THERMAL CONDUCTIVITY OF DINAS CONTAINING ADDITIVES

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In order to boost the productivity of coke ovens, it is important to increase the thermal conductivity of the pier (separating wall), which is made of dinas. Two approaches are known for solving this problem. In some cases [1, 2] we try to increase the apparent density of the refractories to 1.9 g/cm^3 and more with an open porosity of about 18%; and in others [3-6] we use additives mainly of various metal oxides. It was previously shown [7] that with a reduction of 5-7% in the open porosity of dinas goods made by the Pervouralsk and Krasnogorovsk factories, we should expect a statistical increase in their conductivity of 15-25%. The present paper gives the results of studies of the effect of additives on the thermal conductivity of dinas.

Measurements were made on laboratory specimens of two series made on the basis of production batch from the Krasnogorovsk factory. In the specimens of the first series together with lime—iron slip we incorporated additions of ammonium molybdate, copper sulfate, finely dispersed powdered iron, * and titanium. The specimens were pressed at 80 MPa, and fired in a chamber furnace at 1400°C with a soak of 50 h. We prepared two identical batches, one of which was fired in a carbon filling. The composition and properties of the first batch are shown in Table 1.

The second series was prepared to solve the problem of increasing the strength of freshly prepared articles. At the same time, we checked the possibility of increasing their thermal conductivity, for which, in addition to additives made to strengthen the siliceous green brick, we added, in accordance with recommendations stated in [3-5] various oxides (NiO, CuO, TiO$_2$, Fe$_2$O$_3$). The composition and properties of the second series are shown in Table 2.

The thermal conductivity was measured† by the cylinder method [8]. The equipment error was ± 10%. The results for the temperature relationship with conductivity for the first series are shown in Fig. 1. For convenience, the smoothed-out values for λ are shown in Table 3. The concentration of impurities did not

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* In this case the batch was wetted only with lime slip.
† With the participation of D. B. Glushkova, M. L. Litvin, and T. A. Pozdnyakova.

TABLE 1. Porosity and Density of Dinas Specimens in First Series

Specimen No.	Additive	Amount of additive, %	Properties of specimens fired					
			in air			in carbon filling		
			open porosity, %	apparent density, g/cm³	density, g/cm³	open porosity, %	apparent density, g/cm³	density, g/cm³
1	—	—	19,6	1,88	2,34	—	—	—
2	Mo(NH₄)₃	1	22,9	1,85	2,40	20,3	1,93	2,42
		3	20,6	1,86	2,34	20,5	1,91	2,41
3	CuSO₄	1	24,1	1,80	2,37	21,6	1,89	2,41
		3	22,9	1,83	2,37	24,6	1,78	2,36
4	Fe	1	17,6	1,94	2,35	20,0	1,94	2,42
		3	17,6	1,94	2,35	19,7	1,93	2,40
5	Ti	1	18,6	1,93	2,37	19,4	1,97	2,44
		3	21,9	1,88	2,41	19,1	1,93	2,38
		5	19,6	1,90	2,36	20,5	1,89	2,38

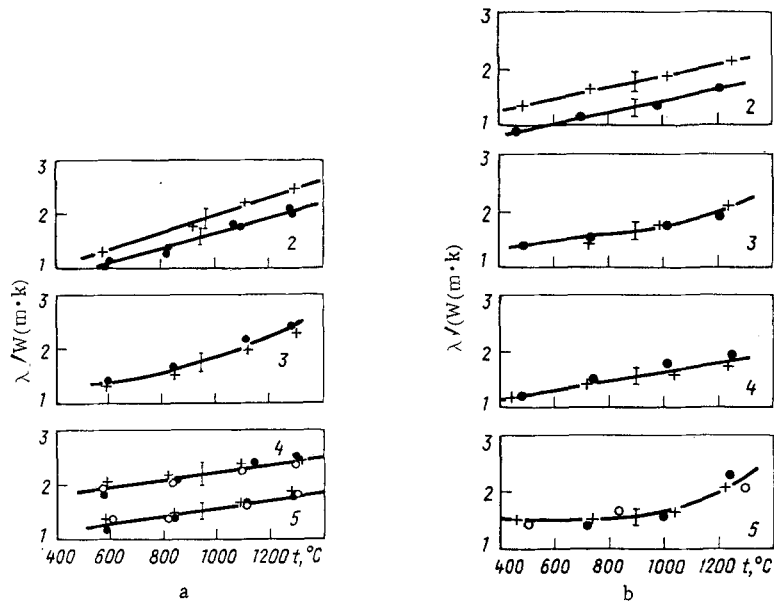* Here and subsequently indicates weight proportions.

