Application of radio frequency Inductively Coupled Plasma (rf-ICP) in the measurement of physical properties of melts

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Abstract: In this new containerless method, an atmospheric radio-frequency Inductively Coupled Plasma (RF-ICP) torch melts horizontal metallic rods, and a high-speed camera records the drop formation process caused by melting. The drop shapes are fitted by the theoretical Young-Laplace (YL) profiles to determine the surface tension. From the photographs of the melting process, the solid-liquid interface was found to be inclined at an angle to the horizontal. For the first time, the effect of this inclination on surface tension measurement is investigated. In addition to the measurements based on the drop shapes, this methodology provides the possibility of validating the results with other methods for measuring surface tension: the drop oscillation method is also implemented.

Keywords: Radio-Frequency Plasma, Physical property measurement, Surface tension.

1. Introduction

The study of the wetting phenomena at elevated temperatures has provided considerable impetus to research the liquid metal and ceramics wetting behaviour for improving industrial processes. Methods to measure wettability parameters, specifically, surface tension are diverse. However, there are only a number of the methods applicable at high temperatures. Melting high melting point samples requires high power heat sources, and radio-frequency Inductively Coupled Plasmas (rf-ICP) provide a reliable heating capable of melting such samples (see **Fig. 1**).

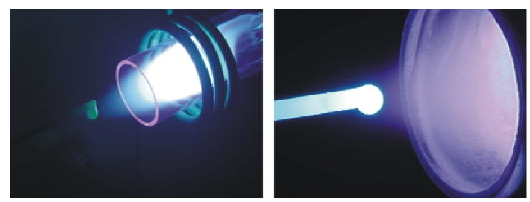

Fig. 1 rf-ICP heating of rod shaped samples

In this study, for the first time, copper samples are heated, and the dynamics of the melts are analyzed. The melting process of rod shaped samples can be categorized into three stages (see **Fig. 2**): First, the period during which a molten drop is pendant from the rods; second, when the drop is detached and oscillates during the free-fall; third, when it is spreading on a substrate. Whereas all the three stages represent the effects of physical properties, current study investigates pendant drop profiles and free-fall oscillations of molten samples to calculate the surface tension, viscosity, and density of melts.

2. Surface Tension Measurement by Matching Pendant Drop Profiles

a) Experimental Drop Profiles

Shape of pendant drops of melts at tip of a melting sample depends on the surface tension of materials. Surface tension holds the drops, during formation, attached to the sample. Eventually, the drop is large enough so that its weight is more than the surface tension force; therefore, the drop starts moving downward and, eventually, detaches from its neck (a small ligament of melt connecting the main drop to the sample). If the break happens at one point, the portion of melt over the breakup point rebounds

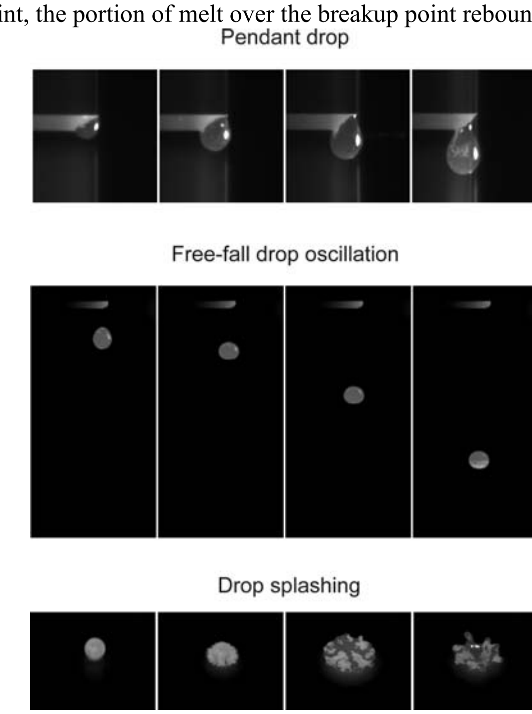

Fig. 2 Melting of the samples, free-fall oscillation, and drop splashing

back to the sample, and the main drop falls down. In cases with long necks (usually in liquids with higher viscosity), the neck breaks at two points; therefore, in addition to the main drop, the portion of the liquid between the two breaking points form a small satellite droplet.

