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Viscosity and Surface Tension Measurements in Microgravity[1]

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The viscosity and surface tension of liquid metals can be measured by observing the oscillations of a levitated drop. The frequency is related to the surface tension, while the viscosity determines the damping of the oscillations. If no external forces are present, as in microgravity, these relations are particularly simple and precise. During the recent Spacelab mission MSL-1, such experiments have been performed on Co–Pd and Pd–Cu–Si using the electromagnetic levitation facility TEMPUS. It was possible to obtain data over a wide temperature range, including the undercooled regime. While the temperature dependence of the surface tension remains linear over the complete range, the temperature dependence of the viscosity is much more pronounced and is discussed in terms of different models.

KEY WORDS: Co–Pd alloy; electromagnetic levitation; liquid metals; microgravity; Pd–Cu–Si alloy; surface tension; viscosity.

1. INTRODUCTION

The thermophysical properties of liquid metals and alloys are difficult to measure, yet they play an important role in many phenomena relevant to both fundamental science and technological applications. In particular, surface tension and viscosity are of interest. The oscillating drop method has been used widely to measure the surface tension of levitated liquid metals [1]. This method makes use of the fact that the frequency of the surface oscillations of a liquid drop is related to the surface tension by Rayleigh's

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formula. If the radius R of a spherical droplet undergoes oscillations of the form

$$R = R_0(1 + \delta \cos(\omega t)\, e^{-\Gamma t}) \tag{1}$$

where δ is the amplitude of the oscillation, ω is the frequency, and Γ is the damping, then the frequency ω is given by

$$\omega^2 = 32\pi\gamma/(3m) \tag{2}$$

where γ is the surface tension and m is the mass of the drop.

Unfortunately, Rayleigh's formula cannot be applied directly to oscillations of levitated drops. The influence of the external electromagnetic and gravitational fields must be taken into account. These fields lead to a splitting of the single peak predicted by Rayleigh for the oscillation spectrum into up to five peaks and a shift of the peak positions. Although an approximate correction [2] has been worked out, it is advantageous to perform such experiments under microgravity, where both fields are negligibly small, and Rayleigh's formula is directly applicable.

In addition, the oscillating drop technique also yields the viscosity of the droplet. This idea is based on Kelvin's work on the oscillations of viscous drops [3]. He derived the following expression for the damping constant Γ:

$$\Gamma = \frac{20\pi}{3} \frac{\eta R_0}{m} \tag{3}$$

where η is the viscosity. Like Rayleigh's formula, this equation is valid only for spherical drops in the absence of external fields. Although attempts have been made to include the effect of the external fields on the damping constant [4], no terrestrial experiments have been reported which make use of the oscillating drop technique for viscosity measurements. Experiments under microgravity may in fact be the only possibility to apply this method.

Based on these considerations, we have performed microgravity experiments to measure the surface tension and viscosity of pure metals and alloys using the electromagnetic levitation facility TEMPUS during the IML-2 Spacelab mission in 1994. Due to contamination and stability problems, the samples could not be processed as planned. However, it was possible to obtain surface tension data over a limited temperature range. More importantly, the presence of a single peak, as predicted by the Rayleigh theory, was clearly demonstrated [5]. Based on the experience gained during IML-2, the TEMPUS facility was modified and reflown on Spacelab mission MSL-1 in 1997. For this flight, we have proposed to measure the surface tension and viscosity of two alloys, namely, $Co_{80}Pd_{20}$ and $Pd_{76}Cu_6Si_{18}$. While the first system is a low-viscosity alloy with excellent undercooling capabilities [6], the latter is a eutectic system which is a good glass former and, consequently, has a high viscosity. The reported values for the viscosity of $Pd_{76}Cu_6Si_{18}$ at the eutectic temperature differ by a factor of 100 [7, 8]. In this paper, we present the results obtained during MSL-1. While no previous data exist for the viscosity of $Co_{80}Pd_{20}$, our results on $Pd_{76}Cu_6Si_{18}$ confirm the data of Lee et al. [8] and rule out those of Steinberg et al. [7]. The former investigators measured the viscosity by a capillary flow viscometer, while the latter team used a rotating viscometer.

