STUDY OF THERMAL SHOCK RESISTANCE OF

FIRED AND UNFIRED ZIRCONIA REFRACTORIES

G. A. Gogotsi, A. G. Gashchenko,
A. G. Karaulov, and I. N. Rudyak

The poor thermal shock resistance of products from zirconium dioxide limits their use in high temperature equipment having sudden variations in temperature [1]. The life of the linings of such installations can be increased by using unfired bodies, which in contrast to fired refractories possess greater resistance to thermal shock.

The literature contains almost no references in which a comparative assessment has been made of the thermal shock resistance of fired and unfired products.

It is not possible to evaluate the thermal shock resistance of rammed bodies and to compare the same factors in fired refractories with specimens by the heat exchange method, since after the first heat cycle the unfired specimens prove to be fired at a particular temperature, and will behave as fired refractories. Determination of the destructive drop in temperature on round specimens is the most suitable method for evaluating the thermal shock resistance of unfired rammed bodies [2], comparing it with the thermal shock resistance of fired refractories, and selecting the most spalling-resistant compositions.

An investigation was made on annular specimens with external diameter 50 and 75, and internal diameter 25 and thickness 12.5 mm. The specimens were prepared from technical zirconia containing (% by weight): 99.0% $ZrO_2 + HfO_2$, 0.17% SiO_2, 0.05% Al_2O_3, 0.11% TiO_2, 0.04% Fe_2O_3, <0.03% CaO and <0.03% MgO.

As the stabilizing additives we used Belgorod chalk containing 54.24% CaO with 42.22% loss on ignition. The stabilizing additive was incorporated on the basis of 6% and 4% by weight. The material was pelletized. The zirconia was stabilized at 1750°C with 18-h soaking. The chemical and phase compositions, and porosity of the pellets after firing are given in Table 1.

The pellets after firing were crushed and screened into fractions 2-1, 1-0.5, and <0.5 mm. Some of the material (<0.5 mm) was further ground in a vibromill to obtain the fine fractions, <0.09 mm. The powder was molded into bodies without additions, and with additions of monoclinic zirconium dioxide preground to particle sizes of mainly less than 0.03 mm.

The body compositions were selected bearing in mind the concentrations in them of 20-40% monoclinic phase which yields products with the maximum spalling resistance [3]. The grain-size distribution of the

TABLE 1. Characteristics of Pellets after Firing

Pellets*	Chemical composition							Phase composition		Open porosity, %	Apparent density, g/cm³
	$ZrO_2 + HfO_2$	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	R_2O	monoclinic	cubic		
4	94,24	0,52	0,25	0,13	4,3	0,33	0,23	15	85	5,1	5,44
6	92,68	0,56	0,17	0,13	6,2	0,27	0,29	—	100	13,5	4,90

*Notation corresponds to the content of stablizing additive, % by weight.

TABLE 2. Characteristics of Specimens of Unfired Bodies and Fired Specimens of Zirconia

Composition	Pellet	Bond	ZrO₂ content, %*		Heat process temperature °C	Open porosity, %	apparent density, g/cm³	Compressive strength, kg/cm²	Phase composition, %*	
			stabilized fraction <0.09 mm	apparent density, g/cm³					monoclinic phase	cubic phase
Kh-11	6	S. s. b.	10	30	120	25,6	4,04	172	30	70
Kh-1	6	H₃PO₄	10	30	300	17,3	4,43	653	30	70
Kh-15	4	S. s. b.	20	20	120	22,7	4,26	95	35	65
Kh-8	4	H₃PO₄	40	—	300	17,4	4,44	480	15	85
R-47	6	—	10	30	1750	17,3	4,43	306	24	76
G	6	—	40	—	1750	23,2	4,30	4200	—	100

*In addition, the specimens contained 25% stabilized ZrO_2 fractions 2-1 mm, 25% 1-0.5 mm, and 10% 0.5-0.09 mm.

bodies was also selected bearing in mind the production of spalling-resistant specimens [4]. The bodies were prepared with sulfite lye which was added in amounts of 1% on the dry weight, and with orthophosphoric acid (5% by weight of an 86% H_3PO_4) ensuring the formation of phosphate bond during heating of the body [5]. The specimens were pressed at 1000 kg/cm². After pressing the specimens with sulfite lye we subjected them to heat processing at 120°C, and for those with the orthosphoric acid at 300°C. The grain-size distribution of the bodies and the properties of the specimens after heating are given in Table 2.