Fig. 1. Temperature relationship of thermal conductivity λ of specimens of first series dinas, fired in air (a) and in carbon filling (b): 2-5) numbers of specimens (see Table 1); •) 1% additive; +) 3%; ○) 5%, vertical sections — deviation ± 10%.

affect the conductivity, within the limits of experimental error; the exception were specimens containing $Mo(NH_4)_3$ whose thermal conductivity with a rise in the amount of additive from 1 to 3% increased by 20-40% (depending on the temperature and atmosphere of firing).

The conductivity of the specimens increased linearly with rise in temperature, with the exception of λ for compositions containing $CuSO_4$ and Ti after firing in the reducing conditions. These materials had a sharper temperature dependence, approximating to a square function.

Reduction firing had a significant effect only on the compositions containing Fe impurities. Firing in the carbon reduced the conductivity of these specimens by 35% at 600°C, and by 25% at 1200°C. In the specimens containing $Mo(NH_4)_3$ after reduction firing the conductivity was somewhat reduced (by $\approx$ 15% at high

TABLE 2. Porosity and Density of Second-Series Dinas

No.	Amount of additive, %					Open porosity, %	Density, g/cm³
	CaO	H₃PO₄	TiO₂	NiO	CuO		
1	—	5	—	2	—	18,4	2,39
2	—	5	2	—	—	22,2	2,36
3	—	5	1	—	1	20,2	2,36
4	2,5	5	1	—	1	24,0	2,36
5	2,5	3,5	1	—	1	22,9	2,36
6	2,5	5	—	2	—	22,9	2,36
7	—	5	2	—	—	19,4	2,37
8	—	3,5	—	5	—	17,8	2,40
9	2,5	5	2	—	—	25,4	2,34
10	—	3,5	1	—	1	19,7	2,34
11	—	5	—	—	—	23,1	2,38
12	—	5	—	—	—	22,5	2,40
13	—	3,5	—	—	5	21,8	2,39

* To all specimens, except Nos. 11 and 12, we added 1% each of Fe_2O_3, and except Nos. 2 and 11 and 12 — 1% each MgO; to No. 11 we added metallurgical slag, to specimen No. 12 — slag obtained from the production of ferrochromium (3% each).

TABLE 3. Thermal Conductivity of Dinas Specimens in First Series

Additive	Amount of additive, %	λ, W/(m · K) at temperature, °C					J, W/m
		600	800	1000	1200	1300	
Firing in air							
Without additive*	—	1,50 / 1,95	1,75 / 2,15	2,00 / 2,40	2,30 / 2,70	2,40 / 2,85	1610 / 1930
Mo(NH₄)₃	1	1,10	1,35	1,65	1,90	2,05	1320
	3	1,35	1,65	1,95	2,25	2,55	1540
CuSO₄	1; 3	1,35	1,50	1,80	2,15	2,40	1500
Fe	1; 3	1,95	2,10	2,25	2,35	2,45	1780
Ti	1; 3; 5	1,25	1,40	1,55	1,70	1,75	1240
Firing in carbon filling							
Mo(NH₄)₃	1	1,00	1,20	1,40	1,60	1,75	1140
	3	1,45	1,65	1,85	2,05	2,20	1430
CuSO₄	1; 3	1,45	1,60	1,75	2,00	2,20	1440
Fe	1; 3	1,30	1,45	1,65	1,80	1,90	1330
Ti	1; 3; 5	1,50	1,50	1,65	1,95	2,25	1410

*In numerator — before service; in denominator — after service.

temperatures); in specimens containing Ti, on the other hand, there was an increase of about the same order; the conductivity of specimens with additions of $CuSO_4$ remained practically unchanged.

Compared with specimens without the additives, not one of the compositions studied showed an increase in conductivity, except specimens containing iron and fired in air. Judging from the absolute values of λ, certain additives can significantly alter the conductivity of dinas at moderate temperatures. Thus, adding 1% $Mo(NH_4)_3$ reduces λ of dinas at 600°C to 1-1.1 W/(m · K), and the conductivity of specimens containing iron, fired in air, is almost double the value. Clearly, such changes are not connected with the conductivity of the additive itself, or the compounds formed on its basis, since the mechanical impurities in such small amounts (the volumetric concentration of the metal is 8-10 times less than its weight concentration) do not markedly influence the thermal conductivity of the composite material [9].

