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Microsecond Laser Polarimetry for Emissivity Measurements on Liquid Metals at High Temperatures—Application to Tantalum[1]

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The aim of this work was to determine accurate and reliable thermophysical properties of liquid tantalum from melting up to temperatures of 5000 K. Temperature measurements on pulse-heated liquid metal samples reported by different authors have always been performed under the assumption of a constant emissivity over the whole liquid range because of the lack of data for liquid metals. The uncertainty in temperature measurement is reduced in this work by the direct measurement of emissivity during the experiments. The emissivity measurements are performed by linking a laser polarimetry technique with the established method for performing high speed measurements on liquid tantalum samples at high temperatures during microsecond pulse-heating experiments. A set of improved thermophysical properties for liquid tantalum, such as temperature dependences of normal spectral emissivity at 684.5 nm, heat capacity, enthalpy, electrical resistivity, thermal diffusivity, and thermal conductivity, was obtained.

KEY WORDS: ellipsometric technique; heat capacity; liquid tantalum; normal spectral emissivity at 684.5 nm; thermophysical properties.

1. INTRODUCTION

It is well known that the spectral emissivity of a surface is a function of its optical constants, and may be modified by extrinsic characteristics such as surface roughness, and the presence of absorbing/non-absorbing overlayers such as oxides, nitrides, etc. Radiometric temperature measurement

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problems of industrial or scientific interest are often limited by the lack of knowledge of the spectral emissivity and its variation with temperature and wavelength for a given material. Multicolour or multi-spectral methods are commonly employed to overcome this problem, but it has been clearly shown [1, 2] that these methods are inaccurate and fail to work on the general problem, although they have been quite successful on specific problems of interest, in which *a priori* information about the emissivity dependence on wavelength is available [3].

Pulse heating techniques can be used to investigate liquid metals, but only optical methods are applicable for temperature measurements. A serious drawback of all pulse-heating experiments has been that the specimen temperature is uncertain because the spectral emissivity of the liquid metal was unknown and methods to measure the spectral emissivity in real-time had not been available up to now. Although the radiance temperature is readily measured by spectral radiation pyrometry, the methods for emissivity measurements on solids cannot be used on the liquid.

The most accurate method available to obtain the spectral emissivity of solid materials is to compare the radiance from the material of interest to a blackbody at the same temperature. This is practically realized by including a blackbody hole in the specimen of interest and comparing the radiance from the surface with that from the blackbody hole. This method has been widely practiced and is considered the standard method by which emissivity data of solid materials may be derived. It has been extensively used in millisecond pulse-heating experiments [4, 5] to measure thermophysical properties of high temperature materials. However, serious drawbacks of this approach include that the specimen of interest may be too small or inaccessible for the inclusion of a blackbody hole. This technique is limited to the solid phase; due to surface tension effects, the blackbody hole in a liquid metal sample usually is not stable.

Another method with millisecond resolution to measure the normal spectral emissivity of solid strip specimens is by an integrating sphere reflectometer under pulse heating conditions [6]. This method uses a high-speed version of an integrating sphere reflectometer of the comparison type in which the reflectivity of the sample, which undergoes pulse-heating, is measured in relation to the known reflectivity of a barium sulphate reference specimen. A modulated laser beam from a laser diode (900 nm) strikes the side of the sample facing the sphere. The reflected beam is collected hemispherically by the integrating sphere. A fast lock-in technique is used to discriminate between the reflected laser radiation and the continuous component generated by the specimen itself, when it reaches high temperatures.

A third approach to obtain normal spectral emissivity at the melting point is to measure the radiance temperature with a calibrated pyrometer and determine the normal spectral emissivity by using Planck's law along with a knowledge of the melting temperature [7].

The use of ellipsometric techniques for emissivity measurements is not new [8], but our implementation to achieve high speed measurements on liquid metals is novel. Although polarization state measurements have been practiced for well over a century, there has been limited progress in the development of instruments capable of measuring the complete state of polarization of light without moving parts. Traditionally, the polarization state of light has been measured with rotating element devices, where the polarizing and/or retarding elements are synchronously or asynchronously rotated. These approaches suffer from the problems of complexity, low speed, and high cost, but are generally very accurate. More recently, Azzam [9, 10] and Krishnan [11] have developed special polarimeters with no moving parts capable of accurately measuring the complete polarization state of light.

