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Ceramics International 28 (2002) 601–607

CERAMICS
INTERNATIONAL

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Thermal conductivity of carbon-containing refractories

Jerzy Tomeczek[a],*, Renata Suwak[b]

[a]Department of Process Energy, Silesian Technical University, ul Krasinskiego 8, 40-019 Katowice, Poland
[b]Institute of Refractory Materials, Gliwice, Poland

Received 9 July 2001; received in revised form 13 August 2001; accepted 27 November 2001

Abstract

The measurements of the heat transfer coefficient of carbon-containing refractories at temperatures up to 800 °C by the hot-wire method are presented. Based on the solution of the Fourier–Kirchhoff equation the criteria of the method application to finite size samples are developed. The appearance of the minimum on the $\lambda(t)$ curve is an indication of an even initial temperature within the sample, while the heat transfer coefficient is equal to the value at the point of minimum. Carbon in refractory materials enhances thermal conductivity, but only above 400 °C.

Keywords: C. Thermal conductivity; D. Carbon; E. Refractories

1. Introduction

The use of new materials in high temperature industrial technologies requires a thorough knowledge of their thermal conductivity. Magnesia products with an addition of carbon or SiC as well as carbonised corundum products belong to future materials in the industry of refractories, due to their potentially favourable properties such as: high thermal conductivity, resistance to high temperature, low density and good mechanical properties. Technological processes of production can be better controlled when the relation between thermal conductivity and the composition of raw input materials and parameters of their firing process is known.

The aim of the work is to present the results of investigations on thermal conductivity of carbon-containing refractories within the temperature range up to 800 °C. Experimental studies were carried out by means of non-stationary measurement method using hot wire as a linear heat source. In this method thermal conductivity is determined on the basis of temperature measurement at a chosen measuring point of the sample material at two moments of time. Since the hot wire method for carbon-containing refractories is not included in international standards, the criteria of its usability for samples with finite dimensions have been established on the basis of numerical solution of Fourier–Kirchhoff equation and its accuracy has been evaluated. Systematic investigations were carried out on magnesia–carbon products where carbon was added in the form of graphite or in the form of coke grains. The research revealed that thermal conductivity of magnesia–carbon products is higher than that for magnesia ones but only at temperature exceeding 400 °C and this refers solely to carbon introduced in the form of graphite. The finer the graphite grains the lower the thermal conductivity.

2. Theoretical basis of hot wire method

The method makes use of the measurement of temperature change at a particular point of the body heated with a linear heat source characterised by steady power P_1 per unit length. Transient temperature field in an infinite solid characterised by an initial temperature T_0, induced by electric current flowing through a thin wire placed in the centre of a cylindrical system of co-ordinates, turned on at moment $t=0$, is described by solution of the Fourier–Kirchhoff equation:

$$\frac{\partial T}{\partial t} = a\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) \tag{1}$$

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* Corresponding author. Tel./fax: +48-32-255-56-16.
E-mail address: kep@rm4.polsl.katowice.pl (J. Tomeczek).

PII: S0272-8842(02)00015-9

Nomenclature

a	thermal diffusivity, m^2/s
c	specific thermal capacity of sample material, kJ (kg K)
c_d	specific thermal capacity of wire, kJ/(kg K)
P_1	linear heat source power, W/m
r	radius, co-ordinate of cylindrical system, m
R_d	radius of linear heat source, m
R_m	distance of measuring thermocouple from linear heat source, m
R_r	distance of reference thermocouple from linear heat source, m
T	temperature, K or °C
T_0	initial temperature of sample, K or °C
T_r	temperature of reference thermocouple, K or °C
t	time, s
ρ	density of sample material, kg/m^3
ρ_d	density of linear heat source, kg/m^3
λ	thermal conductivity of sample material, W (mK)

with boundary conditions

$$T(r \to \infty, t) = T_0, \tag{2}$$

$$r \to 0, \lim\ 2\pi\ r\ \lambda \frac{\partial T}{\partial r} = P_1, \tag{3}$$

and the initial condition

$$T(r, 0) = T_0. \tag{4}$$

Carslaw and Jaeger [1] have developed a solution of the initial-boundary value problem (1)–(4) in the form of the following dependence

$$\Delta\ T(r, t) = T(r, t) - T_0 = -\frac{P_l}{4\pi\ \lambda} Ei\left(-\frac{r^2}{4\,at}\right), \tag{5}$$

