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Surface Tension of Liquid Alumina from Contactless Techniques[1]

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New data for the surface tension of liquid alumina from 2300 to 3200 K are reported. Aerodynamic levitation of CO_2 laser-heated liquid drops allowed contactless measurement of vibration frequencies directly related to surface tension. Consistent data were obtained on drops of different mass ranging from 20 to 160 mg. It was also shown that the oxydo-reducing character of the atmosphere does not modify the results within experimental uncertainty.

KEY WORDS: high temperature; levitation; liquid alumina; surface tension.

1. INTRODUCTION

High temperature properties of liquid alumina have become an industrial challenge particularly in the aerospace domain. Large quantities of liquid alumina are produced when aluminized propergol is burned in solid rockets. The aerodynamic behavior of these liquid residues (temperature being about 3500 K) may produce desired or undesired effects on the efficiency or lifetime of the rocket. Modeling of the aerodynamic properties assumes reliable values of the properties of liquid alumina up to very high temperature.

We have described in previous papers methods of levitation [1, 2], which are particularly well suited to very high temperature studies. They were used to determine the density of liquid alumina. Present work deals with the surface tension of the liquid. The principle of this measurement comes from relations between vibration frequencies n of liquid drops and surface tension s that acts as a spring restraining the liquid drop from

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going very far from a spherical shape. Lord Rayleigh [3] was first to deduce the relation for a spherical drop of weight m:

$$\sigma = 3\pi m v^2/8 \tag{1}$$

Deviations from spherical shape and rotation of the drop modify the vibrations leading to situations where not only one but three or five frequencies must be measured to deduce surface tension. We have recently analyzed situations frequently encountered with aerodynamic levitation [4]. We will refer to this previous work in the present paper and concentrate on the other aspects of measurements.

2. EXPERIMENTAL METHODS

2.1. Levitation Setup

Critical aspects of measurement of high temperature properties are:

- prevention of sample contamination
- homogeneity of temperature
- control of atmosphere.

In order to fulfill these requirements, a two-laser levitation setup has been designed which is schematically shown on Fig. 1. It consists of a convergent-divergent nozzle where gas is flowed with a typical flux of 1 $1 \cdot m^{-1}$.

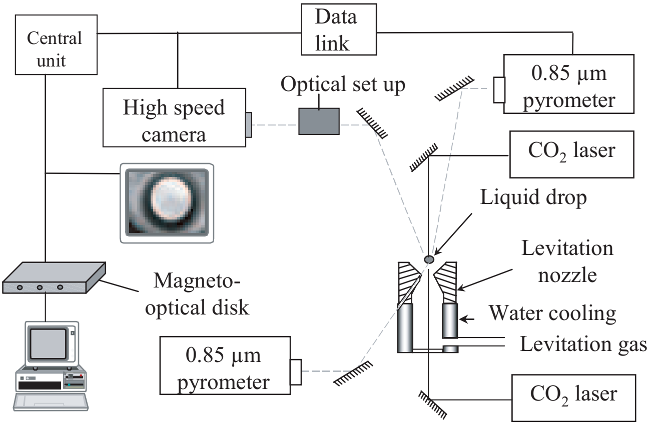

Fig. 1. Two-laser levitation setup for surface tension measurements.

It maintains a drop in levitation. Typical diameters of drops are between 2 and 5 mm.

In contrast to our previous design [2], two 120 W lasers are used to heat efficiently the liquid drop in the nozzle. To that end, the angle of the convergent part of the nozzle is 30 degrees as compared to 60° for the upper part of the nozzle allowing the beam coming from the lower laser to be concentrated from 8 mm diameter to 2 mm diameter by a single or double reflection on the nozzle walls (the drop diameter is larger than or equal to 2 mm).

A small hole is drilled obliquely in the nozzle in order to measure the temperature of the bottom of the drop with a pyrometer. This hole modifies the axial symmetry of the levitation setup and forces the rotation of the drop on a horizontal axis with a typical rotation speed of a few Hz. This movement helps in minimizing temperature gradients.

The image of the drop obtained with a digital high-speed camera (Kodak Ektapro 1000 HRC) indicates, as seen in Fig. 1, a quite homogeneous gray level of the drop apart from a brighter ring, which is due to the light emitted by the drop and doubly reflected by the nozzle walls and the drop itself. An optical setup is adjusted to get the drop image with diameters of 250 to 300 pixels.

