The viscosity of eutectic Pd-Si alloys

I. Egry
Institut für Materialphysik im Weltraum, German Aerospace Center, DLR, 51170 Köln, Germany
E-mail: ivan.egry@dlr.de

Abstract. The viscosity of eutectic PdSi alloys has been measured by different techniques. The conventional oscillating cup viscosimetry was used in the ground-based laboratory, while the oscillating drop technique was applied in a microgravity experiment. Different working equations were utilised to derive the viscosity from the damping of the oscillations, and the results thus obtained were compared to each other and available literature data. Whereas systematic deviations exist, an overall satisfactory agreement was found.

1. Introduction
The viscosity $\eta$ of a liquid is one of its most fundamental thermophysical properties, both from an academic and an engineering point of view. It determines mass transport in fluids, governs the onset of convection and affects to a large extent the glass forming ability of a given alloy. Viscous flow is an activated process, and, therefore, the temperature dependence of the viscosity is often given in an Arrhenius form:

$$\eta = \eta_0 \exp \left( \frac{E_A}{kT} \right)$$  \hspace{1cm} (1)

where $E_A$ is the activation energy and $T$ the absolute temperature.

Among the binary metallic alloys, Pd-Si has one of the highest reported viscosities at its eutectic compositions [1]. According to its phase diagram, two eutectics exist at very similar compositions: Pd$_{82.2}$Si$_{17.8}$ and Pd$_{85}$Si$_{15}$. Before the discovery of the bulk metallic glasses [2], these alloys were considered the best starting point for easy glass formers. Their glass forming ability could be further improved by adding a ternary component in the form of Pd$_{76}$Cu$_6$Si$_{18}$. Due to their relatively simple composition, these alloys are ideal candidates for benchmark experiments. There exist a few published data on these alloys [3, 4, 5]; their results differ by more than two orders of magnitude. Steinberg and coworkers [3] used an oscillating cup viscometer, Nishi et al. [4] used a vibration technique, and Lee et al. [5] used a capillary flow method.

During the STS-83 Spacelab mission, Egry and coworkers [6] measured the viscosity of the Pd$_{76}$Cu$_6$Si$_{18}$ alloy on electromagnetically levitated specimen, applying the oscillating drop technique, while Hyers et al. [7] measured the viscosity of the Pd$_{82.8}$Si$_{17.2}$ alloy on the same mission. The microgravity data agree well with each other, and with the terrestrial data of Lee et al. [5].

The evaluation of the microgravity experiments was based on Lamb’s treatment of an oscillating viscous liquid sphere [8]. When the radius $R$ of a viscous liquid drop performs small (linear) damped oscillations of the form

$$R = R_0 \exp \left( \frac{-2\pi \eta \omega t}{\rho \pi R_0^4} \right)$$
\[ R = R_0 \left( 1 + \delta \cos(\omega t) \exp(-\Gamma t) \right) \]  
then the viscosity \( \eta \) can be calculated from the damping \( \Gamma \) as:

\[ \eta = \frac{3}{20\pi} \frac{m}{R_0} \Gamma \]  
where \( m \) is the mass of the drop.

Lamb’s treatment neglects any effects of surface viscosity, which may arise either from an oxide layer covering the liquid drop, or even from an intrinsic effect due to a varying density profile of the conduction electrons close to the surface [9]. When surface viscosity is taken into account, Lamb’s formula, eqn (3) is no longer valid. Miller and Scriven [10] have derived an expression for the damping of a liquid drop covered by an inextensible surface layer. Their result reads:

\[ \eta = \frac{54}{\pi} \frac{m}{R_0} \frac{\Gamma^2}{\omega} \]  
As can be seen, the surface viscosity itself does not appear in the above expression; however, the viscosity now scales with the damping squared. The physical reason for this qualitatively different behaviour is due to different boundary conditions in both treatments. With surface layer, not only the normal, but also the tangential pressure balance need to be satisfied. As shown by Lyubimova and coworkers in a recent paper [11], Miller and Scriven’s result may also be derived by treating a small surface viscosity as a perturbation to the original problem of Lamb.

