Int J Thermophys (2010) 31:388–398
DOI 10.1007/s10765-010-0721-0

Thermophysical Property Measurements of Liquid Gadolinium by Containerless Methods

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Received: 29 May 2009 / Accepted: 2 March 2010 / Published online: 20 March 2010

Abstract Thermophysical properties of liquid gadolinium were measured using non-contact diagnostic techniques with an electrostatic levitator. Over the 1585 K to 1920 K temperature range, the density can be expressed as $\rho(T) = 7.41 \times 10^3 - 0.46(T - T_\mathrm{m})$ $(\mathrm{kg \cdot m^{-3}})$ where $T_\mathrm{m} = 1585\,\mathrm{K}$, yielding a volume expansion coefficient of $6.2 \times 10^{-5}\,\mathrm{K}^{-1}$. In addition, the surface tension data can be fitted as $\gamma(T) = 8.22 \times 10^2 - 0.097(T - T_\mathrm{m})(10^{-3}\,\mathrm{N \cdot m^{-1}})$ over the 1613 K to 1803 K span and the viscosity as $\eta(T) = 1.7\exp[1.4 \times 10^4/(RT)](10^{-3}\,\mathrm{Pa \cdot s})$ over the same temperature range.

Keywords Density · Gadolinium · Liquid · Surface tension · Viscosity

1 Introduction

Rare earth elements and their compounds are currently used to improve the resistance of certain glasses, to fabricate hydrogen sponges and strong magnets, and as dopants in optical amplifiers [1]. To assist further material development, knowledge of the physical properties of rare earth metals and their temperature dependences is, therefore, paramount. However, rare earths are very reactive, oxidizing rapidly when exposed to air and reacting directly with nitrogen and other elements. This explains why accurate physical properties are difficult to measure in their liquid phase when

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traditional methods are used (e.g., crucible, support) and why there are little data reported.

In the past decade, the electrostatic levitation method has been developed [2] and thermophysical properties of refractory metals were reported using non-contact measurement techniques. Recently, some rare earth metals (La, Pr, Nd [3], Tb [4], and Ce [5]) were also processed with this method and their thermophysical properties were measured.

Gadolinium and its alloys are used for microwave applications, color TV tubes, compact discs, and computer memory [1]. Gadolinium also has unique magnetic properties and is used as an intravenous contrast agent to enhance medical magnetic resonance imaging. In spite of these wide applications, only a few articles [6–9] have been published, which report its thermophysical properties.

In this study, the density, surface tension, and viscosity of molten gadolinium have been measured with the electrostatic levitation method. The containerless technique in vacuum was used to overcome the contamination problems associated with conventional high temperature processing and to allow accurate determination of these properties. This article first briefly describes the experimental facility and the measurement methods, and then presents the experimental results.

2 Experimental Setup and Procedures

2.1 Electrostatic Levitation Furnace

The facility consisted of a vacuum chamber (10^{-5} Pa pressure before processing) (Fig. 1) that housed the levitator. A sample, charged by electrostatic emission, was levitated between two disk-shaped electrodes, separated by 10 mm. These electrodes

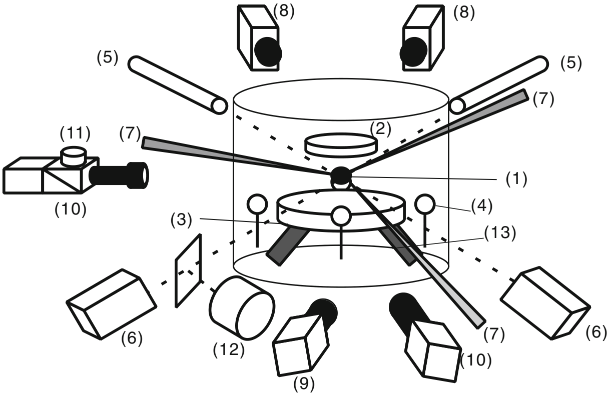

Fig. 1 Schematic view of the electrostatic levitation furnace and its diagnostic apparatus: (1) sample, (2) top electrode, (3) bottom electrode, (4) side electrode, (5) He–Ne laser, (6) position detector, (7) CO_2 laser beam, (8) pyrometer, (9) CCD camera, (10) CCD camera with telephoto objective lens, (11) rotation detector, (12) oscillation detector, (13) coil

