THERMAL DIFFUSIVITY OF RESIN-BONDED REFRACTORIES OVER A WIDE TEMPERATURE RANGE

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Results are shown of thermal diffusivity measurements made on resin-bonded refractories of various compositions and structures.

In order to study processes occurring in resin-bonded refractories, to calculate temperature fields, and to select the most appropriate heating modes, it is necessary to know the thermophysical properties of these materials.

The most important thermophysical property of a material is its thermal diffusivity a.

According to available published information, no study was ever made concerning the thermal diffusivity of resin-bonded refractories; in [1-5] are given test data on their thermal conductivity. Its values suggested in these references differ appreciably – by up to 100%. It is difficult to compare them properly, because the authors do not describe the complete characteristics of their test specimens.

In this study the authors present the results of their measurements, namely the thermal diffusivity of freshly molded, of heat treated, and of coked resin-bonded refractories (dolomite, magnesite, and dolomite–magnesite grades) over the 200-1600°C temperature range.

The test materials experience structural and phase transformations during heating and, therefore, their effective thermophysical properties as $a(t)$, for example, must be determined under test conditions as close as possible to actual operating conditions. The method used in this study was one of monotonically heating flat specimens [6] in an apparatus which had been described earlier [7-10]. Each specimen constituted two identical plates 90 × 90 × 13 mm in size. The temperature was measured with tungsten–rhenium thermocouples. The experiment was performed in a nitrogen atmosphere with a thermal conductivity close to that of air or carbon dioxide. The theoretical principle of this method is based on a linear temperature-dependence of the thermophysical properties within the range of temperature drops across a specimen. In view of this, the heating rate was selected so as not to exceed a 50-70°C temperature drop. All our assumptions could be assumed valid within this range of temperature drops, except at points where the monotonicity of an $a(t)$ curve would break. At those points the error of this method was above the estimated 10-12% level, the curves then indicating only qualitative trends. The very concept of thermal diffusivity becomes rather tentative within the range of strongly nonlinear thermophysical characteristics.

The specimens for our thermal diffusivity tests were prepared from as identical as possible industrial batches. The raw material was roasted dolomite from the Stylsk deposit and roasted magnesite. The chemical composition and the properties of these materials are listed in Table 1. "Solid" coal tar, a common ingredient of converter refractories, was used as the resin binder. Its properties are listed in Table 2.

The specimens were prepared as follows. The raw material was ground in crusher rolls, then sieved into 5-3 mm and 3-1 mm fractions. The fine fraction <0.088 mm was collected in a spherical

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TABLE 1. Chemical Composition and Properties of Raw Materials

Material	Chemical composition, %							Apparent density, g/cm³	Apparent porosity, %
	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	calcination loss	moisture		
Roasted dolomite	37,80	55,4	2,20	1,50	2,4	0,5	0,1	3,08	4,6
Roasted magnesite	92,77	1,68	2,0	0,66	2,24	0,5	0,5	—	—

TABLE 2. Composition and Properties of Anthracite Tar

Density at 20°C, g/cm³		1,23
Water content, %		<0,5
Viscosity $C^{10}_{80\,°C}$, sec		43
Coke number, %		42
Yield of volatile fraction, %	170 °C	—
	270 °C	5
	360 °C	26

receptacle, with only 1% residue remaining on the 0.088 mm sieve. The ground material and the resin were heated up to 100-120°C. The coarse fractions were then mixed with the resin, fine material was added, and mixing was continued until the mass had become homogeneous. Specimens were molded from this mass at a 50-80°C temperature under a pressure of 1200 kg/cm². The weight and the dimensions of a specimen were checked during molding, for the purpose of maintaining a uniform apparent density. Part of the specimens was then either heat treated or coked in a coke bed according to cycles listed in Table 3. The finished specimens were held in desiccators for not longer than 1-2 weeks.

Four specimens of each type of refractory were examined. Each freshly molded specimen was heated up to 1600°C twice during each test. Evidently, data obtained after the second heating would pertain to coked refractories. In order to verify this hypothesis, special thermal diffusivity tests were performed on precoked specimens and a satisfactory agreement was found here with the data for freshly molded specimens after the second heating.

