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# Measurements of Heat Capacity of Pure Titanium and Zirconium by Electromagnetic Levitation

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**Abstract** The heat capacity of titanium and zirconium was measured in the temperature range from approximately 1,300 K to 1,800 K . The measurement technique is based on the modulated power method originally proposed by Fecht and Johnson. The heat capacity of a sample can be derived from the sample's temperature response to the modulated electromagnetic heating power if the sample's total hemispherical emissivity is known. The experiments were performed using an electromagnetic levitator. The solid titanium and zirconium samples were suspended in the center of an induction coil with a very small diameter (0.15 mm) Pt (87 %)-Rh (13 %) wire. The heat capacity measurements of titanium and zirconium are presented, and the uncertainty is estimated to be ±3 %.

**Keywords** Electromagnetic levitation · Heat capacity measurement · Modulated power method

## 1 Introduction

An accurate knowledge of the heat capacity of materials is very important for both fundamental studies on phase transformations and optimization of industrial processes. Experimental measurements of heat capacity can also be used to derive enthalpy, entropy, and the Gibbs free energy—essential thermodynamic parameters.

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The present paper describes heat capacity measurements on titanium and zirconium using an improved modulated power method. The modulated power method was originally proposed in [1,2]. In these pioneering experiments, heat capacity measurements were performed at low temperatures with a small sample (1 mg to 500 mg), in which a silicon chip was used as the sample holder. Fecht and Johnson [3] and their colleagues [4–9] applied the modulated power method to the electromagnetic heating and levitation technique. In this application, the electromagnetically heated and levitated sample is exposed to a slowly varying sinusoidally modulated heating power. The temperature response of the levitated sample slightly lagged behind the imposed power profile with a time constant that depended upon the thermal inertia of the sample. By proper choice of the modulation frequency, the transient effects of external and internal thermal relaxations can be ignored with errors of only approximately 1 % [3], and then as discussed below, the unknown specific heat can be calculated if the sample's emissive properties are known. The electromagnetic levitation technique [10,11], combined with the modulation power method, is an excellent experimental technique that allows containerless heat capacity measurements on electrically conductive samples. This is very important in the case of reactive metals like titanium.

Space-based electromagnetic levitators like TEMPUS [12,13], designed to operate under micro-gravity, use two sets of independent coaxial induction coils. The small positioning forces necessary in low-gravity are provided by one coil while the heating power is provided by an additional higher frequency coil. The sample temperature can thus be controlled over a wide range depending on the specific sample size and properties. Earth-based electromagnetic levitation systems typically use only a single set of opposing coils of the quadrapole design and operate at a single frequency to both levitate and heat the sample. Although the heating and levitation effects are coupled, such systems are easy to fabricate, assemble, and operate. An example of such a single coil system is the Vulcan-I instrument originally developed for operation in the earth-based laboratory as well as parabolic flights of NASA's KC135 low-gravity research aircraft [14,15].

## 2 Experimental Procedures

### 2.1 Experimental Setup and Procedures

The electromagnetic levitator at Auburn University (Fig. 1) uses a commercial 1 KW Ameritherm power supply to provide a high frequency alternating current of approximately 175 A and 280 kHz to the induction coil. The vacuum chamber was maintained at a vacuum level of $10^{-7}$ torr with a turbo-molecular pump. Up to eight samples can be processed without opening the vacuum chamber. The experiments are monitored by a charge-coupled device (CCD) camera. The sample temperature was monitored by a Micron two-color pyrometer with a 0.5 % reported uncertainty.

A solid cylindrical zirconium temperature calibration sample of 6 mm diameter and 6. 2 mm length was suspended by an attached 0.15 mm diameter R-type thermocouple. Four separate transient heating experiments from room temperature to steady temperatures of 1,423 K, 1,498 K, 1,673 K, and 1773 K were conducted in the induction coil.

