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Measurement of Thermophysical Properties of Metals and Ceramics by the Laser-Flash Method

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Several recent advances made in the author's laboratory in the experimental apparatus and measuring procedures for precise measurements of thermophysical properties by the laser-flash method are reviewed. Heat-capacity measurement has been done on metals and ceramics within an accuracy of ±0.5% in the range from 80 to 800 K, and within ±2% from 800 to 1100 K. Thermal diffusivity has been also measured from 80 to 1300 K with reasonable corrections for heat leak and finite pulse width. As an example of the experimental results by the method, the data of heat capacity, thermal diffusivity, and thermal conductivity of vanadium–oxygen alloys containing 1.07 and 3.46 at.% of oxygen from 80 to 800 K are presented and compared with those of pure vanadium metal.

KEY WORDS: heat capacity; laser-flash method; thermal diffusivity; thermal conductivity; vanadium-oxygen alloy.

1. INTRODUCTION

The flash method for measuring the thermal properties of solid materials, first proposed by Parker et al. [1] in 1961, has become one of the most useful methods for high temperature measurements on metals and ceramics. Especially, it permits measurements of thermal diffusivity to be extended up to 3000 K by using IR detectors for temperature measurements. In these high temperatures on the other hand, it has been recognized that several difficulties arise in precise heat-capacity measurements.

We have been working on the laser-flash measurement for more than 10 years, and we proved that the laser-flash method can afford precise

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results of both heat capacity and thermal diffusivity at temperatures between 80 and 1100 K. In particular, the heat-capacity measurement in this temperature range by the laser-flash method gives rather more precise results than those obtained by the conventional adiabatic method. This paper gives the present status and prospects of the laser-flash method for the measurement of thermal properties of metals and ceramics. Some recent advances in experimental methods and analytical procedures, which have been made in the author's laboratory, are reviewed, and experimental results on the vanadium–oxygen alloy system are presented.

2. EXPERIMENTAL METHODS AND ANALYTICAL PROCEDURES

2.1. Heat-Capacity Measurements

Use of the laser-flash method has not been as widely applied in measurements of heat capacity as in those of thermal diffusivity. This is due to a number of experimental difficulties, which have impaired the reliability of the data obtained with this method. In fact, at the earliest stage, the accuracy of the experimental results [2] were rather poor; they were found to differ by about 10% from the results obtained by the conventional methods.

One of the main difficulties encountered in this earlier work was in measuring accurately the energy density of the laser beam absorbed by the sample. This problem was solved by using a measuring system consisting of reflecting glass and a photoelectric cell. Another problem was the difficulty in determining the absolute heat capacity of an unknown sample, due to differences in the absorption efficiency of the laser energy, which depends on the reflectivity of the surface, and which hence varies with the sample. This problem was also successfully solved by the author and coworkers [3] by utilizing an "absorbing disk." These improvements to laser-flash calorimetry have permitted the heat capacity of solid samples to be measured within an accuracy of ±0.5% in the range from 80 to 800 K, and within ±2% from 800 to 1100 K [3].

2.1.1. Procedures and Experimental Results

The principle of heat-capacity measurement by the laser-flash method is as follows [3]. Samples to be measured are heated by a pulse from a ruby laser, and the energy absorbed by the sample and its resulting temperature rise are precisely measured. The sample is in the form of a small disk pellet, 8–12 mm in diameter and 0.5–5 mm thick. The mass of the sample necessary for the measurement is 0.03–5.0 g. On the front surface of the sample, an "absorbing disk" is attached. This is a thin glassy-carbon plate and the advantages of its use were described previously [4].

The most important components of the measurement of heat capacity are the precise measurements of the sample temperature and its increment, and of the energy imparted to the sample. In this method, the temperature rise of the sample is detected by a thermocouple, attached to the back surface of the sample with silver paste. The maximum temperature rise of the sample, T_m, is determined after correcting for the heat loss from the sample during the measurement; details of the method and reliability of this correction were described elsewhere [3]. The amount of energy absorbed by the sample is measured by a Si-photoelectric cell and determined comparatively using a standard material of which the values of heat capacity are well established.

