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Effects of Sample Size on Surface-Tension Measurements of Nickel in Reduced-Gravity Parabolic Flights[1]

S.-F. Chen[2] and R. A. Overfelt[3,4]

Surface tensions of molten metals have been reported in the literature by application of many "standard" techniques: sessile-drop, maximum bubble pressure, pendant-drop, and capillary-rise methods. Great experimental care must be exercised to ensure the absence of contamination, and containerless techniques based upon the classical theory of oscillations of a liquid drop are being developed for high-precision measurements on reactive alloys. Droplet positioning and heating can be efficiently accomplished by electromagnetic levitation, although additional modes of oscillation can be excited and the fundamental oscillation mode can be shifted to higher frequencies due to asymmetries in droplet shape when experiments are performed in earth-based laboratories. These additional factors associated with $1g$ experiments significantly complicate data analysis. An electromagnetic levitator has been developed at Auburn University to test containerless processing methods for characterizing the surface tension of high temperature, reactive melts. Recent oscillating drop experiments with nickel samples utilizing electromagnetic levitation in the low-g environment of NASA's KC-135 research aircraft have shown droplet oscillations in the primary mode and at the fundamental frequency. A series of experiments was performed with droplets covering a range of sizes (i.e., mass), and the largest samples exhibited the largest deviations from Rayleigh's simple theory. The smallest samples exhibited oscillatory behavior consistent with Rayleigh's simple theory. An uncertainty analysis showed that the oscillating-drop technique

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[2] Auburn University, Space Power Institute, 231 Leach Center, Auburn, Alabama 36849, U.S.A.

[3] Auburn University, Materials Research and Education Center, 201 Ross Hall, Auburn, Alabama 36849, U.S.A.

[4] To whom correspondence should be addressed.

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should provide uncertainties in surface tension of ± 0.1 to 2.0% depending upon the uncertainty in the mass of the sample.

KEY WORDS: surface tension; oscillating drop; containerless; electromagnetic levitation; nickel; molten metals.

1. INTRODUCTION

The use of computational simulation in the molten metal processing industries is rapidly growing as manufacturers devise more competitive processes. Unfortunately, simulation results can only be as good as the input thermophysical properties used. Although many techniques exist for determining most of the required properties to accuracies of the order of $\pm 5\%$ or better [1, 2], property measurements on molten alloys are experimentally difficult and considerable errors may be present in the data. For example, Nagashima [3] has reviewed the status of thermophysical property data for high-temperature semiconductor melts and has found considerable uncertainty. Convection effects and crucible contamination in very reactive samples clearly exacerbate the difficulties.

Surface tensions of molten metals can be measured by many techniques: sessile-drop, maximum bubble pressure, pendant-drop, capillary-rise, drop weight, and oscillating-drop methods [2]. The sessile-drop technique has been widely utilized because of its many advantages, for example, measurements over a wide range of temperatures. Although the method is inherently straightforward by utilizing a molten drop resting on a horizontal ceramic substrate, surface-tension data are particularly susceptible to the deleterious effects of contamination. Thus, great experimental care must be exercised to ensure the absence of contaminants.

Bashforth and Adams [4] utilized the fundamental theory of capillarity for the determination of surface tension in 1883 and developed a theoretical description of the contour of a cylindrically symmetrical sessile drop resting on a nonwetting substrate. The calculations are rather tedious, and Butler and Bloom [5] were prompted to develop an iterative computational procedure to automate the curve fitting process by minimizing the error between the theoretical drop shape and the experimental data. Butler and Bloom note that accuracies of 0.1% are possible with extremely careful attention to the parallelism of sessile-drop lighting conditions, scrupulous attention to droplet symmetry, microscopic measurement of drop geometry, and avoidance of contamination. The density of molten alloys can also be determined from careful sessile drop experiments [6].

Reactions between the molten droplet and the substrate are particularly worrisome. Recent research at Auburn University on the surface tension of superalloys has shown that the wetting angles and apparent surface tension values change with time when using typical sessile drops [7]. These changes were presumably due to reactions between the substrate and the molten metal and/or reactions with residual gas species in the vacuum chamber.