The properties of the test specimens are listed in Tables 4 and 5. The measured thermal diffusivity of three resin-bonded refractories is shown in Fig. 1.

The total range of values is: $(0.5\text{-}1.0)\cdot 10^{-6}$ m²/sec for freshly molded refractories; $(1.0\text{-}1.8)\cdot 10^{-6}$ m²/sec at 200°C and $(0.5\text{-}0.8)\cdot 10^{-6}$ m²/sec at 1000-1600°C for heat treated and coked refractories, respectively.

The $a(t)$ curves (Fig. 1a, b, c) indicate that the thermal diffusivity of resin-bonded refractories passes through a characteristic drop within the 200-1000°C temperature range, while at higher temperatures it remains almost constant. The variation in the thermal diffusivity of freshly molded specimens does not exceed 20-30%. The thermal diffusivity of coked and heat treated refractories is much more steeply temperature-dependent. The drop in the thermal diffusivity at low and moderate temperatures is, evidently, related to the phonon mechanism of heat conduction in the component calcium and magnesium oxides.

We will now consider the effect of certain physicochemical processes which occur during the heating of resin-bonded refractories on the temperature characteristics of their thermal diffusivity. According to a special thermographic analysis of tar, its decomposition in an inert atmosphere within the 200-400°C temperature range has a prolonged endothermal effect not capable of causing sharp changes in the trend of the $a(t)$ characteristic. Instead, this effect causes the $a(t)$ curve to shift (downward) within the 200-400°C range (Fig. 1).

It is well known that in resin-bonded refractories there forms an admixture of calcium hydroxide, which becomes dehydrated at 550°C. This is the temperature at which the monotonicity of the $a(t)$ characteristic of freshly molded and heat treated refractories breaks (Fig. 1a). In resin-bonded dolomite – magnesite refractories this effect is very weak (Fig. 1c), while in resin-bonded magnesite refractories it does not appear at all (Fig. 1b).

TABLE 3. Modes of Heat Treatment and Coking

Time, h	Heating treatment		Coking	
	temperature, °C	mode	temperature, °C	mode
1	200		200	
2	400	Hold	500	
3	400	"	800	Hold
4	400	"	800	"
5	400	"	800	"
6	350	Cool	600	Cool
7	300	"	500	"
8	250	"	450	"
9	200	"	400	"

TABLE 4. Composition and Properties of Specimens

Batch No.	Specimen*	Substantial and fractional content of batch,%							Properties of test specimens			
		roasted dolomite			roasted magnesite			resin (tar) content,%	apparent density, g/cm³			coke residue,%
		5–3 mm	3–1 mm	<0,088 mm	5–3 mm	3–1 mm	<0,088 mm		freshly molded	coked	heat treated	
1	RD	52	13	35	—	—	—	5,5	2,79	2,68	—	2,25
2	RDh	50	15	35	—	—	—	5,5	—	—	2,64	2,80
3	RD	28	7	65	—	—	—	5,3	2,76	2,65	—	2,17
4	RD	40	10	50	—	—	—	5,3	2,85	2,74	—	2,17
5	RMh	40	10	50	—	—	—	5,3	—	—	2,64	2,66
6	RDc	40	10	50	—	—	—	5,3	—	2,66	—	2,01
7	RDM	15	20	—	—	—	65	5,5	2,80	2,68	—	2,18
8	RDM	50	15	—	—	—	35	5,5	2,68	2,56	—	2,10
9	RM	—	—	—	50	15	35	5,5	2,74	2,61	—	2,00
10	CMт	—	—	—	50	15	35	5,5	—	—	2,67	3,50
11	RM	—	—	—	40	10	50	8,5	2,70	2,58	—	4,10
12	RM	—	—	—	40	10	50	6,0	2,70	2.59	—	2,20

*R, resin, c, coked; D, dolomite; M, magnesite; h, heat treated.