In this method, the experimental procedure for the heat-capacity determination is divided into two steps. The first step is to determine the absolute heat capacity of the sample at room temperature by utilizing a sample of pure Al_2O_3 single crystal as a standard material. In a series of preliminary measurements at room temperature on several Al_2O_3 specimens having different masses, the experimental results were reproducible to about ±0.5% on different runs. As the second step, the temperature dependence of the heat capacity is determined relative to the absolute value

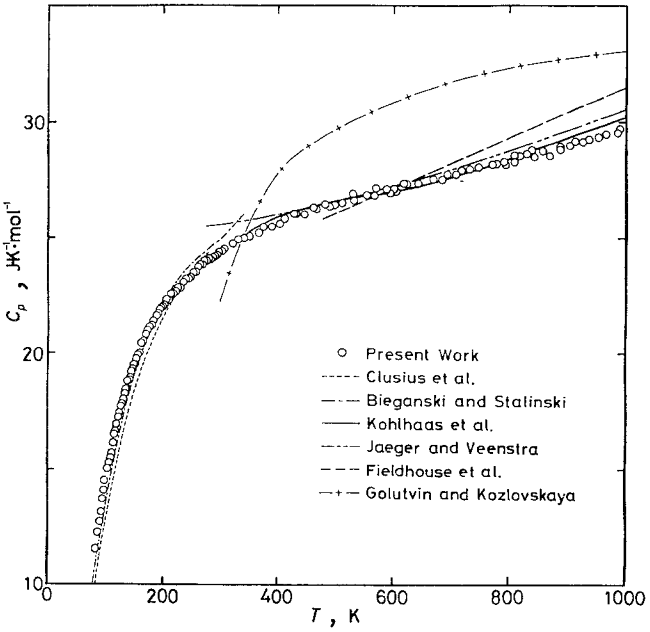

Fig. 1. Molar heat capacity of pure vanadium [11].

determined at room temperature. Measurements of the heat capacity have been made successfully with this method on many metals and ceramics. We have already published experimental results on the heat capacities of ceramics such as UN [5], US [6], $UP_{1-x}S_x$ solid solutions [7], and TiO_2 [8]; and of metals such as Pt [9], Th and U [10], V [11] and Ga [12]. As an example, the results of molar heat-capacity measurement on vanadium [11] are presented in Fig. 1.

2.1.2. Improved Apparatus for Low Temperature Measurements

For the purpose of obtaining more precise data over the temperature range from 80 to 300 K, a new isoperibol type calorimeter has been recently developed [13], which is shown schematically in Fig. 2. In the new calorimeter the sample is surrounded by a heat sink made of copper, whose temperature is kept nearly the same as that of the sample; thus the heat loss from the sample is considerably diminished. The temperature of the heat sink is detected by a Minco platinum resistance thermometer, and the temperature difference between the heat sink and the sample is detected by a copper-constantan thermocouple. In this way, the temperature of the

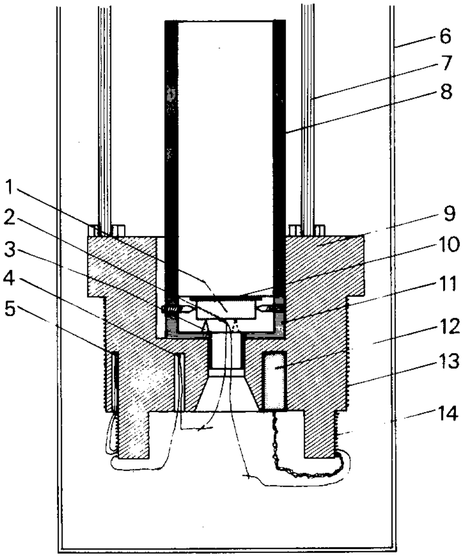

Fig. 2. Heat sink and sample holding assembly of the improved calorimeter [13]. 1, sample; 2, differential thermocouple; 3, quartz pin; 4, differential thermocouple; 5, thermocouple for temperature control; 6, outer thermal shield; 7, holding rod; 8, inner thermal shield; 9, heat sink; 10, absorbing disk; 11, sample holder; 12, platinum resistance thermometer; 13, heater; 14, lead wires.

