

NON-CONTACT MEASUREMENTS OF THERMOPHYSICAL PROPERTIES  
OF TITANIUM AT HIGH TEMPERATURE

Paul-François Paradis and Won-Kyu Rhim  
Jet Propulsion Laboratory, California Institute of Technology  
4800 Oak Grove Drive, Pasadena, CA 91109  
Telephone: (818) 354-2925  
Fax: (818) 393-5039  
Email: [won-kyu.rhim@jpl.nasa.gov](mailto:won-kyu.rhim@jpl.nasa.gov)

## ABSTRACT

Four thermophysical properties of both the solid and the liquid titanium measured using the high-temperature electrostatic levitator at JPL are presented. These properties are the density, the thermal expansion coefficient, the constant pressure heat capacity, and the hemispherical total emissivity. For the first time, we report the density, the thermal expansion coefficient, and the ratio of the constant pressure heat capacity over the hemispherical total emissivity of undercooled titanium over a wide range of temperatures. Over the 1650 ~ 2000 K temperature span, the liquid density can be expressed as  $\rho_l(T) = 4.208 \times 10^3 - 0.508 (T - T_m)$  kg/m<sup>3</sup> with  $T_m = 1943$  K, and the corresponding volume expansion coefficient as  $\alpha_l = 1.169 \times 10^{-4}$  K<sup>-1</sup>. Similarly, over the 1540 ~ 1940 K range, the measured density of the solid can be expressed as  $\rho_s(T) = 4.321 \times 10^3 - 0.212 (T - T_m)$ , giving a volume expansion coefficient  $\alpha_s = 4.76 \times 10^{-5}$  K<sup>-1</sup>. The constant pressure heat capacity of the liquid phase could be estimated as  $C_{pl}(T) = 46.06 - 3.21 \times 10^{-3} (T - T_m)$  J·mol<sup>-1</sup>·K<sup>-1</sup> if the hemispherical total emissivity of the liquid phase  $\epsilon_{Tl}$  remains constant at 0.35 over the 1650 ~ 2000 K range. Over the 1540 ~ 1940 K temperature span, the hemispherical total emissivity of the solid phase could be rendered as  $\epsilon_{Ts}(T) = 0.297 + 5.952 \times 10^{-5} (T - T_m)$ . The heat of fusion has also been calculated as 14.3 kJ·mol<sup>-1</sup>.

Keywords: titanium, thermophysical properties, high temperature, electrostatic levitation.

## 1. INTRODUCTION

Titanium is widely used for various applications (turbine blades, airframes, ship propeller shafts, etc.) because of its low density, good strength, ductility, refractory nature, and its resistance to corrosive chemical environments (acids, chloride solutions, sea water, etc.) [1]. However, its high melting point and the risk of contamination in its molten phase make it difficult to measure its thermophysical properties using traditional methods and hence, necessitate the use of a containerless technique. The advent of the electrostatic levitation, and the recent development of non-contact diagnostic techniques, circumvent these difficulties, allowing an accurate and quick determination of the thermophysical properties of different materials [2-8]. Our experimental facility allowed us to levitate a sample in a high vacuum, and to process it at high temperature using laser radiation, thus isolating it from contaminating container walls as well as surrounding gasses.

An accurate knowledge of thermophysical properties is important for various fundamental studies on phase transformations and nucleation, as well as industrial processes on metals, such as refining, forming and casting. In some cases, the properties can be used to determine other thermodynamic parameters. For instance, enthalpy, entropy, and the Gibbs free energy can be derived from the heat capacity. The present paper focuses on the thermophysical properties of both the solid and liquid titanium at high temperature. The properties include the density, the thermal expansion coefficient, the constant pressure heat capacity, and the hemispherical total emissivity.

## 2. EXPERIMENTAL SET-UP AND PROCEDURES

The measurements reported in this paper have been done using the high-temperature electrostatic levitator (HTESL) at the Jet Propulsion Laboratory [2]. Figure 1 shows a schematic diagram of the HTESL. The sample and electrodes

were housed in a stainless-steel chamber which was typically evacuated to  $10^{-8}$  Torr before heating began. The material, titanium of 99.99 % purity, came from the Johnson Matthey Company, Ward Hill, Massachusetts. For these measurements, samples with diameters close to 2.5 mm were used. The spheres were produced by laser melting the tip of a 1.0 mm diameter wire in a designated vacuum chamber. The HTESL achieved sample positioning between the parallel plate electrodes using a feedback control system. This system relied on He-Ne lasers that projected sample images on position detectors. Typically, the top and bottom electrodes were spaced 12 mm apart (fig. 2). The sample rotation rate was also monitored by detecting the reflected He-Ne laser beam from its surface so that the sample shape remained close to a spherical shape. A 1-kW xenon arc lamp was used for initial sample heating, until thermionic emission regime was attained. Then, the sample was heated further and melted using a Nd-YAG laser. For these experiments, temperatures in excess of 2000 K were reached while keeping a stable sample.