b) Theoretical Drop Profiles

Geometry of an axisymmetric pendant drop can be represented with a set of ordinary differential equations which include different parameters: arc length, s, slope angle of a tangent to a point of the profile, θ, and the curvature at the apex, *b* (see **Fig. 3**). The Young-Laplace equation [1, 2] presents the profiles as a function of the curvatures on two perpendicular planes at each point. A set of three equations can be solved simultaneously to calculate φ, *X*, and *Z* (*S* is the independent variable measured from the apex).

$$\frac{d\varphi}{dS}=\frac{2}{B}-Z-\frac{\sin\varphi}{|X|}$$
$$\frac{dX}{dS}=\cos\varphi \tag{1}$$
$$\frac{dZ}{dS}=\sin\varphi$$

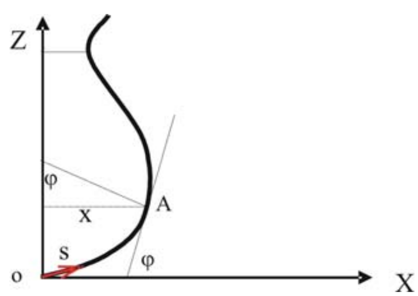

Fig. 3 A schematic of a theoretical pendant drop profile

Where *S, X, Z*, and *B* are dimensionless parameters for (*s, x, z, b*) based on the characteristic length. $\sqrt{\Delta\rho g/\sigma}$.

In order to calculate surface tension, the theoretical profiles can be fitted onto the experimental profiles of the pendant drops. Based on the governing equations, there are two adjustable parameters for matching the profiles. A change in *B* results in different profiles which resemble the evolution of the shape of a drop during the growth process. Moreover, a theoretical profile (dimensionless) should be scaled to fit onto an experimental profile.

Therefore, the scale factor (or characteristic length) provides a value for the surface tension.

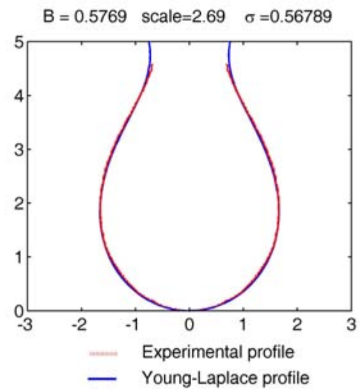

Fig. 4 Fitting experimental drop profiles with YL profiles

c) The effect of the angle of the interface between melt and solid on weight of detaching drops

The experimental aspect of the measurement methodology at high temperature deals with melting of horizontal rods, which results in pendant drops that have an interface forming an angle with respect to the rod (see **Fig. 5**). Since all of the previous studies considered vertical droplet formations, in this study for the first time, a correction factor for drop formation at different angles is presented and some of the hydrodynamic effects in surface tension measurement based on the drop weight method are studied. Results from this study contributed to the common drop weight method for measuring surface tension in a horizontal configuration.

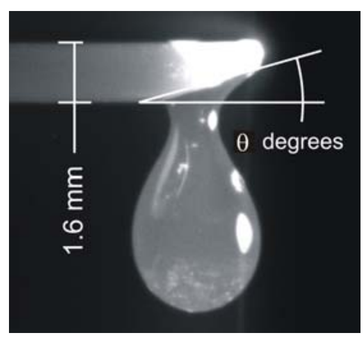

Fig. 5 The angle of interface between melt and its rod in horizontal melting of samples

a new relation was derived as follows [3]:

$$Bo=3.37\Psi^{2.81}\left(1-\frac{2\theta}{\pi}\right)^{n} \tag{2}$$
$$0\le\theta<\frac{\pi}{2}$$

Where θ is the angle, Ψ is dimensionless radius ($r/V^{1/3}$, r is radius of rod, and V is the volume of a detached drop), and *n* is almost 0.3.