Some of the specimens of composition Kh-11 were fired at 1750°C with a 6 h soak (No. R-47 in Table 2). Simultaneously we prepared for comparison specimens of completely stabilized ZrO_2 (composition G). The physical properties of the specimens are given in Table 3.

Studies of the regularity of the breakdown of the specimens with variable cycles of thermal loading were made up to 1200°C on the TS-4 equipment, and up to 2100°C on the TS-5 equipment designed in the Institute of Strength Problems.

The heaters in the TS-4 units consisted of silit rods of diameter 16 and length 320 mm, and in the TS-5 equipment a graphite rod. Heating on the TS-5 unit was done in inert gas, and therefore the equipment was fitted with a protective metal chamber. Before filling with inert gas the air was pumped out of the chamber with a VN-1MG pump to a residual pressure of $1 \cdot 10^{-2}$ mm Hg.

The TS-4 and TS-5 units have automatic control systems for heating the specimens ensuring testing at low (1 deg/min) and high (600 deg/min) rates of temperature rise. During testing we maintained a strict heating cycle (temperature variations ±2°C).

The method of study was based on the following assumptions*: precise measurements of temperature across the thickness of the specimens and determination of temperature fields during heating; precise determination of the moment of development of cracking in the period of thermal stress, with simultaneous registration of the temperature variation across the thickness of the specimen and distribution of the temperature in it.

---

*G. A. Gogotsi, Author's Abstract of Dissertation [in Russian], Kiev, IMP AN UkrSSR (1966).

TABLE 3. Properties of Specimens

Composition	σ_{bend}, kg/cm³ *			$E \cdot 10^{-5}$, kg/cm³			$\alpha \cdot 10^6$, deg⁻¹		
	temperature, °C								
	20	300	600	20	300	600	20	300	600
R-47	103	100	90	0,85	0,65	0,6	4,1	4,1	16,3
G	238	223	200	3,3	3,0	2,9	14,0	14	15
Kh-1	69	92	103	2,45	2,78	2,54	3,0	3	6
Kh-8	64	91,5	105	2,35	2,79	1,16	3,3	3,3	5,0
Kh-11	23	Not determined	4	0,57	Not determined	0,1	3,0	Not determined	
Kh-15	19,5		5	0,59		0,15	3,0	" "	

*The strength limits obtained by testing using the three point bending method.
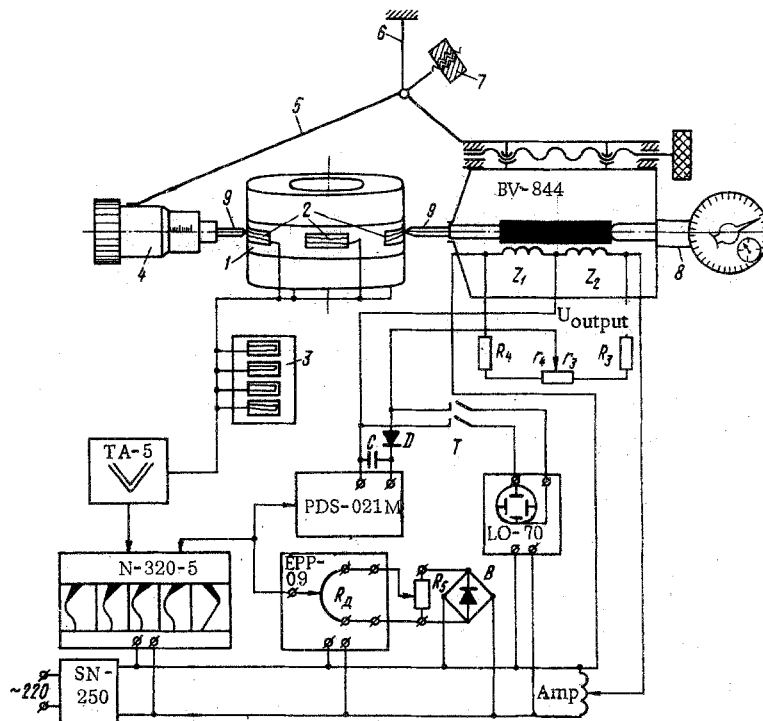
56