sample can be determined with an inaccuracy of ±10 mK, which is much better than that of ±0.2 K for the conventional laser-flash calorimeter using a thermocouple as the temperature detector. In order to test the reliability of the calorimeter, the heat capacity of the α-alumina single crystal was measured from 80 to 300 K. The results were compared with the NBS data, and the standard deviation was ±0.28%. The imprecision and inaccuracy of the heat-capacity measurement using this calorimeter are estimated to be within ±0.3% and ±0.5%, respectively.

2.2. Thermal Diffusivity Measurements

The principle of thermal diffusivity measurement by the laser-flash method is well established and thermal diffusivity, α, is usually given by the equation

$$\alpha = 0.1388\, L^2/t_{1/2} = L^2/t_c \tag{1}$$

where L is the thickness of the sample, $t_{1/2}$ is time elapsed for the rear-surface temperature to reach half its maximum temperature rise, and t_c is the characteristic rise time defined as $t_c = L^2/\alpha$. It should be noted, however, that Eq. (1) holds strictly only under the ideal condition satisfying (a) short duration time of laser irradiation as compared with $t_{1/2}$, (b) uniform energy density of the laser beam, and (c) no heat loss from the sample during the measurement, etc.

We have reported [14, 15] on a new apparatus and the method for measuring thermal diffusivity precisely at high temperatures. The new apparatus, shown in Fig. 3, is of isoperibol type, which has an isothermal block made of tantalum surrounding the sample. The temperature of the sample is detected by a thermocouple or IR detector. The temperature of isothermal block is also measured by a thermocouple, and this ensures the determination of temperature of the sample.

2.2.1. Heat-Leak Correction

The use of the isothermal block diminishes the heat leak as shown in Fig. 4. At temperatures above 1000 K, the temperature decrease due to heat leak has been confirmed to be proportional to $\exp(-kt)$, as is expected from the isoperibol condition, and it can be corrected using the experimental parameter C. When thermal diffusivity is written as

$$\alpha = 0.1388 C L^2/t_{1/2} \tag{2}$$

instead of Eq. (1), the relation between C versus $kt_{1/2}$ has been calculated theoretically, and has been given as a figure in the literature [15]. When

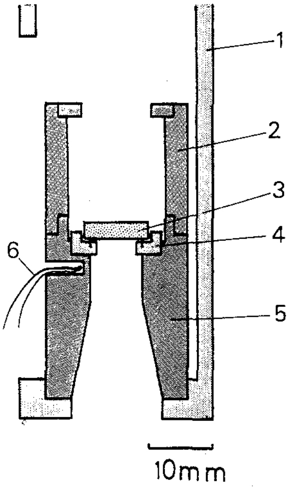

Fig. 3. Sample and sample holding assembly for the thermal diffusivity measurements [15]. 1, holding tube (Al_2O_3); 2, upper isothermal block (Ta); 3, sample; 4, sample holder (Al_2O_3); 5, lower isothermal block (Ta); 6, thermocouple; 7, pin (Al_2O_3).

$kt_{1/2}$ is over 0.01, the value of C becomes 0.97, namely, about 3% smaller than the uncorrected value, indicating the necessity of this correction. Usually, this occurs above 800 K with the isoperibol apparatus.

2.2.2. *Finite Pulse-Width Correction*

As already stated, even in the case of no heat leak from the sample, Eq. (1) is valid only when the pulse-duration time, τ, is sufficiently short as compared with $t_{1/2}$. If this is not the case, Eq. (3) should be used instead of

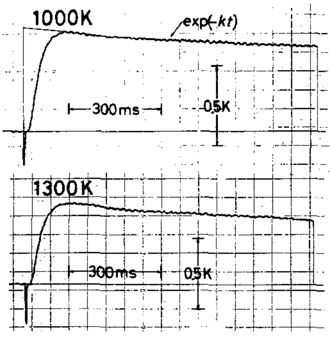

Fig. 4. Temperature history curve at high temperatures [15].