2. EXPERIMENTS AND RESULTS

2.1. Experimental Setup

We prepared spherical samples 8 mm in diameter. The $Pd_{76}Cu_6Si_{18}$ sample was placed in a sample holder consisting of a wire cage made of W–Re and a pedestal of SiC, whereas the $Co_{80}Pd_{20}$ sample was placed into a cup-type sample holder made of SiC. This cup served as an evaporation shield to protect the levitation coil from the expected strong evaporation of the sample. For viewing purposes, it had a lateral slit. Both sample holders were integrated into the TEMPUS facility, where they were kept under inert gas atmosphere until launch. The experiments on $Pd_{76}Cu_6Si_{18}$ were performed in 100-mbar argon of 6 N purity, while those on $Co_{80}Pd_{20}$ were performed in a 100-mbar He–4% H_2 atmosphere. The temperature was measured by a pyrometer equipped with an InAs detector covering the range between 600 and 2000 K. The temperature data were acquired with a 100-Hz resolution, while the coil current was monitored with 10 Hz. The sample oscillations were observed radially with a videocamera, operating at 30 Hz. Using the time stamps on both the temperature signal and the video frames, the two data sets could be synchronized with an uncertainty better than 0.1 s.

After stable positioning, the samples were melted and overheated by 100 to 400 K. Then the heating fields were switched off, allowing the sample to cool due to radiation and conduction. During cooling, a short current pulse was passed through the heating coils, leading to a lateral compression of the sample and subsequent oscillations. Although observing the oscillations during cooling introduces a temperature error of about 5 to 10 K, it has the advantage that the electromagnetic fields are reduced to a minimum, eliminating any fluid flow effects. During one cooling cycle, such an excitation pulse was applied every 50 K, until the sample solidified. The video images were analyzed frame by frame, and the radius of the sample was determined as a function of time. The damping constant was obtained from the time signal directly, whereas the frequency was obtained from the Fourier transform of the signal. Due to the low sampling rate of the camera (compared to the frequency of the surface oscillations), the Nyquist sampling theorem [9] was violated, and aliasing effects had to be taken into account.

2.2. $Co_{80}Pd_{20}$

$Co_{80}Pd_{20}$ has a liquidus temperature of $T_l = 1610$ K and a solidus temperature of $T_s = 1565$ K [10] and, therefore, only a small temperature region where solid and liquid phases coexist. This makes this alloy easy to handle in electromagnetic levitation. During MSL-1, 30 melt cycles could be performed. After initial in situ purification by overheating, it could be undercooled by more than 340 K, which means that the hypercooling limit [6] was exceeded and the Curie temperature $T_c = 1257$ K of the liquid phase [11] was approached. The temperature trace of one typical thermal cycle is shown in Fig. 1. Melting, undercooling, recalescence, and solidification are clearly visible. Note the absence of a recalescence plateau and the fact that, upon recalescence, the liquidus temperature is not reached. This is a consequence of hypercooling. The graph also shows the electrical current through the heating coils. The distinct spikes correspond to the pulses which were used to excite surface oscillations. From the video signal, the onset and decay of these oscillations can be observed. This is shown in Fig. 2. The Fourier spectrum of such a damped oscillation is shown in Fig. 3. As mentioned before, there is an aliasing effect present in this spectrum. The true physical frequency is around 24 Hz, whereas the peak at 6 Hz is an alias of the original peak. We have verified this assignment by a numerical simulation of the recording setup. Bearing this in mind, Fig. 3 once again confirms the theoretical prediction that liquid drops in microgravity are spherical, and hence, their oscillation spectrum consists of one frequency only, the Rayleigh frequency, given by Eq. (2). Using Eqs. (2) and (3) to convert frequencies and damping constants into surface tension and viscosity, we have analyzed all oscillations and obtained surface tension and viscosity as functions of temperature. The results are shown in Figs. 4 and 5, respectively. The surface tension data have been fitted with a linear relation to obtain