where the exponential-integral function is defined as follows

$$Ei(x) = -Ei(-x) = \int_x^{\infty} \frac{e^{-u}}{u} du. \tag{6}$$

For very small arguments $r^2/4at << 1$ of the *Ei* function, Eq. (5) may be written in a simplified form

$$\Delta T(r, t) = \frac{P_l}{4\pi\ \lambda} \ln\left(4\ at/\beta\ r^2\right), \tag{7}$$

resulting from the expansion of the function $Ei(x)$ for $(x \to 0)$ into a series [2,3]

$$Ei(x) = \ln(1/\beta\ x) + x - \frac{x^2}{4} + \frac{x^3}{18}, \tag{8}$$

where $\beta = 1.781072$. Thermal conductivity λ may then be determined by measuring the temperature at one point of the body at two moments of time

$$\lambda = \frac{P_l}{4\pi} \frac{\ln(t_2/t_1)}{T(r, t_2) - T(r, t_1)}. \tag{9}$$

Since it is difficult to meet the requirement $r^2/4at << 1$ for most materials, chiefly because of finite geometrical dimensions of the samples under investigation, the application of Eq. (9) is limited. Then thermal conductivity should be calculated from dependence (5) on the basis of temperature change measurement at a specified measuring point at two moments of time t and $2t$, enabling determination of an appropriate ratio of temperature increment [4]

$$\frac{\Delta T(2t)}{\Delta T(t)} = M = \frac{Ei(x/2)}{Ei(x)}. \tag{10}$$

Eq. (10) makes it possible to calculate the value $x = R_m^2/4at$ for subsequent moments of time at measurement point located in distance R_m from linear heat source, and consequently the function $Ei(x)$. One may also use tables specifying $Ei(x) = f(M)$ value [4]. The knowledge of the $Ei(x)$ function enables calculation of λ from Eq. (5).

3. Accuracy of hot wire method

The most serious errors result from finite geometrical dimensions of the examined sample and heat source. In the case of carbon-containing materials it is necessary to electrically insulate the measuring thermocouple, which is the source of additional errors. Due to that the conditions of initial-boundary value problem (1–4) are not met. The method assumptions are checked during the measurement procedure by means of two thermocouples: a measurement thermocouple placed parallel to heat source in distance R_m from the heat source and a reference thermocouple placed perpendicular to the heat source in distance R_r. During the sample stabilisation at temperature T_0 of the instrument chamber, the indications of both thermocouples should be equalized $T_m = T_r = T_0$. To minimise the method error, one should pay attention to basic error elements such as:

(a) heating wire finite length which disturbs one-dimensional thermal field,
(b) different from zero hot wire diameter,
(c) inadequate power of heat source,
(d) too long measuring time,

(e) non uniform sample temperature at the moment when the wire heating is turned on,

(f) inappropriate distance of the reference thermocouple from the heat source.

In the non-stationary hot wire method, the measuring thermocouple is usually placed parallel to heat source in the distance of several millimetres from the heating wire $R_m = 15–17$ mm, while the reference thermocouple is placed perpendicular to the heat source in the possibly large distance, which in practice means $R_r \geqslant 50$ mm. The time of measurement is limited by the stability of the reference temperature T_r indication during experiments. An error of λ determination increases if the temperature disturbance reaches the reference thermocouple. Maximum measuring time is then dependent on the heat source power, which should be selected according to the initially assumed properties of the examined material: ρ, c, λ. It is assumed [5] that an adequate accuracy in determining thermal conductivity λ is ensured by arithmetic mean value within the range

$$1.5 \leqslant \frac{\Delta T(2t)}{\Delta T(t)} \leqslant 2.4. \tag{11}$$

To check the influence of the above mentioned measurement error elements, an analysis was carried out on the basis of numerical solution of Eq. (1) for cylindrical infinitely long sample with an external radius $R_z = 60$ mm, in which a heating wire with radius $R_d = 0.25$ mm, having density $\rho_d = 11806$ kg/m^3 and specific thermal capacity $c_d = 453.3$ J/kg K was placed. Boundary conditions (2) and (3) were replaced with appropriate ones for finite dimensions of the sample and wire:

$$T(R_z, t) = T_0 = \text{const}, \tag{12}$$

$$-2\ \pi\ R_d \lambda \frac{\partial T}{\partial r}\Big|_{r=R_d} = P_l. \tag{13}$$