It is typical that the less thermally conducting specimens have the higher temperature coefficient of thermal conductivity. Thus, the value b in the equation $\lambda = a + bT$ for specimens with $Mo(NH_4)_3$ is about 2.5 times greater than for specimens containing iron additive. There is a marked change with variation in temperature in the conductivity of specimens containing $CuSO_4$ and Ti (in carbon setting). Since dinas refractories in the piers of coke ovens serve in the range 1100-1400°C, an increase in the temperature coefficient for specimens with a lower λ value should have been equivalent to the thermophysical properties of the materials being studied (see Table 3). However, it must be considered that charging the furnace with cold and moist carbon batch leads to a rapid reduction in the temperature of the walls on the side of the coke chamber (some 2-3 h after loading the temperature is reduced to 600°C). After 3-4 h it increases to 700°C and then in a period of 7-8 h — to 900-950°C, and at the end of the coking period to 1050-1100°C [10]. Thus, the optimum

TABLE 4. Phase Composition and Parameter J for Dinas Specimens

Specimen	Open porosity, %	Volume proportion of phases, %*			J, W/m
		tridymite	cristobalite	quartz	
Without additives	19,6	40—50	40—45	7—10	1610
With addition of 3%, Mo(NH₄)₃ fired in air	20,6	12—18 (15—19)	70—73 (72—76)	9—11 (9—11)	1540
Same, fired in carbon filling	20,5	10—15	35—40	30—33	1430
With addition of 3%, Fe, fired in air	17,6	47—53	32—37	9—11	1680 †
Same fired in carbon filling	19,7	15—20	30—35	30—33	1330
Pervouralsk factory	19,5	43—49 (44—48)	26—30 (31—33)	8—10 (7—9)	1370
Krasnogorovsk factory	20,7	25—29 (28—32)	27—31 (32—34)	23—27 (28—32)	1500
After service	19,0	85—95	not detected	1—3	1930
Same, according to data in [11]	~25	~95	not detected		2000 ± 200 †

*In parenthesis we show the volume of phases in the insoluble residue.
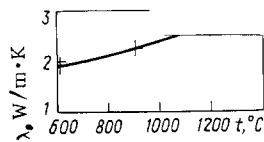†Value corrected for open porosity, %.

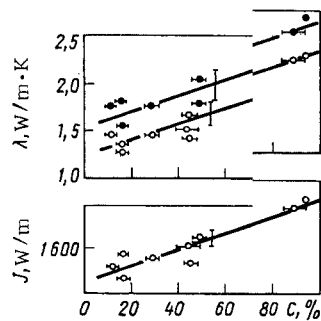Fig. 2.   Fig. 3.

Fig. 2. Thermal conductivity λ of dinas refractories
(eight specimens) after 30 years service in the piers of
coke ovens at Zaporozhe Coke-Chemical Factory. Verti-
cal and horizontal sections — mean-square deviations of
experimental values. Curve drawn for calculated equa-
tion.

Fig. 3. Relationship between the thermal conductivity λ
of dinas and the content of tridymite, C, in it. ○) at
600°C, ●) at 900°C; vertical sections — ±S_{dis}.

heating cycle for working coke ovens can be attained by using dinas refractories having the highest thermal
conductivity in the range 600-1400°C. In the general case we should give preference to material in which the
parameter

$$\tau = \int_{T_1 = 600°C}^{T_2 = 1400°C} \lambda(T)\,dt,$$

proportional to the heat flow is maximum. The computed values of J (see Table 3) show that from this point
of view the best of the materials studied is dinas containing iron additive, fired in air.

Apparently, the differences in the thermal conductivity are due to the modifying effect of the material's
composition on the structure and phase composition. We should mention that the absolute value of the open
porosity cannot completely characterize the structural sensitivity of the specimen to the processes of heat
spread.