TABLE 5. Chemical Composition of Specimens, %

Specimens	MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	C
Resin-bonded dolomite	36,26	53,6	1,89	1,40	2,55	4,3
Resin-bonded magnesite	90,30	1,65	1,75	0,97	2,33	3
Resin-bonded dolomite –magnesite (batch No. 7)	71,57	20,07	1,81	1,13	2,42	3

It is to be noted that an analogous (endothermal) effect at 900°C may be related to the decomposition of calcium carbonate. The effect of $CaCO_3$ decomposition is most pronounced in heat treated resin-bonded dolomite refractories, while it is almost absent in coked specimens. Evidently, during heat treatment at 400°C there forms a certain amount of $CaCO_3$ [1].

With respect to their temperature characteristics, heat treated resin-bonded dolomite refractories are similar to freshly molded ones. For example, the monotonicity of their $a(t)$ curves breaks at 500 and at 900°C. The trend of this curve for heat treated resin-bonded magnesite refractories is similar to that of coked ones.

Noteworthy is the rather significantly higher thermal diffusivity of coked and heat treated refractories above that of freshly molded ones, often 50-100% higher. According to Fig. 1a, b the thermal diffusivity of heat treated specimens is similar to that of coked ones, or is intermediate between the latter and that of freshly molded ones.

This change in the thermal diffusivity (thermal conductivity) of resin-bonded refractories during heat treatment can be explained on the basis of the following analysis. Let us represent the thermal model of a ceramic by a series circuit of thermal resistances: the resistance of resin (or the coke residue) and the resistance of porous dolomite grains (Fig. 2a). The effective thermal conductivity of such a system can be calculated according to the Dul'nev formula [11]:

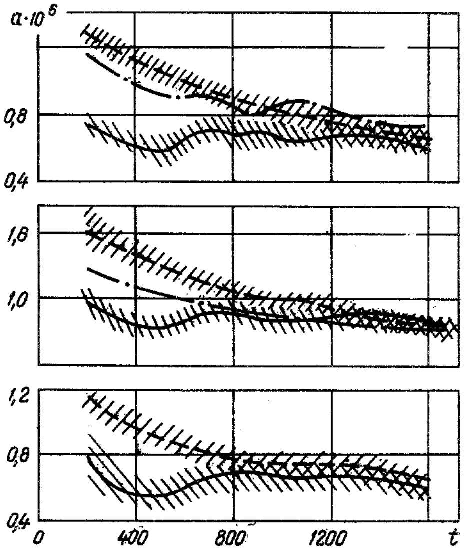

Fig. 1. Thermal diffusivity a (m^2/sec) of resin-bonded refractories: a) dolomite; b) magnesite; c) dolomite – magnesite [solid lines) freshly molded specimens; dashed-dotted lines) heat treated specimens; dashed lines) coked specimens], as a function of the temperature t (°C).

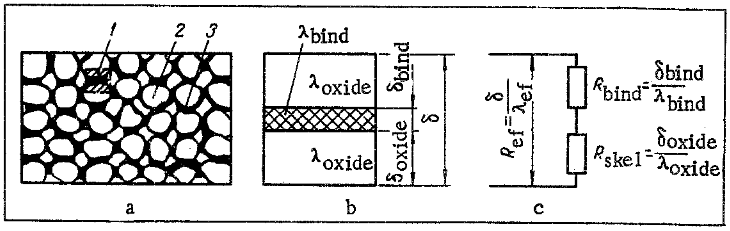

Fig. 2. a, b) Thermal model; c) equivalent circuit diagram of a resin-bonded ceramic: 1) unit cell; 2) pore; 3) resin.

$$\lambda = \lambda_{skel} f(P, \nu). \tag{1}$$

The following expression (Fig. 2b, c) can be reliably used for the thermal resistance of the "skeleton" (material without the pores):

$$R_{skel} = R_{bind} + R_{oxide},$$

i.e.,

$$\frac{\delta}{\lambda_{skel}} = \frac{\delta_{bind}}{\lambda_{bind}} + \frac{\delta_{oxide}}{\lambda_{oxide}}. \tag{2}$$

