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Surface Tension Measurements of Refractory Liquids using the Modified Drop Weight Method

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Liquid surface tension measurements using the sessile drop, pendant drop and drop weight methods are discussed. These measurements refer to high temperature materials which melt at temperatures greater than 2000° C. The liquid surface tension of copper was determined to be 1212 dyn/cm at its melting point, and that of Al_2O_3 to be 600 dyn/cm at its melting point. Discussion is presented giving preference to the drop weight method.

1. Introduction

Within the last ten years, much work has been done on high temperature materials in the range 2000 to 3000° C. In this temperature range, very little data concerning physical properties of materials have been noted in the literature. In particular, the liquid surface tension measurements of refractory materials have been very limited. This has probably been a result of the experimental problems encountered in making such measurements. The liquid surface tension at the melting point of Al_2O_3 is one of the few measured. Von Wartenberg *et al* [1] reported 500 to 640 dyn/cm; on the other hand, Kingery [2], using the pendant drop method, reported the value 663 to 713 dyn/cm. Liquid surface tension measurements on other common metal oxides such as MgO, CaO, ZrO_2, and Cr_2O_3 have not been reported. Since liquid surface tension is an important property in the determination of the viscosity of molten liquids, and in thermodynamic calculations such as surface entropy and surface heat content, it was decided to attempt some liquid surface tension measurements at the melting point.

2. Discussion of Methods

In the literature, there are three commonly used techniques for measuring liquid surface tension. First is the sessile drop method [3-5] which requires the formation of a liquid drop of the test material resting on an inert plate; the dimension of the drop is then measured. This measurement generally employs the use of photography, which is an indirect measurement, and can give inaccurate results. Another important consideration in using the sessile drop method is the choice of material which supports the drop; any chemical reaction or wetting by the support material will adversely affect the measurements.

The second method is the pendant drop technique [6]. Here, a liquid drop of the test material is formed on the end of an inert rod. The dimensions of the drop are measured either photographically at high temperature, or measured directly at low temperature by quenching the liquid drop into the solid state.

It was the desire of the authors to measure the surface tension of refractory materials (melting point >2000° C) at their melting points. The sessile drop and pendant drop methods were tried, but the experimental problems are considerable. In these methods, the critical data depend on the correction factor (F) for the shape of the drop. The correction factor in turn depends on the melting point and liquid density. Accurate experimental determination of these factors is difficult [7]. Al_2O_3 is used as an example, because it is the only refractory oxide for which

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these properties are reported in the literature. The density of Al_2O_3 at the meltıng point is reported as 2.5 [1], 2.97 [2] and 3.03 [8]. The melting point is reported between 1900 to 2072° C [9]. These differences limit the accuracy of the surface tension measurements using the sessile and pendant drop methods.

In both methods, the error inherent in the dimensional measurements cannot be avoided, and the density value is controversial. The presence of pores, which are difficult to detect and to eliminate in the drop, will affect the measurements. Numerous experiments have been attempted, using these two methods in our laboratory, to measure the liquid surface tension of Al_2O_3 at the melting point. Results were scattered in an inconsistent manner. With materials that melt at temperatures above 2000° C, suitable contact materials that have high melting points, and do not react or wet, are difficult to obtain. It was after consideration of the above problems that the drop weight method was employed.

This method is normally used for low temperature liquid surface tension measurements. It consists of passing the liquid to be measured through a glass tube. The weight of the liquid drop and the radius of the tip of the glass tube are employed to calculate the surface tension, using the equation $\sigma = mgF/r$, where σ is the surface energy in dyn/cm, mg is the weight of the drop in grams, F is the correction factor, and r is the radius of the tip of the glass tube in cm. The correction factor (F) is determined by calculating the volume (V) of the drop from the weight of the drop and its liquid density. F is obtained from the set of tables [11] for V/r^3, where r is the radius of the glass tube tip. It was found that variations in the liquid density resulted in an insignificant change in the V/r^3 term. The most significant factor in the surface tension calculation is the weight of the drop. The weight of the drop and the radius of the tip can be measured very accurately.

