Heat Capacities of Boron Nitride and Aluminum Oxide Using an Arc-Image Furnace

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A comparative cooling rate technique for the rapid determination of solid heat capacity in the range of 1300° to 2300° K. has been developed for use with arc-imaging furnaces. A full description of the theory, construction, calibration, and operation of the system is given. Data are reported for boron nitride and aluminum oxide and compare well with previous reports; they are estimated to be accurate to ±3% at the highest temperatures.

A NOVEL TECHNIQUE for the determination of relative heat capacities in the temperature range above 1300° K. has been developed for use with arc-imaging furnaces (*2, 7*). Essentially, cooling rates of different materials were compared in a standard container, whose rate of loss of heat was a function only of its absolute temperature. The furnace, a double ellipsoidal mirror type, operated at a maximum power input of 21 KW and delivered approximately 240 cal./sec. at the image plane. The ⅜-inch anode crater maintained at a brightness temperature of 3800° K., irradiated a sample area slightly greater than 1 square cm. The essentials of the furnace are shown schematically in Figure 1; a full description has been given elsewhere (*3*). The chief advantages of such a heat source were the ease of atmosphere control, the absence of hot furnace walls and the rapid attainment of high temperatures. The major disadvantages were the small total power output which limited sample size and the high energy concentration which created thermal shock problems and also large temperature gradients.

COOLING RATE METHOD

The method was based on the fact that at high temperatures a standard container of unvarying emissivity, E, radiated heat according to the relation $W = E\,\sigma\,AT^4$. Where W is the heat flux per unit area, σ the Stefan-Boltzman constant, A the area, and T its absolute temperature. At a given temperature, the rate of radiative heat loss was dependent only on the external dimensions and properties and the absolute temperature. By maintaining the container dimensions constant and obtaining a highly reproducible surface the heat loss rate at a given temperature became a function only of that temperature. The conductive and convective losses were made functions of temperature by maintaining their sink temperatures relatively constant. They were arranged to be minor compared to radiative transfer, for conduction this was roughly 10% of the total heat loss. Under these conditions, the heat loss rate at any temperature was independent of the contents of the vessel. Measuring the rate of decrease of temperature of the container and contents allowed the heat capacity to be determined ideally, as shown below.

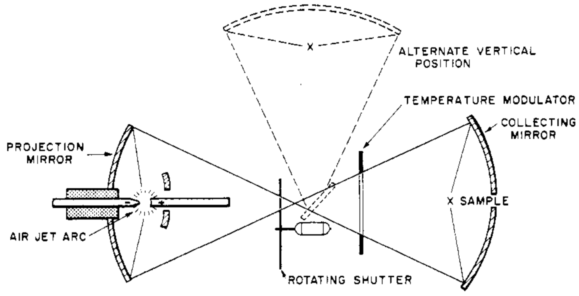

Figure 1. Schematic diagram of the arc-imaging furnace
Normally operated in the alternate vertical position

$$H_T = (m_2C_p + m'C_p')R' \text{ for calibration with known } C_p'$$

and

$$H_T = (m_3C_p + m''C_p'')R'' \text{ for determination of } C_p''$$

Thus

$$C_p'' = [C_p(m_2R' - m_3R'') + m'C_p'R']/m''R''$$

Where

H_T = rate of loss of heat at temperature T
m_2 and m_3 = masses of the empty vessel in the two series
m' and m'' = masses of the calibration material and sample.
C_p, C_p', and C_p'' = gram heat capacities of vessel, calibration, and sample materials
R' and R'' = rates of decrease of temperature at temperature T for calibration and sample series

However in practice the system did not behave ideally, deviating by 2–8%. To correct for this deviation, the temperature of the vessel as read was assumed (*9*) to vary with its cooling rate. To determine the correction, the cooling rate of the empty vessel was also determined, and the assumption was made that the temperatures in the calibration runs were correct. If T is the true temperature and S the observed temperature and $S = T + K$ for a small temperature interval, then at a temperature T_1:

$$(\mathrm{d}T/\mathrm{d}t)_{T=T_1} = R_{S=T_1} + K(\mathrm{d}R/\mathrm{d}S)_{S=T_1} + \frac{K^2}{2}(\mathrm{d}^2R/\mathrm{d}S^2)_{S=T_1}$$

Where

$$R = (\mathrm{d}S/\mathrm{d}t) \text{ for the empty vessel.}$$

If the vessel and calibration material are the same, then the ratio of the cooling rates between the empty and calibration series is given by

$$(\mathrm{d}T/\mathrm{d}t)_{T=T} / R' = (m_2 + m')/m_1$$

Where

m_1 and m_2 = masses of the empty vessel in the empty and calibration series
m' = mass of the calibration material

The value of K for the empty vessel was found by solving the quadratic equation at each temperature of interest.