The power of the two lasers is adjusted in order to have the same temperature with the two calibrated pyrometers, ensuring an optimized homogeneity of temperature. The coldest point of the drop is at the shortest distance from the nozzle and corresponds to the hidden part of it.

An indirect proof of temperature homogeneity is found in the cooling curve of the two-laser heated drop. Figure 2 reveals that, apart from the fact that it follows a perfect $1/T^3$ law expected for perfectly radiative cooling, there is almost no heat redistribution in the drop after the lasers are turned off. In other words, the $1/T^3$ law acts immediately after the shut-off. From previous experience with one-laser heated alumina [2] which induces temperature differences of 200 to 300 °C between the top and bottom of a 3-mm diameter drop, it can be safely concluded that the temperature homogeneity of the two-laser heated drop is much better than 100 °C. A term of comparison is found by the estimated 30 °C difference at 2000 °C between the surface and the center of a free cooling 3 mm alumina liquid drop.

Figure 2 also shows the recalescence, which accompanies the solidification of the strongly undercooled liquid. The temperature plateau of solidification (not completely shown on Fig. 2) which lasts approximately 1 s is used to calibrate the pyrometers, using the known melting point of alumina, 2327 K. The transparency of solid alumina in the visible region probably helps to measure a mean temperature below the surface of the

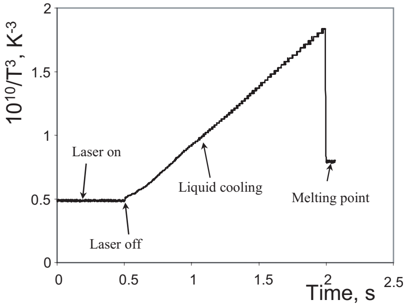

Fig. 2. Cooling curve and recalescence of two laser-heated liquid alumina levitated in oxygen.

semitransparent liquid at some depth, which depends on its absorption coefficient and on the wavelength of the pyrometer [2]. In practice, it is observed that the solidification plateau is not dependent on the previous history of the liquid drop and is also not dependent on the nature of the levitating gas.

2.2. Materials

Alumina comes from 15 mg hollow spheres from Rhone–Poulenc Company obtained by quenching liquid drops in water. We have prepared weighted and purified alumina drops between 4 and 160 mg by overheating (3000 K) levitated spheres in argon.

Various gases have been used for levitation: pure oxygen, pure argon, and mixtures of argon containing 5% hydrogen. The purity of argon-containing gases is of the order of 5 to 10 ppm of O_2 and H_2O. Oxygen contains 10 ppm H_2O impurity.

The nozzle is made of a commercial aluminium-based alloy. This material has the double advantage that it is not a pollution source for alumina if accidental contact happens between the drop and the nozzle, and it is a good metal which is easy to cool and which reflects almost perfectly the 10.6 μm laser beam.

2.3. Image Analysis

Surface tension is derived from vibration frequencies of the liquid drop. We, then, need to measure geometrical properties of the drop as a function of time. The principle of this measurement is similar to that already described in our previous work on liquid alumina density [1].

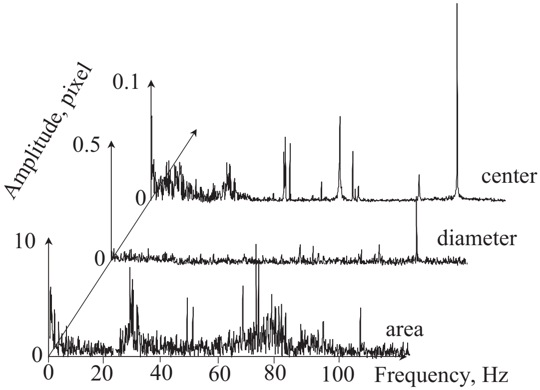

Fig. 3. Fourier transforms of geometrical characteristics of an 83 mg liquid alumina drop heated at 2420 K and recorded at 250 frames/second.

Sequences of 2700 successive images at 250 to 1000 frames per second were transformed to binary images and finally to tables of diameters, areas, and geometrical centers of drop versus time. Fourier transforms were applied to these data in order to detect peak frequencies. An example is shown in Fig. 3.

The common characteristics of the three spectra are as follows:

- Amplitudes are very small, for instance, from the sum of the amplitudes of frequency peaks of the geometrical center, a prediction of total amplitude of the lateral movement of the drop of less than 10 μm can be made. Likewise, the 10 pixel full scale of the area equally means that the relative breathing amplitude is less than 10^{-3}. The ratio of expected signal to noise is too small to predict correctly the shape and the position of vibration peaks of the drop.
- The sharp peaks are always found at the same frequencies and characterize vibrations coming from rotating engines (cooler, compressor etc.) in the vicinity of the experiment and from artifacts of the 50 Hz European current.