Numerical solutions of the initial-boundary value problem (1), (12), (13) and (4) made it possible to determine the thermal field in the sample, which enabled testing the influence of the method parameters upon the accuracy of measurement λ. Since in the calculations the known value $\lambda = 13$ W/m (mK) was assumed, then we could evaluate the ability of the method using Eqs. (10) and (5) to reproduce the assumed value. Fig. 1 presents the effect of the location of the reference thermocouple R_r on thermal conductivity recorded during the numerical experiment. For both investigated cases $R_r = 39$ mm and $R_r = 51$ mm the time interval, when condition (11) is fulfilled, and the mean value λ at this interval were marked. It may be seen clearly that location $R_r = 51$ mm gives exactly the assumed value $\lambda = 13$ W/(mK) at minimum point $\lambda(t)$, while the mean value $\lambda = 13.94$ W/(mK) is higher only by 7%. When the distance is too small $R_r = 39$ mm < 50 mm, the obtained value of the thermal conductivity is by 25% higher than the real one. Fig. 2 shows the influence of the initial temperature difference in the sample presented in Fig. 3. Curves $\lambda(t)$ do not

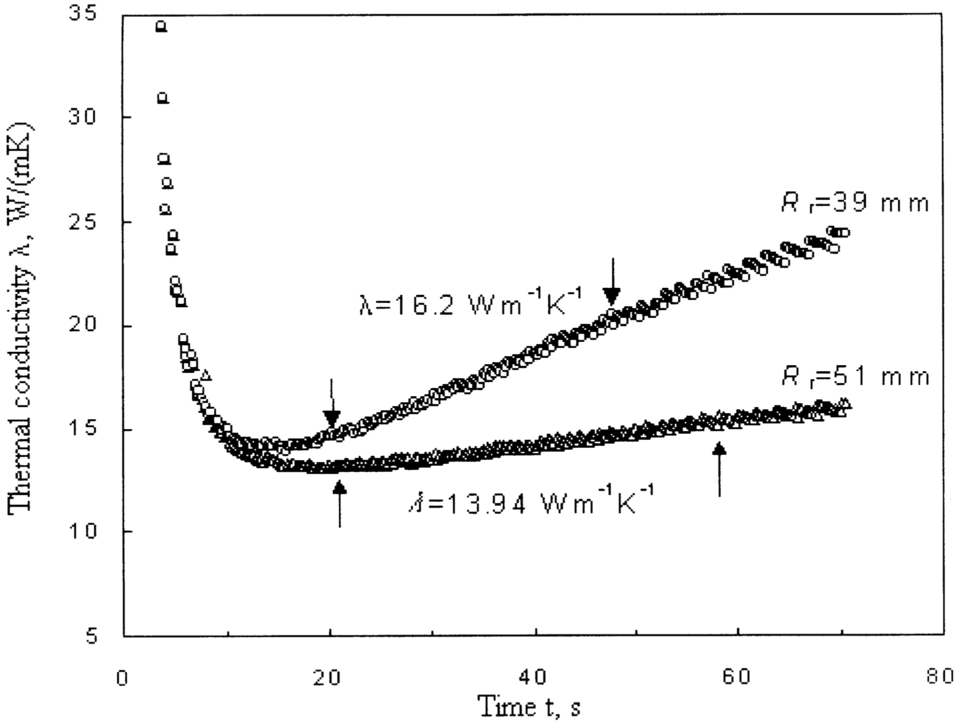

Fig. 1. Calculated thermal conductivity for: $\Delta T_{max} = 0$ °C, $R_m = 17$ mm, $R_z = 60$ mm, $T_o = 200$ °C, $\lambda = 13$ W/(mK), $\rho c = 3.17 \times 10^6$ J/(m^{3}K).

show a minimum as distinct from the case for $\Delta T = 0$. The mean value $\lambda = 12.98$ W (mK) for $R_r = 51$ mm is very close to the assumed one, while the distance $R_r = 39$ mm is too small, as it leads to an increase in λ value. It may be seen clearly that a uniform sample temperature before heating is turned on, produces a curve $\lambda(t)$ with a minimum corresponding to the correct λ value. On the other hand, lack of a minimum point on the function $\lambda(t)$ means initial temperature difference in the sample. In the last case the ratio $\Delta T(2t)/\Delta T(t)$ in Eq. (10) is smaller than unity. Because the exponential-integral function $Ei(x)$ can be determined only for positive and larger than unity values of $\Delta T(2t)/\Delta T(t) > 1$, then the thermal conductivity $\lambda(t)$ can not be calculated by Eq. (5) for very short time t, and the $\lambda(t)$ curve does not have a minimum. The arrows shown in Figs. 1, 2 and 4 stand for the boundaries as determined by irregularities (11).

