International Journal of Thermophysics, Vol. 16, No. 1, 1995

A Quasi-Containerless Pendant Drop Method for Surface Tension Measurements on Molten Metals and Alloys[1]

D. B. Thiessen[2,3] and K. F. Man[2,4]

A quasi-containerless pendant drop method for measuring the surface tension of molten metals and alloys is being developed. The technique involves melting the end of a high-purity metal rod by bombardment with an electron beam to form a pendant drop under ultra-high-vacuum conditions to minimize surface contamination. The magnified image of the drop is captured from a high-resolution CCD camera. The digitized image of the drop is then analyzed to compute the surface tension. A computer program has been developed that reads the pixel intensities from a graphics file containing the digital image. The code searches for the edge of the drop along rows and columns of pixels and stores the edge coordinates in an array. It then computes an optimized theoretical drop shape by solving the Young–Laplace differential equation from which the quantity of surface tension is deduced. This technique has been demonstrated with the surface tension measurement of molten zirconium metal.

KEY WORDS: digital image analysis; electron beam melting; high temperature; liquid metals and alloys; pendant drop method; surface tension.

1. INTRODUCTION

A knowledge of the surface tension of metals and alloys is essential to an understanding of metallurgical processes and low-gravity processing schemes involving a free surface, such as floating-zone crystal growth, and to confirm fundamental theories of molten metal surfaces. On the ground,

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Microgravity Research Group, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109, U.S.A.

[3] NRC-NASA Resident Research Associate.

[4] To whom correspondence should be addressed.

0195-928X/95/0100-0245$07.50/0

under normal gravity conditions, surface tension forces contribute significantly to fluid flow (Marangoni or thermocapillary flows) in crystal growth. In space where buoyancy convection is minimal, surface tension-driven flow is often the dominant type of fluid flow. Obtaining accurate surface tension data is, therefore, particularly important to understanding the process of crystal growth in space. Although the surface tension of many metallic elements have been measured before [1, 2], there remain significant uncertainties as to their magnitude [3]. Many of the surface tension measurements were made in a gaseous environment. A small amount of impurities in the gas could strongly affect the accuracy of the measurement. Even trace quantities of oxygen and other contaminants can change the surface tension of liquid metals [4–6]. Surface tension measurements of the same metal by several investigators often scatter over a wide range of values.

Most of the standard ground-based techniques (sessile drop, maximum bubble pressure, and capillary rise) for measuring molten metal surface tension involve contact of the molten metal with a foreign support material. The support material often contaminates the surface, which in turn can cause very large errors in the measured surface tension [5] since it is highly sensitive to even low concentrations of surface-active impurities. A containerless oscillating drop technique to be performed in the reduced gravity of space promises to yield high-precision surface tension measurements for very clean liquid metal surfaces. Ground-based results for purity levels similar to those in low-gravity experiments have been obtained with a 1*g* version of the oscillating drop method [7]. Unfortunately, gravitational deformation of the drop alone caused uncertainties on the order of 4% in the surface tension measurements.

A potentially more accurate ground-based method that is capable of high surface purity is the quasi-containerless pendant drop method. In 1963, Allen [1] used this method to measure the surface tension of a number of transition metals. The drop shape was analyzed by the selected-plane method that uses two diameter measurements of the drop to calculate surface tension. Improvements in vacuum hardware and the application of digital image analysis will allow the accuracy of this method to be improved.