Fig. 1. Circuit for tensometric measurements and measure-
ments of the radial displacement of the thermally loaded
specimens. 1) Specimen; 2) working tensoresistors; 3)
compensation tensoresistors; 4) micrometric mechanism;
5) load bearing fork; 6) flexible suspension; 7) counter-
weight; 8) clock type indicator; 9) quartz probe; LO-70)
balancing oscillograph; T) tumbler; SN-250) voltage stabi-
lizer; Amp) controllable autotransformer; B, D) rectifiers;
R_5) voltage divider.

The temperatures were measured with thermocouples: up to 300°C with copper/constantan which were
fixed into the specimen with a special solder; from 500-1200°C with platinum/platinorhodium, secured with
silver in an aperture in the specimen; above 1200° with tungsten/rhenium VR-5/20 fitted with a lubricant
made from finely dispersed powdered ZrO_2 slaked with orthophosphoric acid having a density of 1.5.

The thermocouples were placed on the specimen in the form of isotherms for excluding local distor-
tions in the temperature field. The specimens were assembled in a column about 200 mm high which cor-
responded to 3-4 diameters of the specimen.

The specimens were fitted in the central part of the column which excluded end effects, and created
a uniform temperature field from top to bottom in the specimens.

To determine the moment of failure and also to obtain information about the destruction processes we
made tensometric measurements of surface tangential deformations and measurements of the radial dis-
placements of the surfaces of the specimens with the inductive sensor (Fig. 1).

The tensometric measurements of the specimens were done with the tensoresistors of the type 2PKB
with a base of 10 mm, the resistance being about 100 Ω and the nominal tensometric sensitivity being 2.21.
The signal from the tensoresistors was amplified with the tensometric TA-5 and recorded on the rapid-
working milliammeter N-320-5, on one of whose channels we simultaneously recorded the signal propor-
tional to the temperature on the internal surface of the specimen. Considering the sensitivity of the tensor
resistors to the change in temperature, the heat loading cycle was selected so that the external surface was
not heated, and in the case of its being heated the thermal error of the working tensor resistors was com-
pensated by the compensation tensoresistors secured in the axial direction. The error of the measurement
for the deformation with this scheme of tensometric measurement (see Fig. 1) did not exceed ±5%.

Registration of the radial displacement of the external surface of the specimens was done with a
BV-844 inductive sensor whose error was ±1.5%. The windings Z_1 and Z_2 of the sensor (see Fig. 1) were
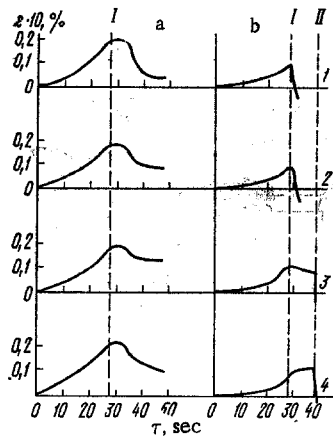
57

