EXPERIMENTAL INVESTIGATION OF THE ENTHALPY AND HEAT CAPACITY OF INDUSTRIAL REFRACTORIES OVER THE TEMPERATURE RANGE 1300-2200°K

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Heat capacity is one of the most important thermophysical parameters of construction materials. The heat capacity of industrial refractories has not been the subject of much research until now. The data given in the various reference manuals differ considerably and in some cases are repeated without an indication of a literature source from which the precision of determination can be checked. Judging by some of the literature references, the heat capacity measurements on refractories were carried out with inferior calorimeters. Information on the relation between the heat capacity and the temperature is scant and on the high-temperature heat capacity of refractories almost completely absent.

A systematic investigation of the enthalpy and heat capacity of industrial refractories at high temperatures has been launched at the All-Union Institute of Refractories. It was intended first to study the refractories which are used in peak-temperature industrial furnaces, viz., magnesite, chrome—magnesite, tar-bonded dolomite, high-alumina, and dinas refractories.

The investigation was carried out with the commercial-grade refractories produced by the largest refractories plants. The selection of representative types of mass-produced refractories was based on State Standards or on the Technical Specifications. The chemical composition of these products is given in Table 1.

The investigation was carried out on high-temperature calorimetry apparatus designed at the All-Union Institute of Refractories and intended for enthalpy measurements on solids at temperatures of

TABLE 1. The Chemical Composition of the Investigated Refractories

Product			Oxides content, %						
type	designation	norming document	MgO	CaO	Cr_2O_3	Al_2O_3	SiO_2	Fe_2O_3	R_2O
Magnesite	M-91	GOST 4689—63	92,70	2,40	—	0,70	2,60	1,40	—
Spinel-bonded magnesite	MGSh	MRTU 14-06-26—63	87,80	2,70	—	4,40	2,90	1,90	—
Periclase-spinel	PShSO	GOST 10 828—64	62,28	2,68	21,42	4,61	3,44	6,03	0,20
Chrome-magnesite	KhM	GOST 5381—50	56,60	2,26	22,14	4,87	4,50	9,64	0,19
Chrome-magnesite for converters	KK	TU/USSR 14-6-276—67	57,21	2,82	22,83	5,38	4,80	7,23	0,29
Tar-bonded dolmite for converters			36,42	54,71	—	1,43	2,60	1,94	—
High-alumina	DV-5*	GOST 10381—63	0,60	0,77	—	65,72	30,7	0,91	0,27
Dinas for coke ovens		GOST 8025—56	—	2,88	—	1,00	94,05	1,32	—

*Contains 1.36% TiO_2.

All-Union Institute of Refractories. Translated from Ogneupory, No. 12, pp. 14-17, December, 1975.

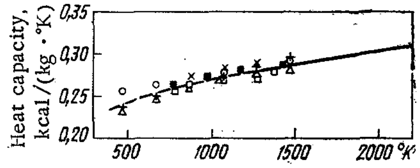

Fig. 1

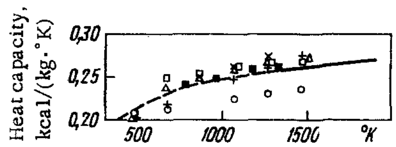

Fig. 2

Fig. 1. The interpolated mean heat capacity of magnesite refractories compared with published data: ——) experimental curve, ----) interpolated curve, ○) [3], ×) [8], △) [10], +) [11], □) [12], ■) [4].

Fig. 2. The interpolated mean heat capacity of dinas refractories compared with published data: ——) experimental curve, ----) interpolated curve, ○) [3], ×) [9], △) [10], +) [11], □) [12], ■) [4].

1300-2500°K. The design is similar to those described by Chekhovskii et al. [1] and Sheindlin et al. [2]. The enthalpy is determined on this apparatus by a combination method with the large isothermic calorimeter used in the diathermal method of temperature measurement.

The apparatus consists of a high-temperature graphite furnace, a calorimetry system, and a power pack (two regulating transformers, viz., an AOSK-40 and an OSU-80) with control panel and high-precision measuring instruments.

The cylindrical specimens 23-25 mm in diameter and 18-21 mm in height were set up in the cylindrical graphite furnace. The latter was evacuated and the specimens were heated in an argon atmosphere. The temperature in the center of the specimens was measured with VR 5/20 thermocouples or with an optical pyrometer.

The calorimeter was calibrated by the direct method of inducing a known quantity of heat with an electric current. The calibration precision was checked by measuring the enthalpy of corundum as reference standard.

The theoretical error of the enthalpy measurements determined as the rms of the maximum instrument errors was about 1.5%.