2. OSCILLATING-DROP TECHNIQUE

Since many high-temperature metals of commercial and scientific interest react with crucibles and substrates, containerless techniques are being developed for high-precision measurements of thermophysical properties [8–10]. These containerless methods are particularly effective in a low-gravity environment. Electromagnetic levitation (EML) is a mature technology and has been utilized in a recent series of orbital experiments with the TEMPUS electromagnetic levitator [8]. In EML, eddy currents are induced in an electrically conductive sample subjected to high-frequency, alternating electromagnetic fields. The induced eddy currents provide both Joule heating of the sample and mechanical forces due to coupling of the induced eddy currents with the applied electromagnetic field. The typical sample shape exhibited by molten samples during terrestrial processing is elongated in the direction of gravity and are clearly not spherical.

The containerless technique for measuring surface tension (γ) is based upon the classical theory of oscillations of a liquid drop. Consider a liquid droplet oscillating along its vertical axis. The linearized theory of Reid [11] gives the following relationship:

$$\gamma = \frac{3M\omega_n^2}{4\pi n(n-1)(n+2)} \tag{1}$$

where ω_n is the oscillation frequency, M is the mass of the drop, and n counts the normal modes of oscillation. The fundamental mode is $n = 2$. When $n = 2$, the oscillation frequency is referred to as the Rayleigh frequency (ω_{R}) from his original work [12]. Thus, the surface tension is related to the natural frequency of drop oscillation. These quantities can be measured if the drop can be excited and its oscillations detected. Cummings and Blackburn [13] note that the mere presence of the magnetic field causes a slight increase in the "stiffness" of the drop (which raises the apparent surface tension and must be corrected for when evaluating the fundamental Rayleigh frequency). The correction factor can be estimated from translational vibration of the drop according to

$${\omega_{\mathrm{Expt}}}^2 = {\omega_{\mathrm{R}}}^2 + 2{\omega_{\mathrm{T}}}^2 \tag{2}$$

where ω_{Expt} is the experimentally measured oscillation frequency and ω_{T} is the frequency of the drop's translational vibration in the magnetic field.

Measurements of the surface tension of several molten metals have been performed using this technique on earth, and these data agree with data from conventional techniques [14]. The fundamental mode ($n=2$) can be the only mode excited, although multiple peaks are often observed [15, 16]. Busse [17] has shown that rotation of a spherical droplet can cause the fundamental peak to split into five separate equally spaced peaks. In addition, Cummings and Blackburn [13] have shown that rotating aspherical droplets can experience splitting of the fundamental frequency into five separate non-equally spaced frequencies. Oscillating, but not rotating, aspherical droplets can exhibit three separate non-equally spaced frequencies. Soda et al. [18] note that large droplet oscillation amplitudes can increase the measured frequencies.

3. EXPERIMENTAL PROCEDURES

The Space Power Institute at Auburn University has developed and flown an instrument for containerless measurements of surface tension on the NASA KC-135 parabolic research aircraft. The apparatus is shown schematically in Fig. 1. The device is powered by a commercial 1-kW Ameritherm power supply and utilizes electromagnetic levitation for

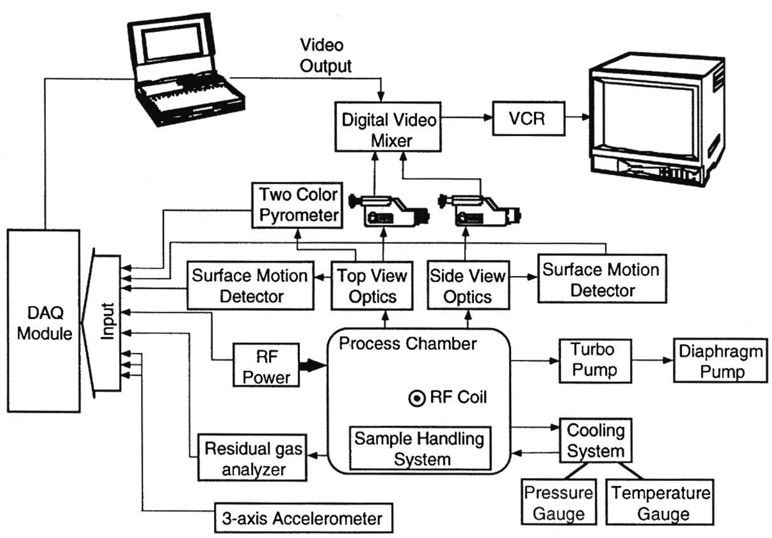

Fig. 1. Schematic diagram of the electromagnetic levitator system.

