J. Chem. Thermodynamics 121 (2018) 145–152

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Thermophysical properties of liquid Co measured by electromagnetic levitation technique in a static magnetic field

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ARTICLE INFO

Article history:
Received 20 September 2017
Received in revised form 30 January 2018
Accepted 4 February 2018
Available online 6 February 2018

Keywords:
Density
Electromagnetic levitation
Heat capacity at constant pressure
Thermal conductivity

ABSTRACT

Density, normal spectral emissivity, heat capacity, and thermal conductivity of liquid Co were measured by an electromagnetic levitation technique in a static magnetic field. High-purity Co (99.9995 mass%) prepared by an anion exchange method was used for the measurements. Uncertainty analysis was conducted for all experimental data. The emissivity data at 807 nm deviated from the Drude model, owing to interband transitions of electrons. The heat capacity was successfully measured at a low magnetic field of 3 T with some residual convection within the droplet. However, for thermal conductivity measurements, a larger magnetic field was required to suppress convection, which made the levitation unstable owing to the magnetic force. Although the thermal conductivity data showed a relatively large scatter, the data agreed with the Wiedemann–Franz law at low temperatures. At higher temperatures, the experimental data deviated from the Wiedemann–Franz law. For heat capacity measurements, translational motion of the Co droplet should be suppressed, while thermal transportation by convection flow in the droplet should be preserved. Conversely, for thermal conductivity measurements, the convection flow should also be suppressed. Therefore, in this study, the heat capacity and thermal conductivity of Co were measured under static magnetic fields of 3 and 9 T, respectively. Moreover, our experimental results were compared with free electron models, namely, the Drude model and Wiedemann–Franz law.

1. Introduction

Cobalt is an important alloying element for Co-based biomaterials such as artificial hip prosthesis and Ni-based super alloys used in jet engine turbine blades of aircraft. Knowledge of the thermophysical properties of liquid cobalt are required to improve manufacturing processes, such as recently developed 3D-printing technologies and casting processes. Accurate thermophysical properties are also required as input parameters for numerical simulations of casting processes.

We have been developing a high-temperature thermophysical property measurement system, namely, PROSPECT, to meet the broad material characterization demands of manufacturing industries. PROSPECT consists of an electromagnetic levitator (EML) and a superconducting magnet [1–6]. A static magnetic field suppresses surface oscillation, translational motion of the droplet, and convection flow within the droplet. This system enables accurate measurements of density, emissivity, heat capacity, and thermal conductivity of liquid metals without any contamination. In this study, density, normal spectral emissivity at 807 nm, heat capacity at constant pressure, and thermal conductivity of liquid Co were measured with PROSPECT. The experimental emissivity and thermal conductivity values were compared with values estimated by free electron theories, such as the Drude model and Wiedemann–Franz law.

2. Experimental

Sintered Co (99.8–99.9 mass% in purity) was used as a source material, which was further purified by anion-exchange separation in chloride media followed by plasma arc melting under oxidizing and reducing conditions [7–9] to obtain high-purity Co (99.9995 mass%). The chemical compositions of the high purity Co, as measured by glow discharge mass spectrometry, are presented in Table 1. Full details of the experimental apparatus and procedures for the thermophysical property measurements are given in previous reports [1–6]. The sample temperature was measured from the bottom of the levitated sample by a single-color pyrometer (Detection wavelength range: 1.45–1.8 μm, IS-140, Impac Electronic, Frankfurt, Germany), calibrated against the melting point of Co (1768 K) [21]. In this study, the sample temperature was

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https://doi.org/10.1016/j.jct.2018.02.004
0021-9614/

Table 1
Chemical compositions of high purity Co. Chemical composition (mass%).

Al	Cr	Cu	Fe	Mn	Ni	Co
<0.000048	0.0000017	0.00011	0.000028	0.0000067	0.000011	99.9995

determined based on the assumption that the emissivity of liquid Co at 1.6 μm featured no temperature dependence.

2.1. Density measurement

The sample was levitated electromagnetically in Ar-5 vol%H_2 gas atmosphere, then, a static magnetic field (B) of 4 T was applied to the sample droplet by a superconducting magnet (JMTD-10T 120SSFX, Japan Superconductor Technology, Kobe, Japan) to suppress sample oscillation and translational motion. Side-view images of samples were recorded for 15 s for each measurement at a frame rate of 200 fps, i.e., the average sample volume was obtained from 3000 images taken by a high-speed camera (MC1310, Mikrotron, Unterschleiβheim, Germany) with a laser back illumination system operating at 532 nm. The sample radius (r) was determined by fitting the sample edge with a series of Legendre polynomials, and its volume (V) was obtained assuming that the sample shape was rotationally symmetric around a vertical axis. Here, three different-sized stainless-steel balls (diameters: 4.760, 6.366 and 6.999 mm) were used as a calibration standard to obtain the real diameter of the sample droplet. The sample mass (m) was measured before and after the density measurements, and its average value was used for the density (ρ) determination.

