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Measurement of spectral emissivity and constant pressure heat capacity of liquid platinum with an electrostatic levitator

Takehiko Ishikawa [a,b,*], Junpei T. Okada [c], Paul-François Paradis [d], Yuki Watanabe [e]

[a] Institute of Space and Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), 2-1-1 Sengen, Tsukuba, Ibaraki 305-8505, Japan
[b] SOKENDAI (The Graduate University for Advanced Studies), 3-1-1 Yoshinodai, Chuo-Ku, Sagamihara 252-5210, Japan
[c] Tohoku University, 2-1-1 Katahira, Aoba-Ku, Sendai 980-8577, Japan
[d] INO, Remote Sensing Group, 2740 Einstein, Quebec City, Quebec G1P4S4, Canada
[e] Advanced Engineering Services Co. Ltd., 1-6-1 Takezono, Tsukuba, Ibaraki 305-0032, Japan

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ABSTRACT

Spectral emissivity and constant heat capacity of molten platinum at its melting temperature were measured. A sample was levitated in an electrostatic levitator and the radiation intensity from the molten sample was measured by spectrometers over a wide wavelength range. The spectrometers were calibrated with a blackbody radiation furnace and the spectral hemispherical emissivity was obtained. The obtained emissivity showed a negative wavelength dependence, which can be explained by Drude model. The total hemispherical emissivity of platinum at the melting temperature calculated by integrating the spectral hemispherical emissivity was found to be 0.25. Also, the constant pressure heat capacity was calculated to be 38.8 $J \cdot mol^{-1} \cdot K^{-1}$.

1. Introduction

To improve the accuracy of computer simulations for material processing involving the liquid phase (i.e. casting, welding, crystal growth), jthe importance of thermophysical properties of molten metals and alloys is increasing. However, due to their high melting temperature and the risk of chemical reactions between samples and crucibles, property measurements of high temperature melts are very difficult with conventional methods.

In the past 20 years, the electrostatic levitation method (ESL) [1] has been developed to measure thermophysical properties of high temperature melts. In this method, a sample is levitated by Coulomb forces and isolated from any contact with a crucible. Coupled with laser heating, the ESL enables non-contact measurements of such thermophysical properties as density [2], surface tension, and viscosity [3] for many refractory metal and alloys [4].

Recently, thermophysical property measurements with ESL have been expanded so that the constant pressure heat capacity (C_p) and the emissivity (ε) can be obtained [5]. Knowledge of the C_p is important to calculate thermodynamic state functions such as enthalpy, entropy, and Gibbs free energy. As for ε, it is important for accurate pyrometric temperature measurements as well as to give some insights about the structural properties because it is related to the index of refraction and extinction coefficient. The total hemispherical emissivity (ε_T), which is the average value of emissivity in wavelength and in direction, is commonly used to calculate radiative heat transfer.

In previous studies, we combine spectrometers with an electrostatic levitator to measure ε_T and C_p. The system measured radiation intensity of the molten sample over a wide wavelength range and the spectral hemispherical emissivity ($\varepsilon(\lambda)$) of the sample was calculated. Then, ε_T was calculated by integrating $\varepsilon(\lambda)$. Following this, C_p could be calculated using ε_T and the time-temperature curve obtained during radiative cooling of the sample. Using this system, ε and C_p of molten zirconium [5], niobium [6], nickel, and rhodium [7] have been obtained.

In this study, ε and C_p of platinum are reported. Platinum is widely used in jewelry, wire, and hardware for laboratory use, and in many valuable instruments including thermocouple elements. There is also much current interest in the use of platinum as a catalyst in fuel cells and in antipollution devices for automobiles [8]. Although platinum plays an important role in many industrial applications, its thermophysical properties, especially in its liquid phase, have only been scarcely measured. This paper explains the experimental setup and presents the ε_T and C_p results for molten platinum at its melting temperature.

* Corresponding author at: Institute of Space and Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), 2-1-1 Sengen, Tsukuba, Ibaraki 305-8505, Japan.
E-mail address: ishikawa.takehiko@jaxa.jp (T. Ishikawa).

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2. Experimental setup and procedures

2.1. Experimental setup

A detailed description of the electrostatic levitation facility and emissivity measurement system is given in our earlier publications [1,5], but it is briefly repeated here for completeness. The schematic drawing of the experimental setup is shown in Fig. 1.

A positively charged sample, which has a typical diameter of about 2 mm, can be levitated between parallel electrodes using Coulomb force in a high vacuum (around 5×10^{-5} Pa) chamber. Using high speed feedback control, the sample position can be maintained within a 20 μm deviation. The chamber has many optical windows through which heating and observations of the sample are made.

Sample heating is achieved using CO_2 lasers (10.6 μm wavelength, total power of 200 W), whose beams hit the sample from three directions separated by 120 degrees from each other in a horizontal plane. The sample temperature is measured using a single-color pyrometer whose observation wavelength was 900 nm (with 200 nm full width at half maximum). An observation camera, equipped with a telephoto objective, provides a magnified view of the sample allowing the measurement of its radius.