3. Surface Tension Measurement by Drop Oscillation

Oscillation of copper drops was studied to measure surface tension, viscosity, and density. For the first time, samples were heated by a radio frequency Inductively Coupled Plasma (rf-ICP) torch. This study confirms that the setup and calculation procedure (oscillation analysis code [4] is capable of measuring physical properties of ceramics and alloys in terrestrial condition without a levitation force field. **Fig. 6** shows oscillation of a free falling drop of copper detached from a rod with the diameter of 1.6 mm.

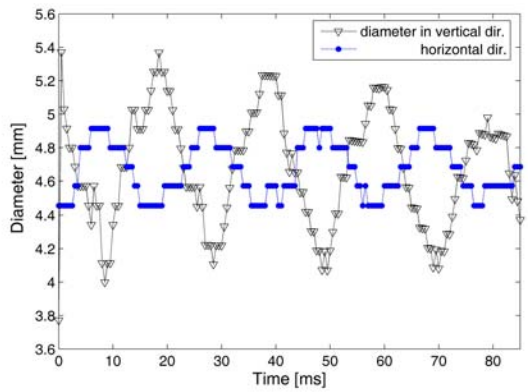

Fig. 6 Oscillations in diameter of a falling drop

a) Surface tension measurement

According to Lord Rayleigh (1879) [5], vibration of a liquid mass about a sphere can be related to surface tension. Resonance of the oscillation represents a peak in the frequency spectrum. In earth's gravitational field, location of the resonance in the spectrum is governed by interfacial restoring forces [6]. The generalized linear solution of the problem which includes the influence of a surrounding medium is given by Lamb (1932) [7]. The solution describes the instantaneous deformation of the droplet shape by an infinite series of surface spherical harmonics, where each term of this function corresponds to one independent natural oscillation mode.

Equation (3) shows the Rayleigh's relation for surface tension of a liquid with mass M.

$$\omega_l^2 = \frac{4}{3}\pi l(l-1)(l+2)\frac{\sigma}{M} \tag{3}$$

Where ω_l is the angular frequency ($\omega=2\pi f$), l is the oscillation mode number, and σ is the surface tension. Accordingly, the density which is a required parameter in most of the surface tension measurement methods is not required in this method. Translation of a liquid drop is assigned to l=1, while l=2 corresponds to the Rayleigh's frequency and manifests the effect of surface tension in the oscillations. It is worth noting that higher modes of oscillation (l > 2) are negligible when the deformation is small.

External force fields can result in shifting or degeneracy splitting of the resonance frequency. This complicates the structure of peaks in Fast Fourier Transformation (FFT) of the oscillations obtained from various external force fields, such as rotation, or procession. On the other hand, when a spherical drop is not rotating, there is one characteristic frequency manifesting the surface tension based on the Rayleigh's relation. However, for droplets deformed due to external fields, the dominant frequency splits into three frequencies. For the case of static deformation and axisymmetric rotation, the characteristic frequency splits into five frequencies. In such cases, the correction equation suggested by Cummings and Blakburn (1991) [8], or more recently, the relation presented by Egry et al. (1995) [9] may be used to consider the effect of external forces or rotations. This frequency is determined by the strength of an externally applied levitation field and by mass of the droplet.

b) Viscosity measurement

According to Lamb [10], viscosity of an oscillating drop can be related to the oscillation characteristics. Lamb's relation shows how the damping constant, Γ, is related to the dynamic viscosity, η, of an oscillating drop with radius a_0 and mass M.

$$\Gamma = \frac{20\pi\eta a_0}{3M} \tag{4}$$

The damping coefficient, Γ, is calculated by fitting a decaying exponential function the oscillation spectrum.

$$y = Ae^{-\Gamma t}\cos(2\pi ft) \tag{5}$$

4. Results and discussion

a) Surface tension

The dynamic surface tension values and results from the pendant drop (PD) [11] and drop weight (DW) [12] methods are shown in **Fig. 7**.

