International Journal of Thermophysics, Vol. 14, No. 2, 1993

An Evaluation of Specific Heat Measurement Methods Using the Laser Flash Technique

J. Xue[1] and R. Taylor[2]

Received November 24, 1992

Different methods for adapting the laser flash technique to measure simultaneously specific heat have been proposed in the literature. Among them are the coating method, the absorbing disk method, the double-specimen method, the pulse heating-cooling method, and the cavity method. These methods are briefly reviewed, and their merits and demerits are evaluated.

KEY WORDS: laser flash technique; specific heat; thermal diffusivity.

1. INTRODUCTION

The flash method for measuring thermal diffusivity α was first proposed by Parker et al. in 1961 [1]. In the same paper, it was also proposed that the technique could be used to measure the specific heat C_p and hence allow thermal conductivity to be determined. In order to do this it is necessary to know the temperature rise ΔT and the energy input per unit area Q whence

$$C_p = \frac{Q}{\rho L \Delta T} \tag{1}$$

where ρ is density and L is sample length. In its basic form this method necessitates that no heat losses occur and that both temperature rise and energy input Q be measured accurately. This poses certain experimental problems and a variety of techniques has been postulated over the years to adapt the laser flash technique to measure specific heat, and these are reviewed.

[1] Powder Metallurgy Research Institute, Central South University of Technology, Hunan, China.

[2] Manchester Materials Science Centre, University of Manchester and UMIST, Manchester M1 7HS, United Kingdom.

840/14/2-10

2. SPECIFIC HEAT METHODS

2.1. Coating Method

Originally proposed by Parker et al. [1], this is an inherently simple method. While the laser energy Q can be measured by such means as laser calorimetry, it is the quantity of heat absorbed by the sample that is needed. This depends on emissivity. The proposed route is to measure the temperature rise of a reference sample of known specific heat, in order to determine the energy input Q. However, in order to ensure the same energy absorption, it is necessary to coat both sample and reference with a coating: usually colloidal graphite or camphor black. For the reference sample the relationship between temperature rise and laser energy is

$$Q\varepsilon' = \rho' L' C'_{\mathrm{p}} \, \Delta T' \tag{2}$$

where the prime refers to the reference sample and ε' is the front surface emissivity. For the unknown sample using the same energy input Q and the same surface coating

$$Q\varepsilon = \rho L C_{\mathrm{p}} \, \Delta T \tag{3}$$

where ε is the sample emissivity. Now if $\varepsilon = \varepsilon'$, Eqs. (2) and (3) give the specific heat of the unknown sample

$$C_{\mathrm{p}} = \frac{\rho' L' C'_{\mathrm{p}} \, \Delta T'}{\rho L \, \Delta T} \tag{4}$$

The accuracy of the method relies critically on two factors. First, it is assumed absorptivities of reference and unknown samples are the same. For this reason coatings are applied to ensure uniform absorptivity. However, for multiple measurements or measurements over a temperature range, maintenance of the integrity of the coating is an important factor. Second, since duplicate experiments are needed for each measurement the reproducibility of the laser pulse is also important. To obviate some of these problems, other techniques have been devised or postulated over the past 30 years.

2.2. Double-Specimen Method

Proposed by Qinqzhao and Likun [2], two reference samples of known specific heat are used. The first reference sample is mounted on the unknown sample with the reference sample facing the laser (Fig. 1). The

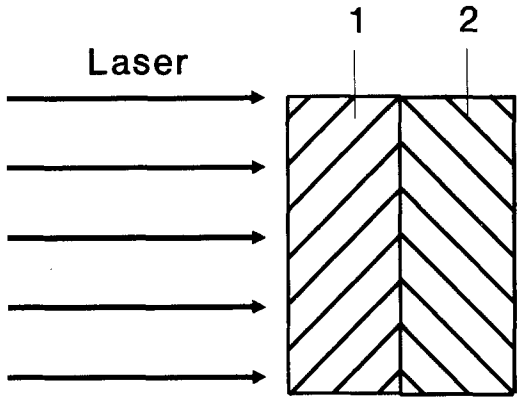

Fig. 1. Schematic diagram of the double-specimen method (after Qingzhao and Likun [2]). (1) Reference sample M_1 or M_2; (2) sample to be measured.

input pulse raises the temperature of both materials by an amount ΔT_1 whence

$$(C'_p M'_1 + C_p M)\,\Delta T_1 = Q\varepsilon \tag{5}$$

where M is the sample mass of the unknown and M'_1 the mass of the reference sample. The suffix refers to the reference sample and the symbols are as before. The reference sample is replaced by a second disk of the same material but of different mass M'_2, and the experiment repeated. If a temperature rise ΔT_2 is recorded,

$$(C'_p M'_2 + C_p M)\,\Delta T_2 = Q\varepsilon \tag{6}$$

Combining yields

$$C_p = \frac{C_p(M'_2\,\Delta T'_1 - M'_2\,\Delta T'_2)}{M(\Delta T_2 - \Delta T_1)} \tag{7}$$

Since two samples of a reference material are used and this is the material pulsed with the laser beam, it does have the advantage that knowledge of sample emissivity is not needed.