An increase in the initial temperature difference within the sample lowers the measured λ value (Fig. 4), but even for $\Delta T = 0.2$ °C the thermal conductivity differs from the real value by about 7% that is within the hot wire method experimental error, if the procedure of calculating a mean value at interval determined by irregularities (11) is applied in each case. The conducted analysis did not reveal any significant errors in the bases of the hot wire method, which was suggested in the work [6].

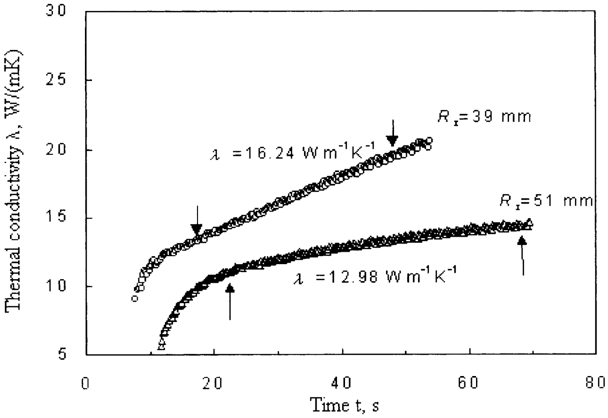

Fig. 2. Calculated thermal conductivity for: $\Delta T_{\max} = 0.1$ °C, $R_m = 17$ mm, $R_z = 60$ mm, $T_o = 200$ °C, $\lambda = 13$ W/(mK), $\rho c = 3.17 \times 10^6$ J/(m^{3}K).

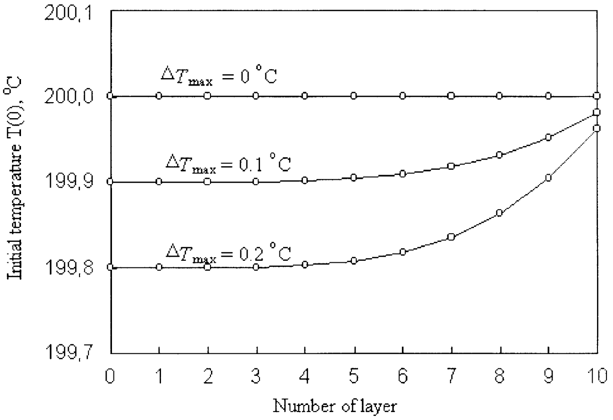

Fig. 3. Analyzed initial temperature fields within the sample divided into 10 layers.

The calculations for thermal capacity within the range $\rho c = 2.4 \times 10^6$–3.4×10^6 J/m^{3}K, thermal conductivity $\lambda = 8$ –15 W/mK and unit power of heat source $P_l = 60$–240 W/m allowed us to determine the maximum measuring time for the sample with external radius $R_z = 60$ mm on the basis of admissible change in the temperature of the reference thermocouple placed in distance $R_r = 51$ mm equal to $\Delta T_r = 0.05$ °C. The obtained results may be described by the following dependence

$$t_{\max} = K\frac{\rho c}{\sqrt{\lambda P_l}}, \qquad (14)$$

where $K = 1.24 \times 10^{-3}$ K$^{1/2}$ m^2.

