drop and the radius at the apex.](image)

![Fig. 6 Relationship between the capillary constant (C.C.) and the radius at the apex.](image)

<table>
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<tr>
<th>Element</th>
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<th>Co</th>
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<td>12.5</td>
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<td>4.14</td>
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Table 1 Capillary constant of pure metals at the melting temperatures.
using Young’s equation considering the line tension. From the relationship between the micro-scale contact angle and the reciprocal of $R_{\text{Max.}}$, we obtained $134^\circ$ and $3.50 \times 10^{-7}$ N for the macro-scale contact angle and the line tension, respectively. Here, the micro-scale contact angle was determined with a new equation

$$\theta = \cos^{-1}\left(1 - \frac{h}{R_{\text{Max.}}}\right).$$

From the simulation results with Laplace equation, the limit size of drop was expressed as a function of the capillary constant.

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REFERENCES