We have been developing and testing an improved quasi-containerless pendant drop method for measuring the surface tension of molten metals and alloys. The technique involves melting the end of a high-purity metal rod under ultra-high-vacuum conditions to form a pendant drop, the shape of which is analyzed using digital image analysis to calculate the surface tension. In this technique, the pendant drop of molten metal is in contact only with its own solid, while any initial surface contamination is

evaporated away by prolonged heating of the sample near its melting point. This is expected to produce a surface purity comparable to or even better than what can be achieved by the low-gravity containerless method. The pendant drop method has the added advantage that it is a static method, thus presenting less uncertainty in the interpretation of results than with the dynamic oscillating drop method. Furthermore, digital image analysis allows the shape of a drop to be determined very accurately. If the experimental and theoretical shapes fail to match closely after optimization, this can indicate nonuniformity in the surface tension arising from temperature gradients or nonuniform impurity distributions along the surface. The full-shape analysis described here should give a lower standard deviation than the standard selected-plane method. This method is well suited for obtaining surface tension measurements at temperatures near the melting point of a given material since it involves a solid–melt equilibrium.

It is expected that the quasi-containerless pendant drop technique will be useful for studying the surface tension of alloys. Of particular interest is the study of the composition dependence of surface tension for binary metallic alloys. The subtle effects of interest can often be hidden by noise in the data arising from impurity effects or random errors in the measurements. Fundamental theories of alloy surface tension [8] predict a nonlinear dependence of surface tension on composition owing to preferential adsorption of one component at the liquid–vapor surface. The experimental data necessary to validate these theories must have high precision.

In this paper, the improved quasi-containerless pendant drop method for measuring the surface tension of molten metals and alloys is described, and preliminary test results and analyses of errors are presented.

2. EXPERIMENTS

2.1. Apparatus

Figure 1 shows a schematic diagram of the quasi-containerless pendant drop apparatus used for measuring the surface tension of molten metals and alloys. The metal and alloy samples are heated by an electron beam (Fig. 1a). The electron source consists of a 1.5-turn loop of tungsten (0.38-mm-diameter wire) filament and a tantalum focusing plate which directs the energetic electrons toward the end of the sample rod. The filament is supported by two copper posts that are isolated from ground by ceramic insulator blocks. The filament power is provided by the main power outlet through a transformer and potentiometer. The acceleration voltage of the electrons is provided by a DC power supply (Varian Model 922-0020) that is fixed at -4 kV. Both the filament and the focusing plate