4. Experimental investigations using the hot wire method

Investigations were carried out for a group of magnesia–carbon products based on pure magnesia clinker having composition by mass: $MgO = 97.22\%$, $Al_2O_3 = 0.05\%$, $SiO_2 = 0.26\%$, $CaO = 2.06\%$, $Fe_2O_3 = 0.22\%$. Into the refractory material in the form of magnesia clinker aggregate obtained by dry moulding of mix carbon was added as: thick-flake graphite, fine-flake graphite or coke dust and resol – phenol-formaldehyde resin. The micrographs of the carbon forms used are presented in Fig. 5. Investigations were conducted for unfired magnesia–carbon products, which were subjected to preliminary thermal treatment in coke powder

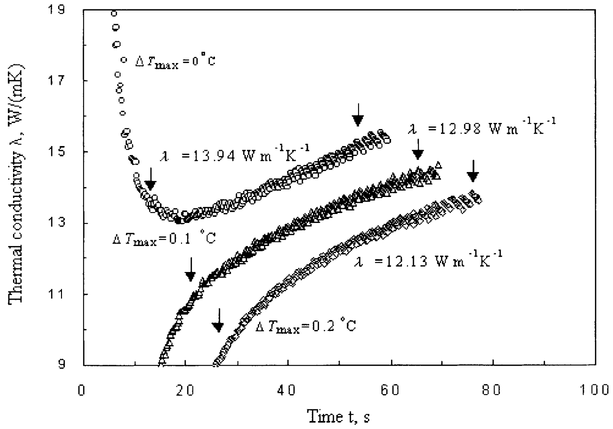

Fig. 4. Influence of initial temperature field on calculated thermal conductivity for: $P_l = 100$ W/m, $\rho c = 3.17 \times 10^6$ J/(m^{3}K), $R_m = 17$ mm, $R_r = 51$ mm, $R_z = 60$ mm, $\lambda = 13$ W/(mK).

layer at 900 °C for 4 h, the rate of reaching the treatment temperature being 3 K/min for each of the samples. Besides, a magnesia product fired at 1680 °C in a tunnel furnace was prepared for research. All the samples had dimensions 230×115×64 mm. Table 1 presents the characteristics of the examined samples for four groups of products: A—containing thick-flake graphite, B—fine-flake graphite, C—coke dust and D—magnesia product with no carbon content. In magnesia–carbon samples open, irregular mutually joined pores were observed. During the heating process a very significant change in open porosity of samples took place, which can be explained mainly by the pyrolysis of the resol-phenol-formaldehyde resin used as a binder for the magnesia and carbon grains. Gases released during the pyrolysis, flowing out of the sample enhance the growing of open pores volume.

Mean values of two measuring series of each sample have been given in Figs. 5–7. Comparison of curves in Figs. 5 and 6 allows us to state that an increase in the amount of the carbon added into magnesia mass does not lead to an unequivocal increase in the thermal conductivity, neither for thick- nor fine-flake graphite. The carbon content in the samples, examined after the preliminary heating at 900 °C, includes not only the graphite or coke from the substrates but also coke formed in consequence of pyrolysis of the resol-phenol-formaldehyde resin used as binding substance. The pyrolysis process leads to uncontrolled development of open and closed porous structure influencing the thermal conductivity of material. Fig. 7 presents the effect of the form of added carbon on λ value in products containing ca 12% mass fraction of carbon after preliminary heating. Coke-containing magnesia–carbon product is

Table 1
Characteristics of the examined samples

No. of sample	Kind of carbon added	Content of carbon subjected to initial heating (% mass)	Open porosity (%)		Apparent density after conductivity measurement (g/cm^3)
			After heating at 900 °C	After conductivity measurement	
AI	Thick-flake graphite	9.1	12.7	13.8	2.87
AII		9.8	11.6	12.9	2.88
AIII		12.0	10.8	11.1	2.90
AIV		15.8	10.7	10.7	2.87
BI	Fine-flake graphite	8.8	12.7	13.9	2.93
BII		10.0	12.7	12.1	2.95
BIII		11.2	11.0	12.6	2.91
BIV		14.0	11.6	12.5	2.86
C	Coke dust	12.3	18.6	Samples scattered	
D	–	–	Unheated	15.1	3.01

