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Observations of the Effects of Oxide Skins on the Oscillations of Electromagnetically Levitated Metal Droplets[1] *

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The surface tensions of liquid metals can be derived from measurements of the natural oscillation frequencies of levitated drops through the Rayleigh relation, $\gamma = \frac{3}{8}\pi m \omega^2$. In general, during terrestrial measurements, a spectrum consisting of three to five dominant oscillation frequencies (in the range of 30 to 60 Hz) are found, rather than the single one predicted by Rayleigh, due to deformation of the drop shape by gravity and the supporting magnetic field. Cummings and Blackburn have derived a correction factor to align the measured frequencies with the Rayleigh frequency, which has been shown to hold through microgravity experiments by Egry et al., for the majority of metals that have a liquid surface. Work at the NPL on more complex, commercial alloys has found that, in some cases, oscillation frequencies may be split into more complex spectra exhibiting seven to nine oscillation frequencies. This has been attributed to formations of oxide from the metal collecting on the surface of the droplet. Observations of the frequency spectra and high speed video images of the levitated drops are discussed.

KEY WORDS: high temperature; image analysis; levitation; liquid metal; steel; surface tension.

1. INTRODUCTION

Metals manufacturing and fabrication industries are increasingly using computer-based mathematical models to obtain a better understanding or control of their processes or to predict defects in the final product. These

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* Dedicated to Barbara Brooks-Bailey, 1952–1998.

models are highly developed in terms of the mathematical equations used, but they rely on the accuracy of the physical property data of the materials they are modeling to give a true prediction. In many cases these data are not available, and this is particularly true in the case of surface tension, which is a critical factor in the modelling of such processes as welding, spray forming, powder and metallic ribbon manufacture, and inclusion removal by electron beam button melting.

Measurement of the surface tension of metals and alloys by analysis of the frequencies of the oscillations of a magnetically levitated drop is now an established technique. Surface tension (γ) can be derived from the Rayleigh relation [1],

$$\gamma = \tfrac{3}{8}\pi m \omega^2 \tag{1}$$

where m is the mass of the droplet, and ω the oscillation frequency of a free-falling droplet. Rayleigh predicted the oscillations to be distortions of a sphere with no external pressure, resulting in a single mode of oscillation at a single frequency. Using a photodiode and dynamic signal analyzer, Keene et al. [2] discovered that electromagnetic levitation provides oscillation spectra with three or five closely spaced frequencies. Cummings and Blackburn [3] showed that these frequencies resulted from three modes of oscillation caused by the distortion of the drop by the magnetic field and were slightly raised by the pressure of the field. They also showed that the magnetic pressure could be correlated with the translational frequency ($\omega_{\rm tr}$) and that Eq. (2) could be used to calculate the Rayleigh frequency ($\omega_{\rm R}$) where a is the radius of the drop, g is the gravitational constant, and the subscripts 1 to 5 denote the various peaks.

$$\omega_{\rm R}^2 = \frac{1}{5}(\omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2 + \omega_5^2) - \omega_{\rm tr}^2\left(1.9 + 1.2\left[\frac{g}{2a(2\pi\omega_{\rm tr})^2}\right]^2\right) \tag{2}$$

Egry and his co-workers have shown the validity of Eq. (2) with measurements made in microgravity [4], where the electromagnetic fields can be minimized, and a nearly spherical drop shape can be attained. The surface tension data show good agreement with the terrestrial data corrected with Eq. (2).

The majority of work carried out with this technique is (for liquid metals) on relatively benign systems which have free liquid surfaces and oscillate in the predicted manner. However, work at the NPL has been aimed at providing data on a wide range of commercial alloys, with complex chemistries, which can result in the formation of surface oxide rafts or films. These oxides can damp or stop the oscillations and thus make oscillation frequency identification difficult or impossible. Observations were reported at the last International Workshop of Subsecond Thermophysics of spectra with up to nine frequencies [5]. Results calculated with all nine frequencies showed agreement with data obtained on the same material where only five frequencies were obtained. Samples exhibiting the nine frequencies were subsequently found to have larger amounts of oxide on their surface, suggesting that the oxide was contributing to the oscillation modes. The aim of the current work is to look at the effects of these oxides on the oscillations of the drop.

