A CALORIMETER FOR MEASURING LIQUID-METAL ENTHALPIES UP TO 2100°K

V. I. Chemykhin, I. N. Zedina,
and S. E. Vaisburd

UDC 536.2.083:536.722

A description is given of a calorimeter using the droplet form of the method of mixtures and test results are presented. The advantages of using droplet specimens are discussed.

The enthalpy and specific heat of molten metals are required particularly in the mathematical description of metallurgical furnaces; these parameters serve to give detail to calculations on processes and equipment, and also assist in improving the efficiency of energy use, while accurate values ensure that possible errors, which can arise particularly if one is forced to assume additivity in the thermal parameters of components, are minimized.

Distinctive features of thermal measurements at high temperatures are the poor accuracy and considerable difficulty; the difficulties for metals arise particularly on account of the high temperatures, the need to correct for heat losses, the restricted range of constructional materials, the need for protective atmospheres or vacuum, and the high chemical activities of the molten substances.

The methods of measurement also have a considerable effect on the results; there are no commercial high-temperature calorimeters for this purpose, so each worker makes his own equipment, and frequently there are no clear-cut limits to the applicability of the instrument, while no analysis of the errors of measurement is made.

We now have reasonably good methods of determining the thermal parameters of solids at high temperatures, even up to 3500°C and above [1], but many difficulties are still encountered in measuring the enthalpy and specific heat for melts.

There are comparatively few papers on the thermal characteristics of high-temperature melts; most of these have used classical methods in calorimetry, namely, mixing in a variable-temperature calorimeter, which may contain a massive metallic block enclosed in a diathermic or adiabatic case. The method of mixtures and the characteristic features of various systems are described in detail in monographs on calorimetry [2, 3], so here we consider only some specific features of certain types.

A mixing calorimeter has distinctive features mainly in the design of the heating oven and in the specimen, since the latter is contained usually in an ampul.

A specimen is usually heated by means of a resistance furnace having a long isothermal zone.

The enthalpy or specific heat of the melt is usually measured by placing the specimen in an ampul or crucible made of refractory material, so additional errors arise because the result is determined as the difference between the enthalpy of the ampul contining the specimen and the enthalpy of the empty ampul, with the latter determined in an additional series of runs. The heat carried by the ampul is comparable to that carried by the specimen, which is one of the main disadvantages of the ampul form of the method. The effect can be reduced by increasing the working volume of the ampul, but this enlarges the entire equipment.

There are also the following two disadvantages in the ampul method.

1. The melt may interact with the ampul at high temperatures, so very careful choice of materials is necessary.

Gipronikel', Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 34, No. 5, pp. 870-874, May, 1978. Original article submitted May 17, 1977.