$$\gamma_{\text{Co-Pd}} = 1675 - 0.17(T - 1610) \qquad (\text{mN} \cdot \text{m}^{-1}) \tag{4}$$

where the temperature T is in K. The viscosity was fitted with an Arrhenius-type expression to obtain

$$\eta_{\text{CoPd}} = 0.15 \exp(9.37 \cdot 10^{-20}/(kT)) \qquad (\text{mPa} \cdot \text{s}) \tag{5}$$

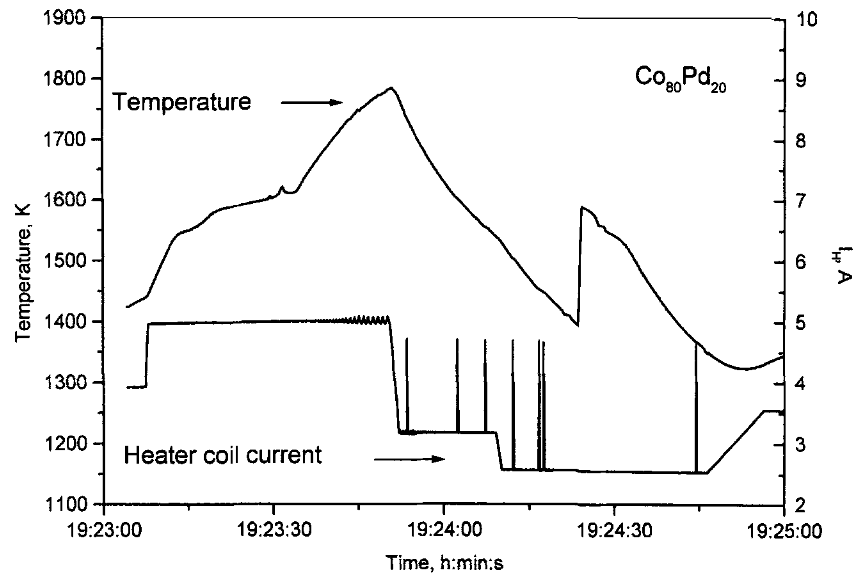

Fig. 1. *One thermal cycle of* $Co_{80}Pd_{20}$ *indicating hypercooling. The lower curve shows the current through the levitation coil. The spikes correspond to pulses used to excite surface oscillations.*

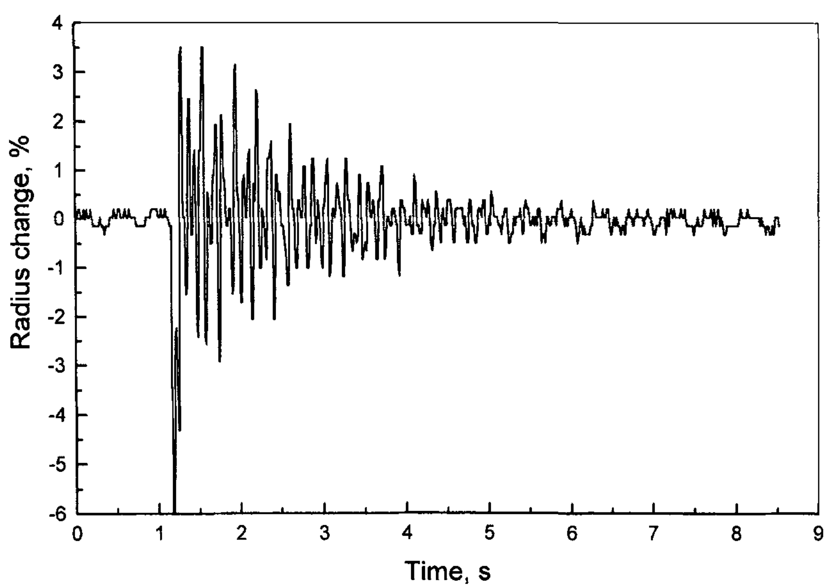

Fig. 2. Excitation and decay of a surface oscillation, as detected in the video signal.