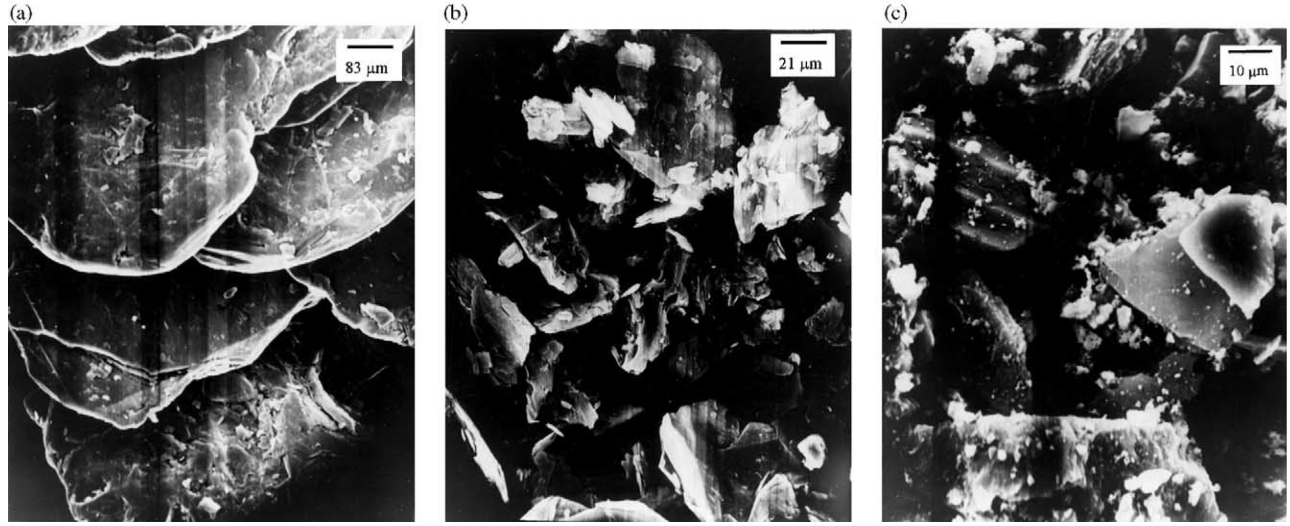

Fig. 5. Micrographs of the carbon forms added to magnesia–carbon products: (a) thick-flake graphite (×120), (b) fine-flake graphite (×480), (c) coke dust (×1000).

characterised by the lowest values of thermal conductivity. It is surprising that the magnesia product with no carbon content (sample D) displays higher thermal conductivity within low temperature range and the addition of graphite increases λ value only for higher temperature. It can be noticed (Fig. 8) that the form of carbon grains influences the temperature at which the thermal conductivity of magnesia–carbon is higher than for magnesia. For thick-flake graphite the thermal conductivity of the carbon containing products is higher than for magnesia already at around 300 °C, while for fine-flake graphite even at 500 °C the thermal conductivity does not exceed that of magnesia. This can be associated with the larger porosity evolution of the fine-flake graphite containing products during the experiments in which larger amount of the binding resins is needed due to higher specific surface. Basically, the investigation results confirm the published values (Fig. 9) of the thermal conductivity characterising magnesia–carbon products [7–9]. The magnesia–carbon products show weaker decrease of the thermal conductivity with increased temperature than the magnesia products [7]. Deeper quantitative comparison of the thermal conductivity values is not possible because the references quote only the amount of the rest carbon, while the form of carbon-grains is not given. It has been found that the total carbon content in the material and the form of the carbonaceous grains do not identify fully the thermal conductivity. Equally important is the amount of the binding substance, because its pyrolysis influences the porous structure of the magnesia–carbon material after thermal treatment.

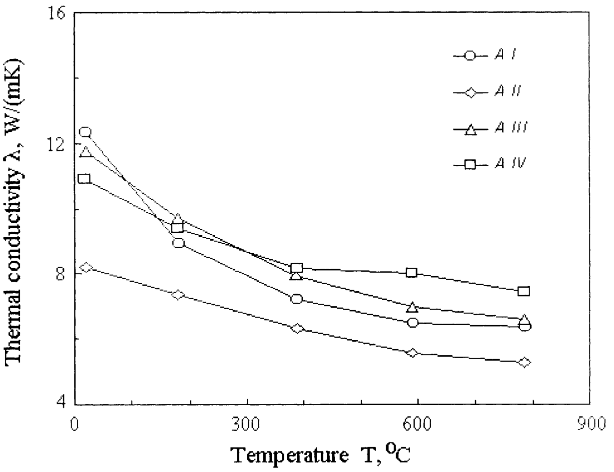

Fig. 6. Influence of thick-flake graphite content on the thermal conductivity of magnesia–carbon material heated initially during 4 h at 900 °C under coke layer protection.