The values (dR/dS) and (d^2R/dS^2) were obtained from R by taking first and second differences. The value of K for the sample series was obtained by interpolating between $K = 0$ for the calibration series and K for the empty vessel. In general, the K^2 term was found negligible in the sample series.

APPARATUS

Because of the limited heat flux available at the image plane, the vessel size determined the maximum temperature attainable and also the rate of cooling. For example a 1.6-cm. diameter, spherical body would have a maximum temperature of 2250° K. and a maximum cooling rate of roughly 135° K./seconds. Such cooling rates were too high to measure accurately and shielding was necessary to reduce them to more reasonable proportions. In order to have the heat loss rate still dependent only on the temperature, it was necessary to have a highly reproducible surface on the shield. This was achieved by casting a heavy-walled gold shield which was highly polished on the inside. The shield had a graphite outer cover in order to increase its total heat capacity and maintain its temperature constant. This was extremely effective and reduced cooling rates to 20–30% of their unshielded values.

The ½ by ½-inch standard container was made from ultra high purity, high density, SPK grade National Carbon graphite. The reasons for choosing graphite were its high emissivity —which relatively insensitive to surface condition—excellent thermal shock resistance, good thermal conductivity, and the ease of working. To provide black body radiation for accurate temperature measurement, a central post contained a re-entrant well. The dimensions of the well were chosen according to the formula of DeVos (*11*) to have a ratio of length to radius of 10. The container was seated on a graphite support which also served to position the sample container exactly in space. The container and support are shown schematically in Figure 2. The small crossectional area of the support served to limit conduction, and the massive brass sample holder acted as a constant temperature heat sink.

The temperature measuring system consisted of a Leeds and Northrup total radiation pyrometer whose output was amplified and recorded on a millivolt recorder. The pyrometer was able to sight on an area of 0.01 square cm. at 12 inches and had a response time of 0.13 seconds for 63% of a change. The output of the instrument was calibrated in position using the freezing point of gold (*10*) at 1336° K. and the platinum carbon eutectic point (*1*) at 2003° K., as the primary calibration points. The standard container held, roughly, 12 grams of gold or platinum and gave well defined plateaus from which the purities were calculated to be 99.8 to 99.95 mole %. The outputs for pure systems were calculated and used for the calibration; the over-all reproducibility of the calibration of the pyrometer was ±1° K. The freezing times, using the gold shielding system, were 17 seconds at 1336° and 7 seconds at 2003°.

The system is shown assembled in Figure 3. The glass envelope was held rigidly in position at its upper end, the brass support fitted exactly in the open base of the envelope. The upper shield was located by the brass cone meshing with the graphite cover. The glass envelope was open at the top so as not to affect the temperature measurement. Argon gas was flowed through the system entering near the base of the envelope and leaving through the open top. The pyrometer was locked in position above the envelope and adjusted to maximum output while sighted on the freezing point of gold. Once the system was aligned, the container could be removed and replaced with ease, and its black body cavity was automatically in correct alignment. The system gave highly reproducible cooling curves, the time taken to cool between two specified temperatures being reproducible to ±0.2%.

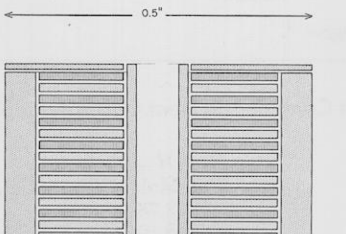

Figure 2. Filled container and support

Interleaved disks of graphite and sample

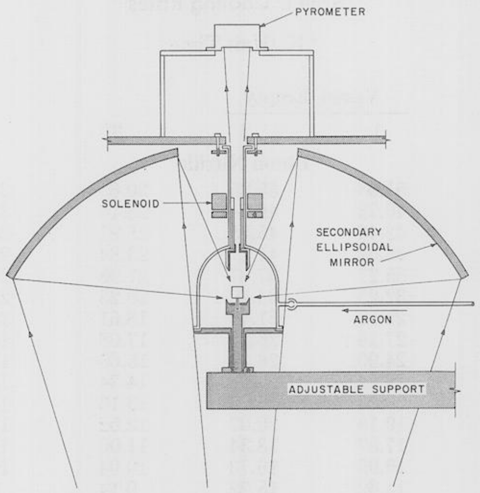

Figure 3. Assembled system

Upper gold shield raised

PROCEDURE

The procedure followed consisted of weighing the container and then placing it in position inside the glass cover. The air was flushed out using argon, which was passed through the system for at least 10 minutes. The gold shield was raised, the arc struck, and the container irradiated by opening a shutter. The rising temperature trace was followed on the recorder until it leveled off, the shutter was then closed as the shield was dropped. The cooling curve was followed, with periodic range changes, until the container cooled below 1300° K. The whole operation from raising the shield to the end of the cooling curve required only 2 minutes. The system was allowed to cool to room temperature, roughly 30 minutes, before the next heat input. The procedure was repeated until two identical cooling curves were obtained—which usually took 3 determinations. This was due to the fact that the first cooling curve after assembly was always much faster than subsequent determinations. The reason for this was not entirely clear, but it was believed to be due to water condensation on the shields.