2. EXPERIMENTAL

2.1. Apparatus

The apparatus is shown in Fig. 1. Samples of between 0.3 and 0.8 g are placed on the turntable and raised on a BN push rod into a 13-mm-outside diameter silica tube, placed within a coil with parallel turns wound in opposite directions at top and bottom. When power is applied to the coil (450-kHz, 15-kW Radyne RF generator), the sample levitates and is inductively heated. A protective atmosphere of Ar + He or $Ar + H_2$ is flowed through the tube to prevent oxidation of the sample, the gas having first been passed through a purification system consisting of a copper catalyst heated to ca. 150°C and a liquid nitrogen cold trap in order to provide levels of oxygen lower than 1 vpm. The temperature of the sample can be controlled by altering the power output of the generator to change the position of the droplet in the coil and thus change the induction heating effect or by changing the gas composition so that the higher thermal conductivity gas (relative to Ar) extracts more heat from the sample. The temperature is measured using a two-color ratio pyrometer (Ircon Modline R; wavelengths, ca. 1 μm) viewing the sample though a quartz prism. The oscillations are usually measured by projecting an image of the drop onto a photodiode through a narrow slit. The photodiode produces a varying electrical signal in response to the changing diameter of the drop, which is fed to a dynamic signal analyzer, which, through a fast Fourier transform (FFT), provides a frequency spectrum. For this work the apparatus was modified by the addition of a high-speed videocamera, frame grabber, and video recorder. A beam splitter in the photodiode optics allowed both systems to view the drop simultaneously. One thousand twenty-six images are recorded at a rate of 150 Hz and saved as individual bit maps. These are saved to disk for off-line analysis.

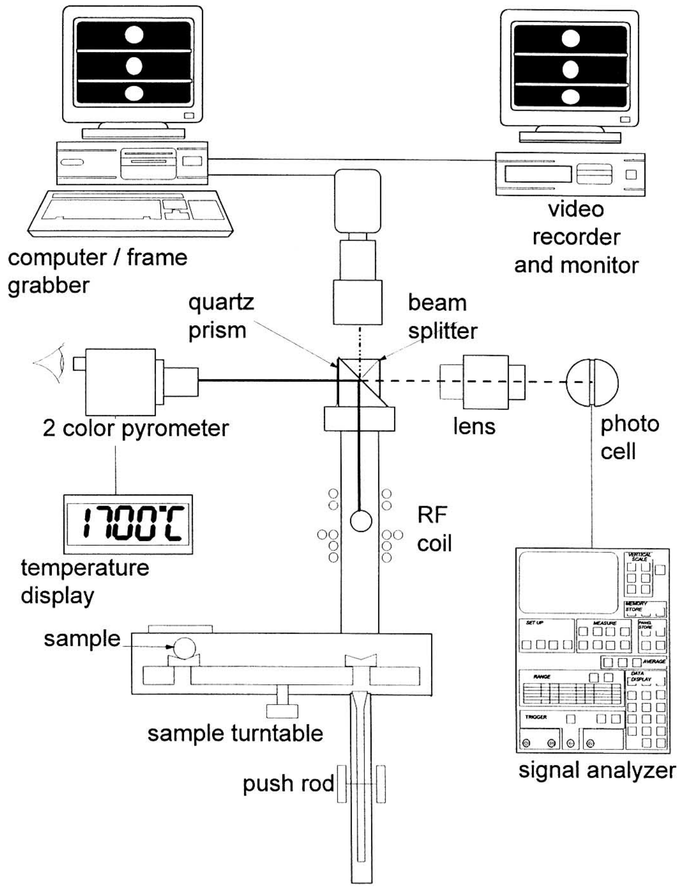

Fig. 1. General arrangement of the levitation apparatus.

2.2. Materials

The work reported previously [5] had been carried out on a nickel-based super alloy, IN718. For this study, however, a steel known to form oxide skins was chosen, as the pyrometer is optimized for steels making temperature measurement more reliable. The partial composition (wt%) of the steel is as follows: Al, 0.036; C, 0.18; Si, 0.026; Mn, 0.98; O_{total}, 0.0015; S, 0.015; and no Ca, was detected. Samples were run in an atmosphere of Ar + He to prevent loss of sulfur. Postmeasurement energy-dispersive x-ray analysis of the surface of the samples was carried out on a Link AN10000 and a CamScan SEM.