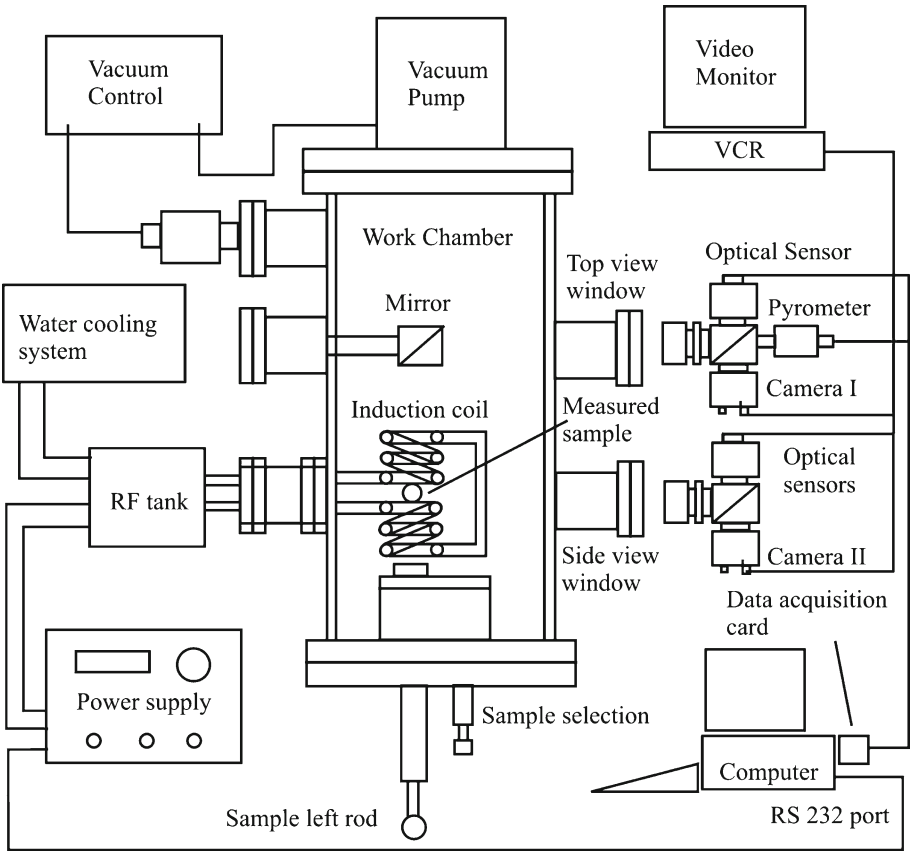


**Fig. 1** Schematic diagram of electromagnetic levitator

The results indicated that the temperature measurements between the pyrometer and the R-type thermocouple agreed to within 0.4 % during steady-state conditions and agreed to approximately 0.8 % during the transient heating conditions. The experimental heat capacity measurements were performed on pure titanium (99.99 %) and zirconium (99 %). The heat capacity samples were suspended in the center of the induction coil with very small 0.15 mm diameter Pt–Rh wire.

## 2.2 Modulated Power Control

In the modulation power technique, a spherical sample is heated with a total power that can be expressed as

$$P_{\text{total}} = P_{\text{o}} + \Delta P_{\text{o}} + \Delta P_{\omega} \cos(\omega t) \tag{1}$$

where $P_{\text{o}}$ is the steady power, $\Delta P_{\omega}$ is the modulation component of power, and $\Delta P_{\text{o}}$ is the net increase in steady power due to the modulation. Therefore, the sample's

temperature response also exhibits three components: the bias temperature $T_o$ related to $P_o$, an oscillatory component $\Delta T_\omega$ induced by $\Delta P_\omega$, and a net increase in the bias temperature $\Delta T_o$ due to $\Delta P_o$. Figure 2 shows a typical thermal response for the model system. Theoretically, the amplitude of $\Delta T_\omega$ of the sample is given by [1–3]

$$\Delta T_\omega = \frac{\Delta P_\omega}{\omega \rho V C_p}[1 + (\omega\tau_1)^{-2} + (\omega\tau_2)^2]^{-1/2}. \tag{2}$$