2.2. Normal spectral emissivity measurement

The normal spectral emissivity $\varepsilon(\lambda, T)$ is defined as:

$$\varepsilon(\lambda, T) = \frac{R_s(\lambda, T)}{R_b(\lambda, T)} \quad (1)$$

where $R_s(\lambda, T)$ and $R_b(\lambda, T)$ are the normal spectral radiance emitted from the sample and a blackbody, respectively. The value of $R_b(\lambda, T)$ is obtained from Planck's law of radiation. On the basis of Eq. (1), the normal spectral emissivity can be determined from radiance measurements of the levitated sample droplet. Normal spectral radiation spectra from the top of the sample droplet were measured by a multichannel spectrometer (wavelength range 530–1100 nm, USB2000, Ocean Optics Inc., FL, USA). The spectrometer was calibrated with the use of a quasi-blackbody as a standard light source of 530–1100 nm. A static magnetic field of 3 T was applied to the sample droplet to suppress sample oscillation and translational motion.

2.3. Laser modulation calorimetry

2.3.1. Heat capacity measurement

The heat capacity of liquid Co was measured by noncontact laser modulation calorimetry. The top of the levitated sample was heated by a modulated laser at a power of $P_0(1 + \cos \omega t)$ with an angular frequency (ω), then, the temperature response was observed at the bottom of the sample with the single-color pyrometer. The temperature amplitude (ΔT_{ac}) and phase shift ($\Delta\phi$) between the laser intensity and temperature response are expressed as follows:

$$\Delta T_{ac} = \frac{\alpha S_h A P_0}{\omega C_P}\left(1 + \frac{1}{\omega^2\tau_r^2} + \omega^2\tau_c^2\right)^{-\frac{1}{2}} = \frac{\alpha S_h A P_0}{\omega C_P} f, \quad (2)$$

$$\Delta\varphi = \arccos\left\{\frac{\tau_c}{\omega}\left(\frac{1}{\tau_c\tau_r} - \omega^2\right)\left(1 + \frac{1}{\omega^2\tau_r^2} + \omega^2\tau_c^2\right)^{-\frac{1}{2}}\right\}$$
$$= \arccos\left\{\frac{\tau_c}{\omega}\left(\frac{1}{\tau_c\tau_r} - \omega^2\right) f\right\}, \quad (3)$$

Here, α is the laser absorptivity, S_h is the area ratio of the laser-irradiated part of the levitated sample, A is the surface area of the levitated sample, C_P is the heat capacity at constant pressure, T is the absolute temperature, and $\tau_r$and τ_c are the external and internal thermal relaxation times, respectively. In this study, the laser absorptivity was obtained from the normal spectral emissivity according to Kirchhoff's law. The correction function f is defined as:

$$f = \left\{1 + \frac{1}{\omega^2\tau_r^2} + \omega^2\tau_c^2\right\}^{-1/2}. \quad (4)$$

Quasi-adiabatic conditions, i.e., $\omega^2\tau_r^2 >> 1 >> \omega^2\tau_c^2$, which satisfies $f \approx 1$, are achieved by a proper choice of the modulation frequency and static magnetic field. Both the heat relaxation times were determined through curve fitting of Eq. (3) to the experimentally measured $\Delta\phi$-ω relation over the whole angular frequency range. For the heat capacity measurements, a relatively low-magnetic field strength (3 T) was applied to the droplet to reduce the internal relaxation time caused by residual convection flow inside the droplet, which contributed to satisfying the adiabatic condition. The value of C_P was determined by τ_c,τ_r and ΔT_{ac} according to Eq. (2).

2.3.2. Thermal conductivity measurement

Thermal conductivity was also measured by noncontact laser modulation calorimetry [1,3]. The heat conduction equation in the spherical coordinate system is expressed as:

$$\rho C_P \frac{\partial T}{\partial t} = \kappa\left\{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)\right\} + Q(r, \theta) \quad (5)$$

where κ is the thermal conductivity, $Q(r, \theta)$ is the heat generated by induction current, and r and θ denote the radial distance and polar angle, respectively. Equation (3) is solved from the relation between $\Delta\phi$ and ω by nonlinear least-squares fitting. Thermal conductivity is determined through curve fitting over the entire frequency range. For the thermal conductivity measurement, a relatively magnetic field of high strength (greater than 8 T) was applied to the droplet to suppress the convection flow inside the droplet.

3. Results

3.1. Density

The temperature dependence of the density of liquid Co together with literature data [10–18] are shown in Fig. 1 and Table 2. The density (ρ) is expressed as a linear function of temperature, including the supercooled temperature region.

$$\rho/\text{kg}\cdot\text{m}^{-3} = (-0.54) \times (T - 1768) + 7783 \quad [\text{Temperature range}: 1757 - 2001\ \text{K}] \quad (6)$$

The error bars in Fig. 1 present the expanded uncertainty, which is discussed in Section 4.1. The present work is in good agreement with previous results reported by Brillo et al. [10] (electromagnetic levitation method), Paradis et al. [16] (electrostatic levitation method), and Sato et al. [18] (pycnometer method) within experimental uncertainty.