2.3. Image Capture and Analysis

In order to reconstruct the oscillations of the droplets at up to 60 Hz, sampling theory dictates a capture rate of at least 120 Hz (Nyquist frequency). This requires the use of a high-speed camera. A Kappa CF camera capable of producing deinterlaced images at frequencies of 50, 100, 150,..., 500 Hz was used. At the usual operating frequency of 150 Hz, the size of each subimage is 768×96 pixels, and because of the removal of interlacing, the image has been vertically compressed by a factor of two.

For the automatic fitting of droplet images to ellipses, the following description of an ellipse was used: the ellipse was parametrized, using polar coordinates relative to the drop center, as

$$r(\theta) = \frac{r_0}{1 + \varepsilon \cos(2\theta - \theta_0)} \tag{3}$$

or, in Cartesian coordinates relative to the origin, as

$$x(\theta) = x_0 + \frac{r_0 \sin(\theta - \theta_0)}{1 + \varepsilon \cos(2\theta)}, \qquad y(\theta) = y_0 + \frac{r_0 \cos(\theta - \theta_0)}{1 + \varepsilon \cos(2\theta)} \tag{4}$$

where (x_0, y_0) is the center of the ellipse relative to the center of the droplet image, measured in pixels; r_0 is the scaling parameter for the ellipse, measured in pixels; θ_0 is the angle the major axis of the ellipse makes relative to the x-axis, measured anti-clockwise in degrees; and ε is the ellipticity factor for the droplet.

The magnitudes of the major and minor axes, a and b, are related to the ellipticity factor by

$$a = \frac{r_0}{1 + \varepsilon} \qquad \text{and} \qquad b = \frac{r_0}{1 - \varepsilon} \tag{6}$$

and the sum and difference of the major and minor axes are related to ε and r_0,

$$a - b = \frac{2\varepsilon \cdot r_0}{1 - \varepsilon^2} \qquad \text{and} \qquad a + b = \frac{2r_0}{1 - \varepsilon^2} \tag{7}$$

Initial values for the center and size of the droplet were determined from a Hough transform of a smaller, averaged version of the droplet image. The intensity at a point (ϕ, d) in Hough space transform is the average intensity in the droplet image along a line that is inclined at an angle ϕ to the x-axis and at a distance d from the center of the image. The Hough transform converts lines into points (or "butterflies"), circles centered on the origin into stripes, and circles offset from the origin into wavy stripes.

Windows 95 software was written in Delphi 2 (Pascal) to fit the drop images to the generalized ellipse. Sequential examples of images, and the fitting are shown in Fig. 2. The method is as follows:

- read the next sequential bit map,
- stretch it vertically by a factor of two using interpolation to fill the missing interlace lines,
- produce a thumbnail image (100×100 pixels) by averaging,
- generate the Hough transform of the thumbnail,
- using the Hough transform data, locate the center and radius of the best-fit circle,
- using the best fit circle data as a starting point, either
  - scan the complete volume of a five-parameter (x_0, y_0, r_0, θ_0, and ε) space in discrete steps to locate the ellipse which represents the global maximum best fit or
  - scan q_0 and e space and use a downhill simplex maximization routine to find the optimal values of x_0, y_0, and r_0—this is much faster but less robust than the former method,
- display the best-fit ellipse data and store results to data file, and
- repeat with remaining images.

By Fourier transforming the x_0, y_0, $a+b$, and $a-b$ data, the oscillation and translational frequencies of the droplet can be calculated.

3. RESULTS

Upon levitation melting, the samples were seen to form an oxide skin, with areas of thicker oxide moving on the surface. The thicker oxides disappeared from view when heating the samples to ca. 1600°C, and frequency spectra (A_D and B_D) as shown in Fig. 3 could be obtained, although the drop was seen to be unstable in the levitator. It was not possible to obtain reliable surface tension data from these spectra. Further heating caused the oxide to disperse at about 1660°C: the drop became more stable and the oscillation spectra took their usual form (Fig. 3, spectrum C_D). From these spectra surface tension–measurements were made and the surface tension-temperature relationship was found to be

$$\gamma = 1.449 + 0.5932 \times 10^{-3}(T - 1500) \qquad (8)$$

with γ in units of $N \cdot m^{-1}$ and temperature in °C.