The most significant are differences in the structure and phase composition of specimens containing
additions of iron and ammonium molybdate,* whose conductivity values are also very different. The speci-
mens with iron additives fired in air appear dense; the bond is uniform and consists of rather coarse (40-
100 μm) crystals of tridymite and uniformly distributed isometric grains of magnetite; the glassy phase is
completely absent. After firing these specimens in carbon filling as a result of which their conductivity is
significantly reduced, the concentration of tridymite is sharply reduced, and in the bond we detect a large
amount of β-cristobalite and glass. In the specimens containing $Mo(NH_4)_3$ the bond is heterogeneous; certain
parts of it consist of crystals of tridymite (10-50 μm) surrounded by fragments of glass; in other sections
there is a predominance of metacristobalite and quartz.

These data confirm the ideas expressed in [11] on the predominant influence of the amount of tridymite
and its excellent crystallization on the thermal conductivity of dinas. A similar structure contributes,
especially in the absence of glass, to the creation of direct bonds between the crystals and to an improvement
in the conditions of heat transmission. This is supported also by the results of studies of dinas refractories
after prolonged service in coke ovens.

The report [12] gives information on the increase in conductivity of coking dinas during service; special
studies were made in work reported in [11]. Specimens taken from the MMK coke battery after 10 years
service contained in the hot zone (open porosity 24.9%) about 95% tridymite with crystal lengths of 0.8-1.5
mm, and in the coking zone (open porosity 16.6%) 75-80% crystals of tridymite of length 0.17-0.20 mm. The
conductivity of the specimens in the range 250-1200°C was 2.0-2.8 W/m·K.

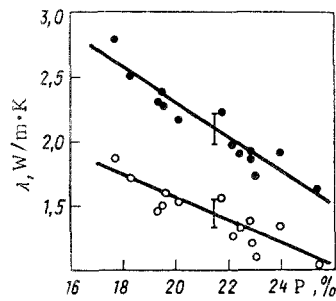* Petrographic studies carried out by N. V. Gul'ko and Z. D. Zhukova.

505

Fig. 4. Relationship between thermal
conductivity λ of specimens of dinas in
the second series and the open porosity
P, $\bigcirc$) at 600°C, $\bullet$) at 1200°C; vertical
sections — $\pm S_{df}$.

Measurements were made of the conductivity of dinas after service over 30 years in coke ovens of the
Zaporozhe Coke-Chemical Factory (ZKZ). From two batteries we selected wall brick at a height of 2-3 m
from the hearth. Specimens were cut so that we could determine the conductivity in the direction of heat
flow through the wall lining. On the side of the coke region in the refractory a certain amount of small grains
of quartz and cristobalite had been preserved. The bond consisted mainly of tridymite with crystal sizes of
up to 0.2 mm, pseudowollastonite and colorless glass (up to 5%). There was no detectable decomposition of
the graphite. The open porosity of the coking zone about 20 mm thick was 12-14%, and apparent density 1.91-
1.96 g/cm^3. On the hot side, the specimens had a uniform structure made of coarse (from 0.2 to 1 mm) tri-
dymite crystals with uniformly distributed sections of brown glass and α-CaSiO$_3$. Quartz and cristobalite
were not detected. The open porosity of the hot zone about 20 mm thick was 19%, the apparent density 1.86
g/cm^3. The properties, structure, and composition of coke and hot zones are close to those described in [11].

The specimens used to determine the conductivity, cut from the coking and hot zones, were characterized
by an open porosity within the range 16.4-20.5%, the apparent density 1.81-1.86 g/cm^3. We measured the
conductivity of eight specimens (four from each battery) and using subsequent statistical processing similar
to that described in [7]. The relationship $\lambda = f(T)$ proved to be curvilinear, and the experimental data ap-
proximated to a parabola of the second order. The best approximation was determined for the minimum value
of the residual dispersion S_{dis} characterizing the spread in experimental points relative to the approximating
curve:

$$S_{dis} = \left[\frac{\sum\limits_{i=1}^{n} (\bar{\lambda}_i - \lambda_i)^2}{n - m - 1} \right]^{1/2},$$

where $\bar{\lambda}_i$ and λ_i are, respectively, the calculated and experimental values of thermal conductivity at tem-
perature T_i, W/m·K; n is the number of measurements, and m is the number of coefficients in the approxi-
mating multiple.

This condition is satisfied by the curve $\lambda = 1.68 + 7.0 \cdot 10^{-7} T^2$, which is illustrated in Fig. 2. That also
shows the averaged values for λ for three samples, grouped close to 600, 900, and 1200°C. The mean-
square deviation of thermal conductivity in each sample does not exceed $\pm 7\%$. This means that within the
limits of experimental error the conductivity values of coke and hot zones coincide, possibly as a result of a
certain compensating action of porosity and phase composition, affecting the thermal properties of dinas in a
contradictory fashion.