were used to control the sample in the vertical position whereas four spherical electrodes distributed around the bottom electrode were used for horizontal control. The positioning of the sample relied on a feedback loop that consisted of two sets of He–Ne lasers and positioning sensors located at right angles of each other. The sample position information obtained by the position sensors was fed to a computer that instructed high-voltage amplifiers to output voltages such that the sample was maintained at a selected position [2]. The lower electrode was also surrounded by four coils that generated a rotating magnetic field that was used for rotation control [10]. In addition, oscillations of the molten sample could be triggered by superimposing an ac electric field on the levitation voltage on the top electrode. For these experiments, the samples were prepared by cutting a rod (99.9 mass% purity, Nilaco Co.) into pieces and then laser melting them into spheroids of about 2 mm in diameter.

The focused radiation of three CO_2 laser beams (10.6 μm emission, total power of 200 W) was used for sample heating. The separation of the beams by 120° and the sample rotation (<10 Hz) provided temperature homogeneity. Temperature measurements were carried out by pyrometers (0.90 μm and 0.96 μm). The sample was observed by three charged-coupled-device cameras. Two black and white high-resolution cameras with telephoto objectives provided magnified views of the sample whereas one color camera offered an overview of the inside of the chamber. The rotation rate was measured by detecting the intensity of the reflected He–Ne laser beam from the sample surface by adding an interference filter and a sensor to one of the telephoto objectives. Another sensor was attached to another telephoto objective to measure the sample oscillation.

2.2 Physical Properties Determination

For property measurements, the samples were levitated using a pre-heating technique [11]. Once levitated, the sample was rotated at a frequency of a few Hertz, melted and re-solidified to confirm pyrometer calibration and alignment. The radiance temperature was measured by the pyrometers and was calibrated to the true temperature using the known melting temperature of gadolinium (1585 K). As shown in Fig. 2, upon closing the shutters of all heating lasers, the Gd sample exhibited the liquid–solid transition as well as the allotropic transition (bcc to hcp, 1508 K) upon cooling. No undercooling was observed even though several heating–cooling cycles were performed. The emissivity values on the pyrometers were adjusted so that the first temperature plateau in Fig. 2 matches the melting temperature within a 10 K tolerance. This heating–cooling process was repeated a few times to get proper emissivity settings of the pyrometers. This process was also advantageous to remove volatile impurities by “vacuum remelt” as described in Ref. [6]. The final temperature adjustment was performed from Planck’s law using in-house developed software in the post-experiment analysis. The emissivity of the gadolinium samples was estimated to be 0.18 in the 0.90 μm to 0.96 μm range.

The density was determined by simultaneously recording the temperature and the magnified images of a sample [12] illuminated from behind with an ultraviolet source