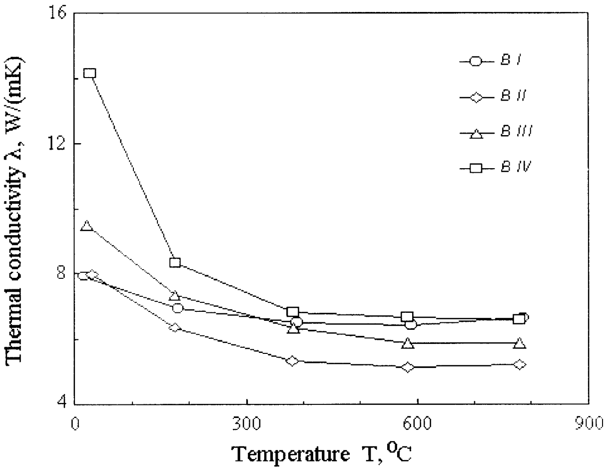

Fig. 7. Influence of fine-flake graphite content on the thermal conductivity of magnesia–carbon material heated initially during 4 h at 900 °C under coke layer protection.

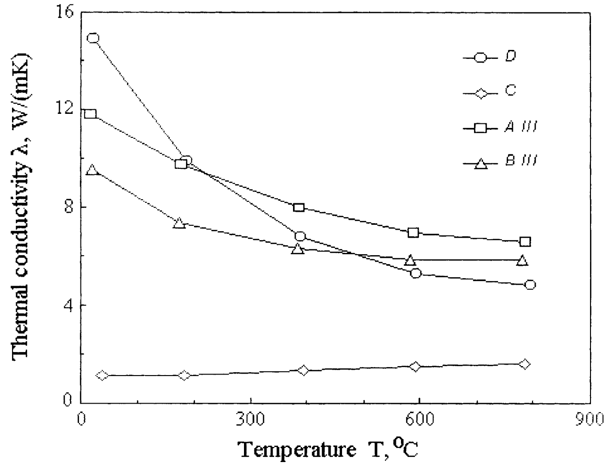

Fig. 8. Thermal conductivity for various carbon forms of 12% carbon mass content in the magnesia–carbon material heated initially during 4 h at 900 °C under coke layer protection.

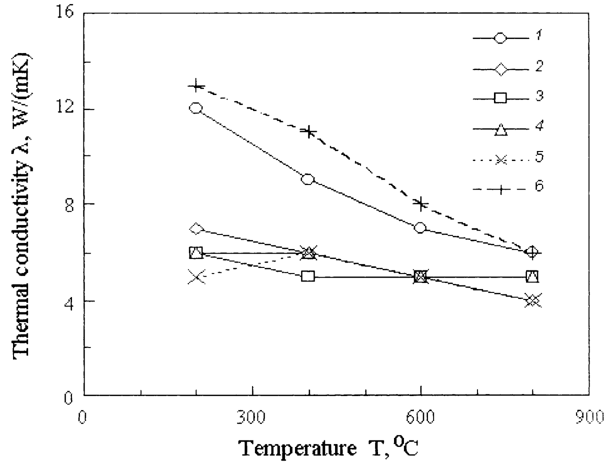

Fig. 9. Thermal conductivity of magnesia–carbon products: 1—burned magnesia, pitch impregnated, 4.8% rest C [7], 2—pitch bounded magnesia, 4.8% rest C [7], 3—burned magnesia–graphite, 7.2% rest C [7], 4—burned magnesia–graphite, 11.7% rest C [7], 5—pitch bounded magnesia, 2.4% rest C [8], 6—burned magnesia–carbon, 10% rest C [9].

5. Conclusions

- The appearance of a minimum on $\lambda(t)$ curve as recorded during measurements proves an effective uniformity of the initial temperature distribution in the sample. Minimum value of $\lambda(t)$ curve is equal to the material's thermal conductivity.
- Maximum measuring time in the hot wire method is dependent on the linear heater's power, thermal capacity of the material and its thermal conductivity as described by Eq. (14).
- The form and amount of graphite added have irregular effect on the thermal conductivity of the examined magnesia–carbon product.
- Thermal conductivity of magnesia–carbon products containing fine coke is much lower than that of products with graphite content.
- Thermal conductivity of magnesia–carbon products containing thick-flake and fine-flake graphite is higher than that of magnesia product only in the case when temperature exceeds 300 °C for thick-flake graphite, and 500 °C for fine-flake graphite.

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