SURFACE TENSION MEASUREMENTS
OF HIGH TEMPERATURE METALLIC MELTS

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ABSTRACT

The surface tension of iron, nickel and aluminium was measured as a function of temperature using the oscillating droplet method combined with electromagnetic levitation. The measurements cover a wide temperature range, including the overheated as well as the undercooled regime. In addition, the effect of oxygen on the surface tension has been determined for the iron and nickel samples. When exposed to an oxygen/helium gas flow of constant composition and flux, the surface tension decreases exponentially with increasing exposure time. The oxygen content in the gas mixture was monitored by a gas analyzer using a zirconia transducer. In the case of aluminium, special care was taken to reduce the oxide skin from the surface of the sample prior to data acquisition.

INTRODUCTION

Capillary effects are of crucial importance in materials processing of melts like casting and welding. The driving force is the liquid-vapour surface tension $\gamma$. For high-temperature, and highly reacting melts, the oscillating drop technique provides a non-contact method for its measurement [1]. This technique not only allows to perform measurements at high temperatures ($>1000 \degree C$), but also the gas phase surrounding the liquid drop can be controlled to a great extent. This is particularly important with respect to oxygen, which is surface active in all metals and reduces the surface tension considerably. In fact, data on surface tension of reactive elements like iron and nickel are of little relevance, unless the experimental conditions and, in particular, the oxygen partial pressure, are specified.

EXPERIMENTAL SETUP

The apparatus for surface tension measurements consists of a small ultrahigh vacuum chamber and an optical system as shown in Fig.1. The levitation coil is powered by a 25 kW high frequency generator operating at 490 kHz. For the contactless temperature measurement, a single color pyrometer was used, calibrated at the melting temperature. The pyrometer covers a temperature range from 550 to 2000$\degree C$ at one wavelength and looks at the sample from the top over a mirror system. The samples have a diameter of typically 6 mm. During the experiments the sample temperature was controlled and maintained by varying the gas flow through the sample holder. The gases used were highly pure He/H$_2$ (99.9999%) for the surface tension measurement and a mixture of He (99.999%) and O$_2$ (99.999%) for the oxygen measurements. For the latter measurements the levitation facility was combined with a Xentra 4100 gas purity analyzer. A zirconia oxygen sensor measures oxygen concentrations from trace level (1 vpm) to 100% accurately.

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Surface tension was measured using the oscillating drop method. This technique utilizes the relationship between the oscillation frequency and the surface tension of a levitated liquid and spherical droplet derived by Lord Rayleigh [2]:

\[ \gamma = \frac{3}{32\pi} M \omega_{nm}^2 \]  

(1)

where \( \gamma \) is the surface tension of the liquid, \( M \) is the mass of a droplet, and \( \omega_{nm} \) is the oscillation frequency of the fundamental mode \( l = 2 \).

Under experimental conditions on earth, the Rayleigh frequency splits into five unequally spaced peaks caused by an aspherical equilibrium shape and rotation of the oscillating droplet. This situation has been considered by Cummings and Blackburn [3]. They have derived the following frequency sum rule to calculate the surface tension:

\[ \gamma = M \frac{3}{32\pi} \left[ \frac{1}{5} \sum_{nm=2}^{1} \omega_{nm}^2 - \omega_0^2 \left( 1.9 + 1.2 \frac{z_0^2}{R^2} \right) \right] \]  

(2)

with

\[ z_0 = \frac{g}{2 \omega_0^2} \]  

(3)

where \( \omega_0 \) is the translation frequency, \( R \) is the radius of the droplet and \( g \) is the gravitational acceleration. The reliability of the correction formula was confirmed by measurements on ground and in space [4].

For the recording of the surface oscillation of the liquid specimen (= 50 Hz), a high speed CCD video camera was used at 100 Hz with a spatial resolution of 192 x 572 pixels. It takes images of the sample from the top. The acquired images were recorded on video tapes.
RESULTS

We have determined the effect of oxygen on the surface tension of the pure elements, iron and nickel [5]. The specimens of 99.999% purity were levitated and overheated up to 300 °C above the melting temperature in a He/H₂ environment. Then the samples were levitated in an adjusted He/O₂ gas flow at a constant temperature. The surface oscillations were recorded as a function of time. Figures 2 and 3 show how the surface tension values decrease with increasing time in a helium atmosphere containing 0.5 vpm oxygen.