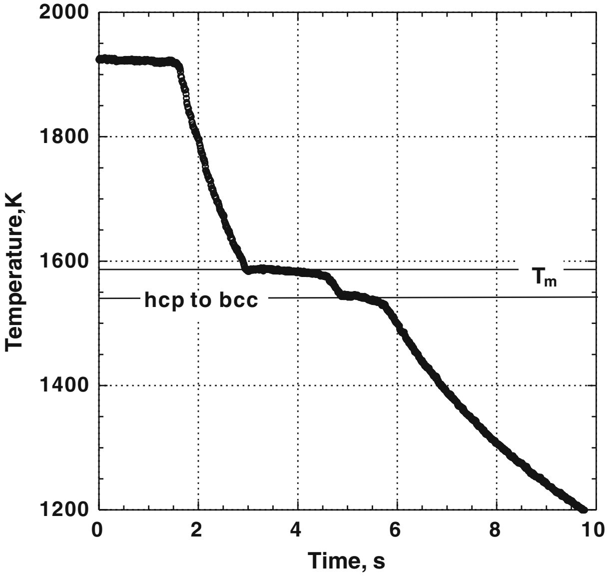

Fig. 2 Radiative temperature profile for a gadolinium sample

[11]. The sample area was extracted from each digitized video image and matched to the temperatures corresponding to the liquid phase. These images were calibrated by levitating a sphere of precisely known diameter under identical conditions. Since the sample was axi-symmetric and because its mass was known, the density could be found for each temperature by dividing the mass by the volume.

The surface tension and viscosity were obtained by inducing an oscillation ($P_2(\cos\theta)$-mode) to a liquid sample by superimposing a small sinusoidal electric field on the levitation field. The sample was slightly rotated (<10 Hz) to prevent oscillations other than mode-2 from happening. The transient signal that followed the termination of the excitation field was detected and analyzed using custom-built software. This was performed a few times at a given temperature and repeated for several temperatures. Using the characteristic oscillation frequency ω_c of this signal after correcting for non-uniform surface charge distribution, the surface tension γ was determined from [13]

$$\omega_c^2 = \left(\frac{8\gamma}{\rho r_0^3}\right) Y \tag{1}$$

where r_0 is the radius of the sample, ρ is the density, and Y is the correction factor that depends on the drop charge, the permittivity of vacuum, and the applied electric field [14,15]. Similarly, using the decay time τ given by the same signal, the viscosity η can be determined [16] by

$$\eta = \frac{\rho r_0^2}{5\tau}. \tag{2}$$

In order to avoid the influence of positive feedback sample position control on the viscosity measurement, the feedback control frequency was reduced to 120 Hz (with a sampling rate at 240 Hz) [17]. Real-time values of the radius and density data, obtained by the image analysis, were substituted in Eqs. 1 and 2 to avoid any detrimental effects of sample evaporation on the surface tension and viscosity data.

As the oxygen contamination can have a dramatic effect on the surface tension of gadolinium, the vacuum chamber was evacuated to around (4.0 to 5.0)×10^{-5} Pa, which was better than the experimental conditions of Ref. [6] ((1 to 2)×10^{-4} Pa). Furthermore, a titanium sublimation pump was used to reduce the oxygen concentration as much as possible.

3 Experimental Results

3.1 Density

The density measurements of liquid gadolinium, taken over the 1585 K to 1920 K temperature range are shown in Fig. 3 with 2 % error bars. In addition, the raw data are presented in Table 1. The density, like that of other pure metals, exhibits a linear behavior as a function of temperature and can be fitted by the following relationship with a confidence interval of 95 %:

$$\rho(T) = (7.410 \pm 0.044) \times 10^3 - (0.46 \pm 0.03)(T - T_\mathrm{m}) \left(\mathrm{kg \cdot m^{-3}}\right) \quad (1585\,\mathrm{K\ to\ }1920\,\mathrm{K}) \tag{3}$$

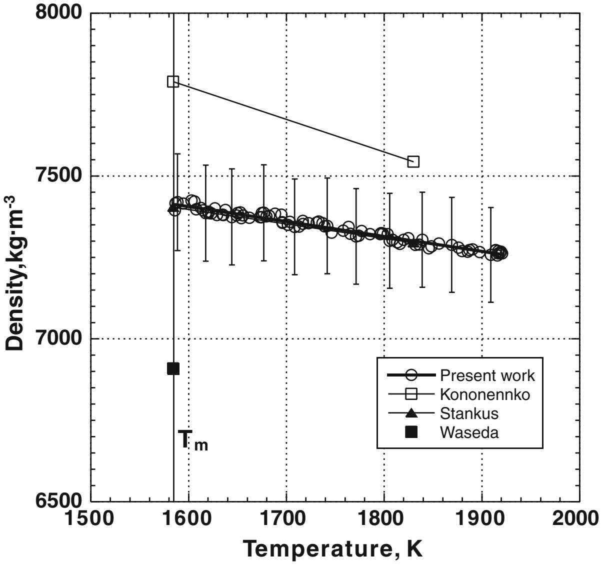

Fig. 3 Density of liquid gadolinium versus temperature

Table 1 Density (ρ) of molten gadolinium as a function of temperature (T)

