

Containerless Property Measurements of Liquid Palladium

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Some thermophysical properties of liquid and supercooled palladium were measured using containerless techniques. Over the 1640–1875 K temperature interval, the density could be expressed as $\rho(T) = 10.66 \times 10^3 - 0.77(T - T_m)(\text{kg}\cdot\text{m}^{-3})$ and the ratio between the isobaric heat capacity and the hemispherical total emissivity could be rendered as $C_P(T)/\varepsilon_T(T) = 132.1 + 5.5 \times 10^{-3}(T - T_m)(\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})$, where $T_m = 1828$ K. The volume expansion coefficient was also determined as $7.2 \times 10^{-5} \text{K}^{-1}$.

KEY WORDS: density; isobaric heat capacity; levitation; liquid metal; melting temperature; palladium; supercooling; thermal expansion.

1. INTRODUCTION

Because palladium does not tarnish in air and can be easily alloyed, it has found applications in dentistry and jewelry, and in the production of surgical instruments, aircraft spark plugs, and electrical contacts. In addition, due to its unusual property of absorbing or diffusing hydrogen, it provides not only storage but also a means of purifying the gas [1]. Palladium is also a good catalyst and is being employed in exhaust emissions systems, in petroleum cracking devices, as well as to speed up hydrogenation and dehydrogenation reactions [1]. In addition, it is being used as a reference point for the calibration of thermocouples to 1820 K [2]. However, its high melting point ($T_m = 1828$ K) [3] and the risk of contamination at elevated

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temperature complicate thermophysical property measurements of the liquid and supercooled phases. Knowledge of these properties and their temperature dependence is crucial in several fundamental studies (e.g., phase transformations, nucleation) as well as for industrial processes (e.g., refining, kinetics of slag/metal reactions, alloy design).

In this study, containerless conditions provided by electrostatic levitation in vacuum and radiative heating overcame the contamination problems associated with processing liquid palladium, and allowed the determination of several properties, even under supercooled conditions [4, 5]. First, this paper briefly describes the facility and the thermophysical property measurement methods and then presents experimental data for the density, thermal expansion coefficient, and ratio between the isobaric heat capacity and the hemispherical total emissivity of liquid and supercooled palladium.

2. EXPERIMENTAL

2.1. Electrostatic Levitation Furnace

The heart of the setup (Fig. 1a) was a vacuum electrostatic levitator (Fig. 1b)($\sim 10^{-5}$ Pa) [6] that allowed noncontact sample processing. The levitator was equipped with four coils (not shown) that generated a rotating magnetic field to control sample rotation [7].

Once levitated, the sample was heated by the radiation ($10.6\mu\text{m}$) of three focused CO_2 laser beams (Fig. 1) separated by 120° in the same plane. This configuration provided temperature homogeneity and sample position stability, and helped to control sample rotation [8]. The radiance temperature was measured with two single-color pyrometers ($0.90\mu\text{m}$ and $0.96\mu\text{m}$, 120 Hz acquisition rate). Calibration to the true temperature was obtained with the help of Planck's law. A temperature profile for a heated and then radiatively cooled palladium sample exhibiting 190 K supercooling ($10\% T_m$) and a sudden temperature rise (release of the latent heat of fusion) is shown in Fig. 2. Because of the lateral motion of the sample with respect to the pyrometer upon cooling and solidification, the noisy data of the temperature profile were numerically smoothed. The largest oscillations occurring at solidification are still observed. A possible emissivity change due to a modification in the sample surface microstructure might explain the slope at the solidification transition (Fig. 2).

The sample was observed by two charged-coupled-device (CCD) cameras located at 90° degrees of each other. They helped to align the heating laser beams to minimize any photon induced effects on the sample [8] and to monitor its position in the horizontal plane. Specifically, one camera