For the current work we measure the change of the polarization of laser light reflected from the liquid surface during pulse heating and derive the spectral emissivity by the methods of ellipsometry. The polarization state changes on a microsecond time scale are detected by a division-of-amplitude photopolarimeter (DOAP). This instrument divides the collected light into four beams detected by four photodetectors capable of simultaneous measurements; the outputs of the four detectors are digitized and the polarization state of the light is calculated from these four measured signals. Emissivity values are then obtained by standard equations of ellipsometry [12].

2. EMISSIVITY AND TEMPERATURE

Temperature is one of the important quantities to be determined when investigating thermophysical properties of metals by pulse heating techniques. Most of the optical pyrometers used for temperature measurements are sensitive to temperatures above 1,000 K. The radiation temperature of the sample is obtained using the voltage output of a calibrated pyrometer, operating on a single wavelength:

$$T_{\mathrm{rad}} = c_2 \left[\lambda \ln \left(\frac{K}{S} + 1 \right) \right]^{-1} \tag{1}$$

where S is the output signal of the pyrometer, T_{rad} is the radiation temperature of the sample at the effective wavelength λ of the pyrometer, K is the calibration-factor of the pyrometer-system, and c_2 is the second radiation constant. The true sample temperature T then can be obtained with the help of Planck's law by the following equation:

$$T = \frac{c_2}{\lambda\{\ln\left[\varepsilon\langle\exp(c_2/\lambda T_{\mathrm{rad}}) - 1\rangle + 1\right]\}} \tag{2}$$

where λ is the effective wavelength of the pyrometer, ε is the normal spectral emissivity at wavelength λ, and c_2 is the second radiation constant. One needs the actual value of the normal spectral emissivity at the wavelength of the pyrometer used for this procedure. The effective wavelength of a pyrometer is always temperature dependent, but this dependence is omitted in the succeeding presentation.

If such a calibrated pyrometer is not available, one can also use the known melting temperature of the specimen as a calibration point [8, 13]. Spectral radiance of the specimen surface is measured, which is related to Planck's law by the following relation:

$$J(T) = g \int_{\lambda=0}^{\infty} \sigma(\lambda)\, \tau(\lambda)\, \varepsilon(\lambda, T)\, \frac{c_1}{\lambda^5[\exp(c_2/\lambda T) - 1]}\, d\lambda, \tag{3}$$

where J is the radiance intensity, T is the temperature, g is the geometric factor of the pyrometer-system, λ is the wavelength, σ is the spectral sensitivity of the detector, τ is the transmittance of the optical systems, ε is the normal spectral emissivity, and c_1, c_2 are the first and second radiation constants.

By forming ratios of the measured radiance intensity at melting $J(T_{\mathrm{M}})$ and the measured radiance intensity $J(T)$ at temperature T, one obtains the unknown temperature T with the melting temperature of the investigated material as the calibration point:

$$T = \frac{c_2}{\lambda \ln\left\{1 + \frac{J(T_{\mathrm{M}})\, \varepsilon(\lambda, T)}{J(T)\, \varepsilon(\lambda, T_{\mathrm{M}})}\left[\exp\left(\frac{c_2}{\lambda T_{\mathrm{M}}}\right) - 1\right]\right\}} \tag{4}$$

where $\varepsilon(\lambda, T)$ is the emissivity of the liquid sample and $\varepsilon(\lambda, T_{\mathrm{M}})$ is the emissivity at the melting temperature. Traditionally, the assumption has been made that the value of the emissivity of the liquid metal has the same value as that at the melting temperature $\varepsilon(\lambda, T)/\varepsilon(\lambda, T_{\mathrm{M}}) = 1$ [14]. The lack of appropriate emissivity data for the liquid metal again results in increased uncertainties of temperature measurements.