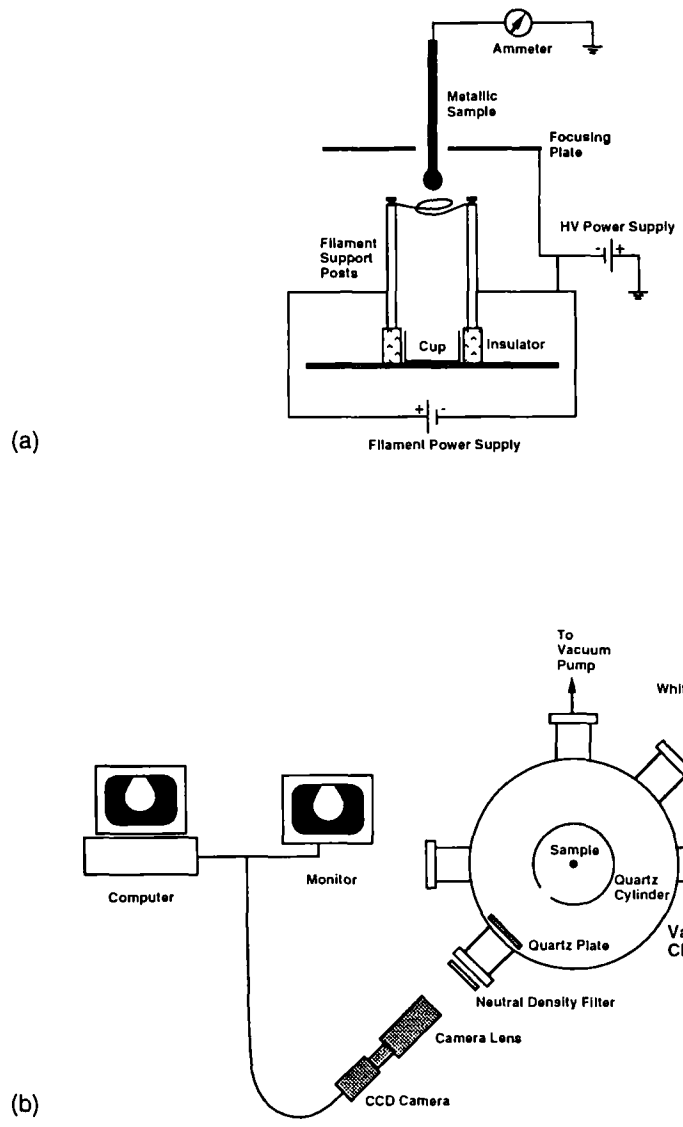

Fig. 1. Schematic diagram of the quasi-containerless pendant drop apparatus. (a) Details of the electron beam heating system. (b) Details of the imaging system. The white light source shown is used only for backlighting of the calibration sphere.

are floating at the same potential. The grounded sample, in the form of a rod or wire, is mounted on a linear micrometer drive feedthrough to allow the sample to be moved up and down along the central axis of the source. The apparatus is housed inside a vacuum chamber that is evacuated by a turbomolecular pump (Balzers Model TSU 180 H) to a base pressure of below 2×10^{-8} Torr.

The accuracy of the surface tension measurements is critically dependent on the imaging system (Fig. 1b). A high-resolution CCD camera (COHU Model 4910) is used to image the molten pendant drop. In order to magnify the image of a small molten drop ($\sim$4-mm diameter) at a minimum working distance of 25 cm, a macrolens of large numerical aperture (Nikon Micro-Nikkor 200 mm f/4 IF) is used with a 40-mm extension tube. This lens allows the image of the drop to fill the full view of the CCD chip for an accurate analysis. For high-temperature molten metals the glowing sample provides good contrast between the drop and the background, thus no external light source is required. A set of neutral density filters is used for adjusting the image brightness to prevent saturation of the camera. The CCD camera and lens are mounted on a stage assembly which permits three-axis translation and two-axis tilt adjustments. The images are digitized using a frame-grabber card (SCION, model LG-3) and the accompanying software (National Institute of Health, Image 1.52), and stored on a Macintosh II computer for subsequent analysis.

2.2. Calibration and Surface Tension Analysis

The calculation of surface tension from pendant drop images requires the magnification factors for the image in both the x and the y directions. These factors are obtained from digital images of precise calibration spheres (Industrial Tectonics) which have diameters specified to within $\pm 2.5\,\mu$m. A calibration sphere with a diameter close to that of the pendant drop is positioned within the vacuum chamber at the same location the pendant drop would occupy during an experiment. A digital image of the calibration sphere is made using collimated back lighting from a fiber-optic white light source. The camera settings are not adjusted in the time between a calibration and a pendant drop experiment. The precise alignment of the CCD camera with the vertical gravity vector is obtained through another calibration procedure. This is achieved by imaging a thin plumb wire at the location of the sample and adjusting the camera orientation until the edge of the wire in the digital image aligns with a column of pixels.

A computer program has been developed [9] to compute the surface tension from a digital image of a pendant drop. The program reads the

pixel intensities from a graphics file containing the digitized image. The code then searches for the edge of the drop along each row or column of pixels and stores the edge coordinates in an array. Approximately 900 points along the edge of the drop are found. The program then computes a trial theoretical drop shape by solving the Young–Laplace differential equation. The theoretical drop shape depends on four parameters. The first three parameters are boundary conditions to the differential equation which include the x and y coordinates of the drop apex and the radius of curvature, R_0, of the drop at its apex. The fourth parameter is the Bond number, β, which is inversely proportional to the surface tension. The trial theoretical drop shape is compared to the experimental edge coordinates via an objective function defined as

$$F = \sum_{i=1}^{N} (\delta n_i)^2 \tag{1}$$

where δn_i is the separation of the ith experimental edge point from the theoretical edge along the normal to the theoretical curve. The objective function is minimized by variation of the four parameters. Following parameter optimization, the surface tension, γ, is then calculated from the following identity:

$$\gamma = \frac{g\,\Delta\rho\,R_0^2}{\beta} \tag{2}$$

where g is the gravitational acceleration, and $\Delta\rho$ the density difference between the drop and its surroundings. Since the drop is in vacuum, $\Delta\rho$ is simply given by the density of the material at the melting point.