0022-0841/78/3405-0596$07.50

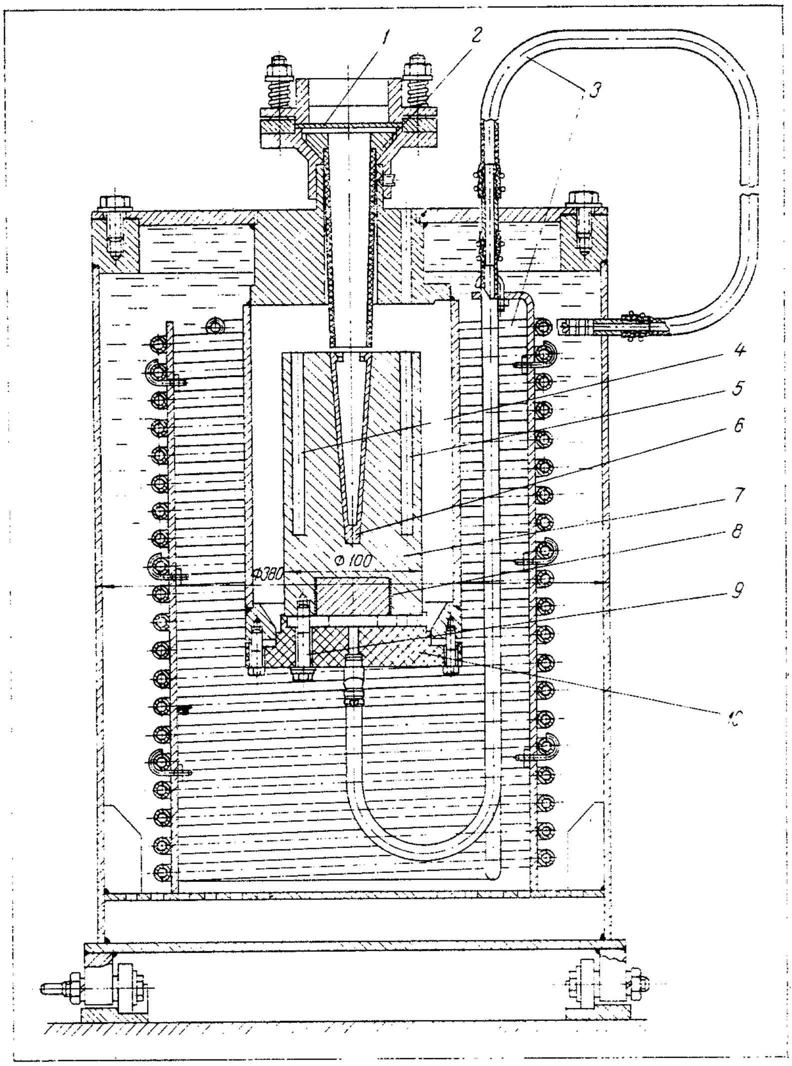

Fig. 1. Massive calorimeter with diathermic jacket: 1) slide; 2) guide tube; 3) system for filling calorimeter with argon; 4, 5) platinum resistance thermometers; 6) reception system for liquid specimen; 7) copper block; 8) calibration heater; 9) plastic sleeve; 10) transparent plastic cover.

2. It is difficult to ensure good contact between the ampul and the wall of the calorimeter, while refractory materials are of low thermal conductivity, so the principal working period in the measurement is fairly prolonged. Therefore, the heat-leak correction becomes substantial. On the other hand, the error in calculating that correction is far greater than the error in measuring the enthalpy itself, so the correction makes a substantial contribution to the reproducibility [4].

The liquid-drop technique represents a promising advance in the method of mixing [5, 6]; a special device is used to throw a drop of the melt into the calorimeter, namely, either a crucible and an extrusion system or a funnel and rod.

The drop technique also has advantages and disadvantages; the advantages include direct measurement of the enthalpy of the molten substance itself and good contact with the calorimeter walls. The disadvantages are as follows: The drop may break up while falling, which can lead to errors in determining the mass, the specimen may oxidize, and heat may be lost by radiation during the fall. These difficulties can be overcome in part by using a guide tube that provides a protective atmosphere in the working space and also by reducing the specific surface of the drop and by making a radiation correction.

We have constructed a calorimeter using this method to measure the enthalpy of a molten metal up to 2100°K.

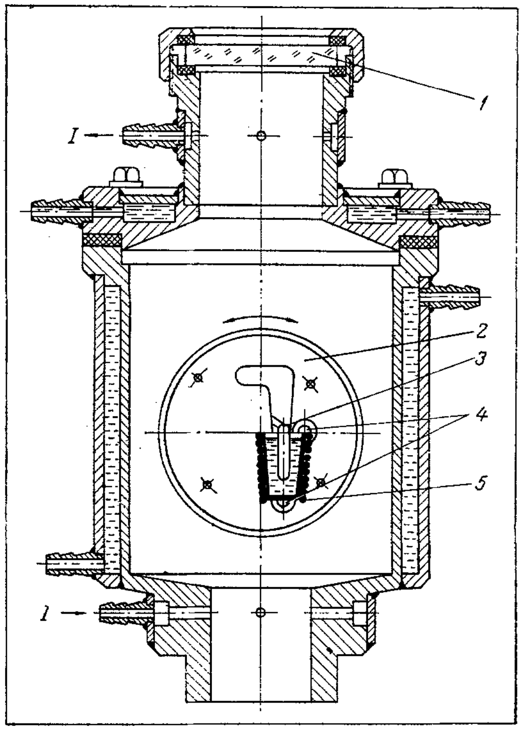

Fig. 2. Miniature electric furnace: 1) viewing port; 2) ejection mechanism; 3) thermocouple; 4) current leads; 5) spiral heater.

The variable-temperature calorimeter contains a massive copper block (mass about 15 kg) and a diathermic jacket, which differs little in design from that of [5]. Figure 1 shows the system. The water jacket is maintained at a constant temperature on account of the thermal inertia of the large body of water in the circulation system, which consists of the calorimeter tank, immersed labyrinth pump, and additional vessel. The thermal equivalent of the calorimeter system is determined by electrical calibration.

The specimen is heated by a small resistance furnace (Fig. 2); this draws about 2.5 kW. The molybdenum wire spiral of diameter 1.5 mm can be used 12-16 times. The jacket and the current leads are water-cooled. The furnace has a means of tipping the cricible and passing the melt into the calorimeter (Fig. 3), as well as a viewing port. Corundum crucibles of capacity about 2 cm^3 are used. The dimensions of the furnace are as follows: height 260 mm; diameter 130 mm. The time needed to heat the specimen to the maximum temperature is 3-5 min.