Once molten as shown in figure 3, the levitated sample assumed a nearly spherical shape, thanks to the action of surface tension. Moreover, since the electrostatic levitation scheme did not transfer any heat to the sample, a heated sample cooled purely radiatively when the cooling was initiated by blocking the laser beam. The energy equation describing the cooling process is given by:

$$\frac{m}{M} C_p \frac{dT}{dt} = -\epsilon_T A \sigma_{SB} (T^4 - T_a^4) \quad (1)$$

where  $m$  is the sample mass,  $M$  the atomic weight,  $C_p$  the molar heat capacity at constant pressure,  $T_a$  and  $T$  are respectively the ambient and sample temperatures,  $\epsilon_T$  the hemispherical total emissivity,  $A$  the surface area of the sample, and  $\sigma_{SB}$  the Stefan-Boltzman constant ( $5.6705 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$ ).

The temperature was measured using a single color custom-made pyrometer operating at 750 nm and was then digitized and calibrated using a LabView software. Since the heating was achieved with a laser at 1.06  $\mu\text{m}$ , the risks of spectral interference were avoided. The emissivity of the sample was determined with respect to the melting temperature (1943 K) and was assumed constant throughout the cooling. A typical cooling curve showing undercooling and recalescence is depicted in figure 4.

The simultaneous measurements of both the density and the heat capacity over temperature was initiated after the laser beam had been blocked and the sample allowed to cool. To measure the density, video images of the sample were recorded during the cooling process. In our case, the sample was axisymmetric and only a side view was needed (fig. 3). The recorded images were digitized and the sample area was extracted from each video frame. This area was converted to the true sample area using the images from a calibrated sphere and by an analysis software developed at JPL [5]. The volume could then be calculated, and, knowing the mass of the sample, the density was found. Finally, the temperature time dependency was extracted from the cooling curve and was correlated with video frames allowing the density to be expressed as a function of the temperature.

The ratio of heat capacity over hemispherical total emissivity was found as a function of temperature using equation (1) since all the other parameters were known. The temperature-time dependency ( $dT/dt$ ) was extracted from the cooling curve (fig. 4) and the sample area was found from the video images.

### 3. RESULTS AND DISCUSSION

#### 3.1. Density

The results of our density measurements for liquid titanium are shown in figure 5. The measurements were taken over the 1650 ~ 2000 K temperature range

and also cover the undercooled region by nearly 300 K. As that of other pure metals, the density of titanium exhibits a linear nature as a function of temperature and can be fitted by the following equation:

$$\rho_l(T) = 4.208 \times 10^3 - 0.508 (T - T_m) \text{ kg}\cdot\text{m}^{-3} \text{ (1650 ~ 2000 K),} \quad (2)$$

where  $T_m$  is the melting temperature (1943 K). In this experiment, the accuracy of the measurements was estimated to be  $\pm 0.5\%$ . To our knowledge, these measurements were the first reported that include the undercooled region. Many values that appear in various references are given in the vicinity of the melting point and are summarized in table 1. Our value agrees within 1.4 % with the result obtained by Saito et al [9] and is about 2.5% greater than those measured by Maurakh [10] and by Eljutin et al [11]. Our value is 11% larger than that estimated by Peterson et al [12], however, it agrees with the Allen's calculated value within 1.4 % [13]. Also, our temperature coefficient is smaller by nearly 30% compared to that measured by Maurakh and 1.25 times larger than that of Saito et al.

The volume variation  $V_l(T)$  of the molten state, normalized with the volume at the melting point  $V_m$ , can be derived from equation (2), and be fitted with the following equation:

$$V_l(T)/V_m = 1 + 1.17 \times 10^{-4} (T - T_m), \quad (3)$$

where  $1.17 \times 10^{-4}$  represents the volume expansion coefficient  $\alpha_l$  ( $\text{K}^{-1}$ ) which is within 25% of the value obtained by Seydel et al [14], considering only the first order term (low temperature approximation).