In view of these controversial results, it seemed therefore appropriate to re-investigate the viscosity of Pd-Si again. This paper reports on measurements of the viscosity of the Pd\textsubscript{82.8}Si\textsubscript{17.2} alloy in microgravity on board a sounding rocket during the TEXUS 46 campaign. The results obtained are compared with those of previous microgravity experiments and ground based values obtained using the new high-temperature viscometer available at DLR [12]. The new TEXUS data were evaluated by both, the Lamb and the Miller-Scriven equation.

In the next chapter, the terrestrial results will be presented and discussed, whereas chapter 3 deals with the microgravity experiment. The final chapter is devoted to the discussion of the results and some conclusions.

2. Terrestrial experiments

2.1. The instrument

All experiments have been carried out in an oscillating cup viscometer described in detail in [12]. In short, a vacuum furnace with a graphite heater is used to heat the sample. The temperature inside the furnace is controlled by a pyrometer, calibrated to the melting points of pure metals (Al, Ag, Cu, Ni, Fe). The sample inside the furnace is placed in a cup made of a temperature resistant and chemically inert material. The sample is then set in torsional oscillations, which are detected by a reflected laser beam on a position sensitive device (PSD). The oscillation period \( T_{osc} \) and the logarithmic decrement \( \delta \) are extracted from the oscillation and inserted into the Roscoe-equation [13]

\[ \eta Z^2(\eta) = \left( \frac{\delta}{\pi R^3_c H} \right)^2 \frac{1}{\pi \rho T_{osc}} \]  
for calculating the viscosity. In equation (5) \( \eta \) is the viscosity, \( Z \) is a known function of \( \eta \), \( I \) is the moment of inertia of the whole oscillating system, \( R_{cup} \) is the inner radius of the cup, \( H \) is the height of the liquid sample inside the cup, and \( \rho \) is the density of the liquid sample. This implicit equation is then solved numerically.

In the experiments cups of yttria (99.9% Y\textsubscript{2}O\textsubscript{3}, Cesima) with an inner diameter of 16.5 mm, a height of 50 mm, and a wall thickness of 2 mm were used.
2.2. Results

Both alloys could be measured close to their melting points and up to 1800 K (Pd$_{82.8}$Si$_{17.2}$) and 1950 K (Pd$_{85}$Si$_{15}$), respectively, covering a temperature range of at least 700 K. Except for temperatures very close to the melting point, an Arrhenius fit describes the data correctly. The corresponding Arrhenius-fits are given by:

\[ \eta_{85-15} = 0.3391 \times \exp(4866/T) \text{ [mPa s]} \]  
\[ \eta_{83-17} = 0.5730 \times \exp(4557/T) \text{ [mPa s]} \]

where the temperature $T$ is in K.

The resulting activation energies and melting point viscosities are listed in Table 1.

| Composition (at%) | $T_L$ (K) | $\eta_L$ (mPa s) | $E_A$ (kJ/mole) |
|-------------------|----------|-----------------|-----------------|
| Pd$_{82.8}$Si$_{17.2}$ | 1089 | 37.62 | 37.8 |
| Pd$_{85}$Si$_{15}$ | 1094 | 28.97 | 40.5 |

The two alloys have similar viscosities. As expected, the deeper eutectic (Pd$_{82.8}$Si$_{17.2}$) has the higher viscosity by about 30%.

3. Microgravity experiments

3.1. The mission

The experiments were carried out in the framework of the TEXUS 46 sounding rocket mission using the TEXUS-EML electromagnetic levitation facility. This mission provided about 6 minutes of microgravity, to be shared by two experiments accommodated in the EML facility. The experiment time allotted to the Pd-Si experiment was 170 s. The EML has two separate high-frequency current circuits: one for positioning the sample against microgravity disturbances, providing a quadrupolar electromagnetic field, and one for heating the sample through a homogeneous dipolar electromagnetic field. More details of the EML can be found in [14].