Measurements are reported at high temperatures, up to 1200°C, but the method as reported seems to have two serious deficiencies; (a) it does not appear to consider or allow for heat losses from the specimen, and (b) the effects of interfacial contact resistance between unknown and reference samples are not even considered. Both of these need to be addressed.

2.3. Absorbing Disk Method

Recognition of the difficulty of obtaining a uniform front surface absorptivity led Takahishi and co-workers [3–5] to propose the absorbing disk method. In this method a thin (0.2-mm) disk of glassy carbon is attached to the front surface of the sample to be measured either by silicone grease or, for high temperatures, a thin layer of silver paste (Fig. 2). The maximum temperature rise of the composite sample is determined by a thermocouple and extrapolatek back to zero time. The specific heat of the unknown sample is given by

$$C_s = \frac{1}{M}\left\{\frac{Q}{\Delta T_m} - C'\right\} \tag{8}$$

where C' is the heat capacity of the absorbing disk, which also includes the silver paste or silicone grease and the thermocouple. The term C' is estimated to account for 5 to 40% of the energy absorbed, dependent on the geometrical configuration used. Unfortunately, the energy balance is not given so it is not clear how this term is derived. Again, accurate knowledge of the energy input is required, although the use of the glassy carbon ensures a reproducible emissivity on the front surface. Measurements are reported over the temperature range 80–1100 K.

2.4. Laser Pulse Heating-Cooling Method

This method again requires a reference sample of known specific heat and that careful precautions be taken to ensure that reference and

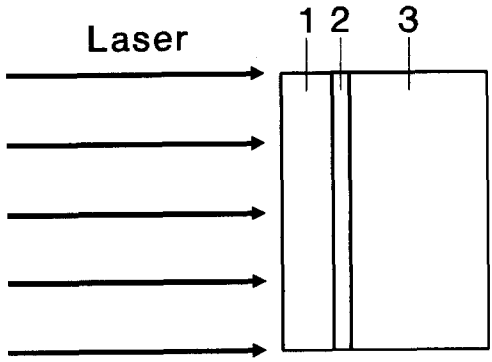

Fig. 2. Schematic diagram of the absorbing disk method (after Takahishi [3]). (1) Glassy carbon; (2) silicone grease or silver paste; (3) sample to be measured (or reference sample).

unknown samples have the same emissivity. However, the thermogram for the flash technique is considered in two separate parts: the heating and cooling regimes. The sample reaches its maximum temperature, which then decays as the sample cools. If the energy exchange between the sample and its surroundings is assumed to be only by heat radiation, the heat balance differential equation is [6, 7]

$$A\varepsilon_n\sigma(T^4 - T_0^4) = -MC_p\,\delta T/\delta t \tag{9}$$

where A is the surface area of the sample ($=\pi D^2/2 + \pi DL$), ε_n the effective emissivity, σ the Stefan Boltzmann constant, M the sample mass, T the instantaneous temperature rise of the sample, and T_0 the ambient temperature. This equation is rearranged and integrated between two times during the cooling portion of the curve t_1 and t_2 which correspond to temperature values T_1 and T_2. This yields an expression for the specific heat/emissivity ratio:

$$\frac{C_p}{\varepsilon_n} = F(t_2 - t_1)T_0^3\left[\ln\frac{T_1 - T_0}{T_2 - T_0} - \ln\frac{T_1 + T_0}{T_2 + T_0} + 2\left(\arctan\frac{T_2}{T_0} - \arctan\frac{T_1}{T_0}\right)\right] \tag{10}$$

where $F = 4A\sigma/M$.

It is therefore necessary to have a known emissivity to calculate specific heat. The procedure advocated is to carry out measurements on a reference sample of known specific heat while endeavoring to ensure that the reference and the unknown samples have the same surface conditions.

The effective emissivity depends not only on the thermal emissivity of sample and sample holder but also on the position of the sample within the furnace. He and co-workers [6] coat the sample with colloiodal graphite, oxidize the stainless-steel sample holder for several hours, and preheat the sample to $\sim$950°C under vacuum in the experimental chamber before measurements commence. Results are reported for 21-6-9 [6] and 304 [7] stainless steels, using Armco Iron as a reference material.

Unlike the coating and absorbing disk methods, this method does not depend on any knowledge of the energy input Q. It does require a standard reference material of known specific heat and needs great experimental care to ensure reproducible condition in order that emissivity may be determined. Hence, it necessitates that the standard reference material and the unknown sample possess identical emissivities. This will, to some extent, limit the choice of material combinations.