Oscillations of a Levitated Drop Captured at 150 Hz

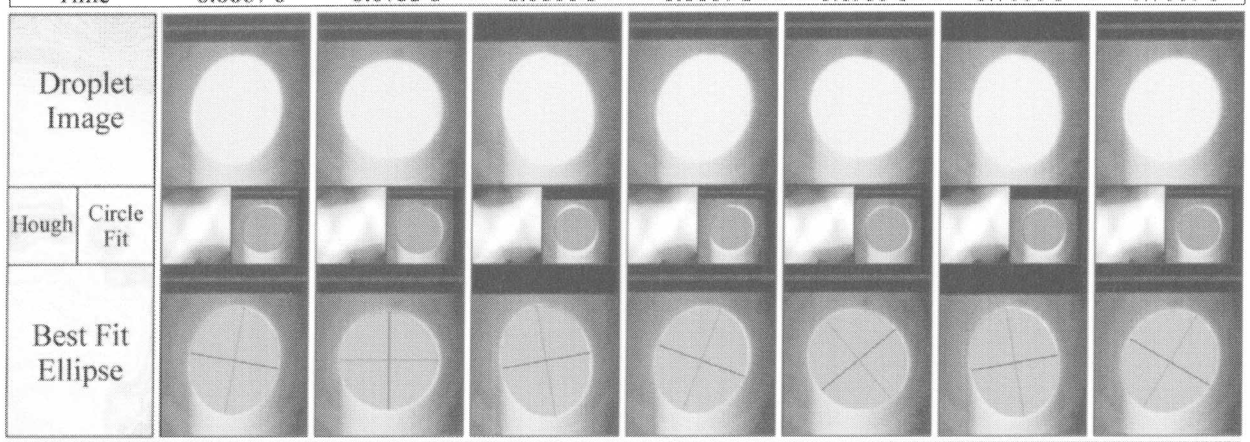

Image file	162_1000	162_1001	162_1002	162_1003	162_1004	162_1005	162_1006
Time	6.6667 s	6.6733 s	6.6800 s	6.6867 s	6.6933 s	6.7000 s	6.7067 s
x_0	0.5	0.0	0.8	1.0	1.5	2.2	2.2
y_0	-12.2	-12.1	-12.4	-11.6	-11.3	-15.1	-13.9
r_0	28.95	29.15	29.20	29.05	29.30	28.75	29.15
Ellipticity, %	9.0	0.5	11.5	8.5	3.5	11.0	6.0
Theta, °	80	0	100	70	130	100	60
Fit	70.1	69.1	70.0	72.6	72.5	66.5	68.4

Fig. 2. Seven levitated drop image examples (top row); their Hough transforms (center row, left); best-fit circles (center row, right) and ellipses (bottom row). Best-fit ellipse data are tabulated below the relevant image.