There is another approach to obtain the temperature of a surface when a pyrometer is used, which also demonstrates the need of the value of the normal spectral emissivity. Again the measured quantity is the radiance, or apparent, temperature T_{rad}. The value of T_{rad} is related to the true surface temperature T, through Planck's law. If the product of the temperature T and λ_{eff}, the effective wavelength of the radiometer is less than 2472 μm · K, Wien's approximation to Planck's law deviates less than 0.5% and the relationship between T and T_{rad} is given by

$$\frac{1}{T}-\frac{1}{T_{\mathrm{rad}}}=\frac{\lambda}{c_2}\log(\varepsilon_\lambda) \tag{5}$$

Equation (5) demonstrates that values of the normal spectral emissivity are required in order to derive the true temperature from measurements of T_{rad} and is quite often used for industrial applications.

The main problem in surface temperature measurements using pyrometers is the necessity of knowing the spectral emissivity $\varepsilon(\lambda, T)$, which is, in general, unknown for liquid metals. Two trends of thought exist on the best approach to minimize the problem: Some investigators tried to keep the uncertainty of the determination of temperature low, using measurements at many wavelengths simultaneously, while others recommend to confine the measurements to only one wavelength as outlined above.

Multiwavelength-pyrometry tries to determine both temperature and emissivity, by measuring the spectral radiance of the surface at different wavelengths. In this case, a mathematical relation for the dependence of emissivity on wavelength must be assumed. The validity of the assumption cannot be determined from the experimental data, and so the magnitude of the resulting systematic error cannot be predicted [15]. Multiwavelength-pyrometers have been developed and described by various authors [16–18]. But when there is little or almost no information available about the emissivity, an increasing number of wavelengths used does not increase the accuracy of temperature measurements [19].

These facts indicate that there is a strong need for a technique to measure emissivity of liquid metals which may be applied to the general problem of non-contact temperature measurements on freely radiating surfaces. Within this work the solution is the measurement of normal spectral emissivity using fast laser polarimetry. Here spectral emissivity measurements on microsecond pulse-heated liquids are provided via an ellipsometric method, which has already proved reliable in millisecond pulse-heating experiments for the solid phase [8] and does not need any rotating device. The technical basis of the experiment is to reflect polarized laser light from the pulse-heated liquid wire and then analyze the change in polarization of the light upon reflection from the wire. Four intensities are measured and, with the help of a calibration matrix, four Stokes parameters can be obtained. By means of standard equations of ellipsometry, the optical constants are deduced, and thus the spectral emissivity of the material. Emissivity measurements in conjunction with the radiance temperature measurements are used to derive the true temperature of the liquid material of interest. Using these techniques, progress in the determination of the temperature of the liquid material has been achieved. A detailed description of the system and the needed equations are given elsewhere [12].

The measurement of emissivity at 684.5 nm is performed simultaneously with those of current through the sample, voltage drop across the sample, the surface radiation intensity and sample geometry [20] until the end of the stable liquid phase. Evaluation of the experimental measurements gives a set of improved thermophysical properties for liquid tantalum, such as temperature dependencies of heat capacity, enthalpy, electrical resistivity, and density. Also, the thermal diffusivity and thermal conductivity can be estimated from the obtained data by means of the Wiedeman–Franz law.

3. RESULTS

Wire shaped tantalum samples of 0.5 mm diameter and 50 mm length and a purity of 99.99 (Goodfellow metals) have been volume heated as part of a fast capacitor discharge circuit. The temperature range measured was in the solid from 2500 K up to melting ($T_m = 3270$ K [22]) and then in the liquid from T_m up to 5000 K. The obtained results are presented in Figs. 1–4.

4. DISCUSSION

Tantalum provides at melting a large drop of measured emissivity, as the surface smoothens due to melting and also a possible contamination of the surface will vanish. At the end of melting the emissivity values measured by means of this fast polarimetry match the values of Ref. 21, which are obtained from radiance temperatures at melting within our evaluated uncertainty. The measured emissivity values of the solid phase depend on the surface treatment before the experiment [24] and thus can deliver quite different values, in our case all samples are treated with grade 1000 sandpaper. For the liquid phase a significant decrease of emissivity with increasing temperatures is measured (see Fig. 1).