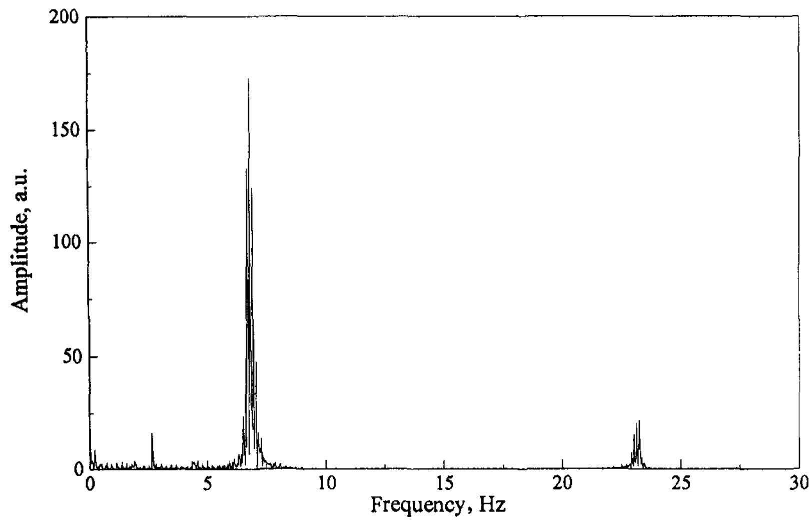

Fig. 3. Fourier spectrum of one damped surface oscillation, showing the physical peak around 24 Hz and its alias around 6 Hz.

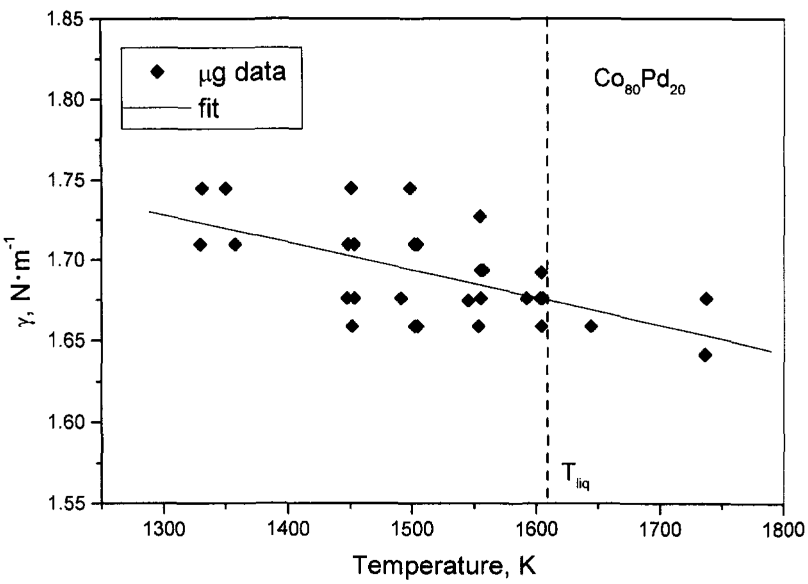

Fig. 4. Surface tension of $Co_{80}Pd_{20}$ as a function of temperature. The vertical line represents the liquidus temperature.