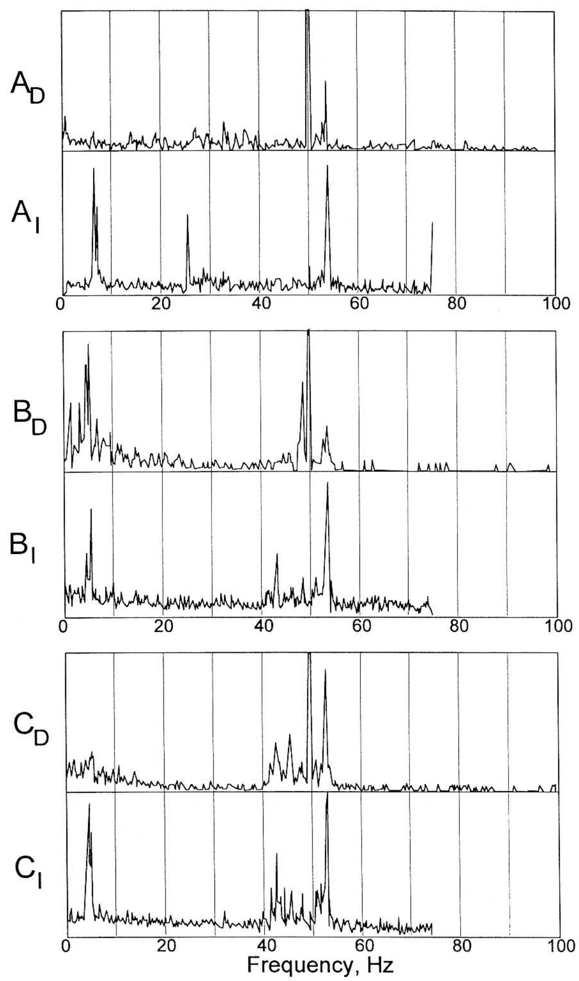

Fig. 3. Frequency spectra in the range of 0 to 100 Hz obtained in this study at temperatures of (A) 1600°C, (B), 1615°C, and (C) 1688°C. Spectra labeled with subscript D were obtained from the diode system, and those labeled with subscript I were obtained simultaneously with the video system.

A temperature in excess of 1670°C was maintained for a period of time (ca. 15 min), after which an oxide skin was seen to form spontaneously on the surface of the droplet, and the indicated temperature of the droplet would fall to ca. 1500°C. No explanation for this behavior has been found, and it will be the subject of a future study.

Analysis of the oscillation spectra (A_I, B_I, and C_I) from the video system, taken simultaneously with the diode system, is shown in Fig. 3. It can be seen that the spectra show good agreement for A_I and C_I with the diode system, but for B_I, the image analysis has been able to resolve more of the oscillation spectrum. It is possible that at the slightly lower temperature (A_D and A_I), the oxide reduces the oscillation amplitude beyond the resolution of the analysis system. Currently, the software cannot identify the individual oscillation modes and further work will be required to achieve this and decide the optimum resolution. It may then be possible to determine the modes occurring when nine oscillation frequencies can be resolved by the diode system. It should be noted that pyrometer calibration, which is usually performed by undercooling the sample and monitoring the apparent temperature during spontaneous recalescence to provide a correction of $T_{measured} - T_{solidus}$ cannot be performed when an oxide forms and may affect the emissivity of the material. SEM analysis of the droplets, made after rapid solidification, showed the following

- All droplets showed that the aluminium content (0.036 wt% of the original composition) had segregated to the surface and appeared in various compositions, including those rich in manganese or silicon. These are probably oxides.

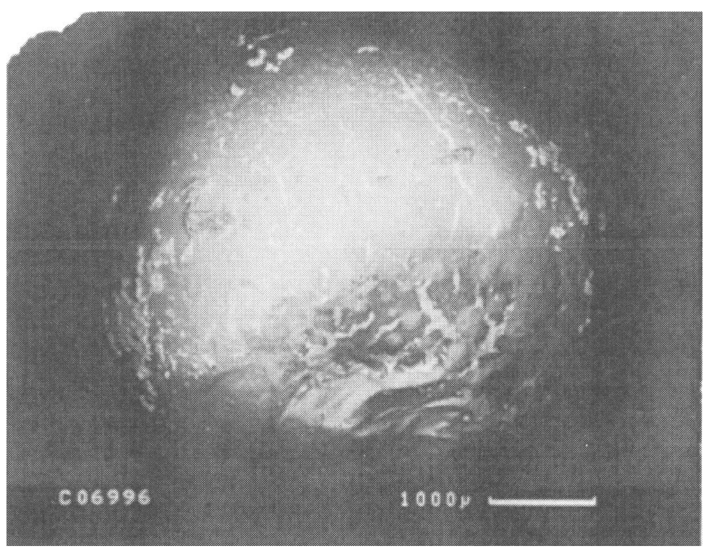

Fig. 4. SEM micrograph example showing aluminium-rich skin of varying thickness over the surface of a solidified drop.

- Copper (0.082 wt% of the original composition) also appeared in some regions.
- Several regions of predominant aluminium with a thickness of at least 1 μm were found.
- Most of the surface was covered by a thin aluminium-rich layer, probably less than 0.25 μm thick.
- Where the oxide skin was broken, regions of pure iron were found.

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