In Figs. 2–4 the thermophysical properties of tantalum are plotted against temperature calculated with a constant emissivity assumption (dashed line) and against temperature calculated with the measured emissivity (full line). For the liquid phase of tantalum there is a significant

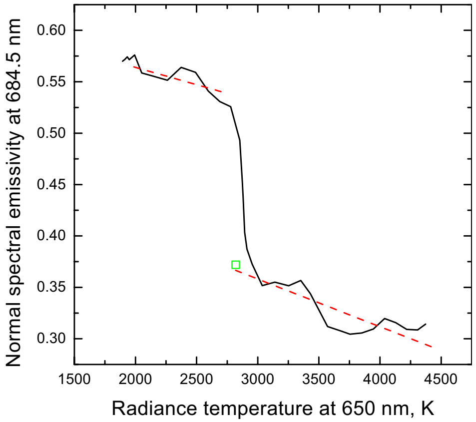

Fig. 1. Normal spectral emissivity of tantalum at a wavelength of 684.5 nm versus temperature. Full line: average of 7 measurements; dashed line: least squares fits; square: emissivity obtained from radiance temperature at melting interpolated for a wavelength of 685 nm [21].

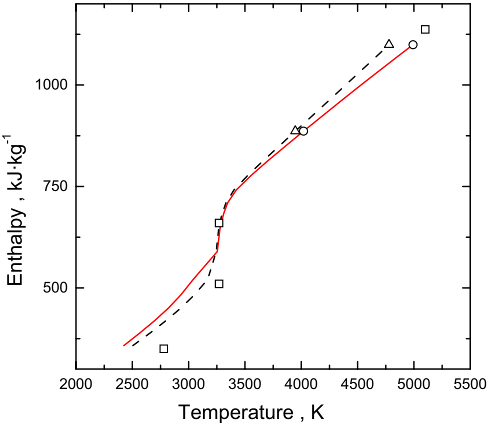

Fig. 2. Specific enthalpy versus temperature for tantalum. Full line: calculated with measured emissivity values; dashed line: temperature evaluated under the assumption of constant emissivity for the whole temperature range, which is equal to the value at melting $\{\varepsilon(\lambda, T)/\varepsilon(\lambda, T_M) = 1\}$; squares: values from Ref. 22. Triangles show two data points calculated with constant emissivity assumption, circles show the values evaluated from the same data points, but this time with the measured emissivity values.

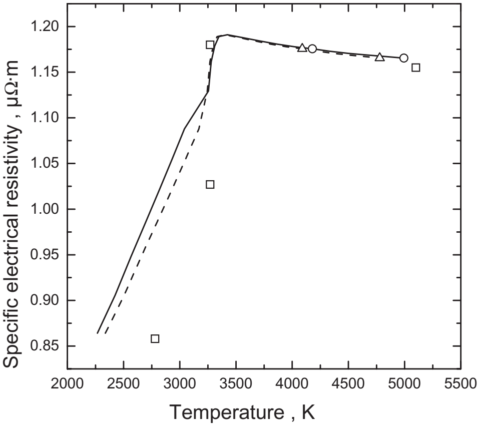

Fig. 3. Specific electrical resistivity without correction for volume expansion versus temperature for tantalum. Full and dashed lines, see comments on Fig. 2; squares: values from Ref. 22. Triangles show two data points calculated with constant emissivity assumption, circles show the values evaluated from the same data points, but this time with the measured emissivity values.

change in the obtained values for enthalpy (Fig. 2); for specific electrical resistivity (Fig. 3) and thermal conductivity (Fig. 4) versus temperature there is a shift of data-points to higher-temperature values in the liquid phase is to be observed—see, e.g., dots and triangles of Figs. 2 and 3 which show two data points calculated with constant emissivity and two corresponding data points calculated with the measured emissivity values which indicates this shift to higher temperatures. For thermal diffusivity calculated via the Wiedeman–Franz law [23] from measured resistivities (Fig. 4), a very strong change for the data of the liquid phase is observed, so that the data of the liquid phase now give an increase at melting, which was not expected and still needs explanation. Figure 4 shows the strongest deviation between "old" and "new" values. For comparison data-points at the beginning of melting and at the end of melting from literature [21–23] are given. From Figs. 2 and 3 and Table I for liquid tantalum, the difference between the results of the two methods is found to be 14%. Thus, the value of the specific heat capacity c_p for liquid tantalum up to 5000 K drops from 257 to 226 $J \cdot kg^{-1} \cdot K^{-1}$.