Until recently, the temperature dependence of the heat capacity of refractories was expressed in the form of a first-order [3, p. 332] or second-order [4, p. 457] polynomial. This approximation was justified by the fact that the measurements were conducted over a comparatively narrow temperature range (800-1300°K). Subsequently it was established that the temperature dependence of the enthalpy and heat capacity of solids over an extensive temperature range, viz., from room temperature to melting point, can be described by the following equations:

$$\Delta H = H_T - H_{298} = a + bT^2 + \frac{c}{T} + d, \qquad (1)$$

$$C_p = \frac{d(\Delta H)}{dT} = a + 2bT - \frac{c}{T^2}, \qquad (2)$$

where ΔH is the variation of the enthalpy of a substance being heated from standard temperature ($T = 298$) to a given temperature T [5, p. 19], kcal/kg or kJ/kg; C_p is the true heat capacity of the substance, kcal/(kg · °K) or kJ/ (kg · °K).

Equation (2) is a good description of the temperature dependence of C_p, it is near linear at high temperatures, and agrees with experimental data. At medium temperatures the function is curvilinear because the value of the third term cT^{-2} increases which again agrees with experimental findings.

The present writers evaluated experimental enthalpy data for 1300-2200°C based on the heat capacity at room temperature (C_{p298}) bearing in mind that the resulting functions can be used for interpolating experimental data in the medium-temperature range (298-1300°K). The quantity C_{p298} of the materials concerned was determined on the RK-1 instrument developed at the Leningrad Institute of Optical Mechanics. The error of measurement was 3-7%.

This method has been used extensively for deriving the equations of the heat capacity of solid materials [6, pp. 144-145]. There is a combined graphic and analytical method of evaluating data for $H_T - H_{298}$ with account taken of C_{p298} [7, pp. 35-37] but it is not precise enough and difficult to use.

TABLE 2. The Coefficients of Temperature-Dependence Equations (1) and (2)

Designation of product	Temp. range, °K	Coefficients*			
		a	$b\cdot10^{6}$	c	d
M-91	1300—2200	$\frac{0,2448}{1,0249}$	$\frac{2,866}{11,999}$	$\frac{3716,6}{15561}$	$\frac{-87,958}{-368,26}$
MGSh	1300—2200	$\frac{0,2175}{0,9106}$	$\frac{3,913}{16,383}$	$\frac{2030,1}{8499,6}$	$\frac{-75,114}{-314,49}$
PShSO	1300—2200	$\frac{0,1756}{0,7352}$	$\frac{5,101}{21,357}$	$\frac{356,85}{1494,1}$	$\frac{-58,061}{-243,09}$
KhM	1300—2200	$\frac{0,1203}{0,5037}$	$\frac{7,177}{30,049}$	$\frac{-2301,9}{-9637,6}$	$\frac{-34,499}{-144,44}$
KK	1300—2200	$\frac{0,1378}{0,5769}$	$\frac{6,414}{26,854}$	$\frac{-971,85}{-4068,9}$	$\frac{-43,508}{-182,16}$
Tar-bonded dolomite	1300—2200	$\frac{0,1581}{0,6619}$	$\frac{4,302}{18,01}$	$\frac{-996,41}{-4171,8}$	$\frac{-47,602}{-199,3}$
DV	1300—2050	$\frac{0,1865}{0,7808}$	$\frac{5,060}{21,185}$	$\frac{3964,2}{16597,4}$	$\frac{-73,368}{-307,18}$
Dinas for coke ovens	1300—1950	$\frac{0,2567}{1,075}$	$\frac{1,198}{5,016}$	$\frac{7533,97}{31543,2}$	$\frac{-102,84}{-430,58}$

*The coefficients for determining $H_T - H_{298}$ in kcal/kg and C_p in kcal/(kg·°K) in the numerator, in kJ/kg and kJ/(kg·°K) in the denominator.

The method of least squares for approximating Eq. (1) gives more precise and reproducible results when the following additional conditions are introduced:

$$H_{298} = 0;\quad \left.\frac{d(\Delta H)}{dT}\right|_{T=298} = C_{p_{298}}.$$

The minimum of the sum of the squares of the deviations is then determined by the Lagrangian method of indeterminate multipliers. The algorithm was set up in the "Odra—Algol" language and the calculations were carried out on an "Odra-1204" computer.

The coefficients $H_T—H_{298}$ and the true heat capacity C_p in the equations of the temperature dependence of the enthalpy of the refractories concerned were obtained by processing* the experimental data in Table 2.

The rms deviation of the individual measured enthalpies from the approximating function was 1.32% for M-91, 1.51% for KhM, and 1.69% for dinas.

For functions derived in the form $H_T—H_{298} = f(T)$ from experimental data over a high-temperature range with account taken of C_{p298}, a limited interpolation in the range of medium temperatures is permissible. This is confirmed by data relating to the mean heat capacity

$$\bar{C}_p = \frac{H_T - H_{298}}{T - 298}\ \text{kcal/(kg·deg K)}$$

of magnesite and dinas refractories (Figs. 1 and 2).

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*The processing was carried out by G. Ya. Zeliger.

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