Eq. (1):

$$\alpha = K_0 L^2 / t_{1/2} \tag{3}$$

where K_0, defined as $K_0 = t_{1/2}/t_c$, is a parameter which now depends on the values of τ and t_c. The values of K_0 can be evaluated as a function of τ / t_c by resolving analytically the thermal diffusion equation. Several authors have developed, by specifying the shape of pulses, the relation between K_0 and τ / t_c [16–19]. The calculated results show that K_0 can be represented as

$$K_0 \simeq 0.1388 + b\tau / t_c \tag{4}$$

These relations are shown in Fig. 5.

We have found [20] that the dependence of K_0 on τ / t_c, which is denoted as b, can be changed by introducing a new time axis having the same scale but a different origin. After shifting the time axis, a new parameter K_g can be given as

$$K_g = (t_{1/2} - t_g)/t_c = K_0 - t_g/t_c \tag{5}$$

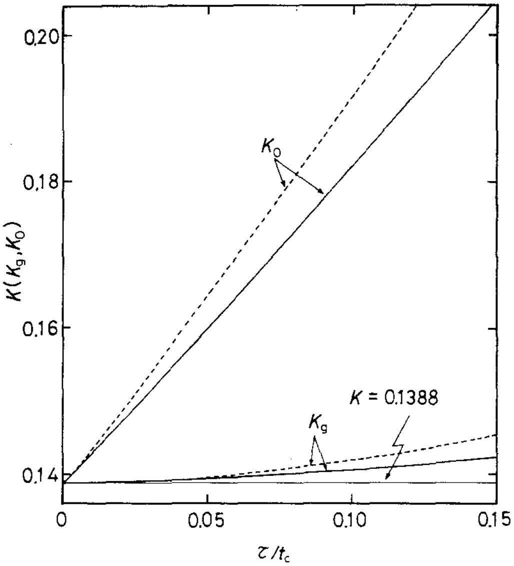

Fig. 5. Numerical values of parameters K_0 and K_g vs $\tau / t_{1/2}$ for two pulse shapes: (pyramidal) ———; (square) --- [20].

where t_g is the value of the shift. A subsequent major concern should be to find a suitable value of the shift that can make K_g nearly independent of τ / t_c. When we choose t_g as

$$t_g = \int_0^\tau t f(t)\,dt \Big/ \int_0^\tau f(t)\,dt \tag{6}$$

where $f(t)$ is the intensity function of a pulse, then $t_g \simeq b\tau$, and K_g becomes nearly constant. This indicates that t_g should be regarded as an adjustment for the infinite pulse width with respect to the "effective" irradiation time. Taking this adjustment, we can give the thermal diffusivity by the following equation:

$$\alpha = K_g L^2 / (t_{1/2} - t_g) \tag{7}$$

Thus, the present scheme of obtaining the correct thermal diffusivity values consists of two steps: (a) adjustment for the "effective" irradiation time and (b) correction of the K_g value. We have found that after the adjustment for the "effective" irradiation time, no further correction is needed for any shape of pulse, even for a very short $t_{1/2}$ such as $t_{1/2} = 2\tau$. The relation K_g versus τ / t_c is also shown in Fig. 5 for two different pulse shapes.

The thermal diffusivity of metallic tantalum determined by this method at high temperatures [15] is shown in Fig. 6. The results after the correction for the heat leak are shown as solid symbols. It can be seen that the correction becomes significant above 900 K.