The area spectra may be described by three frequency regions having broad signals:

- below 10 Hz, amplitudes are increasing inversely to frequency.
- around 25 Hz, there is always a broad peak whatever the size of the drop and the nature of the gas. We believe that it corresponds to an acoustic frequency characteristic of the geometry of the gas circuit.

- around 75 Hz, a broad peak is found. The position of this peak depends on the mass of the drop. It is presumed that it corresponds to its natural vibrations.

In order to increase the ratio of signal to noise, approximately 8 sequences of 2700 frames for every drop have been collected. The drops were left free to cool immediately after every sequence, and they were weighed in order to verify that mass loss was less than 1%. When evaporation occurred, grains of alumina were added in order to keep the mass approximately constant during the 8 measurement cycles. Averaged Fourier spectra have been deduced from these data, which are used as the basic information for the evaluation of surface tension.

3. RESULTS

We have already analyzed the relations between characteristic frequencies of vibration and surface tension [4]. With the experimental conditions described above, characteristic frequency spectra with three equally spaced peaks are expected. The surface tension σ is related to the mass m of the drop and the mean frequency ν by Eq. (1). Examples of Fourier transforms are shown in Fig. 4.

The high frequency part of the spectra shows characteristic masses of peaks. At the highest temperature and for the lightest drops (around 20 mg), three equidistant peaks are clearly separated with the distances between these three peaks being a direct measure of the rotation speed of the drop (we could verify in some instances changes of the position of the two

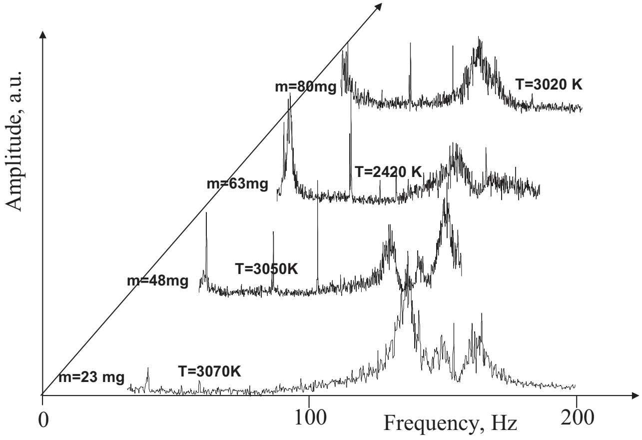

Fig. 4. FFT spectra of liquid alumina vibrations in oxygen.

extreme peaks without change of the position of the central peak during successive recordings). The central peak amplitude is generally smaller than that of rotation satellites, and this may make the assignment of the central peak difficult (for instance, on the two upper curves), particularly when the rotation peak width is large (at lower temperatures) or when the distance between peaks is small (for heaviest drops, >80 mg). The width of peaks is a measure of an apparent viscosity resulting from the true viscosity of the liquid and convection. It is difficult to modify this parameter in order to improve the definition of the vibration frequency.

Experiments have been performed in oxygen and in a mixture of argon with 5% H_2. Influence of drop mass changes have also been examined. The data are shown in Fig. 5.

Some data scatter is observed which is difficult to assign to mass change. It is certainly the ill-defined position of the vibration frequency peak that accounts for the spread of surface tension measurements.

Comparison between data obtained in oxygen and in Ar/H_2 indicates a slight effect of the atmosphere, values in oxygen being 5% higher than in a reducing atmosphere.

For practical purposes, the following equation represents the data:

$$\sigma = 0.65 \times (1 - \alpha \times (T - 2500))\ \mathrm{J \cdot m^{-2}} \tag{2}$$

with T in K and the surface tension temperature coefficient $\alpha = 6 \times 10^{-5}\ \mathrm{K}^{-1}$.