Here $\tau_1$ is the sample's external relaxation time and $\tau_2$ is the sample's internal relaxation time, defined as

$$\tau_1 = \frac{\rho V C_p}{4A\varepsilon\sigma_{SB}T_o^3} \tag{3}$$

$$\tau_2 = \frac{3\rho V C_p}{4\pi^3 \kappa R} \tag{4}$$

where $\kappa$ is the sample thermal conductivity, $\rho$ is the sample density, $V$ is the sample volume, $A$ is the sample surface area, and $\sigma_{SB}$ is the Stefan-Boltzmann constant. As noted by Fecht and Johnson [3], if the modulation frequency is appropriately chosen ($\sim$ 0.1 Hz to 0.5 Hz for typical metal samples in earth-based levitation systems), the transient effects of external and internal thermal relaxations can be ignored with errors of only approximately 1 %. Thus, Eq. 2 reduces to

$$\Delta T_\omega = \frac{\Delta P_\omega}{\omega \rho V C_p} \tag{5}$$

A control voltage is applied with the power supply of the rf system, and the current in the electromagnetic coil can be represented as

$$I_{peak}(t) = I_o + I_m \cos(\omega t) \tag{6}$$

Okress et al. [16], Fromm and Jehn [17], and Xuan [18] assumed that the sample is much smaller than the size of the induction coils and treated the levitated sample as a circular current loop. Xuan derived the time-averaged axial (i.e., $z$) power absorption $P(z)$ expressions for a EML coil system in Fig. 3 as

$$P(z) = \frac{3}{4} R\pi\sigma^{-1} I_{peak}^2 F(x) H(z) \tag{7}$$

where

$$F(x) = \frac{x\sinh(2x) + x\sin(2x) - \cosh(2x) + \cos(2x)}{\cosh(2x) - \cos(2x)} \tag{8}$$

$$H(z) = \left\{ \sum_n \frac{b_n^2}{[b_n^2 + (z - z_n)^2]^{1.5}} \right\}^2 \tag{9}$$

and

$$x = R\sqrt{\pi \mu f \sigma} \tag{10}$$

Here, $\mu$ is the magnetic permeability of the sample, $R$ is the radius, and $\sigma$ is the electrical conductivity of the sample. $I_{\text{peak}}$ is the current in the induction coil and $f$ is the alternative current frequency. $H(z)$ is a geometric term solely dependent on the coil configuration. Substituting Eq. 6 into Eq. 7, the total power can be expressed as

$$P_{\text{total}} = P_{\text{o}} + \Delta P_{\text{o}} + \Delta P_{\omega} \cos(\omega t) + \Delta P_{2\omega} \cos(2\omega t) \tag{11}$$

where

$$P_{\text{o}} = \frac{3}{4} R\pi\sigma^{-1} I_{\text{o}}^2 F(x) H(z) \tag{12}$$

$$\Delta P_{\text{o}} = \frac{3}{8} R\pi\sigma^{-1} I_{\text{m}}^2 F(x) H(z) \tag{13}$$

$$\Delta P_{\omega} = \frac{3}{2} R\pi\sigma^{-1} I_{\text{o}} I_{\text{m}} F(x) H(z) \tag{14}$$

and

$$\Delta P_{2\omega} = \Delta P_{\text{o}} \tag{15}$$

At steady-state conditions in vacuum, the input power $P_{\text{o}}$ is just balanced by the radiative heat losses. When the coil current is modulated, the bulk sample temperature will rise by $\Delta T_0$ due to the increase $\Delta P_{\text{o}}$ in the average absorbed power as shown in Fig. 2. Although the temperature signal theoretically contains a $2\omega$ frequency component, this component was <1 % and negligible due to $I_{\text{m}} \ll I_{\text{o}}$. Determination of the specific heat from Eq. 14 requires a knowledge of the power modulation amplitude $\Delta P_{\omega}$ from the sample's temperature response. $\Delta P_{\omega}$ can be estimated from $P_{\text{o}}$ as

$$\Delta P_{\omega} = \frac{2 I_{\text{m}}}{I_{\text{o}}} P_{\text{o}} \tag{16}$$

where $P_{\text{o}}$ is experimentally obtained using the Stefan-Boltzmann law,

$$P_{\text{o}} = A\sigma_{\text{SB}}\varepsilon \left[ T_{\text{o}}^4 - T_{\text{env}}^4 \right] \tag{17}$$

The total hemispherical emissivity of the sample was determined from the spectral normal emissivity measurement by coupling a FTIR spectrometer with the electromagnetic levitator [19]. The sample specific heat was then calculated from measurements of $T_{\text{o}}$ and $\Delta T_{\omega}$ using the methodology described above, i.e., Eqs. 5, 16, and 17.

