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Measurement of the Surface Tension of Undercooled Liquid $Ti_{90}Al_6V_4$ by the Oscillating Drop Technique[1]

S. Schneider,[2,3] I. Egry,[2] and I. Seyhan[2]

The surface tension of liquid $Ti_{90}Al_6V_4$ was measured. The samples have been processed containerlessly by electromagnetic levitation, which allows the handling of highly reactive materials and measurements in the undercooled temperature region. The use of digital image processing allows the identification of oscillation modes and calculation of the surface tension from the $l = 2$ and $m = 0$, $m = 2$ oscillation modes. A linear least squares fit to the data showed the following temperature dependence:

$$\gamma = 1.389 \pm 0.09 - 9.017 \times 10^{-4} \pm 5.64 \times 10^{-5}(T - 1660\,°\mathrm{C}) \quad [\mathrm{N \cdot m^{-1}}]$$

KEY WORDS: liquid metal; surface tension; titanium alloy.

1. INTRODUCTION

The surface tension of liquid metals is of both technical and scientific importance. It is a central parameter for casting and welding processes and is also relevant for wetting phenomena.

One method for measuring the surface tension is the oscillation drop technique. This method uses the oscillation frequencies of a levitated droplet to determine the surface tension. As a containerless technique, it has the advantage to avoid impurities and can be used to undercool the liquid below its solidus temperature due to the reduction of the heterogeneous solidification. It is also possible to observe the oscillations of the liquid droplet without distortions from a mechanical contact of a support

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[2] Institut für Raumsimulation, DLR, Linder Höhe, D-51170 Köln, Germany.

[3] To whom correspondence should be addressed. E-mail: stephan.schneider@dlr.de

(as in the sessile drop method). Due to the absence of a container, it provides a good possibility to process highly reactive materials at high temperatures, which is necessary for a material such as $Ti_{90}Al_6V_4$ with a liquidus temperature of 1660°C [1]. The reason for the investigation of $Ti_{90}Al_6V_4$ is its importance in the medical field, because it is an often used alloy for medical implants. The surface tension is one of the parameters, which is crucial for the casting of the implant.

2. MEASUREMENT TECHNIQUE

With the oscillating drop method the frequency of surface oscillations of the sample around the equilibrium shape is measured. According to Rayleigh [2] the relation between the surface tension γ of a nonrotating spherical sample and the oscillation frequency ω_R (called Rayleigh frequency in the following) is given by the Rayleigh law:

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

$l > 1$ is an integer, which is explained later. The mass M of the droplet is determined by weighing or can be calculated via the density

$$M = \frac{4\pi}{3} R^3 \rho \tag{2}$$

where ρ is the density of the liquid metal and R is the radius of the sphere.

The deformed sample shape is described with spherical harmonics:

$$R(\vartheta, \varphi, t) = \sum_l \sum_{m=-l}^{m=+l} a_{l,m}(t)\, Y_l^m(\vartheta, \varphi) \tag{3}$$

where l and m are the indices of the spherical harmonics. The oscillation frequency is $2l+1$-fold degenerate. In electromagnetic levitation the lowest observed oscillation mode belongs to $l = 2$. Oscillation modes with $l > 2$ are not observed, because of their strong damping. The geometry of the oscillations for $l = 2$ and $m = 0$ is shown in Fig. 1 and for $l = 2$ and $m = 2$ in Fig. 2.