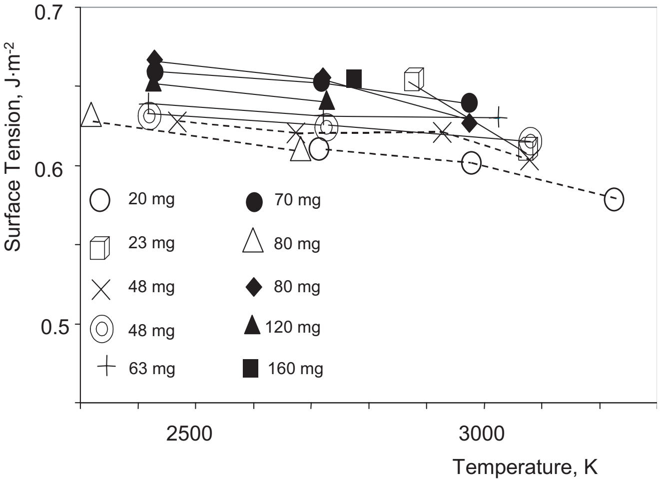

Fig. 5. Surface tension versus temperature of various liquid alumina drops in O_2 (full lines) and Ar-H_2 mixtures (dashed lines).

4. DISCUSSION

We have previously reported data for the density of liquid alumina. One of the main conclusions of this work was that comparison with previous data obtained with crucible techniques revealed the dramatic effect of crucible pollution at 3000 K. The same conclusion can be drawn from the same comparison for surface tension (see Fig. 6).

We have already published an analysis of literature results [17]. Many different techniques have been used in the past to measure the surface tension of liquid alumina, most of them in a crucible at the melting temperature. With the exception of the drop weight technique, all other methods are measurements of the ratio of surface tension to specific weight. Our data are, then, the first direct measurement obtained at very high temperature.

The variations of surface tension with temperature (approximately $(6 \pm 2) \times 10^{-5}\ \mathrm{K}^{-1}$) can be compared with that obtained in our former study of density of liquid alumina, $4 \times 10^{-5}\ \mathrm{K}^{-1}$. These two values are not very different, and this is what is expected from simple considerations [18] on semiconductor melts.

Another comparison is that of the surface entropy, $S_\sigma = dv/dT$ for a large number of compounds. This has been already done by Lyklema [19]

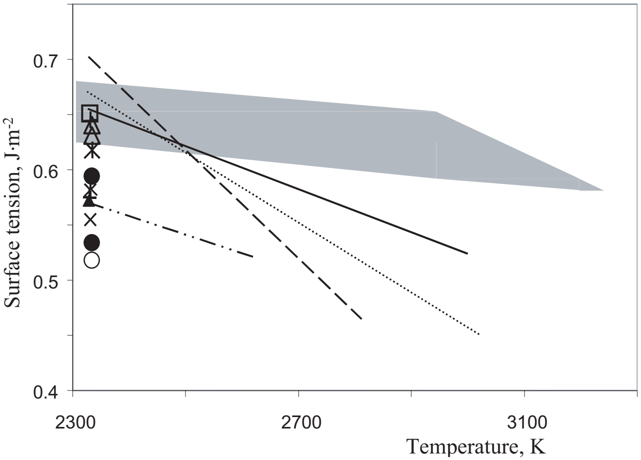

Fig. 6. Comparison of published surface tension: grey area corresponds to our data. (–––) Zubarev et al. [5], (···) Shpil'rain et al. [6], (—) Elyutin et al. [7], (–··–) Elyutin et al. [8], (○) Bartlett and Hall [9], (●) Rasmussen [10], (×) Ikemiya et al. [11], (⁎) Lirhmann and Haggerty [12], (▲) McNally et al. [13], (+) Wartenberg et al. [14], (△) Maurakh et al. [15], (□) Kingery [16].

who examined the data available mainly on halogenides, sulphates, nitrates, and metals. S_σ was found in the range 0.05 to 0.17 $\mathrm{mJ \cdot m^{-2} \cdot K^{-1}}$ which should be compared to our value for alumina: $0.04 \pm 0.01\ \mathrm{mJ \cdot m^{-2} \cdot K^{-1}}$. It was concluded by this author that contrary to the surface energy, the surface entropy is a generic property. Our result compares favorably with other available results. It is difficult to get into a more detailed analysis because it presumes many hypotheses on the composition and the structure of the liquid surface and volume that are not known for alumina.

5. CONCLUSION

Surface tensions of liquid alumina between 2300 and 3200 K have been obtained from the vibration frequencies of levitated droplets of various masses and in various atmospheres. The results indicate that the typical scatter between data is approximately 5%. The typical value of surface tension is $(0.650 \pm 0.03)\ \mathrm{J \cdot m^{-2}}$ at 2500 K with a temperature coefficient of $6 \times 10^{-5}\ \mathrm{K^{-1}}$. Comparison with literature values stresses the importance of contactless diagnostics at very high temperature.

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