simultaneous heating and positioning of metallic samples. A vacuum level of 5×10^{-6} Torr was maintained during the experiments by an Alcatel turbopump. Partial pressures of background gases were measured with a Leybold Transpector residual gas analyzer and the partial pressure of oxygen was 3×10^{-7} Torr. Aircraft acceleration levels are measured with a three-axis accelerometer. Up to eight samples can be processed without breaking vacuum. A Mikron two-color pyrometer is utilized for temperature measurements. The pyrometer was calibrated in the system using a nickel sample with an internal B-type thermocouple.

Sample imaging from the top and side is accomplished by Sony high-resolution videocameras, and oscillations are detected by imaging the top of the sample on an On-Trak Photonics high-speed photodetector (SiTek 2L10SP with a rise time of 800 ns). Voltage outputs from the photodetectors were acquired using a National Instrument DAQCard-700 data acquisition card with a sampling rate of 1 kHz. The acquired voltage spectrums were then filtered and frequency analyzed via a numerical fast Fourier transform algorithm. A 166 MHz laptop computer using Labview software provides the instrument's data acquisition (image, temperature, *g*-level, and oscillation data). Part of the data stream is also recorded to a videotape for later analysis.

Pure nickel samples of 99.99% purity were selected for these initial experiments. The size of the samples ranged from 3 to 5 mm in diameter, and all samples were weighed before and after the measurements. The coil was designed such that a quadrupole magnetic field provided for both sample positioning and heating. A maximum current of 210 A at a frequency of 300 kHz was passed through the induction coil.

In the KC-135 experiments, eight nickel samples of different masses were loaded in the sample carousel for each day's flight of 40 parabolas. The low-*g* portion of each parabola lasts approximately 21 s. Before each parabola a solid nickel sample was introduced into the coil from the carousel using a ceramic pedestal. Each sample was preheated on the pedestal for 5 s before going into the low-gravity period. In the 21 s of low gravity, the coil was fully energized and the sample was melted by the induced eddy currents. Surface oscillations usually started after each sample was completely molten.

4. RESULTS AND DISCUSSION

4.1. Experimental Results

The fundamental mode is often the only mode excited and clearly dominates in low-*g* experiments, as shown by the typical Fourier-transform

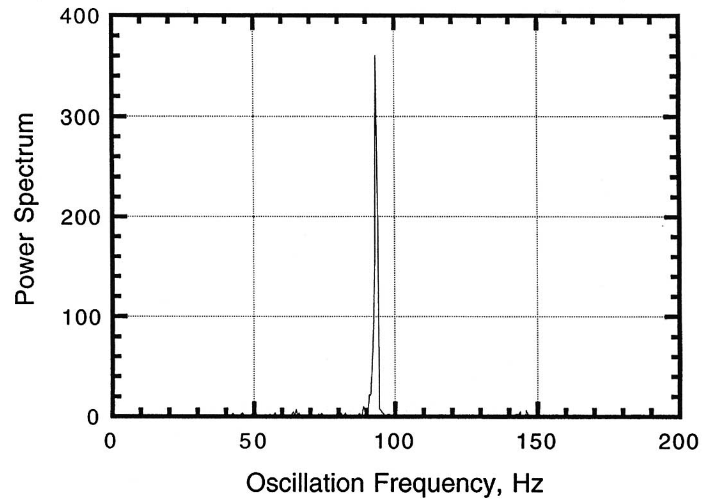

Fig. 2. Typical FFT of droplet oscillation data from the low-gravity period of a parabola.

spectrum of Fig. 2. Multiple peaks were not observed in the spectra when the oscillation response was well behaved. The apparent surface tension data calculated from Eq. (1) from these oscillating-drop experiments are shown versus sample mass in Fig. 3. Although the smallest samples exhibited good agreement between the measured surface tension values and the literature value of 1.78 $N \cdot m^{-1}$ [19], the apparent surface tension increases rapidly with increasing sample mass exhibiting a 60% deviation from the literature value for a sample size of 493 mg.