The sample for the microgravity experiment had a nominal composition of Pd$_{82.2}$Si$_{17.8}$ and was prepared from the same material as used in the terrestrial viscosity measurement. The sample mass was 1.599 g. The experiments were carried out under argon atmosphere. Pyrometer and video signals were acquired with a frame rate of 200 Hz. The pyrometer signal $T_p$ was converted to true temperatures $T$ by adjusting its reading to the known melting temperature [15]:

\[ \frac{1}{T} = \frac{1}{T_p} + \left( \frac{1}{T_L} - \frac{1}{T_{L,p}} \right), \quad \left( \frac{1}{T_L} - \frac{1}{T_{L,pyro}} \right) = 8.3 \times 10^{-5} \]  

Here, $T_L = 1089$ K is the known liquidus temperature, and $T_{L,pyro}$ is the pyrometer reading at the melting temperature.

Two melt cycles were performed, both consisting of a heating and cooling phase. The heating phases heated the sample above 1400 K, in order to destroy potentially existing Pd$_3$Si clusters. In the cooling phase, sample oscillations were triggered every 6 seconds by applying a short pulse through the heater coil, leading to a compression of the liquid sample near the equatorial plane. No attempt was made to provide isothermal conditions, i.e. to perform the oscillation analysis at constant temperature. The reason for this is twofold: first, the experiment time is not sufficient for achieving thermal equilibrium, and second, isothermal conditions require heating of the sample by the electromagnetic field. This would lead to turbulent flow in the sample, disturbing the viscosity measurements.
The temperature profile of the experiment is shown in Figure 1. The melt plateau at 1089 K is clearly visible. The spikes on the cooling curve correspond to the heater pulses, used for triggering the sample oscillations.

![Figure 1. Temperature profile of the TEXUS 46 microgravity experiment.](image)

Two video cameras provided axial (=top) and radial (=side) view. From the video images it was possible to extract the relevant geometrical parameters (radii in two perpendicular directions, cross section) of the drop. Due to some microgravity disturbance, the sample did not show the expected oscillation behaviour during melt cycle #1. Consequently, only cycle #2 was further analysed. The corresponding video signal is shown in Fig. 2.

3.2. Data analysis

For the analysis, all radius and area data were normalized to zero average by subtracting a linear fit from the original data. In addition, the absolute time was replaced by a relative time, starting at the beginning of cycle #2. This avoids dealing with large numbers and improves the accuracy of the fits and Fourier transforms. The damping constant $\Gamma$, eqn (2), was determined in two different ways:

![Figure 2. Sum of two perpendicular radii of oscillating drop, mean value subtracted. Axial view, cycle #2.](image)
Method 1:
The absolute value of the radius (or area) was taken, and its maxima were determined:

\[ S(t_i) = \text{Max} \{ |R(t)| \} \]. The resulting data set was fitted by a simple exponential \( A \exp(-\Gamma t) \).

Method 2:
The radius (or area) signal was squared, and its logarithm taken:

\[ \ln \left( R^2(t) \right) = \ln \left( A^2 \sin^2(\omega t) \right) - 2\Gamma t \]

The maxima were determined and fitted by a linear function, whose slope equals \(-2\Gamma\).
Both method yielded consistent results.

The temperature attributed to each pulse corresponds to the temperature at the beginning of the oscillation. This overestimates the temperature, but is reasonable, since the data points at the beginning of the oscillation, where the amplitude is large, dominate the data analysis.

3.3. Results
The damping constants, determined as described above, are shown in Table 2 together with the associated temperatures.

| \( T \), K | \( \Gamma \), s\(^{-1}\) | \( \omega \), s\(^{-1}\) |
|------------|----------------|-------------|
| 1447       | 0.510          | 175.4       |
| 1381       | 0.515          | 175.9       |
| 1328       | 0.641          | 176.8       |
| 1252       | 0.781          | 177.6       |
| 1223       | 0.775          | 177.5       |

For the application of eqns (3) or (4), the mass and radius of the sample are required. For the mass \( m = 1.599 \) g was used. This value was determined before flight, a post-flight analysis was not possible. Consequently, possible mass losses due to evaporation are not considered. The radius was determined indirectly from the mass and density of the drop, assuming a spherical shape. For the liquid density a temperature-dependent value of \( \rho(T) = 10.0 - 0.001(T - 1089K) \) g cm\(^{-1}\) was used, as determined before flight [16].

In eqn (4), the frequency \( \omega \) of the oscillation is required in addition. This was obtained by Fourier transforming the time signal of each pulse individually and determining the peak position.