The full-shape analysis described here has several advantages over the standard selected-plane analysis, which uses only two diameter measurements to calculate surface tension. The full shape analysis generally gives a substantially lower standard deviation than the selected-plane method. Furthermore, if the theoretical and experimental shapes fail to match closely after optimization, this can indicate nonuniformity in the surface tension arising from temperature gradients or nonuniform impurity distributions along the surface or significant drop oscillations as a result of instrument vibration.

2.3. Sample Preparation and Experimental Procedure

Zirconium was used as a test of the method. It was chosen for this study because of its low evaporation rate, which minimized the coating of

windows during long runs. Samples were produced from a 6.5-mm-diameter zirconium rod of 99% purity in which hafnium is the main impurity (Johnson Matthey). The end of the rod was machined to form a stem of 2.5-mm diameter. The rod was etched for several minutes in a nitric acid solution consisting of 1 part nitric acid to 3 parts water to remove any initial oxide layer or other surface contamination. The sample was rinsed in water and then in ethanol, dried by evaporation, mounted on the micrometer drive, and quickly put inside the vacuum chamber. During the experiment, the sample temperature was raised slowly to just below melting for several hours while maintaining good vacuum conditions (10^{-7} Torr range) to allow thorough outgassing and evaporation of surface impurities. When the pressure fell to the low 10^{-7} Torr range, the temperature of the sample was raised slowly until the tip of the rod was molten to form a drop. The temperature of the drop could be controlled very precisely, such that the solid–melt interface could be moved slowly upward from the drop apex to the neck where the drop joins the stem. Since the drop was small (typically a few millimeters in diameter) and the thermal conductivity of metals is good, the temperature gradient across the surface of the drop was estimated to be small. Every attempt was made to melt the drop uniformly across the diameter of the stem and to maintain it at this condition for subsequent image capture.

During a typical run approximately 25 images of a single sample were captured over a period of several hours. These digitized pendant drop images were stored on the computer hard drive for later analysis to compute the surface tension. The time at which each image was captured was also recorded to study the variation of surface tension as a function of the length of time the drop has been kept molten.

3. RESULTS AND DISCUSSION

3.1. Surface Tension Measurements

Preliminary measurements have been made on zirconium samples to evaluate the technique described in this paper. A typical set of results is shown in Fig. 2. They were taken over a period of approximately 4 h. The surface tension values appear to increase as a function of time. This increase may have been due to a gradual removal of surface contaminants through evaporation. In this run seven images were also captured in a period of nine minutes at the end of the experiment, when the sample was likely to be cleanest. They gave an average surface tension value and a standard deviation of $1463 \pm 12\ \mathrm{mN \cdot m^{-1}}$. Separate measurements made on 3 different days gave average surface tension values and standard devia-

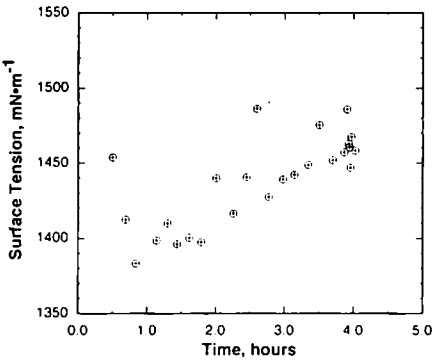

Fig. 2. A typical set of surface tension measurements of zirconium as a function of the time for which the sample has been molten.

tions for zirconium of 1435 ± 25, 1445 ± 14, and 1346 ± 18 mN · m^{-1}. The first three results were made with a sample that was prepared as described in Section 2.3 and thoroughly outgassed until the pressure was in the low 10^{-7} Torr range before image capture began. The last result was obtained with the sample exposed to room atmosphere for more than 1.5 h and the pressure in the vacuum chamber was 2×10^{-6} Torr during image capture. The latter surface tension value is substantially lower than the former three measurements. These results indicate that surface tension measurements are rather sensitive to sample preparation and vacuum conditions.