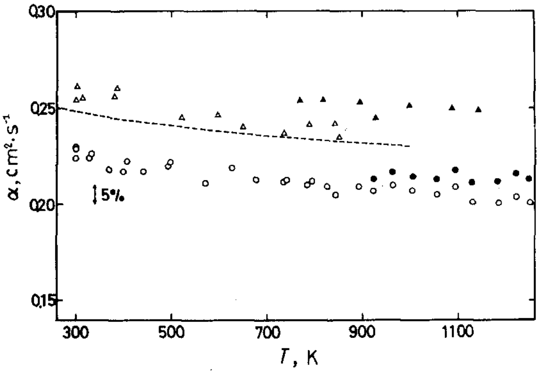

Fig. 6. Thermal diffusivity of tantalum [15]. ○, present results (before heat-leak correction); ●, after correction; △, ▲, Denman (1969) [27]; ---, TPRC recommended values.

3. THERMAL PROPERTIES OF THE V–O SYSTEM

Heat-capacity and thermal diffusivity measurements by the laser-flash method have been performed from 80 to 800 K on well-characterized vanadium–oxygen alloys containing 1.07 and 3.46 at.% oxygen, which were prepared at the Ames Laboratory, U.S.A. The thermal conductivity values are also calculated from these data.

3.1. Heat Capacity

Figure 7 shows the results of heat-capacity measurements on alloys [21] together with those of pure vanadium shown in Fig. 1. It should be noted that the C_p curves of V–O alloys can be normalized to that of pure vanadium by shifting the temperature scale, that is, multiplying by 0.95 for V–O (1.07%) and 0.90 for V–O (3.46%) below 300 K. The analysis of these data has been made in the usual manner, and the Debye temperatures are estimated as follows: pure V, 370 K; V–O (1.07%), 390 K; V–O (3.46%), 410 K.

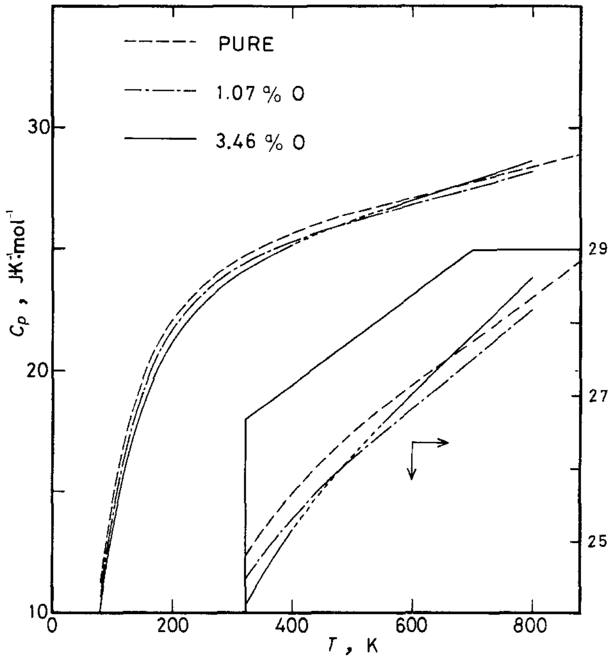

Fig. 7. Comparison of the heat-capacity data for the V–O system.

It can be seen that below 300 K, C_p values are decreased with increase of oxygen content in metallic vanadium, corresponding to the increase of the Debye temperature. At higher temperatures, the contribution of anharmonic terms to the heat capacity becomes larger with oxygen content; thus the trend of C_p versus T curves (Fig. 7) is reversed above 600 K.

3.2. Thermal Diffusivity and Thermal Conductivity

Thermal diffusivity has been also measured on the same set of samples, including pure vanadium metal. The results are shown in Fig. 8, where the literature values on pure vanadium [22, 23] are also given. The smoothed values of the present study at selected temperatures are given in Table I. The marked effect of dissolution of oxygen atoms in metallic vanadium in the case of thermal diffusivity measurements should be noted. The difference between the present data and literature values on pure vanadium might be attributed to the impurity effects.