An immersed thermocouple is used to measure the temperature of the specimen at the moment of ejection, and this takes the form of a sealed hinge, which means that the working end can be displaced within the furnace. The leads were made of tungsten—rhenium wire type VR-5/20 of diameter 0.35 mm. A correction was applied for the cold-junction temperature. There was no appreciable recrystallization of the wire during the working period. The temperature was recorded with a portable PP-63 potentiometer of accuracy class 0.05. The electromagnetic forces produced vigorous mixing in the melt, so the effects of temperature gradients within the crucible were undetectable within the error of measurement.

The specimen was melted and handled in an inert atmosphere (argon). When the furnace had reached the steady state, the crucible was tipped and the drop of melt was ejected into the calorimeter. The temperature rise in the copper block was only 2-4°. The time from loading the furnace to extracting the specimen from the calorimeter was not more than 30 min.

The usual scheme [2] was used to process the data; the Renault—Pfaundler method was used to perform the heat-leak correction, which did not exceed 1% of the enthalpy.

The system was tested with iron, nickel, and silicon; reduced iron of reagent grade or nickel of NO grade and fragments of silicon single crystals were employed. The data were processed by least squares, and the results were found to be reproducible with a coefficient of variation from 0.5 to 1.0%. The discrepancies between our values and those recommended

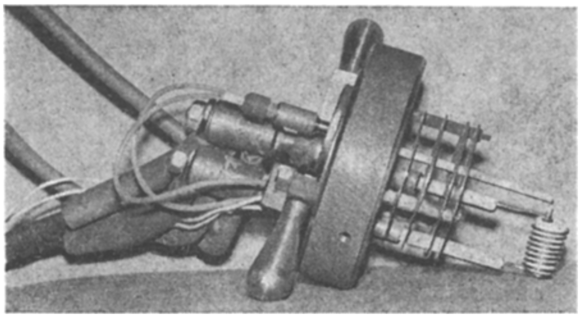

Fig. 3. Mechanism for ejecting the melt.

in the usual handbooks [7, 8] were not more than 2% for iron or 1.6% for silicon, while for nickel the measurements were essentially in agreement with the published values, which is definitely related not only to the errors of the equipments, but also to the purity of the specimens.

The enthalpies of these materials ($H_T - H_{298}$) up to 2100°K were as follows (in J/g): iron 0.686 T + 75 (±10); nickel 0.665 T − 43 (±7); and silicon 0.933 T + 1444 (±13).

LITERATURE CITED

1. V. I. Tyukaev and A. G. Shashkov, Inzh.-Fiz. Zh., 12, 263 (1967).
2. M. M. Popov, Thermometry and Calorimetry [in Russian], MGU, Moscow (1954).
3. S. M. Skuratov, V. P. Kolesov, and A. F. Vorob'ev, Thermochemistry [in Russian], Part 1, MGU, Moscow (1964); Part 2 (1966).
4. A. N. Kornilov, Zh. Fiz. Khim., 37, 2296 (1963).
5. S. E. Vaisburd and I. N. Zedina, in: Papers from the Gipronikel' Design and Research Institute [in Russian], No. 46, Leningrad (1970).
6. L. L. Osinovskikh and S. V. Shavrin, in: Papers from the Urals Ferrous Metallurgy Research Institute [in Russian], Vol. 8 (1968), p. 54.
7. O. Kubashewski and E. L. Evans, Metallurgical Thermochemistry, Pergamon.
8. J. F. Elliott, M. Gleiser, and V. Ramakrishna, Thermochemistry for Steelmaking [Russian translation], Metallurgiya, Moscow (1969).

A METHOD OF MEASURING THE THERMAL CONDUCTIVITY OF POOR HEAT CONDUCTORS UNDER MONOTONIC CONDITIONS

E. A. Tombasov, V. Ya. Cherepanov,
P. S. Glazyrin, G. P. Polukeev,
and V. E. Chelmodeev

UDC 536.2.08

A method of measuring the thermal conductivity of poor heat conductors under monotonic conditions is described which enables one to make measurements on large specimens at different rates of heating and over a wide temperature range.

Existing calorimeters for measuring the thermal conductivity of laminar specimens under monotonic conditions are based on the use of a heat sink to collect the heat passing through the specimen. Blocks of metal with a thermal capacity C_A somewhat exceeding the thermal capacity of the specimen C_0 ($C_0/2\,C_A \leqslant 0.1$) are usually employed as heat sinks [1, 2].

To investigate specimens of low thermal conductivity (λ = 0.1-0.5 W/m·°K) such a ratio of the thermal capacities does not enable one to obtain convenient values of the measured quantities occurring in the theoretical equation. For example, for a rate of heating of about 5°K/min, the drop in temperature of specimens of thickness 5 mm reaches 100°K. A reduction

---

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 34, No. 5, pp. 875-879, May, 1978. Original article submitted March 1, 1977.