Under real experimental conditions the Rayleigh frequency splits into five unequally spaced peaks caused by the magnetic force on the sample, aspherical shape, and rotation of the sample. The degeneracy of the oscillation frequency is cancelled and the oscillation frequencies for $m = -2$,

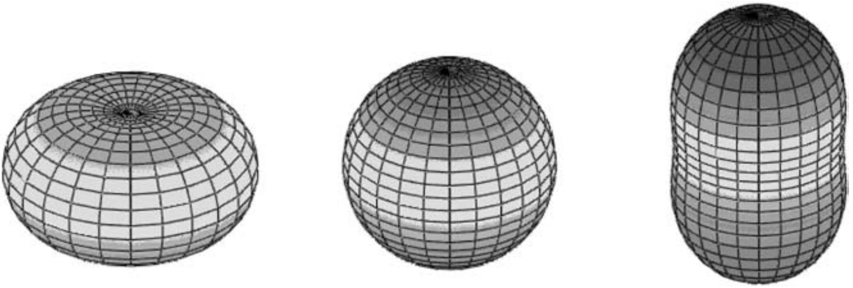

Fig. 1. Geometry of the $l=2$, $m=0$ oscillation mode.

$-1, 0, 1, 2$ are distinguishable [3, 4]. Cummings and Blackburn [3] calculated a formula to derive the Rayleigh frequency from these shifted oscillation frequencies $\omega_{2,m}$ (in our experiments only the $|m|=2$ and $m=0$ was visible, see Figs. 3a and b):

$$\omega_{2,0}^2 = \omega_R^2 + \omega_t^2 \left(3.832 - 0.1714 \frac{z_0^2}{R}\right) \tag{4}$$

$$\omega_{2,2}^2 = \omega_R^2 + \omega_t^2 \left(-0.9297 + 2.571 \frac{z_0^2}{R}\right) \tag{5}$$

with

$$z_0 = \frac{g}{2\omega_t^2} \tag{6}$$

where ω_R^2 is the Rayleigh frequency for $l=2$, ω_t^2 denotes the mean translation frequency of the sample, and g is the gravitational acceleration. During the experiment the oscillation frequencies $\omega_{2,0}$, $\omega_{2,2}$ and the translation frequency ω_t are measured. Then, with the help of Eqs. (4) and (5), the Rayleigh frequency ω_R can be calculated via Eq. (1) from which

Fig. 2. Geometry of the $l=2$, $m=2$ oscillation mode.

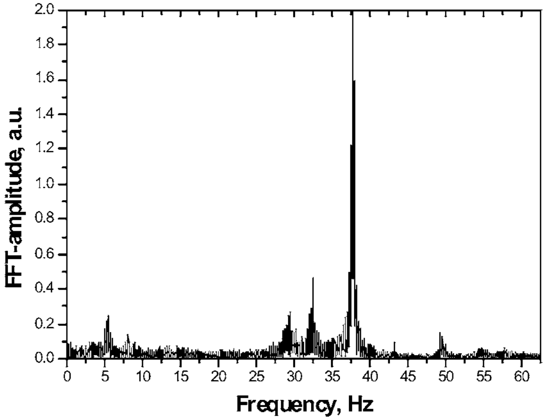

Fig. 3a. Spectrum obtained from the digital image processing.

the surface tension is finally determined. Processing of the data with digital image processing enables the association of the oscillation modes with the corresponding oscillation frequencies [5]. These oscillation frequencies $\omega_{2,0}$ and $\omega_{2,2}$ are the input data for the above formulas.

3. EXPERIMENT

We used industrial grade material of nominal composition Ti90 at% Al6 at% V4 at% for the sample preparations. Samples have been cut from a

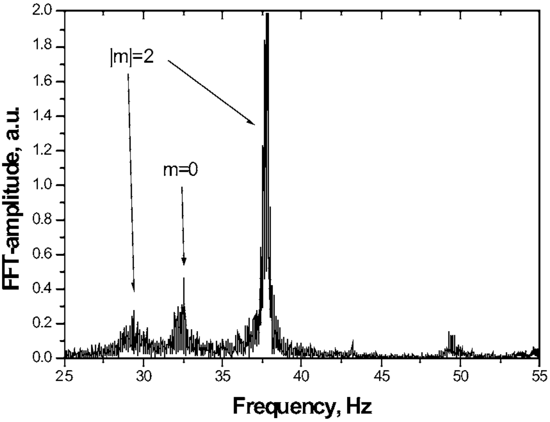

Fig. 3b. Section of the spectrum, the oscillation frequencies for the $m = 0$ and $m = 2$ oscillation mode are marked with arrows.