Figure 2. Surface tension of iron in a helium atmosphere with 0.5 vpm oxygen as a function of time at different temperatures.

Figure 3. Surface tension of nickel in a helium atmosphere with 0.5 vpm oxygen as a function of time at different temperatures.
After approximately 7 minutes for iron and 15 minutes for nickel, the oxygen concentration at the surface reaches a stationary value and the surface tension remains constant. In this region, the temperature dependence of the surface tension can be studied and is shown in figures 4 and 5 respectively for an oxygen concentration of 0.5 vpm at the inlet. For comparison, the values of the pure elements taken from Sauerland [6] are also shown. As to be expected, the surface tension is reduced by the presence of oxygen. Surprisingly, however, the slope, \(-\frac{\partial \gamma}{\partial T}\) is steeper for the iron sample exposed to 0.5 vpm oxygen than for pure iron. This may either be due to a residual oxygen concentration in the “pure” sample, or to the fact that, especially at lower temperatures, the stationary state with respect to oxygen concentration has not yet been reached.

For iron in 0.5 vpm O\(_2\) we find:

\[
\gamma_{\text{Fe}}(T;[O_2] = 0.5\text{vpm}) = 1722 - 0.56(T - 1536^\circ\text{C}) \text{ mN/m}
\] (4)

while we obtain for nickel:

\[
\gamma_{\text{Ni}}(T;[O_2] = 0.5\text{vpm}) = 1733 - 0.26(T - 1453^\circ\text{C}) \text{ mN/m}
\] (5)

For nickel, the slope of the surface tension measured in the presence of oxygen is smaller than for pure nickel.

![Figure 4](image_url)

**Figure 4.** The surface tension of iron as a function of temperature in a helium atmosphere containing 0.5 vpm oxygen. For comparison, the result for pure iron, taken from Sauerland [6] is also shown by the dashed line. The melting temperature \(T_m\) is indicated by the dotted vertical line.
Finally, we have also measured the surface tension of liquid aluminium [7]. In this case, the aim was to obtain data for pure aluminium, i.e. to reduce the oxygen content of the surrounding atmosphere as much as possible. The oxide skin which covers the droplet’s surface at temperatures near the melting point, was reduced by strongly overheating the sample in 0.1 mbar He. Above approximately 900 °C, Al₂O₃ is transformed into volatile Al₂O which leads to a purification of the sample [8]. The measurements were performed sequentially, starting from high temperatures and reducing the temperature stepwise.

In Fig. 6 the experimental data on Al with 99.9999 % purity (dataset #1) and of commercially pure Al (dataset #2) are presented in comparison with the results obtained by the sessile drop method [9, 10]. In addition, the mean γ(T)-relation according to Keene [11] which is derived from data obtained by different authors is also included. Due to the limited number of data points no significant difference between the two types of Al samples can be derived. Both datasets together can be fitted to a linear relation and we obtain

\[ \gamma_d(T) = 881 - 0.2(T - 660^\circ C) \text{ mN/m} \]  

(6)

which is in good agreement with previously published data [9-11]. Nevertheless, the data measured must be considered with some caution. Due to the high temperatures needed for the purification process, there is a strong evaporation from the sample. This can lead to a mass loss at high temperatures, which according to eqn (1) yields a too high apparent surface tension value. On the other hand, the evaporated material coats the windows in the optical path of the pyrometer, leading to a too low temperature. Accordingly, the data points plotted at apparent temperatures below the melting point, may indeed correspond to higher temperatures and are probably too high by 1-5%.
Figure 6. Surface tension of aluminium measured by the oscillating drop technique (dataset #1: Al 99.9999%, dataset #2: commercially pure Al) and by the sessile drop technique [9, 10] as a function of temperature. The full line is the linear fit to our experimental data. The dashed line is the $\gamma(T)$-relation recommended by Keene [11] on the basis of sessile drop measurements where the scatter of these data points is indicated by the shadowed area. The melting temperature $T_m$ is shown by the dotted vertical line.

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