International Journal of Thermophysics, Vol. 10, No. 1, 1989

Accurate Determination of Specific Heat at High Temperatures Using the Flash Diffusivity Method[1]

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The flash diffusivity method can be extended, very simply, to measuring simultaneously thermal diffusivity and specific heat and thus obtaining the thermal conductivity directly. This was accomplished by determining the amount of heat absorbed by a sample with a well-known specific heat and then using this to determine the specific heat of any other sample. The key to using this technique was to have identically reproducible surfaces on the standard and the unknowns. This was achieved earlier by sputtering the surfaces of the samples with a thin layer of graphite. However, the accuracy in determining the specific heat was within ±10% and there was considerable scatter in the data. Several improvements in the technique have been made which have improved the accuracy to ±3% and increased the precision. The most important of these changes has been the introduction of a method enabling the samples to be placed in exactly the same position in front of the light source. Also, the control of the thickness and the application of the graphite coating have turned out to be very important. A comparison of specific heats obtained with this improved technique and with results obtained using other techniques has been made for two materials.

KEY WORDS: flash method; heat capacity; high temperatures; niobium; specific heat; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

The "flash method" [1] to measure thermal diffusivity is now well established and widely used. However, the use has remained primarily one of measuring thermal diffusivity, α, and not the specific heat, C_p. The

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[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

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advantage, of course, of measuring both simultaneously is that the thermal conductivity, Λ, can then the expeditiously obtained on the identical sample as long as the density, ρ, of the sample is known:

$$\Lambda = \alpha C_p \rho \tag{1}$$

This direct determination of thermal conductivity has the advantage of not needing a laborious additional method (e.g., a DSC or drop calorimeter) to measure specific heat separately which often requires a sample of dimensions quite different from those of the thermal diffusivity sample. Of course, the accuracy of the direct method should be comparable to or better than that of the indirect method. During the past 20 years, several research groups [2, 3] have attempted to measure specific heat using the flash diffusivity method. Generally, such attempts have not been very successful at high temperatures. The primary difficulty involves the accurate determination of the amount of heat, Q, absorbed by the sample, which is related to the specific heat by

$$C_p = \frac{Q}{m\,\Delta T_{\max}} \tag{2}$$

where m is the mass of the sample and $\Delta T_{\max}$ the maximum temperature rise of the sample. Different sample materials (or even the same material under different surface conditions) differ markedly in their ability to absorb radiation. It is thus necessary that a calibrated surface be used. Surface paints are usually damaged by repeated intense radiation pulses, are usually unstable at high temperatures, and are difficult to apply with any reproducibility and uniformity (thickness and weight). A thin "absorption disk" (glassy carbon) attached to the front face of the samples has been used successfully [4] but has the disadvantage of having to subtract out the specific heat of the disk and the adhesive.

In earlier work reported by us [5] these problems were overcome by sputtering a thin layer of graphite on the test and reference samples. However, even though this layer was reproducibly applied, the accuracy in determining the specific heat was only within about ±10% and there was considerable scatter in the data. Several improvements in the technique and the experimental setup have been made and are reported here. These improved techniques have increased the accuracy of the specific heat results to ±3% and the precision of the measurements.

2. EXPERIMENTAL

The thermal diffusivity and specific heat were determined by the flash method in an apparatus described elsewhere [5, 6]. Briefly, a xenon flash lamp applies a heat pulse to one side of the sample, by means of a sapphire light pipe, while an InSb infrared detector measures the temperature rise of the rear surface of the sample. The output of the detector is fed through a Textronic differential amplifier into a Nicolet digital storage scope which displays the rear-face sample temperature rise (in μV) versus time (in ms). A flash lamp has several advantages over a laser. The main ones are that it is inexpensive, is capable of higher power levels, and has a very reproducible flash intensity. The main disadvantage is a larger finite pulse time but corrections to that have been developed [7–9].