T (K)	ρ ($\mathrm{kg \cdot m^{-3}}$)	T (K)	ρ ($\mathrm{kg \cdot m^{-3}}$)	T (K)	ρ ($\mathrm{kg \cdot m^{-3}}$)
1920.6	7262.3	1757.9	7332.8	1617.4	7386.0
1919.6	7268.2	1746.4	7325.9	1620.3	7390.6
1918.7	7264.1	1741.7	7346.9	1614.5	7395.2
1916.8	7270.3	1738.8	7346.3	1612.6	7402.6
1916.8	7263.0	1736.9	7355.3	1607.8	7397.7
1915.8	7256.1	1733.1	7360.6	1605.9	7421.9
1913.9	7272.3	1731.2	7357.9	1603.0	7424.9
1913.9	7273.0	1722.6	7356.0	1594.4	7415.4
1909.2	7258.0	1716.8	7362.6	1588.7	7419.8
1897.8	7267.0	1716.8	7352.9	1586.7	7417.0
1890.2	7274.8	1713.0	7345.0	1585.8	7394.8
1887.3	7273.3	1708.2	7344.3		
1885.4	7267.6	1703.5	7359.9		
1879.7	7270.0	1701.6	7350.1		
1875.9	7280.6	1695.8	7356.2		
1869.3	7288.9	1695.8	7359.0		
1856.0	7292.9	1694.9	7381.8		
1848.3	7284.9	1688.2	7384.4		
1845.5	7278.5	1682.4	7378.3		
1838.8	7304.5	1679.6	7376.1		
1836.0	7289.9	1676.7	7387.3		
1832.2	7288.6	1674.8	7386.6		
1824.6	7309.6	1674.8	7373.7		
1819.8	7304.9	1672.9	7373.8		
1816.0	7292.0	1662.4	7371.7		
1813.1	7296.7	1655.7	7379.1		
1808.4	7304.7	1653.8	7370.7		
1805.5	7301.3	1652.8	7388.9		
1803.6	7321.7	1649.9	7386.3		
1798.8	7324.2	1649.0	7379.5		
1796.9	7325.1	1644.2	7374.5		
1796.0	7322.4	1637.5	7396.2		
1785.5	7322.7	1635.6	7380.5		
1776.9	7331.2	1634.6	7381.7		
1774.1	7316.4	1628.9	7381.0		
1771.2	7314.7	1627.0	7400.8		
1765.5	7323.4	1623.1	7385.8		
1763.6	7344.2	1620.3	7386.3		

where T_m is the melting temperature (1585 K [18]). In these measurements, the uncertainty is 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) [19]. Around the melting temperature, our value is in excellent agreement with the value obtained by Stankus et al. [7] using a radioscopic method based on a monochromatic beam of γ-radiation. Moreover, our value is 5 % lower than that measured by Kononenko et al. [6] by the sessile drop method and is 7.2 % larger than that obtained by Waseda and Tamaki [8].

As for the temperature dependence of the density, our value showed good agreement with that by Stankus et al., but is much smaller than that reported by Kononenko et al. Our value also compared well with the theoretical estimation of Kiselev and Kononenko [20] ($0.539\,\mathrm{kg}\cdot\mathrm{m}^{-3}\cdot\mathrm{K}^{-1}$) that used the hard-sphere model and thermodynamic parameters.

The volume variation $V(T)$ of the molten state, normalized with the volume at the melting temperature V_m, was derived from Eq. 3, and can be expressed by

$$V(T)/V_m = 1 + 6.2 \times 10^{-5}(T - T_m) \quad (1613\,\mathrm{K\ to\ }1803\,\mathrm{K}) \tag{4}$$

where 6.2×10^{-5} (K^{-1}) represents the volume expansion coefficient.