The theoretical values of droplet oscillation frequency were calculated as a function of droplet mass from Rayleigh's small amplitude droplet oscillation theory [Reid's linear theory, Eq. (1); $n = 2$] and assuming a value of 1.78 $N \cdot m^{-1}$ for the surface tension of pure nickel. These data and the experimentally observed values are shown in Fig. 4. The oscillation behavior of samples with masses less than 200 mg is well described by Rayleigh's theory. However, the simple Rayleigh theory consistently underpredicts the oscillation frequencies for droplets with masses greater than 200 mg.

Increases in the measured oscillation frequencies due to the presence of the magnetic field have been noted by Cummings and Blackburn [6]. Sauerland et al. [14] found that the measured oscillation frequencies increased with increasing sample mass during terrestrial levitation experiments. Unfortunately, the smallest nickel samples investigated by Sauerland et al. [14] were 500 mg, approximately the size of our largest sample.

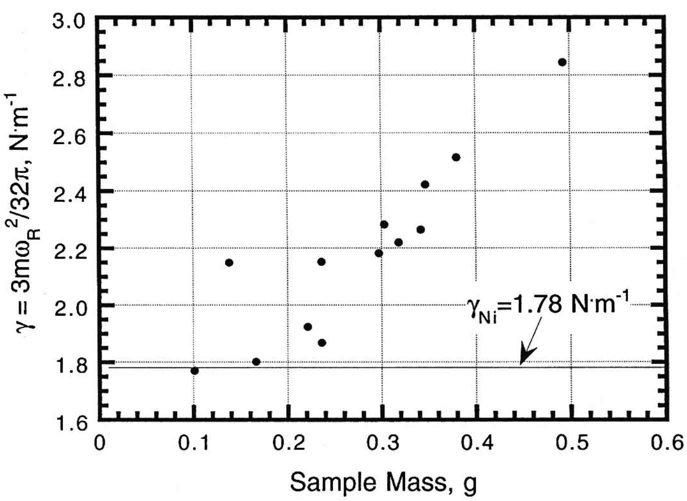

Fig. 3. Apparent surface tension data measured from oscillating-drop experiments with the masses shown.

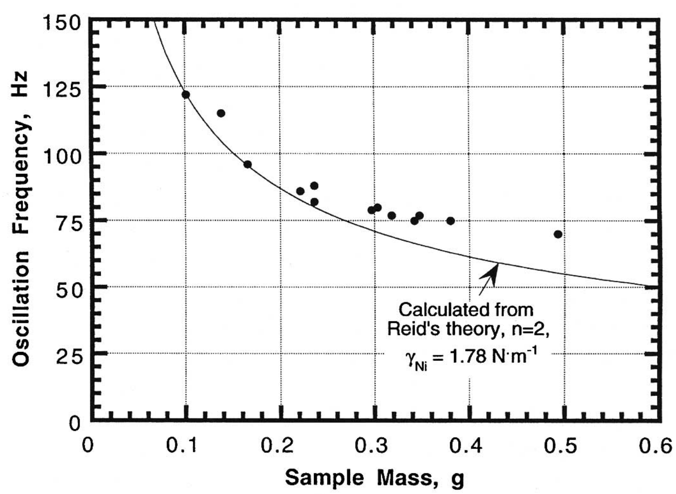

Fig. 4. Measured and calculated droplet oscillation frequencies as a function of sample mass. Experimental measurements conducted during the low-*g* periods of parabolic maneuvers on NASA's KC135 aircraft.

More recent orbital experiments on gold have shown that even very large samples ($m = 5.21$ g) exhibit droplet oscillation frequencies in agreement with the simple Rayleigh frequency when the confining magnetic field pressure is minimal [8]. Perhaps the magnetic fields in the vicinity of the null point were low enough in the present experiments for the smaller samples to experience minimal magnetic field pressure affects and consequently oscillate near the Rayleigh frequencies. Electromagnetic field calculations of the levitation system are needed to address this issue.

4.2. Uncertainty Considerations

The total uncertainty, ΔG, in any experimental measurement can be estimated using the procedure of Moffat [20]. When j independent variables are utilized in a function G, the individual contributions, ΔX_i, to the total uncertainty, ΔG, can be estimated by the root-sum-square method. Thus

$$\Delta G = \left[\left(\frac{\partial G}{\partial X_1} \Delta X_1 \right)^2 + \left(\frac{\partial G}{\partial X_2} \Delta X_2 \right)^2 + \cdots + \left(\frac{\partial G}{\partial X_i} \Delta X_i \right)^2 \right]^{1/2} \tag{3}$$

where the partial derivative of G with respect to X_i is the sensitivity coefficient for the function G with respect to the measurement X_i.