The viscosities, derived from the damping constants, by either using Lamb’s or Miller’s formula, are shown in Figure 3 together with our ground-based result and the earlier microgravity result of Hyers [7], evaluated according to Lamb.

4. Results
The results obtained with the oscillating cup method on ground and those obtained under microgravity show reasonable agreement, especially in the high-temperature region. Surprisingly, the evaluation using Miller’s equation, eqn (4), yield higher viscosities than Lamb’s equation, eqn (3). This is unexpected, since eqn (4) has an additional term \( \Gamma/\omega \), which in the sense of a perturbation expansion is a small quantity of the order of \( 10^{-3} \). However, this is compensated by the different numerical prefactors, whose ratio has the same order of magnitude.

The data obtained with Lamb’s formula yield viscosities somewhat smaller than those measured on ground, but with a very similar temperature dependence, whereas the evaluation according to Miller & Scriven agrees better with the ground-based data, but yields a different temperature dependence. The
microgravity results from TEXUS46 and MSL-1, evaluated according to Lamb’s formula show good agreement.

In summary, the results obtained do not allow to clearly decide which equation works better. In order to do so, the parameter $\Gamma/\omega$ needs to be varied, such that the two formulae should give results which differ by at least an order of magnitude. This is possible by varying the mass of the sample, as damping and frequency depend differently on sample radius. Such experiments are planned for the future.

Figure 3. Viscosity of Pd$_{82.2}$Si$_{17.8}$, as obtained by different methods. Data points correspond to the TEXUS 46 results, full line is our ground based result, and dotted line is Hyers’ result [7].

Acknowledgements
The microgravity experiments would not have been possible without the excellent support of many people involved, namely the ESRANGE launch team, the MORABA team, the EADS teams from Bremen and Friedrichshafen, and the MUSC team from DLR Cologne. Their help and advice and their professional attitude during extreme work load is highly appreciated. Last, but not least, many thanks go to the DLR Agency in Bonn for providing this flight opportunity.

References
1 L. Battezzati and L. Greer, *Acta Met.* 37 (1989), 1791
2 A. Inoue, T. Zhang, and T. Masumoto, *Mater. Trans. JIM*, 31 (1991), 425.
3 J. Steinberg, S. Tyagi, A. Lord Jr., *Appl. Phys. Lett.* 38 (1981), 878
4 Y. Nishi, N. Kayama, S. Kiuchi, K. Suzuki, T. Masumoto, *J. Japan Inst. Metals* 44 (1980), 1336
5 S. Lee, K. Tsang, H. Kui, *J. Appl. Phys.* 70 (1991), 4842
6 I. Egry, G. Löhöfer, I. Seyhan, S. Schneider, B. Feuerbacher, *Appl. Phys. Lett.*, 73, (1998), 462
7 R. Hyers, G. Trapaga, M. Flemings, in: *Solidification 1999*, W. Hofmeister, J. Rogers, N. Singh, S. Marsh, P. Voorhees eds., TMS Warrendale, 1999, p.23
8 H. Lamb, *Proc. London Math. Soc.* 13, (1881) 51
9. J. Earnshaw, in: *Marangoni and Interfacial Phenomena in Materials Processing*, E. Hondros, M. McLean, K. Mills, eds., IOM Communications Ltd, London, 1998, p.41.

10. C. Miller and L. Scriven, *J. Fluid Mech.*, 32 (1968), 417

11. D. Lyubimov, V. Konovalov, T. Lyubimova, I. Egry, *J. Fluid Mech.*, doi:10.1017/jfm.2011.76, (2011)

12. Kehr M, Hoyer W, Egry I. *Int. J. Thermophys.* 28 (2007) 3

13. R. Roscoe, *Proc. Phys. Soc.* 72 (1958)

14. W. Soellner, A. Seidel, Ch. Stenzel, W. Dreier, B. Glaubitz, *J. Jpn. Soc Microgravity* 27 (2010), 183.

15. G. Nutter, in: *Theory and Practice of Radiation Thermometry*, D. DeWitt, G. Nutter, eds., Wiley, New York, 1989, p.231.

16. D. Dorow-Gerspach, *DLR internal report*, 2009