The observed discrepancies between our results and those of Maurakh and Eljutin et al could be attributed to the difference in processing techniques and the extent to which evaporation losses have been considered. We used a containerless

approach isolating our samples from container walls, whereas Maurakh and Eljutin et al used traditional schemes for which possible chemical reactions between the highly reactive molten titanium and crucibles could have altered the final density values. It is interesting to note that our result and that of Saito et al, both obtained using containerless techniques, are identical at the melting point within the experimental errors.

Figure 5 also shows the density measurements for the solid phase over the 1540 ~ 1940 K temperature range. Again, a linear behavior is observed and the data can be fitted by the following equation:

$$\rho_s(T) = 4.321 \times 10^3 - 0.212 (T - T_m) \text{ kg}\cdot\text{m}^{-3} \text{ (1540 ~ 1940 K)}. \quad (4)$$

These are the first data to be reported on the density of solid titanium over a wide range of high temperatures. Our value for the density of the solid at the melting temperature compares well with those found in the literature. Our density is, within our experimental errors, identical to that reported by Peterson et al.

From equation (4), the volume variation  $V_s(T)$  of the solid, normalized with the volume at melting temperature  $V_m$ , can be derived and it can be expressed by the following equation:

$$V_s(T)/V_m = 1 + 4.76 \times 10^{-5} (T - T_m), \quad (5)$$

where  $4.76 \times 10^{-5}$  represents the volume expansion coefficient  $\alpha_s$  ( $\text{K}^{-1}$ ). To our knowledge, this is the first time that this value is reported.

As can be seen in figure 5, there is a discontinuity in density at the melting point, characteristic of a first order transition. The figure also reveals a crossing point (~ 1550 K) between the solid curve and the extrapolated liquid curve. This

point, being 393 K below the melting temperature and 97 K below the heterogeneous nucleation limit achieved in these experiments, may correspond to the undercooling limit before the homogeneous nucleation comes into effect. To further reduce heterogeneous nucleation, undercooling experiments with samples smaller than the one used for the present experiments ( $\ll 2$  mm) are being planned.

### 3.2. Constant-Pressure Heat Capacity

The ratio between the constant-pressure heat capacity and the hemispherical total emissivity as a function of the temperature is shown in figure 6 for both the solid and the liquid titanium. To our knowledge, this is the first time these data are reported. For the liquid state,  $C_{pl}(T)/\varepsilon_{Tl}$  is nearly constant over temperature and can be fitted as:

$$C_{pl}(T)/\varepsilon_{Tl} = 151.17 - 9.29 \times 10^{-3} (T - T_m) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ (1650 ~ 2000 K)}. \quad (6)$$

If the value of  $C_{pl} = 45.50 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$  given by Treverton et al [15] at the melting temperature is used, the  $\varepsilon_{Tl}$  that can be determined from equation (11) is given by  $\varepsilon_{Tl} = 0.35$  at that temperature. Then, assuming that  $\varepsilon_{Tl}$  remains to be constant at 0.35 over the temperature range, the temperature dependency of  $C_{pl}$  can be determined from equation (6) by simply multiplying by  $\varepsilon_{Tl} = 0.35$ . The heat capacity  $C_{pl}(T)$  so obtained (fig. 7) can be expressed by the following equation:

$$C_{pl}(T) = 46.06 - 3.21 \times 10^{-3} (T - T_m) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ (1650 ~ 2000 K)}. \quad (7)$$

In addition, the heat of fusion has been determined by adding the enthalpy contributions of the undercooled liquid and that of the isothermal region following the recalescence (see fig. 4)[3]. The contribution of the undercooled portion was



found by integrating  $C_{pl}$  over temperature from  $T_m$  to the lowest temperature of undercooling whereas that of the isothermal solid was obtained by integrating  $\epsilon_{Ts} A \sigma_{SB} (T^4 - T_a^4)$  over the time at which the solid stays at  $T_m$ . The heat of fusion found was  $14.3 \text{ kJ}\cdot\text{mol}^{-1}$ , which is 8% higher than that measured by Treverton et al [15] but 17% lower than that reported by Maurakh et al [16]. Uncertainty in  $C_{pl}$  might account for the difference. The HTESL can measure  $C_{pl}(T)/\epsilon_{Tl}(T)$  accurately, however, the accuracy of  $C_{pl}(T)$  or  $\epsilon_{Tl}(T)$  is limited by the accuracy of the reference value,  $C_{pl}(T_m)$  or  $\epsilon_{Tl}(T_m)$ , available in the literature.