From this we have

$$\lambda_{skel} = \frac{1}{\frac{1}{\lambda_{bind}} \cdot \frac{\delta_{bind}}{\delta} + \frac{1}{\lambda_{oxide}} \cdot \frac{\delta_{oxide}}{\delta}}; \tag{3}$$

with λ_{skel}, λ_{oxide}, λ_{bind} denoting, respectively, the thermal conductivity of the solid phase ("skeleton"), the component oxides (CaO and MgO), and of the binding resin; δ, δ_{oxide}, δ_{bind} denoting their respective thicknesses in a unit cell and proportional to their volume concentrations; and $f(P, \nu)$ calculated by the Dul'nev formula [11].

Since the resin concentration is small, hence $\delta = \delta_{oxide}$. Then

$$\lambda_{skel} = \frac{\lambda_{oxide}}{1 + \frac{\lambda_{oxide}}{\lambda_{bind}} \cdot \frac{\delta_{bind}}{\delta}}. \tag{4}$$

The thermal conductivities of MgO and CaO do not differ by more than a factor of 5.0 [12], and their effective thermal conductivity can be calculated according to the formula in [13]:

$$\lambda_{skel} = \lambda_{CaO}^{n_{CaO}} + \lambda_{MgO}^{n_{MgO}}; \tag{5}$$

with n_{CaO} and n_{MgO} denoting the volume concentrations of these oxides in the skeleton. The final formula for the effective thermal conductivity of resin-bonded refractories becomes thus

$$\lambda = \frac{\lambda_{CaO}^{n_{CaO}} \lambda_{MgO}^{n_{MgO}} f(P, \nu)}{1 + \frac{\lambda_{CaO}^{n_{CaO}} \lambda_{MgO}^{n_{MgO}}}{\lambda_{bind}} \cdot \frac{\delta_{bind}}{\delta}}. \qquad (6)$$

TABLE 6. Relative Thermal Diffusivity $a(b, t)/a_{skel}(t)$ as a Function of the Heating Rate

b, deg/min	t, °C 400	800	1600
1	0,81	1,0	1,0
30	0,54	0,76	0,95

We will specify values of the various parameters at 200°C. The thermal conductivity of the component oxides with a zero porosity is $\lambda_{CaO} = 10$ W/m·deg and $\lambda_{MgO} = 28$ W/m·deg [12]. On the assumption that the volume concentrations of both oxides are equal, formula (5) yields $\lambda_{oxide} = 17$ W/m·deg. According to the data in [14], the thermal conductivity of tar is 0.14 W/m·deg. Since tar is pressed into the pores during the molding process, hence δ_{bind} is almost equal to the height of the granular micro-asperities. Let $\delta_{bind}/\delta_{oxide} \simeq 0.01$. Then formula (4) yields $\lambda_{skel} = 7.7$ W/m·deg. The porosity of coked and of freshly molded specimens may be assumed the same and equal to $\simeq$14%.

Finally, the effective conductivity of freshly molded specimens is

$$\lambda = 7.7 \cdot 0.62 = 4.8 \text{ W/m} \cdot \text{deg},$$

according to formula (1).

In coked refractories the binder constitutes porous graphite. Its thermal conductivity at 50-60% porosity may become as low as 5-10 W/m·deg [15]. Nevertheless, estimates have shown that in this case $\lambda_{skel} = 13$-15 W/m·deg, i.e., its thermal conductivity is close to that of the oxides λ_{oxide}. Then

$$\lambda = 15 \cdot 0.62 = 9.3 \text{ W/m} \cdot \text{deg}.$$

These estimates show that the thermal conductivity of freshly molded refractories is much lower than that of coked ones. This agrees with test data.

It has also been shown that a change in the thermal conductivity and in the thermal diffusivity of specimens as a result of heat treatment is associated with the formation of a graphite-like binder at the contact between grains: in heat treated specimens the formation of binder is not yet complete, while in coked specimens it is already complete.