Fig. 2   Fig. 3

Fig. 2. Diagrams for deformations of specimens during thermal loading. a) Unfired; b) fired; I) moment of crack formation; II) moment of crack development over entire thickness of the specimen: 1-4) number of sensors.
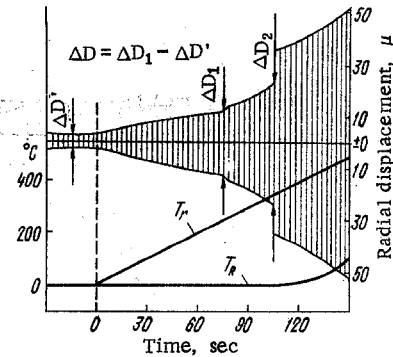
Fig. 3. Oscillogram of the recording by the inductive sensor of the radial displacement of the fired specimens during thermal loading: T_r, T_R, are the temperatures of the internal and external surfaces of the specimen: $\Delta D'$) signal of initial inbalance; ΔD_1) readings of sensor at the moment of crack formation; ΔD_2) same at the moment of crack development over the entire thickness of the wall of the specimen: ΔD) elastic deformation preceding the formation of cracks.

switched into a bridge circuit with resistances R_3 and R_4 supplied from the stabilized source of alternating voltage of 100 V. The balancing of the bridge was done with the alternating resistances r_3 and r_4. The signal taken from the bridge was delivered to the double coordinate potentiometer PDS-021M to which was also transmitted a signal proportional to the temperature of the internal surface of the specimen. To obtain a synchronized signal of the temperatures the internal surfaces on the specimen, the potentiometer ÉPP-09 of the regulator PRT 1 was fitted with an additional potentiometer R_D.

The graduations of the inductive sensor and also visual observation of the radial displacement were made with the clock type inductor with a scale division of 0.001 mm installed in series with the core of the sensor.

The sensor was placed on one side of the rigid fork, on the other side of which we fitted a micrometric mechanism. The sensor and the mechanism had quartz probes, the distance between which, depending on the dimensions of the specimens, was determined before the experiment using the micrometric screw. The fork was suspended on a flexible thread and balanced with a counterweight. This suspension was necessary for free displacement of the fork as a function of the displacement of the package of specimens during their thermal expansion.

The results of determining the variations in temperature causing the development of the first crack at temperatures on the external surface of 20-100°, are given in Table 4. The big variations in the temperature were recorded in the fired specimens. It is noted that the drop in temperature before the development of the first cracks increases with an increase in the heating rate. In the temperature region above 1200°C this drop in temperature was substantially greater than in the region of the low temperatures, and reached about 700°C for the compositions R-47, and 302°C for the composition G. In the high-temperature region some of the stresses are relaxed as a result of the development of plastic deformations. Therefore, with an increase in the temperature such refractories become less sensitive to thermal shock.

For the unfired specimens in contrast to the fired the development of the first cracks during thermal loading is observed with less pronounced drops in temperature. This agrees well with data obtained from the well known criterion for thermal shock resistance (see Table 4)

$$R = \frac{\sigma_t(1 - \mu)}{E\alpha},$$

TABLE 4. Results of Determining the Thermal Shock Resistance of Specimens

Composition	Rate of temperature rise θ, deg/min	Destructive drop in temperature ΔT, °C	ε_{therm}, % *	ε_{tech}, % *			R, 1/deg			R''', cm²/kg		
				temperature, °C								
				20	300	600	20	300	600	20	300	600
R-47	200	591	—	0,125	0,154	0,150	167	205	200	8,5	6,5	7,4
G	200	223	—	0,072	0,074	0,110	51	19,6	49,9	5,8	5,6	7,2
Kh-1	200	166	0,029	0,028	0,34	0,53	94,0	111	67	52	33	24
	600	237	0,030	0,028	0,34	0,53	94,0	111	67	52	33	24
Kh-8	200	143	0,023	0,024	0,33	0,92	87,5	110	182	59	33,4	11,6
	600	225	0,020	0,024	0,33	0,92	87,5	110	182	59	33,4	11,6
Kh-11	200	203	—	0,046	—	0,4	135,0	Not determined		108	—	625
	600	225	—	0,046	—	0,4	135,0	"	"	108	—	625
Kh-15	200	203	—	0,033	—	0,33	110	"	"	155	—	600
	600	230	—	0,033	—	0,33	110	"	"	155	—	600