For the density, it is reasonable to attribute the discrepancy between our measurements and those reported in Ref. [6] to the uncertainty of the surface profile of the drop. Literature values were reported more than 20 years ago. At that time, the analysis of the drop images was performed by manual methods in which human errors could not be avoided. Moreover, with this method, it was hard to process several points along the drop perimeter, which reduced the accuracy of the measurements.

3.2 Surface Tension and Viscosity

The measured surface-tension data are listed in Table 2. For these experiments, the typical characteristic oscillation frequency of the gadolinium sample was around 150 Hz, which was far enough to avoid the effect of the sample position control (120 Hz). In addition, the correction factor Y in Eq. 1 ranged from 1.03 to 1.04. Figure 4 depicts the results (5 % error bars) for the surface tension of gadolinium. In this experiment, the uncertainty of the measurements was estimated to be better than 5 % from the response of the oscillation detector, from the rotation, and from the density measurements [19]. Data available from the literature were superimposed on the same figure for comparison. The surface-tension data, obtained over the 1613 K to 1803 K temperature range, can be expressed with a confidence interval of 95 % by

$$\gamma(T) = (8.22 \pm 0.33) \times 10^2 - (0.097 \pm 0.02)\,(T - T_m)\,(10^{-3}\,\mathrm{N}\cdot\mathrm{m}^{-1}) \\ (1613\,\mathrm{K\ to\ }1803\,\mathrm{K}) \tag{5}$$

The scatter observed in the data is due to the motion of the sample with respect to the oscillation detector upon exciting the drop oscillation. At the melting temperature, our result exhibited good agreement with that obtained by Brissot and Martres [9] with

Table 2 Surface tension (γ) of molten gadolinium as a function of temperature (T)

T (K)	γ (10^{-3} N · m^{-1})	T (K)	γ (10^{-3} N · m^{-1})
1803	801.24	1803	801.76
1803	799.50	1803	800.87
1773	804.03	1773	802.76
1773	801.47	1773	803.10
1773	807.48	1773	803.88
1773	806.61	1723	808.72
1723	809.76	1723	807.17
1723	812.42	1723	808.16
1723	807.23	1673	810.66
1673	815.47	1673	809.78
1673	815.86	1673	808.93
1673	814.37	1643	813.66
1643	820.47	1643	813.63
1643	820.75	1643	814.24
1643	821.19	1613	818.21
1803	799.79		

the drop-weight method, but was 23.7 % higher than that measured by Kononenko et al. [6] with the sessile-drop method.

The large discrepancy between our data and that of Ref. [6] is possibly due to the difficulty of accurate measurements of drop dimensions by the sessile-drop method. A small difference could lead to significant errors in the calculation. Also, those previous data were obtained without computer image analysis and are likely to contain a certain amount of human error.

By extracting decay times from the drop oscillation signals, it was possible to determine the viscosity of liquid gadolinium over the 1613 K to 1803 K range. The measured viscosity data are shown in Table 3. Figure 5 illustrates our data that can be fitted by the following Arrhenius function:

$$\eta(T) = 1.7\exp[1.4 \times 10^4/(RT)] \left(10^{-3}\,\mathrm{Pa}\cdot\mathrm{s}\right) \quad (1613\,\mathrm{K\ to\ }1803\,\mathrm{K}), \tag{6}$$

where R, the universal gas constant, is equal to 8.31 J · mol^{-1} · K^{-1}. The experimental uncertainty is estimated to be around 20 % and is mainly attributed to the measurement error of τ that is affected by the sample translation [19]. Our data are, to the best of our knowledge, the first to be reported for liquid gadolinium. Previous experiments done with several elemental metals, for which literature data are available, have shown the validity of the technique. To ensure that the data obtained in this work were not distorted by the fact that Rayleigh's analysis [21] of the drop oscillation was developed for inviscid liquids, the parameter,