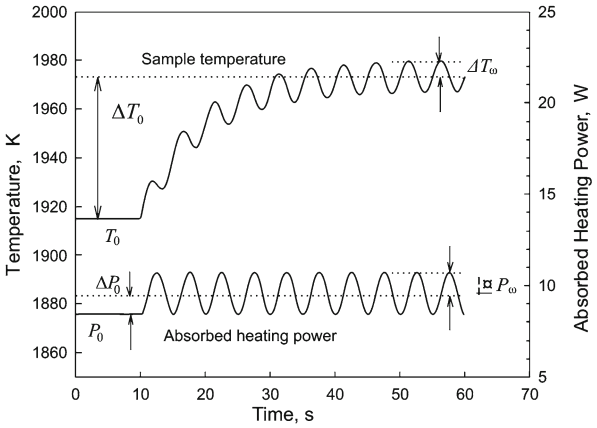


**Fig. 2** Schematic diagram of modulation heating power method

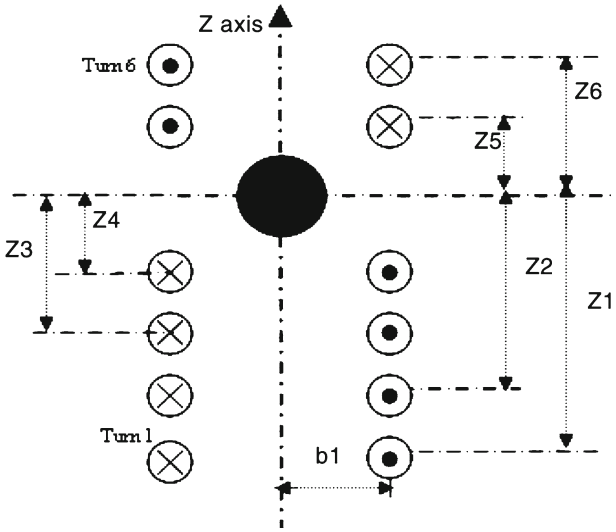


**Fig. 3** Vulcan-I EML coil system with a conducting sample in the middle of the system

## 3 Results and Discussion

The heat capacities of titanium and zirconium were evaluated in the temperature range of 1,300 K to 1,800 K. The experimentally measured heat capacities of titanium and zirconium as functions of temperature are compared to selected literature data as shown in Figs. 4 and 5, respectively. The measurements were performed for each material using two samples with different diameters as noted in the figures. The reproducibility of measurements for individual samples was ±3 %. The least-squares fit polynomial functions that represent the results for the heat capacity for titanium and zirconium in the measured temperature range are as follows:

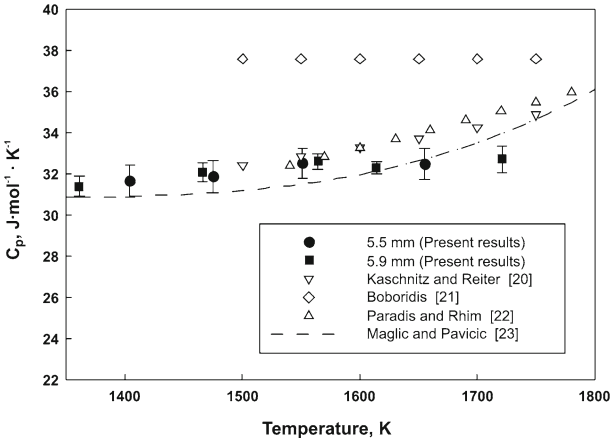


**Fig. 4** Heat capacity of titanium: present work and data reported in the literature

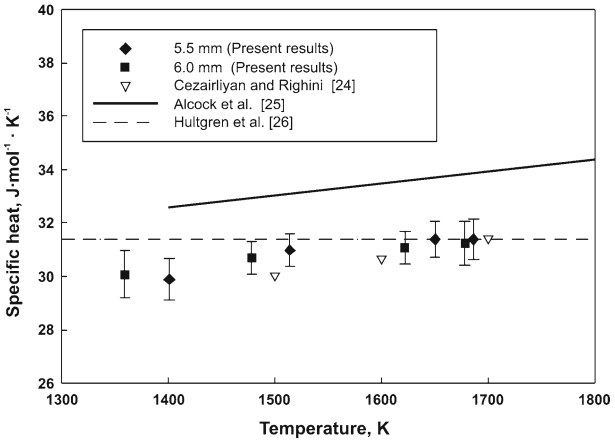


**Fig. 5** Heat capacity of zirconium: present work and data reported in the literature

Titanium:

$$C_{\mathrm{p}} = 75.767178 + 0.190T - 1.112 \times 10^{-4}T^2 + 2.194 \times 10^{-8}T^3 \qquad (18)$$

Zirconium:

$$C_{\mathrm{p}} = 121.315 - 0.2014T + 1.4415 \times 10^{-4}T^2 - 3.3410 \times 10^{-8}T^3 \qquad (19)$$

where $C_{\mathrm{p}}$ is in $\mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$ and T is in K. In the computation of heat capacity, the molar masses of titanium and zirconium were taken as 47.88 and 91.224.

Figure 4 shows that the experimentally determined heat capacity of titanium from the present work agrees with Maglic and Pavicic [20], Kaschnitz and Reiter [22], and Paradis and Rhim [23] up to approximately 1,600 K. The present data indicate lower

**Table 1** Uncertainty estimates of the specific heat measurement using the EML-modulated power method

| Parameter | Estimated $\pm 2\sigma$ confidence limits (%) | Specific heat change ($J \cdot mol^{-1} \cdot K^{-1}$) | Specific heat change squared $(J \cdot mol^{-1} \cdot K^{-1})^2$ |
|---|---|---|---|
| Temperature $T = 1500\,K$ | 0.5 | 0.648 | 0.420 |
| Modulation frequency $\omega = 0.2\,Hz$ | 0.2 | 0.065 | 0.004 |
| Sample mass $m = 484\,mg$ | 0.1 | 0.033 | 0.001 |
| Temperature amplitude $\Delta T_m = 10\,K$ | 0.5 | 0.162 | 0.026 |
| DC control voltage $V_o = 90\,V$ | 0.2 | 0.065 | 0.004 |
| AC control voltage $V_m = 21.8\,V$ | 0.2 | 0.035 | 0.001 |
| Emissivity $\varepsilon = 0.27$ | 4.0 | 1.294 | 1.674 |
| Total uncertainty in specific heat, $J \cdot mol^{-1} \cdot K^{-1}\left[\sum(\triangle\mu)^2\right]^{1/2}$ | | | 1.46 |
| Total % uncertainty in specific heat ($32.31\ J \cdot mol^{-1} \cdot K^{-1}$) | | | 4.52 % |

heat capacity values than the literature values in the 1,600 K to 1,700 K temperature range. Additional testing is required to better understand the reason for this divergence. Figure 5 shows that the experimentally determined heat capacity of zirconium from the present work is in good agreement with Hultgren et al. [24] and the pulse heat experiments reported by Cezairliyan and Righini [25]. Alcock et al. [26] reported slightly higher values of the heat capacity as well as a larger temperature dependence.

Moffat's uncertainty estimation procedure [27] was used to theoretically analyze the various contributions to the experimental uncertainty. The results of these calculations are shown in Table 1. The total estimated uncertainty (95 % confidence limits) is approximately 4.5 % for a typical specific heat measurement for a titanium sample. The largest contributor to the uncertainty in the specific heat measurement was the uncertainty in emissivity (primarily due to the $\pm 0.5$ % uncertainty in the temperature measurement of the noncontact pyrometer). Improvements in accuracy of the temperature characterization are possible on measurements of solid samples of pure elements evaluated incrementally below the melting temperature as well as pure liquid elements just above the melting temperature.

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