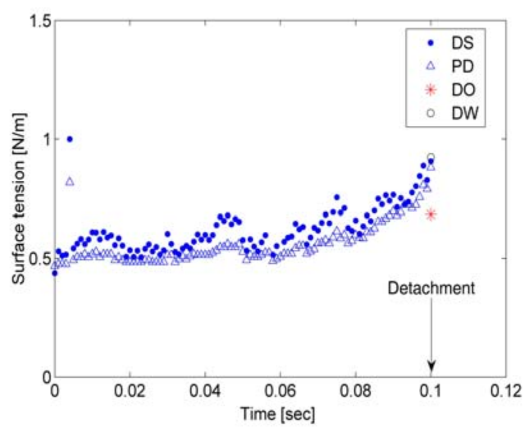

Fig. 7 Surface tension of the sample measured by the drop shape (DS) method (profile fitting)

b) Viscosity and Density

Viscosity of the samples was measured based on the damping factor calculated from the two last consecutive peaks in the oscillation; the oscillations were based on the change in the length of the diameter parallel to the horizontal direction. The damping constant was 1.72 which resulted in a value of 5.03 *mPa.s* for the dynamic viscosity. This reveals a 16.0% difference compared to the value for pure copper, 4.30 *mPa.s*, reported in the literature [13]. Peaks in the beginning of the oscillation are possibly disturbed more because of the breakup and the drag force induced by the argon flow.

In addition, the peaks at the end of the spectrum may have been affected because of cooling during the free-fall. Images of molten nickel showed a change in the brightness of drops between the initial and final instants of free-fall.

Mass of the copper droplets 0.300 g was averaged over more than 20 samples quenched in water. The result of density measurement for copper was 12.5% different with respect to the literature values for pure copper. The drop oscillation method underestimated the density with respect to the values in the literature.

5. Error Analysis

a) Error Sources in Fitting Drop Profiles

The systematic errors involved in the study of surface tension are of two kinds; one is associated with the methods used, and the others are those related to the heating method. Since the neck (where the drop detaches) is close to the solid-liquid interface, the temperature must be close to the melting point of the sample; therefore, any possible temperature gradient in the pendant drops is ignored, and the samples were cleaned chemically and mechanically. Estimating the effect of contaminations and impurities is complicated while some impurities are highly surface active and some are not. Due to the effect of possible active impurities, higher values of the measurements are preferred in this field on the argument that they shall be closer to the true value for totally pure metals [14]. Nevertheless, quantifying the possible oxidations or determining the precision in heating the samples at such temperatures is difficult.

b) Uncertainty Analysis in Drop Oscillation

Uncertainties in analyzing the images, slight motion of the falling drop in the horizontal direction (during free fall), and relatively short flight-height for observing the oscillating droplets were the major sources of errors. Uncertainties due to blurry edges at high temperature, mechanical oscillations due to the breakup and drag force were other challenges in this method. Uncertainties in the measurement of surface tension and viscosity were 4.01% and 7.91%, respectively [4].

6. Conclusion

Agreement between the results from different measurement methods validated the measurement methodology for surface tension measurement at high temperatures. The method was established by using copper samples; however, the method is applicable for alloys and ceramics with high melting points. Effect of angle of the interface between a pendant drop and its solid rod was investigated for the first time; the correction was implemented in the drop weight method (one of the methods used for validating the profile fitting method).

The procedure of fitting drop profiles was validated by a separate numerical study; however, the results from that study were not presented here.

The drop oscillation method was also applied; that method is based on the same apparatus with no further modification to the system. This containerless method is another validating method that can be implemented in addition to the drop shape method (comparing experimental and theoretical drop profiles). Compared to other methods for measuring surface tension, this method does not require density of liquids for measuring surface tension. Density and viscosity of melts were also calculated based on image analysis and damping rate of free-falling drops, respectively.

Acknowledgment

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