The evaluation of the rates of cooling from the cooling curve trace was done as follows: The outputs were read off at even intervals of roughly 1.3 seconds, and these were converted to temperature readings. The temperatures were then fitted by computer to the equation

$$\text{Time} = a + b(T - T_0) + c(T - T_0)^2 + d(T - T_0)^3 + e/(T - T_0)^2$$

T_0 is as an arbitrary temperature of the order of 1000° K., used to obtain improved fits. The cooling rate, or slope of the line, was calculated at specified intervals. Unfortunately, the power form of the equation allowed it to flex slightly through the points and this caused the derivative to flex to an even greater extent. Because the values given by the computer were not accurate enough, they were plotted, and a perfectly smooth line was drawn through them. This part of the procedure was most unsatisfactory, but so far no better way of determining the cooling rates has been found. If the temperatures could be read out with greater precision, then a least-squares fit of successive differences at the mean temperature would probably be more accurate.

RESULTS

The heat capacities of hot pressed boron nitride and sintered aluminum oxide have been measured. The samples were in the form of thin annular disks 0.010-inch thick and interleaved with graphite. This was necessary in order to maintain temperature equilibrium in the system. As a check, the apparent heat capacity of a single solid piece of

Table I. Cooling Rates

° K./Unit Time

Temp., ° K.	Vessel Empty 1	Vessel Empty 2	3[a]	4[b]
		Boron Nitride		
2200	51.68	55.25	30.63	33.75
2150	46.73	49.84	28.16	31.02
2100	42.46	45.35	25.91	28.51
2050	38.62	41.27	23.84	26.20
2000	35.27	37.67	21.98	24.07
1950	32.25	34.40	20.23	22.11
1900	29.58	31.48	18.61	20.29
1850	27.16	28.78	17.08	18.61
1800	24.90	26.29	15.65	17.05
1750	22.84	24.03	14.34	15.64
1700	20.95	21.95	13.13	14.33
1650	19.19	20.07	12.02	13.11
1600	17.57	18.34	11.00	11.97
1550	16.05	16.73	10.04	10.90
1500	14.62	15.22	9.14	9.90
1450	13.24	13.76	8.30	8.97
1400	11.91	12.35	7.44	8.06
1350	10.59	10.98	6.61	7.15
1300	9.30	9.61	5.77	6.25
		Aluminum Oxide		
		5	6	7
2000		36.07	23.01	25.06
1950		33.09	21.11	22.97
1900		30.33	19.36	21.05
1850		27.77	17.74	19.27
1800		25.40	16.24	17.63
1750		23.21	14.85	16.11
1700		21.19	13.56	14.70
1650		19.32	12.36	13.39
1600		17.59	11.25	12.18
1550		15.98	10.22	11.06
1500		14.47	9.25	10.00
1450		13.05	8.34	9.01
1400		11.70	7.47	8.07
1350		10.25	6.60	7.11
1300		8.81	5.65	6.08

[a] Vessel + graphite. [b] Vessel + graphite + compd.

Table II. Weights of Materials Used

Grams

Series	Vessel	Graphite	Boron Nitride
1	1.73310	...	...
2	1.74715	...	...
3	1.78409	1.03079	...
4	1.80022	0.34520	0.47347
			Aluminum Oxide
5	1.82038	0.01987	...
6	1.81336	1.02884	...
7	1.83308	0.41331	0.61110

Table III. Calculated Molar Heat Capacities

Boron Nitride Temp., ° K.	Boron Nitride C_p[a]	Aluminum Oxide Temp., ° K.	Aluminum Oxide C_p[a]
1300	11.23	1300	30.73
1350	11.40	1350	30.71
1400	11.41	1400	30.66
1450	11.65	1450	30.94
1500	11.63	1500	31.07
1550	11.57	1550	31.06
1600	11.50	1600	31.19
1650	11.43	1650	31.27
1700	11.46	1700	31.31
1750	11.57	1750	31.34
1800	11.70	1800	31.38
1850	11.77	1850	31.46
1900	11.80	1900	31.41
1950	11.74	1950	31.41
2000	11.71	2000	31.36
2050	11.60		
2100	11.65		
2150	11.68		
2200	11.80		

[a] Cal. mole^{-1} degree^{-1}.