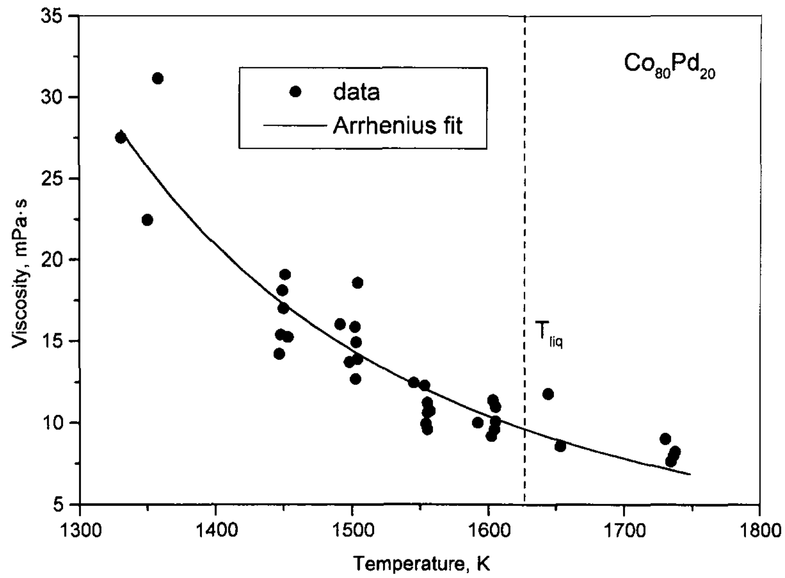

Fig. 5. Viscosity of $Co_{80}Pd_{20}$ as function of temperature. The vertical line represents the liquidus temperature.

Here, Boltzmann's constant k is given in $J \cdot K^{-1}$ and temperature in K. The measured viscosities range from 5 to 30 mPa · s, covering nearly an order of magnitude. An undercooling of approximately 300 K leads to an increase in viscosity by a factor of three.

2.3. $Pd_{76}Cu_6Si_{18}$

At the chosen composition, PdCuSi forms a eutectic at a temperature of $T_e = 1033$ K. This means that melting and solidification take place at a fixed temperature, which can be used to calibrate the pyrometer reading. The addition of Cu to the binary Pd–Si system is supposed to improve the glass-forming ability of the alloy. Unfortunately, its presence limits the undercooling under quasi-isothermal conditions to approximately 70 K, due to the formation of CuO.

The experiments on $Pd_{76}Cu_6Si_{18}$ were carried out during the MSL-1 Spacelab mission, consisting of two Space Shuttle flights, STS-83 and STS-94. STS-83 was a minimum-duration flight of only 4 days. Three thermal cycles could be performed on $Pd_{76}Cu_6Si_{18}$ during STS-83, and an additional 16 cycles were run on STS-94. A trace of a typical melt cycle is shown in Fig. 6. As can be seen, there is only moderate undercooling

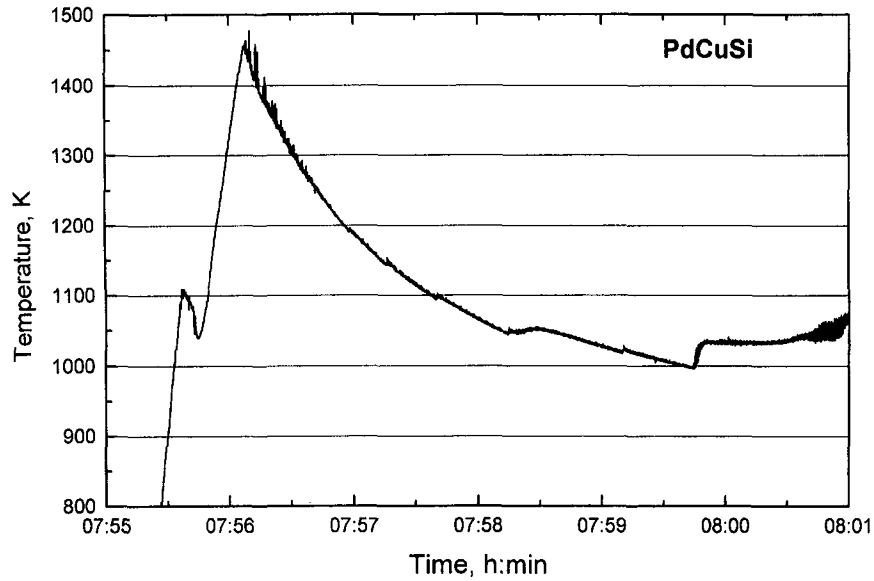

Fig. 6. One melt cycle of $Pd_{76}Cu_6Si_{18}$.