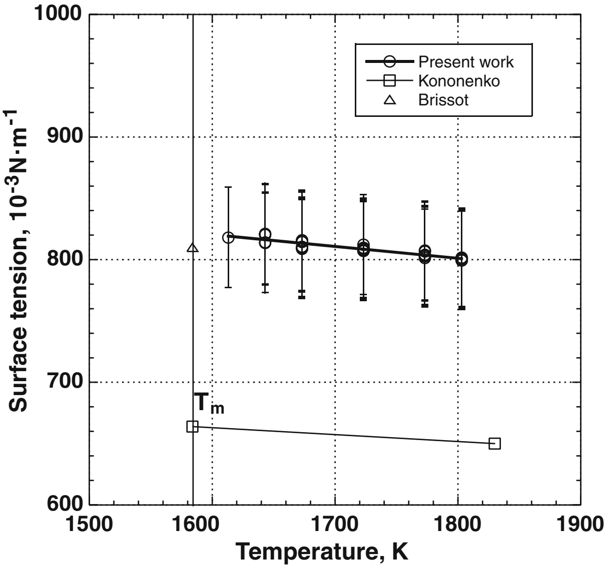

Fig. 4 Surface tension of gadolinium versus temperature

Table 3 Viscosity(η) of molten gadolinium as a function of temperature (T)

T (K)	η (10^{-3} Pa · s)
1803	4.577
1803	4.756
1803	4.265
1773	4.458
1773	4.485
1773	4.419
1723	4.519
1723	4.756
1723	5.108
1673	4.598
1673	4.494
1673	4.443
1643	4.700
1643	4.768
1643	5.019
1613	5.615

$$\alpha^2 = \frac{\sqrt{8\gamma\rho r_0}}{\eta} \tag{7}$$

as given by Suryanarayana and Bayazitoglu [22], was calculated. For $\alpha^2 > 59$, the deviation from the resonant frequency from Rayleigh's analysis is less than 1 % [23]. In our experiments, the lowest value of this parameter was higher than 1200 over the

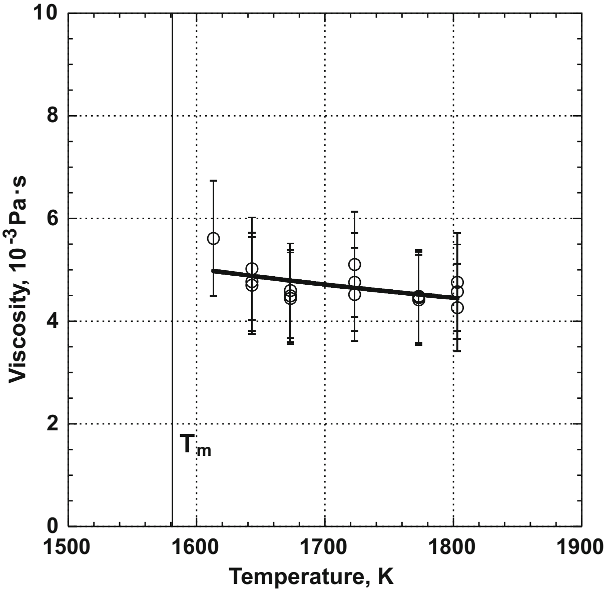

Fig. 5 Viscosity of gadolinium versus temperature

entire temperature range, and therefore, the deviation of the resonant frequency from Rayleigh's analysis for an inviscid droplet was much less than 1 %.

4 Conclusions

Thermophysical properties of liquid gadolinium were measured with an electrostatic levitator. For the first time, the viscosity of liquid gadolinium was reported. Also given in this article were the density, the thermal expansion coefficient, and the surface tension over wide temperature ranges.

Acknowledgment We would like to express our deepest gratitude to the Japan Society for the Promotion of Science for their Grant-in-Aid for Scientific Research (B).

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