Data [11] and results obtained in the present work suggest that it is precisely the structure of the dinas
refractories after service — approximating to a monophase composition from the large directly bonded
crystals — which governs their essentially higher thermal conductivity compared with those produced at the
present time at the Pervouralsk factory and Krasnogorovsk factory [7], and the specimens studied with ad-
ditives. Compared with industrial products with a porosity of about 20% the conductivity of dinas after service
is 40-55% higher. We disagree with the viewpoint expressed in [11] to the effect that the maximum possible
tridymitization of dinas contributing to the growth of tridymite crystals is the most effective factor contributing
to an increase in the thermal conductivity. To a less degree this contributes to a reduction in porosity [7].

506

The combination of the above data provides evidence that the conductivity of dinas should correlate with its phase composition. To establish this correlation, we determined the concentration of crystalline phases in certain laboratory specimens with additives, for dinas refractories after service, and specimens of refractories from the Pervouralsk and Krasnogorovsk factories (Table 4) using the x-ray phase method. * The conductivity of these specimens† correlates linearly with the content of tridymite (Fig. 3). For the parameter J (see Table 4) the regression equation takes the form:

$$J = 1.3 \cdot 10^3 + 7.0 \cdot C,$$

where C is the volume proportion of tridymite, %. The correlation coefficient is

$$r = 7.0 \left[\frac{n \sum_{i=1}^{n} C_i^2 - \left(\sum_{i=1}^{n} C_i \right)^2}{n \sum_{i=1}^{n} J_i^2 - \left(\sum_{i=1}^{n} J_i \right)^2} - \right]^{1/2}$$

which is close to unity (r = 0.93) which indicates the presence of a strong and practically linear relationship between J and C for the compositions studied.

The specimens of the second series in which, together with the additions of the oxides CuO, TiO_2, NiO, Fe_2O_3, we added strengthening additives to the green brick, showed a marked difference in porosity (from 17.8 to 25.4%). Between the conductivity and the porosity there exists practically a functional relationship, shown in Fig. 4, for 600 and 1200°C. The equation for the straight lines for this function takes the form

$$\lambda_{600°C} = 3.34 - 0.089 \ P,$$
$$\lambda_{1200°C} = 5.00 - 0.135 \ P.$$

The correlation coefficients found by the least-squares method equal: $r_{600} = 0.89$, $r_{1200} = 0.95$.

As for the dinas made by industrial methods [7] with a rise in temperature, the relationship $\lambda = f(P)$ for specimens of the second series is reinforced ($r_{1200} > r_{600}$, and in equation $\lambda = \alpha + \beta P$ the coefficient $\beta_{1200} > \beta_{600}°C$). For all temperatures the function for conductivity and porosity in laboratory specimens made on the basis of production batches of the Krasnogorovsk factory proved to be stronger than for industrial products [7]: $\beta_{lab} / \beta_{fact} \approx 1.60$, and the absolute values of λ with equal P values is somewhat higher (when P = 20%, by about 10%).

Apparently, for specimens of the second series the open porosity is the most statistically significant parameter, determining the change in thermal conductivity. The effect of the additives on thermal conductivity was not established by the authors.

LITERATURE CITED

1. Patent No. 1012363 (England).
2. A. Patto, Refractory, 3, No. 3, 135-144 (1967).
3. Patent No. 3024122, Patent Re. 25572 (USA).
4. Patent No. 1300051 (Federal Republic of Germany).
5. Patent No. 3216838 (USA).
6. Patent No. 55693 (Polish People's Republic).
7. I. I. Vishnevskii et al., Ogneupory, No. 5, 8-12 (1980).
8. I. I. Vishnevskii et al., Ogneupory, No. 5, 227-231 (1964).
9. G. N. Dul'nev et al., Thermal Conductivity of Mixtures and Composition Materials [in Russian], Leningrad (1974).
10. I. S. Kainarskii, et al., Refractories for Coke Ovens [in Russian], Moscow (1966).
11. K. K. Strelov et al., Ogneupory, No. 2, 48-52 (1973).
12. I. S. Kainarskii, Dinas [in Russian], Moscow (1961).

*Carried out by S. V. Lysak.
† We also studied data for $\lambda = f(T)$ from [7] and [11].