The present surface tension measurements obtained under proper experimental conditions are somewhat lower than the best value, 1480 mN · m^{-1}, obtained by Allen [1] using the drop weight method. However, our best value, 1463 ± 12 mN · m^{-1}, agrees well with Allen's value of 1469 ± 4 mN · m^{-1}, obtained with a similar pendant drop method but using the selected-plane analysis. The present results also agree well with a more recent measurement of 1435 mN · m^{-1} by Vinet et al. [10] using the drop weight method.

3.2. Analysis of Errors

One major advantage of using digital image analysis of pendant drop shapes is the ease of which sources of error in the surface tension measurements can be diagnosed. The objective function itself [Eq. (1)] is a measure of how well the measured drop shape corresponds to the theoretical shape. The magnitude of the objective function generally arises from a combination of drop shape distortion and noise in the imaging

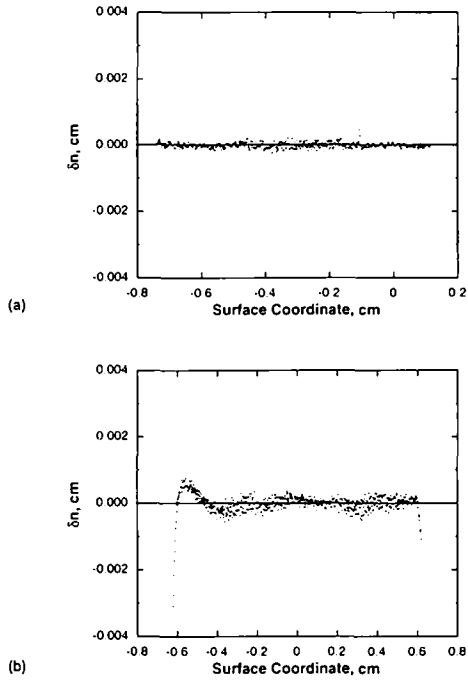

Fig. 3. Drop shape comparison plots of the deviation, δn, of each experimental edge point from the theoretical edge as a function of the arc length along the edge for (a) a calibration sphere and (b) a zirconium pendant drop, with no optical distortions.

system. Values above the noise level may indicate the presence of drop shape oscillation, optical distortion, camera misalignment, surface tension gradients, or nonuniform melting of the pendant drop. Further information on specific sources of error can be obtained by examining a plot of δn as a function of the arc length along the edge. Such shape comparison plots are shown in Fig. 3 for a calibration sphere and for a molten zirconium pendant drop. A positive δn indicates that a given experimental point lies outside, and a negative δn indicates that it lies inside, of the theoretical curve.

Optical distortion can be deduced by examining shape comparison plots for the high precision calibration spheres. When optical distortion is not significant the experimental points are randomly distributed about $\delta n = 0$ as shown in Fig. 3a for a calibration sphere. Noise in the imaging system caused a consistent scatter of approximately $\pm 2\,\mu$m in the edge coordinates. When optical distortion is present the experimental points

show a sinusoidal pattern. Optical distortion was found to be present in the initial runs of this study which was caused by a quartz cylinder in the optical path. A notch was cut in the cylinder to eliminate this distortion in later measurements.