despite considerable overheating of the melt. Such large overheating is necessary to destroy Pd_3Si crystallites which serve as nucleation centers [12], but it cannot prevent formation of CuO.

The experiments on PdCuSi were analyzed as described above for CoPd. The data obtained for the surface tension are shown in Fig. 7. They can be fitted with the following linear relation:

$$\gamma_{\mathrm{PdCuSi}} = 1399 + 0.26(T - 1033) \qquad (\mathrm{mN \cdot m^{-1}}) \tag{6}$$

As before, temperature is in K. Filled squares correspond to data taken during STS-83; open diamonds represent measurements during STS-94. As can be seen, there is considerable scatter in the data. We attribute this as well as the positive temperature coefficient to the formation of CuO at the surface.

The data obtained for the viscosity are shown in Fig. 8. The scatter of the STS-94 data set is larger than that of STS-83, which may be due to microgravity disturbances. We have fitted the data with different theoretical models for the viscosity, namely, to a simple Arrhenius-type exponential, $\eta = \eta_0 e^{\Delta E/kT}$, corresponding to an activated (hopping) process, as well as to the Vogel–Fulcher formula [13] for the viscosity of a glass-forming alloy,

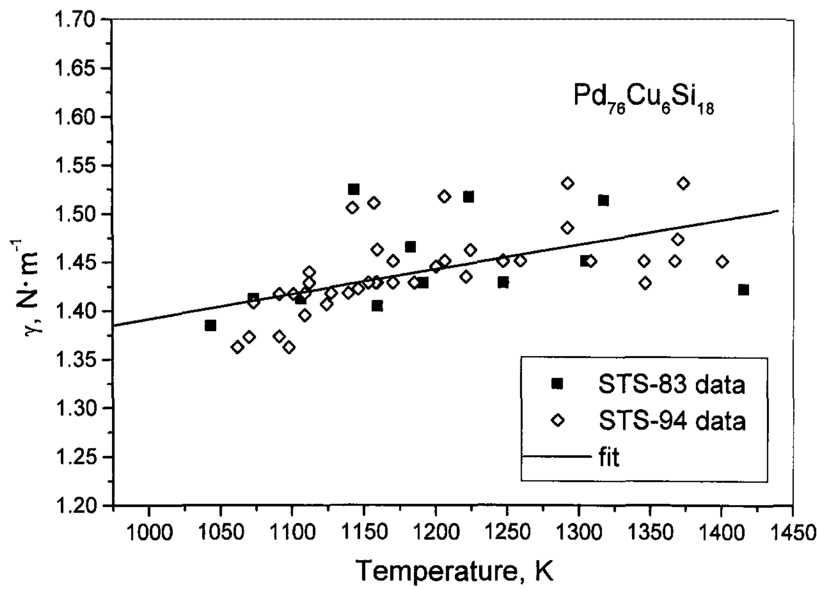

Fig. 7. Surface tension of $Pd_{76}Cu_6Si_{18}$ as a function of temperature.