One purpose of this study was to detect a relation between the thermal diffusivity and the fractional distribution (Table 4). The fine-fraction content was varied over the 35-65% range. No such relation could be established. The total spread of averaged and smoothed thermal diffusivity curves is indicated in Fig. 1. The upper limit of this spread corresponds to 65% fine fraction and its lower limit corresponds to 50% fine fraction. Within this band lie the data for specimens with 35% fine fraction. The total spread of curves does not exceed 20-25%.

In Fig. 3 we compare the thermal diffusivity of specimens with the same fractional composition but different substantial composition. Among the freshly molded specimens with a low fine-fraction content (Fig. 3a), the thermal diffusivity of resin-bonded magnesite refractories is highest. This is, evidently, related to the high content of coarse-fraction magnesite, whose thermal conductivity is higher than that of dolomite. Among freshly molded specimens of the same compositions but with a higher fine-fraction content (Fig. 3b), the thermal diffusivity of resin-bonded dolomite, magnesite, and dolomite–magnesite refractories is almost the same. This can be explained by the large contribution of the contact resistance between fine particles to the total thermal resistance, "overshadowing" the effect of the thermal conductivities of the component materials.

As has been shown here, the thermal resistance of intergranular contact is lower in coked than in freshly molded specimens. The thermal diffusivity of coked refractories is determined mainly by the properties of the component oxides and, therefore, the curve for resin-bonded magnesite specimens lies far above the curve for resin-bonded dolomite specimens, regardless of the fractional composition (Fig. 3c). The difference decreases at higher temperatures. This agrees with the differences between the thermal conductivities of the component oxides [12]:

$$t = 200\,°C, \quad \lambda_{MgO} = 28 \text{ W/m} \cdot \text{deg}, \quad \lambda_{CaO} = 10 \text{ W/m} \cdot \text{deg};$$

$$t = 600\,°C, \quad \lambda_{MgO} = 12 \text{ W/m} \cdot \text{deg}, \quad \lambda_{CaO} = 7 \text{ W/m} \cdot \text{deg};$$

$$t = 1600\,°C, \quad \lambda_{MgO} = 7 \text{ W/m} \cdot \text{deg}, \quad \lambda_{CaO} = 7{,}8 \text{ W/m} \cdot \text{deg}.$$

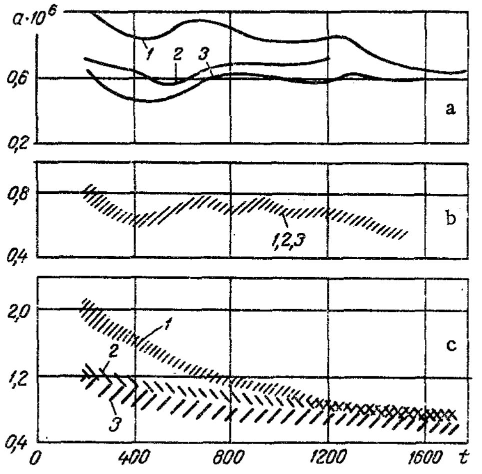

Fig. 3

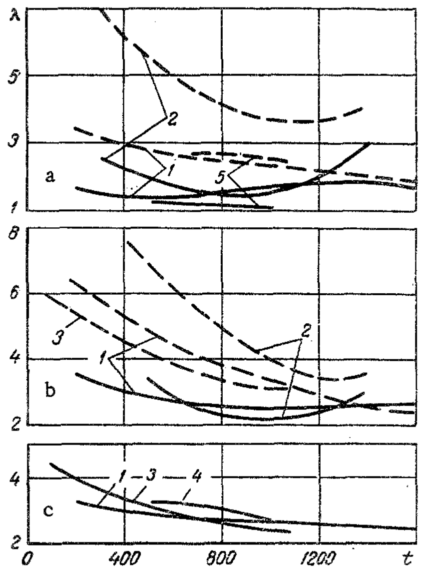

Fig. 4

Fig. 3. Thermal diffusivity a (m^2/sec) of resin-bonded refractories with various fine-fraction contents, as a function of the temperature t (°C): a) freshly molded with 35% fine fraction; b) freshly molded with 65% fine fraction; c) coked with 35% and with 65% fine fraction; 1) magnesite; 2) dolomite; 3) dolomite–magnesite.