Using the data of heat capacity and thermal diffusivity stated above, the values of thermal conductivity have been calculated and are presented in Table I. These values are plotted in Fig. 9, where the literature values of

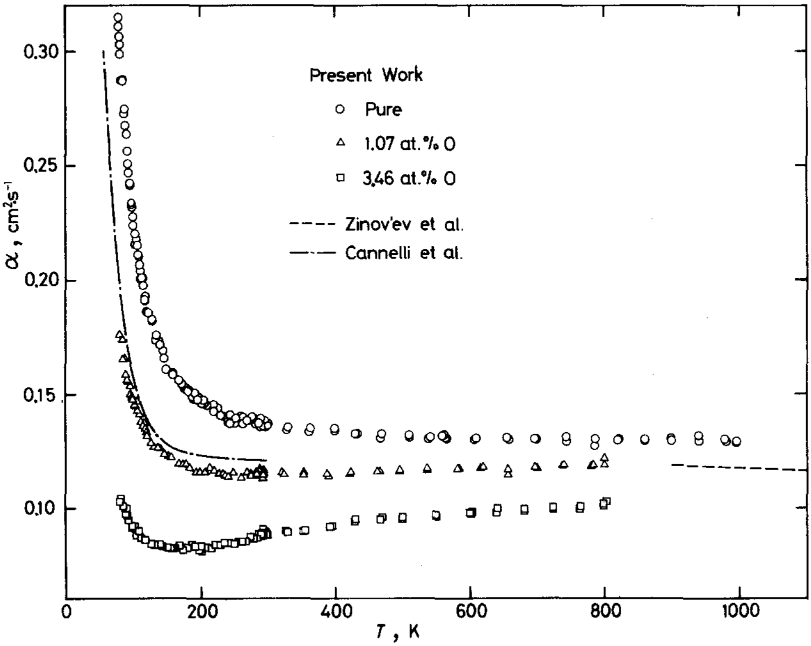

Fig. 8. Thermal diffusivity of the V–O system.

Table I. Thermal Diffusivity and Thermal Conductivity of Pure Vanadium and V–O Alloys.

T (K)	α (cm$^2\cdot$s^{-1})			λ (W$\cdot$m$^{-1}\cdot$K^{-1})		
	Pure V	V–O (1.07)[a]	V–O (3.46)[b]	Pure V	V–O (1.07)	V–O (3.46)
80	0.305	0.177	0.104	41.4	22.6	12.8
100	0.226	0.146	0.091	39.6	24.4	14.7
200	0.146	0.115	0.082	38.5	30.0	21.2
300	0.138	0.115	0.090	40.1	33.1	25.5
400	0.134	0.115	0.092	41.1	35.2	28.5
500	0.132	0.116	0.096	41.6	36.5	30.6
600	0.131	0.117	0.098	42.1	37.6	32.2
700	0.130	0.118	0.100	42.8	38.7	33.7
800	0.130	0.120	0.102	43.5	40.1	35.2

[a] V–O alloy containing 1.07 at.% of oxygen.
[b] V–O alloy containing 3.46 at.% of oxygen.

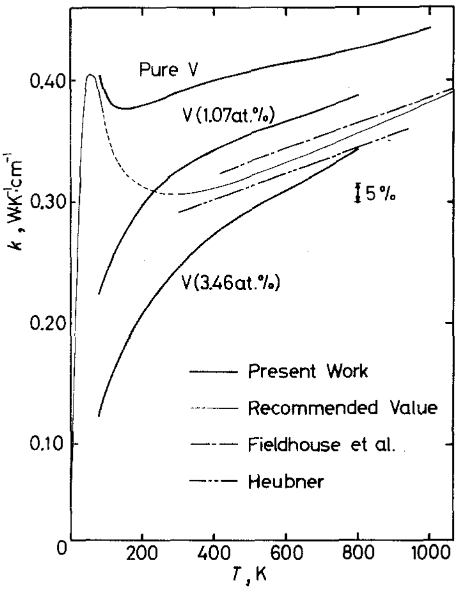

Fig. 9. Thermal conductivity of the V–O system.

other investigators on pure vanadium [24, 25] and the recommended values by TPRC [26] are also presented. Our data on pure vanadium are rather high as compared with others. It should be stressed that our samples of vanadium and V–O alloys are very pure and well characterized, and probably the high thermal conductivity is attributable to the high purity of our samples.

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