Figure 6 also gives the variation of  $C_{ps}/\epsilon_{Ts}$  as a function of temperature for high temperature solid titanium. The ratio can be expressed as:

$$C_{ps}(T)/\epsilon_{Ts} = 76.59 + 2.73 \times 10^{-2} (T - T_m) \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ (1540 ~ 1940 K)}. \quad (8)$$

Cezairliyan and Müller [17] measured  $C_{ps}(T)$  and  $\epsilon_{Ts}(T)$  using a pulse heating technique. According to these authors, their results of  $C_{ps}(T)$  are more reliable than those for their  $\epsilon_{Ts}(T)$ . Using their value for  $C_{ps}(T)$  and our value for  $C_{ps}(T)/\epsilon_{Ts}$  (fig. 6), it is possible to estimate  $\epsilon_{Ts}$  as a function of temperature (fig. 8). The hemispherical total emissivity so obtained can be fitted as:

$$\epsilon_{Ts}(T) = 0.297 + 5.952 \times 10^{-5} (T - T_m) \quad (1540 \sim 1940 \text{ K}). \quad (9)$$

If the values reported in the literature are extrapolated to the melting point, then at the melting point, our value of  $\epsilon_{Ts}$  is 20% lower than that reported by Cezairliyan and Müller, 15% lower than that reported by Landersperger et al [18], 3.5% lower than that of Zhorov [19] and 5% higher than those of Arutyunov et al [20] and Peletskii et al [21]. The present coefficient is 34% lower than that reported by Zhorov, 10% lower than that of Arutyunov et al, and 44% lower than that of

Peletskii et al. The above discrepancies may be attributable to differences in sample surface conditions. As the samples solidified from deeply undercooled liquid states, the smooth surface condition seemed to have preserved. This is probably due to the fact that the solids resulting from deeply undercooled liquids tends to produce fine micro-structures, leading to a smooth surface [22]. Cezairliyan and Müller, however, noticed during their work that the initial smooth surface of their sample changed to an uneven rough surface as a result of repeated heating and cooling. This may partially account for their higher values of emissivity.

#### 4. CONCLUSION

We have presented several thermophysical properties of solid and liquid titanium, measured using the high temperature electrostatic levitator (HTESL) at JPL. For the first time, we reported the densities and the thermal expansion coefficients of undercooled titanium over a wide temperature range. We also presented results of the densities and the thermal expansion coefficients of both solid and liquid titanium as a function of temperature. The constant pressure heat capacity of molten Ti as well as those of the hemispherical total emissivity of the solid phase complemented the data that can be found in the literature.

All the thermophysical properties presented were determined or derived from cooling curves and images acquisition. Therefore, to improve our data, efforts should still be directed onto ways to increase image sharpness, resolution, and contrast. Efforts should also be put in new numerical techniques to determine  $dT/dt$  from the cooling curves to diminish numerically induced errors.

As a final note, we would like to mention that our facility also possesses the capability to determine the spectral emissivity, surface tension, viscosity [8], and the electrical conductivity [6]. Some instrument modifications are currently

underway to implement these capabilities to titanium, and the results will be published elsewhere.

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## FIGURE CAPTIONS

- Figure 1. A schematic diagram of the high-temperature electrostatic levitator.
- Figure 2. A schematic arrangement of the electrode assembly.
- Figure 3. A side image of a molten, levitating titanium sample.
- Figure 4. A radiative cooling curve of titanium exhibiting a deep undercooling and the recalescence.
- Figure 5. Density of titanium versus the temperature, obtained from the video image analysis and the cooling curve data.
- Figure 6. Ratio between the constant-pressure heat capacity and the hemispherical total emissivity of titanium versus the temperature.
- Figure 7. Heat capacity of liquid titanium versus the temperature, calculated using the data in figure 6 and  $\epsilon_{Tl} = 0.35$  [15].
- Figure 8. Hemispherical total emissivity  $\epsilon_{Ts}$  as a function of the temperature estimated using the data from figure 6 and the  $C_{ps}(T)$  from reference [16].

Table 1. Density of liquid titanium at or in the vicinity of its melting temperature.

$\rho_l$ (kg·m <sup>-3</sup> )	T. coeff. (K <sup>-1</sup> )	T (K)	Reference
4208	0.508	1943	Our group
4140	0.226	1943	Saito et al [9]
4110	0.702	1958	Maurakh [10]
4100		1943	Eljutin et al [11]
3800		1943	Peterson et al [12]
4150		1943	Allen [13]

