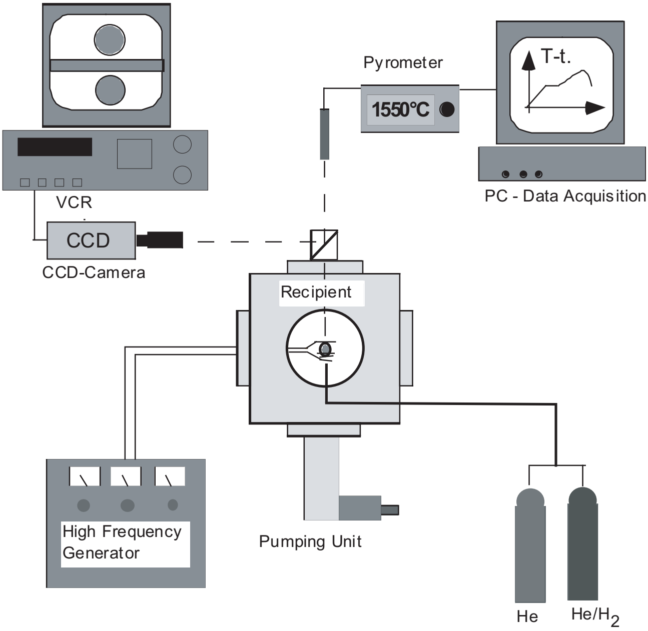

Fig. 4. Experimental setup of the levitation facility.

rod; the surface was polished with Si-C polishing disks and cleaned in an ultrasonic bath. To get a sample form which is suitable for our levitation facility, the sample was finally melted to a sphere in an arc furnace.

The electromagnetic levitation facility consists of a small ultrahigh-vacuum chamber and an optical system which is shown in Fig. 4. For further details concerning the electromagnetic levitation, see Ref. 6. The levitation coil is powered by a 24 kW Huettinger HF-generator operating at 300 to 500 kHz. A schematic of the facility is given in Fig. 4. The temperature, which is controlled by convective cooling with helium gas (99.999% purity), was measured with a single-color infrared pyrometer covering a temperature range from 550 to 2000°C. The liquidus temperature T_{liq} was taken as $T_{\text{liq}} = 1660$°C from the phase diagram [1], and the emissivity was adjusted such that the pyrometer reproduced this temperature at the end of the melting plateau.

The surface oscillations of the liquid droplet were observed with a digital camera with a frame rate of 125 Hz and for one measurement we recorded 8192 images. Via digital image processing, we determined two perpendicular diameters of the sample, the area and the coordinates of the center of mass and their dependence on time. From a fast fourier transformation (FFT) of the monitored sample diameter changes with time, we obtained the frequency spectra of the surface oscillations and sample translations. From these data and the equations of Cummings and Blackburn, the surface tension can be calculated.

The image processing also relates an oscillation frequency with the appropriate oscillation mode by comparison of different frequency spectra. This is necessary because the correction terms in the Cummings and Blackburn equation depend on the observed oscillation mode. As can be seen in Figs 3a and b, we did not observe the $|m| = 1$ mode. In some spectra it has been possible to evaluate three oscillation peaks and calculate the values of the surface tension from the $m = 0$ and $|m| = 2$ modes, while in other spectra only the $m = 0$ mode was clearly visible and so only one oscillation frequency could be used for the calculations.