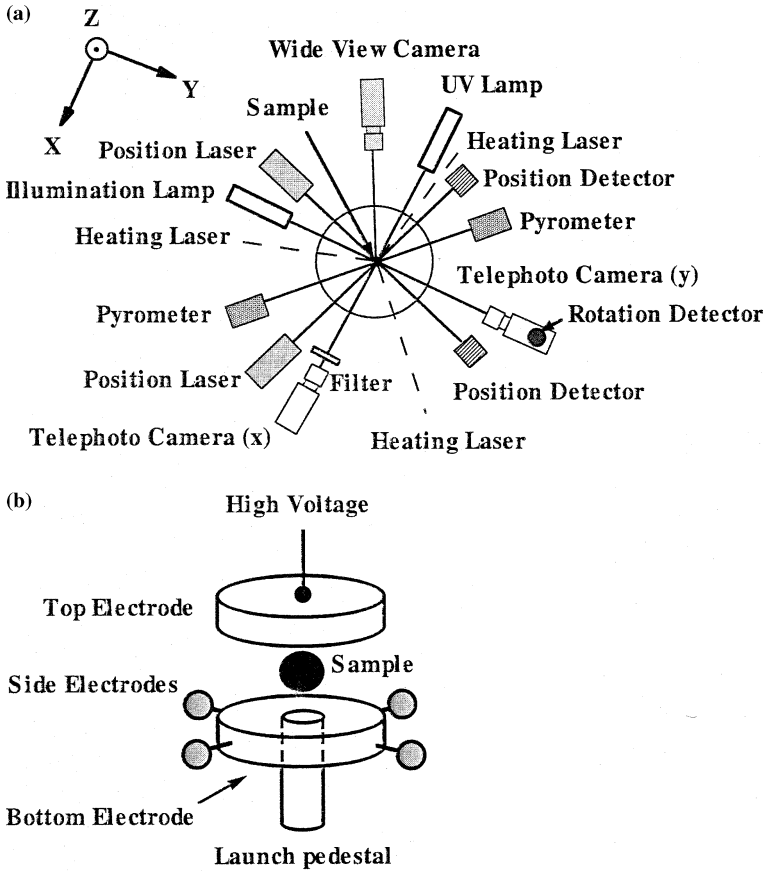


Fig. 1. Schematic diagrams of the (a) experimental setup and (b) details of the levitator.

offered a view of both the electrodes and the sample whereas a second black and white high-resolution camera equipped with a telephoto objective in conjunction with a background light provided a magnified view of the sample. A sensor was also attached to the telephoto objective, allowing the sample rotation rate to be measured by detecting the reflection of a He-Ne laser beam. Since the surface of a molten sample is free of contamination, the sample had to be solidified to measure its rotation rate. A sample was brought in a slow or non-rotating state using coils and photon pressure. It was imperative to do so as a rotating and slightly wobbling sample leads to erroneous density or surface tension data [7].

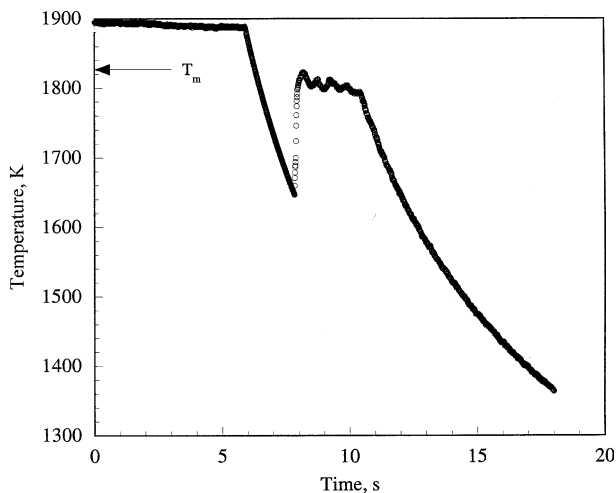


Fig. 2. Temperature profile of a heated and radiatively cooled Pd sample showing supercooling and recalescence.

For the property measurement experiments, the samples were prepared by arc melting 99.95 mass % purity palladium wire (Nilaco Corp., Japan) into spheroids with diameters of ca. 2 mm.

2.2. Property Measurements

Property measurements were carried out once a levitated sample was melted (ca. 1.92 mm diameter, 39.78 mg) and when its shape was spherical. The density was measured using a UV imaging technique [9,10]. In short, images at the rate of 30 frames per second and temperature data were simultaneously recorded. The laser beams were then blocked with mechanical shutters allowing the sample to cool radiatively. After the experiment was completed, the video images were matched with the thermal history of the sample (Fig. 2) and digitized to find the sample radius. Since the sample was axi-symmetric and because its mass is known, the density could be found as a function of temperature. The images were calibrated by levitating a sphere with a precisely known radius under identical experimental conditions. Although the Pd sample evaporated as evidenced by a change in radius during long levitation duration (several tens of minutes), the density data were recorded for only ca. 2 s during which the sample was above the melting temperature for less than 1 s (Fig. 2). Therefore, the effect on density was negligible.

Moreover, since electrostatic levitation does not inject any heat, a liquid sample experiences radiative cooling when the heating beams are blocked and the resulting energy equation reduces to

$$(mC_p/M)dT/dt = -\varepsilon_T A \sigma (T^4 - T_{\text{amb}}^4) \quad (1)$$

where m is the sample mass, M is the molar mass, C_p is the isobaric molar heat capacity, ε_T is the hemispherical total emissivity, A is the sample area, σ is the Stefan–Boltzmann constant, and T and T_{amb} are, respectively, the sample and ambient temperatures. The ratio of isobaric heat capacity and hemispherical total emissivity could be found from Eq. (1) since all parameters were either known or measured from the images (A) and pyrometry (dT/dt , T) [11].