It is impossible to find a "glass tube" that will contain a liquid at 2000 to 3000° C. Therefore, Peterson *et al* [10] melted the ends of the solid Ti, Zr, and Hf rods and used the radius of the rod and weight of the liquid metal drop in each case to calculate the surface tension of these metals at their melting points. They did not discuss the validity nor present any experimental confirmation on the values measured using this modified drop weight method.

3. Experimental

The surface tension of Al_2O_3 and Cu were determined using the modified drop weight method, in which rods of the material were suspended in an induction furnace through a specially designed water-cooled lid [12]. It was observed in this laboratory that the flow of the argon gas in the furnace caused the drop to fall from the rod prematurely, thereby resulting in low weights. To avoid this, the flow gas was turned off just before the first drop formed.

In the case of Al_2O_3, a single-crystal sapphire rod was used. The rod was suspended through a water-cooled protrusion on a water-cooled stainless-steel lid before the experiment was started (fig. 1). The lid acted as a cover for the induction furnace. The furnace was then heated slowly to the melting point of Al_2O_3 (2043° ± 10° C) [7, 12]. The pyrometer was sighted directly on the sample through a fused-silica window. At the melting point, drops formed on the end of the rod, and were allowed to fall through the furnace, and out of the bottom into water. The drops were weighed using an analytical balance. The surface tension was calculated from the weight of the drops and the radius of the rod, using the equation previously described.

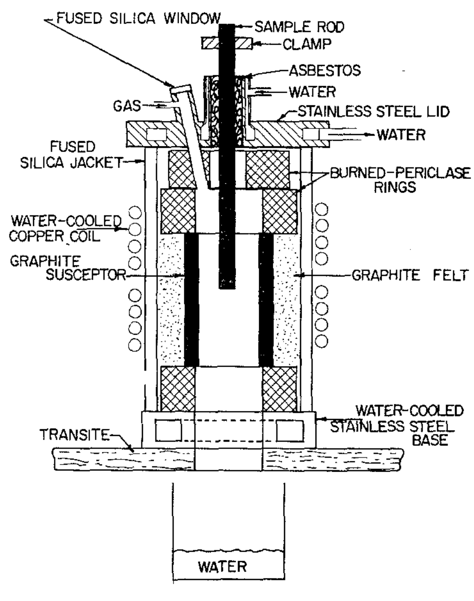

Figure 1 Induction furnace used for the modified drop weight surface tension measurements.

4. Discussion and Conclusions

To check the validity of the modified drop weight method for the case in which the glass tube is replaced by a rod of the test material, we first measured the liquid surface tension of copper. The surface tension of liquid copper near the melting point was previously found to be 1103 to 1350 dyn/cm, using the sessile drop, pendant drop, and bubble pressure techniques [13]. Our resulting value for the surface tension of copper is an average of 1212 dyn/cm near the melting point. This indicates that the modified drop weight method for liquid surface tension determinations is reasonable.

The value obtained for Al_2O_3 is an average of 600 dyn/cm at its melting point. The Al_2O_3 value is reasonable because 905 dyn/cm at 1850° C in the solid state is reported by Livey [14], and the surface tension decreases with increasing temperature. The liquid surface tension of Al_2O_3 at the melting point has been reported in the literature as from 551 [15] to 690 [2] dyn/cm. Using the correlation of the surface tension of the liquid metal and that of the liquid metal oxide at their melting points, as described by Eberhart [16], it can be shown that the value of 600 dyn/cm for the liquid surface tension of Al_2O_3 falls on the curve.

From the comparison of liquid surface tension measured by the modified drop weight method to those measurements reported in the literature, it is reasonable to believe that this method is as accurate as, if not more accurate than, the pendant drop and sessile drop methods for measuring liquid surface tension values of high temperature materials. This method does not require an inert material or an accurately known liquid density value to determine the liquid surface tension of high temperature materials.

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