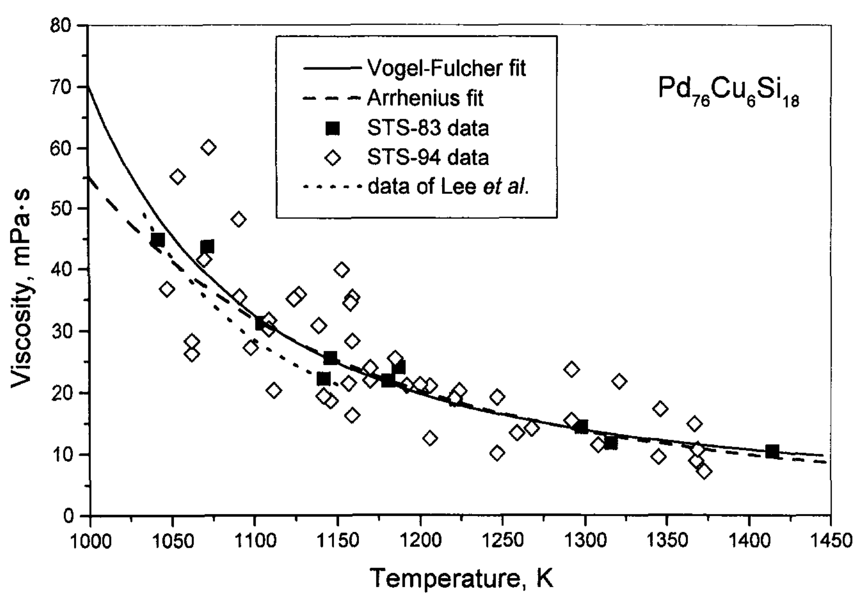

Fig. 8. Viscosity of $Pd_{76}Cu_6Si_{18}$ as a function of temperature.

$\eta = \eta_0 e^{\Delta E/(k(T-T_0))}$. These two fits are shown in Fig. 7. We have also fitted our data with a power-law relation, $\eta = A(T-T_0)^{-\alpha}$, as predicted by the mode-coupling theory [14]. For clarity, this fit is not shown. In the temperature range considered, it is indistinguishable from the Arrhenius fit. Figure 7 also shows the fit obtained by Lee and co-workers [8] indicating the temperature range of their measurements. There is good agreement, but our data extend to much higher temperatures, allowing a more reliable fit. In summary, our fitting procedure yields the following expressions for the viscosity (in mPa · s) of $Pd_{76}Cu_6Si_{18}$:

$$\eta = 0.134 \exp(8.35 \times 10^{-20}/kT), \qquad \text{Arrhenius} \tag{7}$$

$$\eta = 1.97 \exp(1.82 \times 10^{-20}/k(T-630)), \qquad \text{Vogel–Fulcher} \tag{8}$$

$$\eta = 7.49 \times 10^{7}(T-630)^{-2.38}, \qquad \text{Power law} \tag{9}$$

All dimensions are the same as in Eq. (5). The measured viscosities range from 10 mPa · s at 1400 K to 50 mPa · s at 1100 K, very similar to the case for CoPd. Therefore, we expect that viscosities in the range from 1 to 100 mPa · s can be measured using the oscillating drop technique.

Despite the large temperature range, it is not possible to decide which of the proposed theoretical models describes the viscosity of $Pd_{76}Cu_6Si_{18}$ best. The Vogel–Fulcher equation starts to deviate from the other models only in the close vicinity of the glass transition, where it predicts a much steeper increase. Up to now it was not possible to approach the glass transition with low cooling rates as offered by electromagnetic levitation. In addition, when the viscosity exceeds 100 mPa · s, the excitation of the oscillations becomes increasingly difficult, and the oscillations are damped out very quickly. It seems therefore unlikely that the oscillating drop technique can be used to verify the Vogel–Fulcher equation.

3. CONCLUSION

The oscillating drop technique is a useful tool for measuring the surface tension and viscosity of high-temperature melts, in particular, in the undercooled region. In microgravity, the drop is spherical and simple formulas can be used to derive these data from the oscillation spectrum. We have demonstrated the feasibility of this approach and were able to resolve a long standing controversy regarding the viscosity of $Pd_{76}Cu_6Si_{18}$. Future experiments will concentrate on the application of this technique to technologically important materials.

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