* ε_{therm} and ε_{tech} are the limiting deformations obtained at the moment of destruction of the specimen during testing for thermal shock resistance and strength respectively.

where R is the criterion of thermal shock resistance, determining the resistance to crack development during thermal loading [2], σ_t is the strength, E is the elasticity modulus, α is the coefficient of thermal expansion, and μ is the Poisson ratio.

However in evaluating the compositions investigated from the criterion $R''' = E/[\sigma_t^2(1-\mu)]$, characterizing the resistance of the material to the spread of cracking we observe no correspondence between the values R''' and ΔT. The resistance of the ramming bodies proved to be much greater than that of the fired bodies (see Table 4). This possibly explains the well-known fact of the greater resistance of linings made from ramming bodies in equipment with sudden variations in temperature. In connection with this, it is of interest to note the data on the maximum deformations at the moment of failure of the specimens given in Table 4 both for cases of mechanical loading and for thermal loading, the values of which prove to be close for each of the refractory materials being tested.

The maximum deformation prior to failure is shown by compositions which exhibit the greatest resistance to the spread of cracking: the unfired bodies based on sulfite lye, and then those based on orthophosphoric acid. The minimal deformation prior to failure is shown by fired specimens of composition G which actually are characterized by the least thermal shock resistance during service.

We should also note the different nature of the failure in the fired and unfired specimens which is seen from the curves for tangential deformation (Fig. 2) determined by the tensosensors (four tensosensors were secured simultaneously on each specimen). The fired specimens had a more pronounced drop in deformation than the unfired. It can be assumed that in the unfired specimens there is a process of gradual movement and development of the destructive cracks; at the same time in the fired specimens destruction occurs irregularly.

From the curve in Fig. 2b we can also conclude something about the nature of the distribution of the cracks in the fired specimens. The development of the cracks between the sensors 1 and 2 causes a sharp reduction in the deformation recorded by the sensors, and a reduction in the rate of growth of the deformation recorded by sensors 3 and 4, more remote from the site of crack development.

During the development of radial cracks across the entire thickness of the wall of the specimens sensors 3 and 4 also fixed a sudden drop in deformation. With the inductive sensors it was more difficult to determine the moment of development of the cracks in the material of this type (Fig. 3).

CONCLUSIONS

Comparative studies were made of fired and unfired refractories based on zirconium dioxide. The fired refractories are more resistant to cracking. However, the unfired materials possess a higher resistance to the development of cracking which is noted during the registration of surface deformations in the process of destruction of the specimen; and this is confirmed by analytical criterial evaluation.

The determination of the destructive drop in temperatures before the development of the first crack in specimens based on granular bodies should not be considered as a reliable evaluation of the thermal shock resistance of the refractories.

A new method was developed for observing the nature of the failure in specimens during thermal loading.

LITERATURE CITED

1. P. M. Chaikin, Élektrotermiya, No. 77, 70-71 (1968).
2. G. A. Gogotsi et al., Ogneupory, No. 11, 54-57 (1968).
3. A. G. Karanlov et al., Neorgan. Materialy, No. 6, 1101-1104 (1967).
4. A. A. Grebenyuk et al., Avt. Svid. No. 285579, Byull. Izobr. i Tov. Znakov, No. 33, 185 (1970).
5. A. A. Grebenyuk et al., Avt. Svid. No. 210008, Byull. Izobr. i Tov. Znakov, No. 5, 175 (1968).