Table IV. Heat Content and Heat Capacity of SPK Graphite (*4*)

Temp., ° K.	$H_T - H_{298.15}$, Cal. Mole^{-1}	C_p, Cal. Mole^{-1} Deg.$^{-1}$
300	3.78	2.05
400	248.10	2.82
500	564.56	3.49
600	941.96	4.03
700	1365.7	4.44
800	1825.4	4.74
900	2310.8	4.97
1000	2817.5	5.15
1100	3339.8	5.30
1200	3876.0	5.43
1300	4425.2	5.56
1400	4988.5	5.67
1500	5560.7	5.77
1600	6143.4	5.86
1700	6730.7	5.93
1800	(7327.5)	(6.00)
1900	...	(6.06)
2000	...	(6.11)
2100	...	(6.16)
2200	...	(6.20)

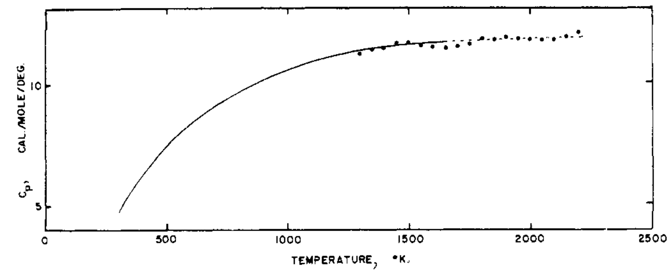

Figure 4. Heat capacity of boron nitride
● This work —— Data of McDonald (5)

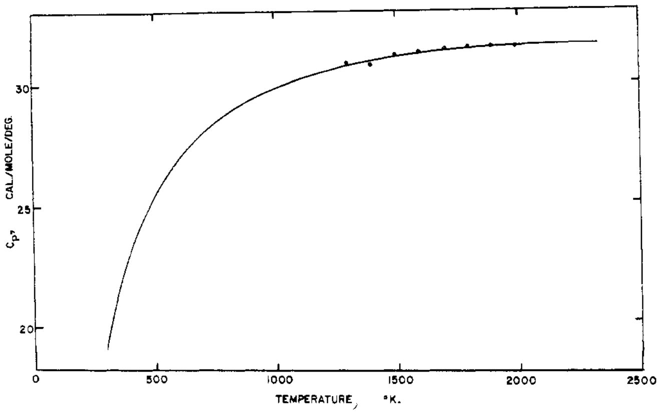

Figure 5. Heat capacity of aluminum oxide
● This work —— NBS table (6)

BN was also measured; this was found to be 8 to 10% lower than the value from the equilibrated disks. The boron nitride was 98% pure and had a chief impurity (1.7%) of boron oxide, which was removed by preheating the disks to 2300° K. in an argon atmosphere. The aluminum oxide was 98.7% pure and had a chief impurity of 1.0% SiO_2; no correction was made for this as the thermal effect would be negligible, 1 gram of Al_2O_3 having almost the identical heat capacity as 1 gram of SiO_2 at high temperatures. The uncorrected cooling rates, or (dS/dt) values, obtained for the two systems are given in Table I, unit time being roughly 1.3 seconds. Table II contains the weights of material in the systems during the determination and calibration. In Table III the heat capacities are given as an average of the two sets obtained from initial and final calibrations. The data is plotted with drop calorimetry values in Figures 4 and 5.

The whole method depends on the comparison with the calibration material in this case National Carbon SPK graphite. The heat content and heat capacity of this material was determined separately in a drop calorimeter by R.A. McDonald of this laboratory. The heat capacity was measured from 300° to 1720° K. and was extrapolated using the Shomate function (*8*) to 2200° K.; the values are given in Table IV. The estimated error of the cooling rate method, including the measurement and extrapolation of the calibration graphite, would be ±2% below 1800° K. and ±3% above 1800° K. With the coming of faster and more precise temperature measuring systems, the errors could be reduced to the order of ±0.5%.

The fact that the method worked as well as it did was due mainly to the calibrating out of many inherent errors. When a temperature gradient existed within the container, it changed the output of the black body cavity slightly. However, the effect in calibration and determination was made nearly identical by having similar cooling rates and thermal diffusivity. Also, due to the temperature difference between the inside and outside of the container, the equations for heat loss were not strictly applicable; however, any error was calibrated out. Lastly, the effect of using very thin disks is important not only to increase the thermal diffusivity by conduction but also by radiation between the large surface areas. In a system of 20 sample and 20 graphite disks the total radiated energy transferred per second would be 5 to 10 times as great as the heat loss of the system.

The most serious limitation of the method is reaction between the sample and graphite and puts an effective limit of 2300° K. on the system. However, the very short hot contact times may allow many reactive systems to be measured. Generally less than 20 seconds per heat would be spent above 2000° K. and only 100 seconds above 1000° K.

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