Fig. 4. Thermal conductivity λ (W/m · deg) of resin-bonded refractories, as a function of the temperature t (°C): a) dolomite; b) magnesite; c) dolomite–magnesite: 1) test curves; 2) data from [4]; 3) data from [3]; 4) data from [5]; 5) data obtained by the standard method of determining the thermal conductivity [solid lines) freshly molded specimens; dashed lines) coked specimens].

In order to study the effect which the amount of resin binder has on the thermal diffusivity, we prepared resin-bonded magnesite specimens with the resin content varying from 6 to 8.5%. According to measurements, the thermal diffusivity remains almost independent of the resin content within the test range. This has apparently to do with the earlier hypothesis that the amount and the properties of resin at the intergranular contacts, rather than of the resin in the pores, affect the thermal conductivity and the thermal diffusivity mostly.

As has been mentioned earlier, the effective thermophysical properties of materials undergoing physicochemical transformations depend not only on the composition and the structure but also on the mode of temperature variation. It was of interest, therefore, to estimate how the effective thermophysical properties of the test materials depend on the heating rate in thermal diffusivity measurements. Such an estimate could be made on the basis of available test data.

The apparatus for measuring the thermal diffusivity of resin-bonded refractories had not been designed for low heating rates and, therefore, all tests were performed at a rate of ~30 deg/min. The values of $a(t)$ for low rates were then obtained in the following manner. First the specimens were heat treated (up to 400°C) or coked (up to 800°C) at heating rates of 1-2 deg/min. Then the thermal diffusivity of these specimens was measured at 400 and 800°C, respectively, after fast heating. One could evidently assume that the specimen composition and structure had remained almost without change during the fast second heating to the preliminary heat treatment temperature. Moreover, the values of the thermal diffusivity could be referred to heating rates of the order of 1-2 deg/min. The tests have also shown that the ratio $a(b, t)/a_{skel}(t)$ ($a(b, t)$ denoting the thermal diffusivity of freshly molded specimens when heated to temperature t at the rate of b deg/min; and $a_{skel}(t)$ denoting the thermal diffusivity of coked specimens of the same material) does not depend on the substantial composition of specimens but, essentially, on the thermal history of such specimens. The test data obtained here and shown in Table 6 indicate the characteristic dependence of the thermal diffusivity on the heating rate. The values here represent averages of 10-20 readings. The maximum deviation from these values did not exceed 5-10%, regardless of the composition of specimens.

TABLE 7. Specific Heat of Resin-Bonded Refractories, J/kg · deg

Specimen	t, °C							
	200	400	600	800	1000	1200	1400	1600
Resin-bonded dolomite	876	936	1006	1073	1140	1207	1273	1341
Resin-bonded dolomite –magnesite	1038	1111	1169	1199	1237	1273	1308	1349
Resin-bonded magnesite	1080	1158	1201	1253	1295	1335	1374	1412

As has been mentioned earlier, the thermal diffusivity of resin-bonded refractories was never measured directly before. In order to compare the test data with published values, we converted the thermal diffusivity into thermal conductivity. The necessary values of the specific heat were obtained experimentally by the mixing method for resin-bonded dolomite refractories; for resin-bonded dolomite–magnesite and magnesite refractories they were calculated according to the additive law on the basis of the chemical composition of the specimens, as given in Table 5 (the specific heat of component oxides was taken from the handbook [16]). The values of the specific heat are listed in Table 7.

In the compilation we have included data for refractories with compositions close to those of industrial grades (items 4, 7, 9 in Table 4).

Values calculated from our test data and those published in the technical literature are compared in Fig. 4a, b, c. The graphs indicate that our test results lie within the same limits as in [3-5] and within the same limits as results obtained by the standard method.

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