The specific heat at constant pressure, C_p, is obtained from Eq. (2), with $\Delta T_{\max}$ being the maximum temperature rise of the sample. Radiation heat losses, which can be significant at high temperatures, especially for low-thermal conductivity materials, will result in $\Delta T_{\max}$ being reduced below the value of the adiabatic case, resulting in too high a value for the specific heat. A correction thus needs to be applied. Parker and Jenkins [7] and Cowan [8] give theoretical curves of heat-loss corrections to the diffusivity as a function of the actual increase in back-face and calculated front-face temperatures, sample thickness, emissivity, and thermal conductivity. Since the effect of heat losses is to reduce the height (temperature rise) and, thus, the shape of the back-face signal, those corrections were used to correct the measured specific heat as well. To confirm the suitability of applying this diffusivity heat-loss correction to the measured specific heat, a sample of lanthanum sulfide, a very low-thermal conductivity material, with different thicknesses was measured. The specific heats after the corrections were found to agree within the experimental error.

The Cowan type of correction, which is tedious to apply, was chosen because it was available and it gave the correct result. A simpler to apply

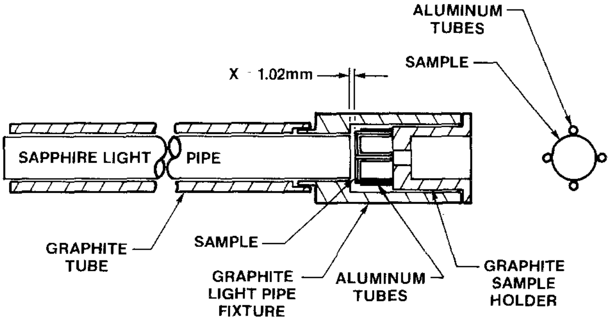

Fig. 1. The schematic of the sample holder and light pipe configuration showing how the sample is clamped between four alumina rods and is positioned in front of the light pipe.

analytical method, which uses the actual measured $t_{1/2}$, $\Delta T_{\max}$, and $T_{\max}$, has been developed [9] very recently.

The amount of heat Q absorbed by the sample is found from a comparative method by using a material with a well-known [10] specific heat as a standard (graphite AXM5Q). This standard, as well as the test samples, were sputtered with graphite, to ensure identical surface conditions, for 1.5 h on each side. This resulted in a surface layer approximately 3 μm thick as determined both from a direct method (added mass and dimensions) and by using a profilometer. Using the published specified heat for graphite AXM5Q, the Q was calculated as a function of temperature and the resulting curve used for the test samples [5]. The positioning of the front surface of the sample with respect to the end of the light pipe was found to be crucial both for the standard (to obtain an accurate repeatable determination of Q) and for the test sample (to obtain an accurate determination of C_p). To achieve a reproducible juxtaposition, the sample was originally clamped between three alumina tubes, threaded over tungsten wires that were embedded in a graphite holder. The length of the alumina tubes was varied to accommodate samples of various thicknesses, ensuring that the front face of the sample was always at exactly the same position from the end of the light pipe (1.02 mm). Clamping the sample in this way resulted in identical separation each time but almost always resulted in a slight sideways shifting of the sample so that part of the sample of 12.6-mm diameter was not covered by the light pipe (12.6-mm diameter). A shift of about 1 mm resulted in the specific heat increasing by up to about 10–15% above the correct value. This sideways shifting was prevented by using four instead of three alumina rods and ensuring that the sample was properly

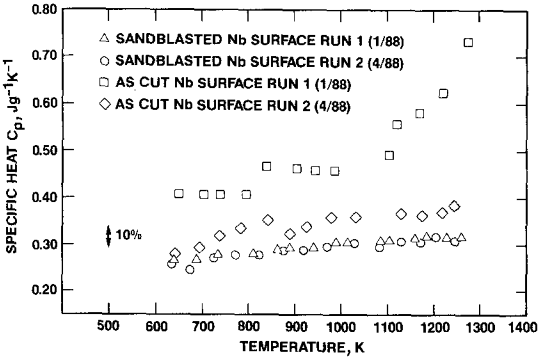

Fig. 2. Variation of specific heat versus temperature for four niobium samples. Two samples had the graphite sputtered on the cleaned ascut surfaces, while the other two had the graphite sputtered onto sandblasted surfaces.

centered (by spinning the sample holder). The sample holder and light pipe setup are shown in Fig. 1.