Two spectrometers are placed around the chamber to measure the spectral intensity of the radiation from the levitated sample. A multichannel photo spectrometer (MPCD) (Otsuka Electronics Co. Ltd. MCPD-3000) covers the wavelengths ranging from 700 nm to 1000 nm, while a Fourier Transform Infrared spectrometer (FTIR) (Newport Co. 80251) covers a spectral interval from 1.2 μm to 5.5 μm. A blackbody furnace (BBF) (MIKRON M335) which can reach a temperature as high as 1773 K is used to calibrate these spectrometers.

The measurement concept was to measure the spectral intensity of the radiation from the levitated sample, compare it with that of a blackbody, and to calculate the spectral emissivity. This technique is widely used and was recently implemented in conjunction with other containerless method including cold crucible [9], electromagnetic levitation [10], and electrostatic levitation [11].

2.2. Measurement procedure

For the measurements, spheroid samples with diameter of about 1.5 mm diameter were prepared by arc-melting pieces of Pt wire of 99.98 wt% purity. Information about the samples is given in Table 1.

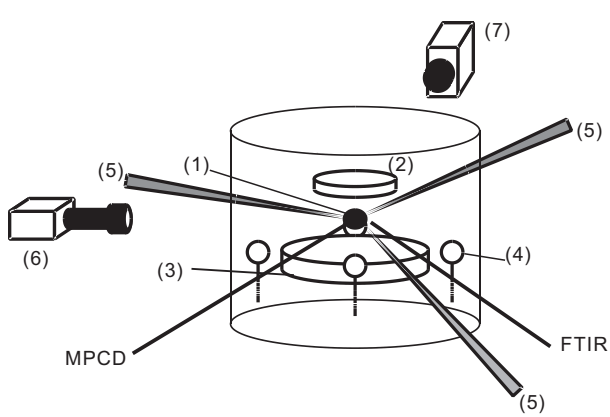

Fig. 1. Schematic view of the electrostatic levitation furnace and apparatus for emissivity measurement: (1) sample, (2) top electrode, (3) bottom electrode, (4) side electrode, (5) CO_2 laser beams, (6) CCD camera with telephoto objective lens, (7) pyrometer. The two arrows indicate radiation from the sample to spectrometers.

Once a sample was levitated in the chamber, it was heated by the CO_2 lasers and fully melted. Then, all CO_2 lasers were turned off to let the sample cool by radiation. A typical cooling curve (sample temperature vs time) is shown in Fig. 2. Since there was no crucible around the sample, it could reach undercooled temperatures. After the recalescence (release of latent heat at solidification from undercooled phase), the sample temperature exhibited a plateau which corresponds to its melting temperature (point c to d in Fig. 2). Melting temperature of platinum (2041.2 K) found in the literature [8] was used to adjust the pyrometer setting. Then, the power of the CO_2 lasers was adjusted so that the sample temperature matched that of the temperature plateau (melting temperature). The sample temperature was maintained for a few minutes and measurements of light intensity from the sample were made with the spectrometers. Throughout the experiment, the magnified sample image was monitored and recorded to keep the sample at a fixed position as well as to obtain the sample size for calibration.

Three detectors were used with the FTIR to cover a wide spectral range: an InGaAs detector (Newport 80020) (1.2 μm to 1.7 μm), an extended InGaAs detector (Newport 80014) (1.7 μm to 2.5 μm), and a HgZnCdTe detector (Newport 77258) (3.4 μm to 5.5 μm). Since only one detector could be equipped with the FTIR, experiments were repeated three times.

After the experiments, the spectrometers were calibrated using the BBF. The temperatures of the BBF were changed from 1373 K to 1673 K with 100 K intervals to get the intensity as a function of temperature. Since the measured signals from the detectors are sensitive to the sample size, a pinhole whose diameter is close to that of levitated sample was placed in front of the BBF. Using the calibration data, the measured signals from the detectors (a. u.) were converted to the radiation intensities from the sample.

The spectral emissivity is the ratio of radiation intensity of the sample (I_s) and that of the blackbody (I_B), defined as:

$$\varepsilon(\lambda,\theta,T) = \frac{I_s(\lambda,\theta,T)}{I_B(\lambda,T)} \tag{1}$$

where λ is the wavelength, T is the temperature, and θ represents the direction of radiation. The directional emissivity with $\theta = 0$ (normal direction from the sample) is called the normal spectral emissivity, which is commonly measured with a variety of methods [12]. The radiation intensity of the blackbody (I_B) is given by Planck's law of radiation as follows:

$$I_B = \frac{2C_1}{\lambda^5} \cdot \frac{1}{\exp(C_2/\lambda T) - 1} \tag{2}$$

where λ is the wavelength, C_1 and C_2 are Planck's first and second constants, being respectively 5.96×10^{-17} W·m^2·sr^{-1} and 1.44×10^{-2} m·K.

Averaging values of Eq. (1) over all directions gives the spectral hemispherical emissivity $\varepsilon(\lambda)$. A merit of ESL is that the levitated molten sample is spherical. When the shape of the emission source is spherical, the radiation becomes isotropic. Therefore, the measured spectral emissivity from the spherical sample is homogeneous in any direction, and the measured emissivity with ESL is equal to the spectral hemispherical emissivity.

The total hemispherical emissivity ε_T can be calculated by integrating the spectral hemispherical emissivity over all wavelengths:

Table 1
Source and mass fraction purity of samples used in this study.

Chemical name	Source	Initial mass fraction purity	Purification method
Platinum	Nilaco	0.998	None