It should be noted here, that the values obtained for the solid phase show quite a significant change for all three graphs, but the main interest of this work was to obtain data of the liquid phase. As mentioned earlier,

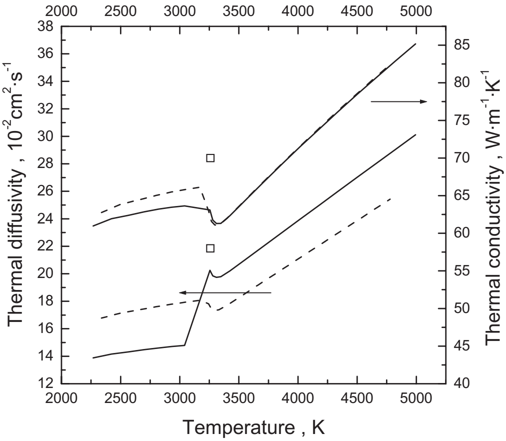

Fig. 4. Thermal conductivity and thermal diffusivity versus temperature for tantalum. Full and dashed lines, see comments on Fig. 2; squares: values for thermal conductivity at the begin and the end of melting from Ref. 23.

Table I. Least Squares Fits for Results on Tantalum. (The physical properties in the solid state are expressed in the form: physical property $= a + bT$, temperature T from 2500 K up to T_m, and in the liquid state: physical property $= c + dT + eT^2$, temperature T from T_m up to 5000 K. With ε: normal spectral emissivity; H: specific enthalpy; ρ_0: specific electrical resistivity without correction for volume expansion; λ: thermal conductivity; a: thermal diffusivity.)

		solid	state		liquid	state
Property		a	b	c	d	e
ε		0.5		0.4661	-3.792×10^{-5}	
H	$\varepsilon/\varepsilon_m = 1$	−255.9	0.2429	−131.87	0.257	
H	$\varepsilon_{measured}$	−329.1	0.2794	−26.32	0.226	
ρ_0	$\varepsilon/\varepsilon_m = 1$	0.2307	2.7007×10^{-4}	1.356	-6.99×10^{-5}	6.29×10^{-9}
ρ_0	$\varepsilon_{measured}$	0.2037	2.9027×10^{-4}	1.3401	-6.243×10^{-5}	5.503×10^{-9}
λ	$\varepsilon/\varepsilon_m = 1$	53.877	3.9277×10^{-3}	11.603	1.488×10^{-2}	
λ	$\varepsilon_{measured}$	53.69	3.341×10^{-3}	12.581	1.4606×10^{-2}	
a	$\varepsilon/\varepsilon_m = 1$	13.296	1.5235×10^{-3}	−1.291	5.592×10^{-3}	
a	$\varepsilon_{measured}$	11.339	1.1494×10^{-3}	−1.350	6.302×10^{-3}	

data in the solid phase strongly depend on the surface treatment of the sample and thus seem to be not very reliable.

5. UNCERTAINTIES

Uncertainties reported here are expanded uncertainties with a coverage factor of $k = 2$. Only a list of the individual uncertainties is given here: current I, 2%; voltage drop U, 2%; temperature T, 4%; mass m, 0.5%; enthalpy H, 4%; not volume-corrected specific electrical resistivity ρ_o, 4%; density d, 5%; volume-corrected specific electrical resistivity ρ, 6%; normal spectral emissivity, 6%; thermal conductivity λ, 12%; and thermal diffusivity a, 15%.

6. SUMMARY

This work presents the first measurements of emissivity of liquid tantalum. This helps to resolve a 25 year old problem, with the observed behavior of normal spectral emissivity of liquid tantalum up to 5000 K determined experimentally. We obtained in the liquid phase decreasing emissivity values with increasing temperatures for tantalum. The specific heat of liquid tantalum obtained within this work is 226 $\mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ up to 5000 K.

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