The graphite sputtering was originally performed on cleaned as-machine surfaces. For several of the tested materials, this presented no problems (graphite, Si_xGe, $La_{3-x}S_4$, $La_{3-x}Te_4$, etc.), as the graphite adhered even up to temperatures as high as 1300 K. However, in the case of metals such as niobium, nickel, and molybdenum, the sputtered graphite coating usually partly or wholly delaminated upon heating to 1300 K. This, of course, resulted in poor data and results. To overcome this problem, the surfaces of the metal samples were sandblasted first before being sputtered with graphite. It was felt that this type of surface provides better adhesion for the graphite. The experimental results of sandblasted and as-cut niobium samples confirm this, as Fig. 2 shows. The specific heats for two samples with sandblasted and then graphite-sputtered surfaces agreed to within a few percent, while for the as-cut and then graphite-sputtered surfaces the results varied greatly.

3. RESULTS AND DISCUSSION

Two types of materials (silicon–germanium alloys and niobium) were tested, using the modified equipment and technique as described in the previous section, to determine if the changes made indeed result in both

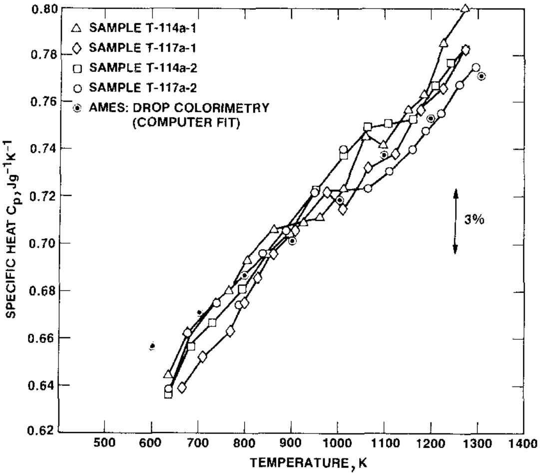

Fig. 3. Variation of specific heat versus temperature for four n-type $Si_{80}Ge_{20}$ plus 2 mol% GaP samples. A computer fit to the literature data using the drop calorimetry method [11] is shown as a comparison.

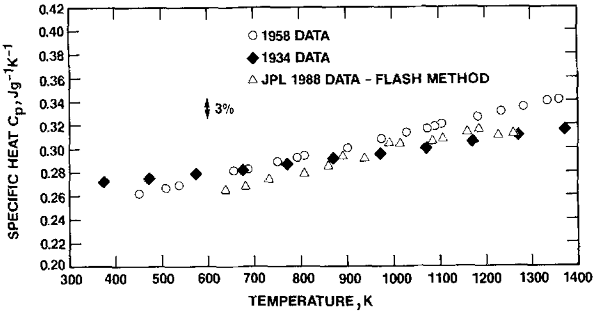

Fig. 4. Variation of specific heat versus temperature for one of the niobium samples from Fig. 2 (the run 1, sandblasted surface). Data reported in the literature [13, 14] are shown as a comparison.

greater accuracy and greater precision when determining specific heat using the flash method.

The specific heat of four n-type $Si_{80}Ge_{20} + 2$ mol% GaP was measured from 600 to 1300 K. The results are shown in Fig. 3. The heat-loss corrections were calculated using the method developed by Cowan [8] as discussed earlier. The specific heat data, obtained on a similar sample by Amano et al. [11], using the drop calorimetry method, are shown as a comparison. The agreement is within ±3%. The agreement with earlier data [12], using a very different technique, is also within a few percent (not shown on curve). Also, the precision of the data using the flash method is generally about ±1 to ±2% for each of the four samples.

The specific heat of a 3,9's pure niobium sample, with sandblasted surfaces, is shown in Fig. 4 and is compared to data obtained earlier [13, 14]. The agreement again is within ±3% over the measured temperature range 600–1300 K. The data shown in Fig. 4 are also the data shown in Fig. 2 (run 1, sandblasted surface).

4. CONCLUSION

It has been shown that the flash diffusivity method can be used up to at least 1300 K to measure accurately the specific heat of test samples simultaneously with the diffusivity, thus obtaining the thermal conductivity directly. The accuracy of the data obtained on two materials was ±3% when compared to previous data. This accuracy and a precision of ±1 to ±2% can be obtained if great care is taken with the experimental technique and setup as described here. The results show that a relatively inexpensive experimental setup can be used to obtain reasonably accurate specific heat data at moderately high temperatures.

ACKNOWLEDGMENTS

The work described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration. We would like to thank H. Awaya for assistance with the calibration fits.

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