As noted above, Butler and Bloom [5] report that accuracies of 0.1 % are possible with sessile-drop measurements where extremely careful attention is devoted to (i) the parallelism of sessile-drop lighting conditions, (ii) droplet symmetry conditions, (iii) microscopic measurement of drop dimensions, and (iv) avoidance of contamination.

The uncertainties of the individual terms of Eq. (1) for the surface tension of the oscillating drops were estimated from actual measurements. If splitting of the fundamental frequency can be avoided so that $n = 2$, then the uncertainty in surface tension is due only to uncertainties in (i) the mass of the drop and (ii) the measured oscillation frequency (including sample translational vibration frequency, if present, to correct for magnetic field effects).

The mass of the drop can be very accurately measured before experimentation begins and after the measurements are concluded. Molten metals are typically processed in a vacuum of 10^{-5} torr or better and can lose mass due to evaporation. Thus, the mass of the droplet at the actual measurement conditions must be estimated from vaporization kinetics. This can be accomplished to within 0.1 to 2% depending upon the complexity of the alloy system and the length of processing time. Quickly cooling the

Table I. Uncertainty Estimate for Oscillating-Drop Measurement of Surface Tension of Nickel

Parameter	Estimated $\pm 2\sigma$ confidence limit (%)	Surface tension change $(N \cdot m^{-1})$	Surface-tension change squared $(N \cdot m^{-1})^2$
Mass of drop, $M = 0.894$ g	2.0	0.034	0.001156
Normal mode of oscillation, $n = 2$	NA	NA	NA
Oscillation frequency, $\omega = 251\ rad \cdot s^{-1}$	0.1	0.0034	1.13×10^{-5}
$\Sigma(\Delta\gamma_i)^2$			1.17×10^{-3}
Total uncertainty in surface tension, $[\Sigma(\Delta\gamma_i)^2]^{1/2}$		0.034	
Total % uncertainty in surface tension ($\gamma = 1.78\ N \cdot m^{-1}$)		1.9 %	

sample after a successful experiment enables a very accurate measurement of the sample's mass.

Oscillation frequencies can be detected either by high-speed video image processing [15] or by focusing the drop image on high-speed photodetectors. Although video image processing is slow and tedious, all sample image data are retained. The utilization of photodetectors is much faster. A SiTek 2L10SP photodetector with a rise time of 800 ns enables better than 0.1% accuracy in oscillation frequency detection, but image information is lost. This information can be critical if assignment of appropriate degenerate frequencies through digital filtering is required due to a multiplicity of peaks. Very careful attention to (i) coil design, (ii) ripple on the RF signal, and (iii) external vibrations is required to minimize peak splitting.

Moffat's uncertainty estimation procedure [20] was applied to the linearized Reid [11] equation for the surface tension of nickel [Eq. (1)], and the individual uncertainties are shown in Table I. The total estimated measurement uncertainty (95% confidence limits) is approximately ± 0.1 to 1.9% depending upon the uncertainty in sample mass, the largest contributor to the experimental uncertainty.

5. SUMMARY

Electromagnetic levitation has been utilized to study droplet oscillations of molten nickel in the low-gravity environment of parabolic aircraft flights. The fundamental mode is typically the only mode excited. The oscillation behavior of molten droplets with a mass of less than 200 mg is well described by Rayleigh's low-amplitude oscillation theory. Droplets with masses greater than 200 mg exhibit droplet oscillations at frequencies higher than predicted by the simple Rayleigh theory.

The primary techniques for measuring surface tension (sessile drop in 1g and oscillating drop in either 1g or low-g) have been compared with respect to their potential accuracy. The sessile-drop technique has been reported to provide uncertainties in surface tension of better than $\pm 0.1\%$ when sample contamination is not an issue. The oscillating-drop technique is expected to provide uncertainties in surface tension of ± 0.1 to 2.0% depending upon the uncertainty in the mass of the sample.

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