2.5. Cavity Method

This method was proposed by Xue [8] in 1984 and consists of placing a hollow cone over the test sample (Fig. 3), the cone and sample being thermally isolated from one another. A laser pulse of known thermal energy Q is focused on the small hole at the apex of the hollow cone so that it reaches the interior of the cavity. The absorptivity of the cavity a_0 is given by

$$a_0 = 1 - \left\{ \frac{r_s \eta}{\pi} + r_h r_s \left(1 - \frac{\eta}{\pi}\right) \frac{s}{s_0} \left[\frac{1}{1 - r(1 - s/s_0)} \right] \right\} \tag{11}$$

where r_h and r_s are the reflectivities of the hollow cone and sample, respectively, η is the solid angle substended by the hole from the point of reflection, s is the area of the hole, and s_0 is the total area of the cavity, and

$$r = \frac{r_h s_h + r_s s_s}{s_0} \tag{12}$$

where s_h and s_s are the areas of the inner surfaces of the holow cone and sample, respectively. Since the hole is small, all laser light entering the cavity is totally absorbed either by the cone or by the sample. The temperature rises of hollow cone ΔT_h and sample ΔT_s are measured using thermocouples and the specific heat of the sample C_s given by [8, 9]

$$C_s = \frac{Q - C_h M_h \Delta T_h}{M_s \Delta T_s} \tag{13}$$

In this method, the sample does not require any surface treatment to give a known emissivity. Although it does not, per se, require the use of a

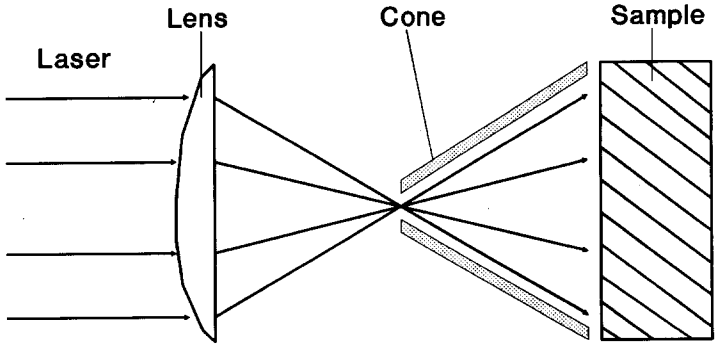

Fig. 3. Schematic diagram of the cavity method (after Xue [8]).

reference sample, it does necessitate that the specific heat of the materials comprising the cavity be known. Details of various configurations to improve the accuracy will be given in a separate paper [10].

3. DISCUSSION

Accurate knowledge of energy is crucial to the generation of specific heat data using the flash technique. This requires either a surface treatment or coating to ensure a reproducible emissivity or the use of a standard reference material. Two of the techniques, the simple coating method and the pulse heating and cooling method, necessitate the use of a standard reference sample and require that the emissivities of sample and reference be the same. The double-specimen method eliminates the need to know the sample emissivity but has the disadvantage that it is not clear how contact between the reference sample and the unknown is considered. The absorbing disk method proposed by Takahishi [3] does ensure a uniform reproducible front surface emissivity and also obviates the need for a standard reference material. Unfortunately, it is not clear from the analysis how the correction for the heat capacity of the disk and adhesive is applied. The pulse heating/cooling method has been used over a wide temperature range but appears limited to specific reference/unknown combinations of identical emissivities. The cavity method does not require knowledge of any specimen emissivity. While this technique does not require a standard reference material, it does necessitate that the heat capacity of the material comprising the cone be known. For only two of the methods, the absorbing disk and pulse heating-cooling methods, are results reported over a wide temperature range. The various methods proposed to adapt the flash technique to measure specific heat all have inherent limitations in that they either necessitate measurement of materials of known specific heat or knowledge of surface emissivity or operate over a limited temperature range. No solution has yet been devised to adapt the technique as a general tool for the absolute measurement of specific heat over a wide temperature range.

ACKNOWLEDGMENTS

The authors would like to acknowledge financial support from the British Council for one of us (J. Xue). Travel assistance from the Committee of China Scientific Foundation for J. Xue is also gratefully acknowledged.

REFERENCES

1. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, *J. Appl. Phys.* **32**:1679 (1961).
2. Y. Qingzhao and W. Likun, in *Proceedings of the First Asian Symposium on Thermophysical Properties* (China Academic, Beijing, 1986), p. 325.
3. Y. Takahishi, *J. Nucl. Mat.* **51**:17 (1974).
4. H. Yokokawa, Y. Takahishi, and T. Mukaibo, in *Thermodynamics of Nuclear Materials, Vol. 2* (IAEA Vienna, 1973), p. 419.
5. Y. Takahishi, *J. Appl. Chem.* **47**:323 (1970).
6. G. He, J. Tao, D. Cao, S. Dong, and B. Zhou, in *Proceedings of the First Asian Symposium on Thermophysical Properties* (China Academic, Beijing, 1986), p. 321.
7. G. He, J. Tao, D. Cao, S. Dong, H. Wang, and B. Zhou, in *Proceedings of the First European Conference on Thermoelectrics*, D. M. Rowe, ed. (Peter Peregrinus, London, 1988), p. 142.
8. J. Xue, *High Temp. High Press.* **17**:691 (1985).
9. X. Liu and J. Xue, in *Proceedings of the First Asian Symposium on Thermophysical Properties* (China Academic, Beijing, 1986), p. 213.
10. J. Xue and R. Taylor, in press.