Figure 3b is a shape comparison plot for a molten zirconium pendant drop after the optical distortion problem was eliminated and the camera carefully aligned. The surface coordinate in this plot is measured with respect to the drop apex. This drop shows some systematic deviation, which is most pronounced near the top of the drop where it contacts the solid stem. The solid melt transition at the top of the drop often appeared slightly nonuniform. A nonaxissymmetric solid–melt vapor contact line, which may result from nonuniform melting, can cause distortion of the pendant drop shape. The observed deviation persisted throughout the set of 25 measurements made on the same day. This deviation could well have caused a systematic error in the measurements, although the magnitude of such an error could not be easily estimated. A similar deviation pattern is also seen when the camera is misaligned with the vertical, but in this case the deviations have opposite signs on opposite sides of the drop.

Problems were also encountered with drop oscillation, which may have originated from vibration of the vacuum pump or, more likely, from vibration in the building. No vibration isolation is being used at present. It was also possible that the drop shape oscillation was caused by the electron beam heating as has been suggested by other workers [11]. Drop shape oscillation is believed to be the main contributor to the random error indicated by the standard deviation of the surface tension measurements.

Other sources of systematic error arise from uncertainties in the parameters in Eq. (2). Errors in the surface tension are linearly proportional to errors in the gravitational acceleration, and the density of the melt. The pendant drop technique with full shape analysis actually measures the Bond number, which is a dimensionless quantity containing the gravitational acceleration, melt density, radius of curvature at the drop apex, and surface tension. The Bond number, surface tension, and radius of curvature for each measurement are recorded so that surface tension values can be corrected in the future for improved values of melt density or gravitational acceleration. A final source of systematic error to be considered is the magnification factors. They are dependent on the sharpness of focus obtained. To estimate the error associated with focusing, five images of the same calibration sphere were captured. The camera was moved to defocus and then refocus on the sphere between consecutive frame grabs. The magnification factors obtained from the five images gave a standard deviation of approximately 0.1%. An error of 0.1% in the magnification factor would translate into a 0.2% error in the surface tension.

4. CONCLUSIONS

A quasi-containerless pendant drop method for measuring the surface tension of molten metals and alloys has been tested with zirconium. The measurements agree well with those in the literature. Shape comparison plots indicate that nonuniform melting caused shape distortion near the top of the pendant drop. Shape distortion over most of the drop surface is quite small, thus confirming that surface tension gradients are small. Work is ongoing to test this method on other metals and, more importantly, to obtain measurements on alloys.

ACKNOWLEDGMENTS

This work was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA). We are grateful to NASA and the National Research Council for supporting a Research Associateship for one of us (D.B.T.). We thank Dr. Eli Jacobsohn and Mr. Dan Barber for their assistance.

REFERENCES

1. B. C. Allen, *Trans. AIME* **227**:1175 (1963); B. C. Allen, in *Liquid Metals, Chemistry and Physics*, S. Z. Beer, ed. (Marcel Dekker, New York, 1972), pp. 161–212.
2. K. Nogi, K. Ogino, A. McLean, and W. A. Miller, *Metallurg. Trans. B* **17B**:163 (1986).
3. T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon Press, Oxford, 1988), pp. 109–146.
4. B. J. Keene, K. C. Mills, A. Kasama, A. McLean, and W. A. Miller, *Metallurg. Trans. B* **17B**:159 (1986).
5. S. C. Hardy, *J. Crystal Growth* **69**:456 (1984); S. C. Hardy, *J. Crystal Growth* **71**:602 (1985).
6. W. D. Kingery and M. Humenik, *J. Phys. Chem.* **57**:359 (1953).
7. I. Egry, G. Lohofer, P. Neuhaus, and S. Sauerland, *Int. J. Thermophys.* **13**:65 (1992).
8. W. Shih and D. Stroud, *Phys. Rev. B* **32**:804 (1985).
9. D. B. Thiessen, D. J. Chione, C. B. McCreary, and W. B. Krantz, *J. Colloid Interface Sci.* (in press).
10. B. Vinet, J. P. Garandet, and L. Cortella, *J. Appl. Phys.* **73**:3830 (1993).
11. J. C. Kelly, *J. Sci. Instrum.* **36**:89 (1959).