4. RESULTS

We measured the surface tension of $Ti_{90}Al_6V_4$ over a broad temperature range of 340 °C and for undercoolings of 200 °C. In Fig. 5, we present the measured surface tensions. As mentioned above, surface tension values from the $m = 0$ and $|m| = 2$ modes could not be obtained in all spectra, so

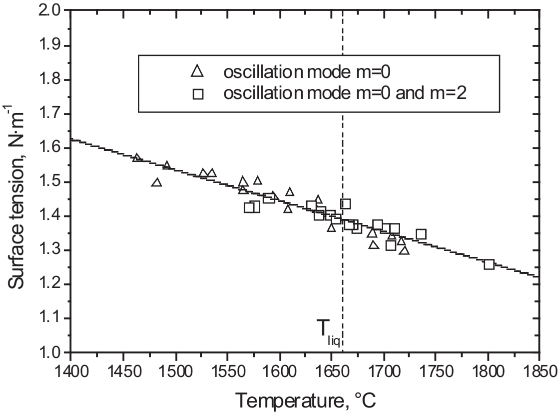

Fig. 5. Surface tension as a function of temperature. The open squares represent data where only the $m = 0$ oscillation mode was evaluated and the open circles show values resulting from the analysis of two oscillation modes ($m = 0$ and $m = 2$). The straight line represents the least squares fit of the data. T_{liq} is taken from Ref. 1.

we used circles as symbols for the values where both modes could be observed and squares for the values where only the $m = 0$ mode could be observed. The data represent a compilation of the results from seven different levitation experiments. The temperature error is about ±10°C.

For the surface tension data a least-squares fit with a linear function has been performed. The resulting linear fit function in the temperature range from 1460 to 1800°C is:

$$\gamma = 1.389 \pm 0.09 - 9.017 \times 10^{-4} \pm 5.64 \times 10^{-5} (T - 1660\,^{\circ}\mathrm{C})\ [\mathrm{N \cdot m^{-1}}] \tag{7}$$

5. UNCERTAINTIES

The error in temperature measurement is due to two efffects, namely the error in the determination of the liquidus temperature and the temperature dependence of the emissivity.

We estimate that the combined error of both effects is ±10°C in the entire temperature range.

The error in the surface tension data is due to the error in mass determination and frequency measurement. We estimate $\Delta M = 0.1\%$ and $\Delta\omega = 1\%$. Therefore we expect $\Delta\gamma = 2\%$. The linear fit yields $\gamma = 1.389 - 9.017 \times 10^{-4}(T - 1660\,^{\circ}\mathrm{C})$ $[\mathrm{N \cdot m^{-1}}]$ with a standard deviation of 0.09 for the value of the surface tension at the liquidus temperature and 5.64×10^{-5} for the slope. Additional sources of error may be due to nonlinear effects.

6. DISCUSSION

It was possible to process the highly reactive melt of $Ti_{90}Al_6V_4$ and measure its surface tension. Due to the containerless processing technique, we could achieve a high undercooling of 200°C. We did not use the $|m| = 1$ oscillation mode for the calculation of the surface tension, because the geometry of this oscillation mode leads to decrease of the amplitudes of the peaks in the frequency spectrum if the sample is observed from the top. An unambigious identification of the oscillation frequencies for the $|m| = 1$ oscillation was not possible. An observation from the side would increase the amplitude of the peaks of the $|m| = 1$ oscillation mode but would also lead to a decrease of the amplitude of the peaks for the $|m| = 2$ oscillation mode. For a surface tension calculation it is not necessary to measure all oscillation freqencies, because for the use of the correction of Cummings and Blackburn only an identification of the observed oscillation frequencies with the oscillation modes is necessary. As shown before the surface tension can be derived from any oscillation mode. The surface tension data showed a linear behavior. We found no anomalities in the undercooled region, which leads to the conclusion that there is no structural change in the undercooled liquid. A comparison with data for pure titanium shows that the surface tension of the $Ti_{90}Al_6V_4$ alloy at the melting point is lower than the value for the pure metal. For pure titanium the surface tension at the melting point is $\gamma = 1.675\ [\mathrm{N \cdot m^{-1}}]$ [7].

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