3. EXPERIMENTAL RESULTS

The density measurements of liquid palladium, taken over the 1640–1875 K range and covering the supercooled region by nearly 190 K, are shown in Fig. 3. The density of Pd, like that of other platinum group metals [12–14], exhibited a linear dependence with temperature and could be fitted by the relationship:

$$\rho(T) = 10.66 \times 10^3 - 0.77(T - T_m)(\text{kg} \cdot \text{m}^{-3}) \quad (1640 - 1875\text{K}) \quad (2)$$

where T_m is the melting temperature (1828 K). In these measurements, the uncertainty was estimated to be less than 2 % from the resolution of the video grabbing capability (640×480 pixels) and from the uncertainty in mass measurement (± 0.0001 g). To our knowledge, these measurements were the first to be reported that included such a large temperature excursion into the supercooled region. At the melting temperature, our value was, within the stated uncertainty, identical with those already reported in the literature [15–19]. The temperature coefficient was, however, 37% lower than that measured by Lucas [15] with the maximum bubble pressure method in Ar and 34% lower than that measured by Vatolin et al. with the sessile drop method in He [18]. Considering a 2% error bar in the data, the temperature coefficient obtained in the levitation experiments was also in agreement with those reported elsewhere [15, 18].

The volume variation $V(T)$ of the molten state, normalized with the volume at the melting temperature V_m , was derived from Eq. (2), and could be expressed by

$$V(T)/V_m = 1 + 7.2 \times 10^{-5}(T - T_m)(1640 - 1875\text{K}) \quad (3)$$

where 7.2×10^{-5} represents the volume expansion coefficient.

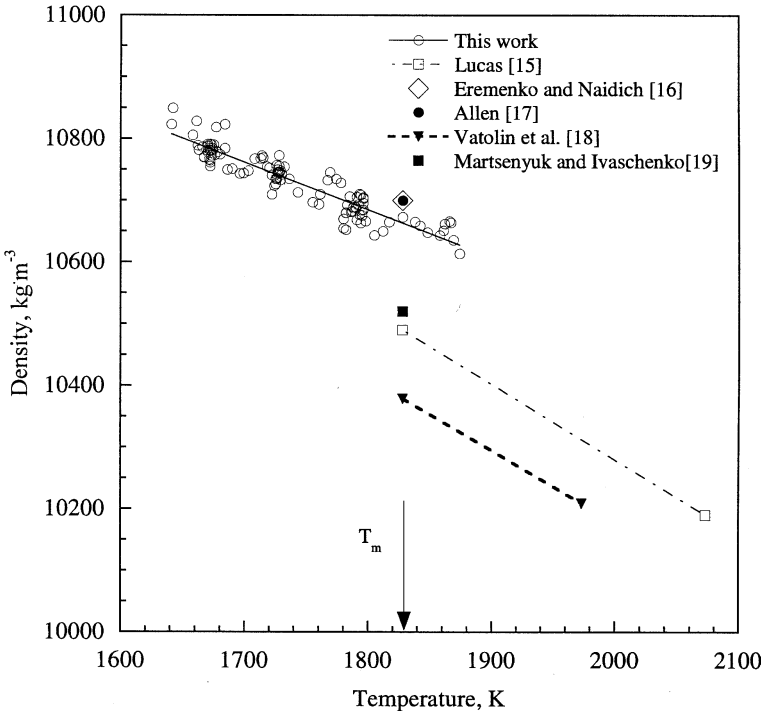


Fig. 3. Density of Pd versus temperature.

Using the method outlined in Section 2.2., the ratio between the isobaric heat capacity and the hemispherical total emissivity as a function of

Table I. Values of the Density of Liquid Palladium

Density @ T_m ($\text{kg}\cdot\text{m}^{-3}$)	Temperature coeff. ($\text{kg}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$)	Temperature range (K)	Reference	Technique
10660	-0.77	1640-1875	Present work	levitation
10490	-1.226	1828-2073	Lucas [15]	bubble pressure (Ar)
			Eremenko and Naidich [16]	calculated
10700	-	-	Allen [17]	calculated
10379	-1.169	1828-1973	Vatolin et al. [18]	sessile drop (He)
			Martsenyuk and Ivaschenko [19]	pendant drop
10520	-	-		

temperature for liquid palladium was found. The $C_P(T)/\varepsilon_T(T)$ was nearly constant with temperature and could be linearly fitted as

$$C_P(T)/\varepsilon_T(T) = 132.1 + 5.5 \times 10^{-3}(T - T_m)(\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ (1640 - 1875\text{K}). \quad (4)$$

Knowing accurately the values of either the isobaric heat capacity or those of the hemispherical total emissivity for the liquid and undercooled phases would help to estimate the other quantity over a large temperature range using Eq. (4). Unfortunately, to the best of our knowledge, such properties are not presently available. [20]

4. CONCLUSIONS

The density of liquid palladium was measured in the supercooled, as well as in the superheated, phases with an electrostatic levitation furnace. Also reported in this paper are the thermal expansion coefficient and the ratio between the isobaric heat capacity and the hemispherical total emissivity of the liquid phase. Future work will focus on platinum and osmium to complete the series of property measurements of the platinum group metals.

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