PERICLASE-ZIRCON PACKING COMPONENTS FOR GLASS-MELTING FURNACE REGENERATORS

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The company has developed the technology and production of periclase-zircon components for glass-melting furnace regenerators. Tests have shown that they have substantial advantages over analogous items made in Russia. The distinctive features of the new refractories are high mechanical strength, together with chemical and erosion resistance to corrosive alkaline components. Physicochemical and thermophysical tests have shown that the items have good performance when used in glass-industry furnace regenerators.

Glass-melting furnaces are operated in runs lasting more than eight years in the production of the main types of industrial glasses, which has required the use for lining the regenerators and particularly packing them with refractory materials that provide for successful operation throughout the run without replacement, or in the extreme case of replacement in hot repairs of individual parts of the refractory lining subject to conditions of ongoing temperature change in the gas (every 20 – 30 min) in the upper part of the regenerator from 1550 – 1600°C (hot side) to 1100 – 1300°C (cold side), and in the lower part from 400 – 500°C to 650 – 750°C, with high concentrations in the flue gases of dusty components of the charge and corrosive gases. In the middle (60 – 80% of the height) the damage to the refractories in the main is associated with the interaction of sulfur trioxide with periclase in the upper parts of that zone and with condensation of corrosive volatile components, mainly alkali-metal sulfates, in the middle and lower parts of that zone at 800 – 900°C. For these parts of the packing, it is best to use periclase-zircon refractories, which on heating show reaction of the zircon with the periclase with the formation of zirconium dioxide and forsterite, which form a protective film around the grains of periclase and prevent damage to them [1].

The company has developed a technology for making highly refractory periclase-zircon components, which have high density, high mechanical strength, and good alkali resistance.

Table 1 gives the physicochemical characteristics of these periclase-zircon components made by the company.

Petrography shows that these components have good density and structural features, with uniform distributions for the components (Fig. 1).

[1] Borovichi Refractories Company, Russia.

Physicochemical changes occur in the material on high-temperature heating, and the reactions give rise to highly refractory phases such as forsterite $2MgO \cdot SiO_2$ (t_{mp} = 1890°C) and zirconium dioxide ZrO_2 (t_{mp} = 2715°C). The forsterite-zircon bonding agent produces a dense structure and strong adhesion in the periclase matrix.

Creep determinations indicate the technical working life of the periclase-zircon refractories made by the company as a high-temperature material for regenerative chambers in glass industry furnaces. The refractory deformation is dependent not only on the load and temperature but also on the service duration. Creep measurements enable one to calculate the behavior under load at high temperatures.

ISO 3187–89 deals with creep determination under compression. The tests were performed in a vertical tubular electric oven with a loading device. A specimen was a cylinder of diameter and height 50 ± 1 mm with an axial hole of diameter 12 ± 1 mm, and it was loaded before the start of heating with a calculated load of 0.2 ± 0.003 MPa, with the heating performed at 5°C/min and the specimen kept at 500°C for 50 h. The following results were obtained with periclase-zircon specimens:

Deformation in % during times in h of:	
15	1.80
25	2.27
50	3.16
Creep rate in %/h in the following time interval in h:	
15 – 25	0.046
25 – 50	0.036

The low creep rates of these PTs-1 plagioclase-zircon components is due to the formation of a dense structure during high-temperature heating, which is highly refractory

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TABLE 1. Physicochemical Parameters of PTs-1 Periclase-Zircon Components Made by the Bakor Company*

Parameters	PTs-1 (Bakor)		Analogous Russian products [2]		Analogous imported product
	of simple shape	of complicated shape	of simple shape	of complicated shape	
Mass fraction, %:					
MgO	71.5		80.8	82.6	74.0
ZrO_2	16.4		10.7	10.3	16.0
SiO_2	8.7		5.93	5.02	8.8
Fe_2O_3	0.93		0.6	0.59	0.4
CaO	1.07		–	–	–
Open porosity, %	9.8	10.8	16.4	13.0	12.0
Apparent density, %	3.34	3.32	–	–	3.22
Strength in MPa:					
in compression	117.5	103.6	73.2	90.0	110
in bending at 20°C	18.7	17.8	–	–	–
in bending at 1300°C	12.1	14.0	–	–	–
Temperature start of deformation under a load of 0.2 MPa, °C	1650	1650	1650	Not determined	1670
Additional linear shrinkage (–) or growth (+) at 1650°C, %	–0.5	–0.5	–	–	+1.8 (1400°C)
Thermal conductivity (1000°C on hot side), W/(m·K)	3.84	–	–	–	2.7

* The parameters of analogous Russian and imported components are given for comparison.

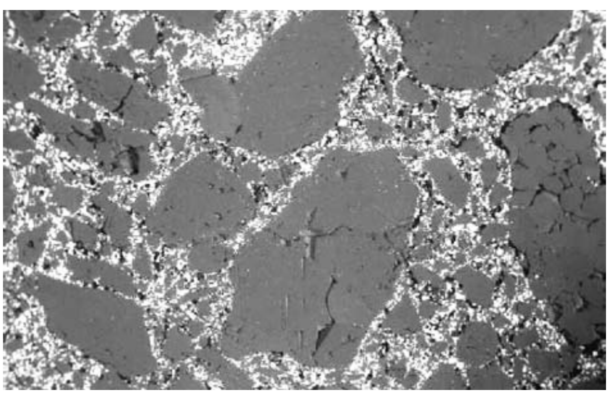

Fig. 1. Part of structure of periclase-zircon component produced by Bakor. The gray corresponds to periclase and the white to the zirco-

TABLE 2. Dilatometric Results on PTs-1 Periclase-Zircon Components Made by Bakor

Temperature, °C	$dL/L_0 \cdot 10^{-3}$	α, 10^{-6}/°C
1000	12.0	12.6
1200	15.1	12.8
1400	18.1	13.2

and highly viscous at the service temperature of the forsterite-zircon binder. In combination with the use of high-grade periclase filler, it provides successful operation for prolonged periods under mechanical and thermal stress.

To produce stability in the lining, the periclase-zircon components should have a low temperature coefficient of linear expansion α. Table 2 gives dilatometric results on PTs-1 specimens.

Prolonged service at high temperatures for refractories produces changes in phase composition, recrystallization, and additional sintering. These reduce or increase the volume (p. 29 of [3]). Our periclase-zircon components show a volume reduction of not more than 0.7% at 1650°C. The constant volume at high temperatures and the high mechanical strength provide reliable service in glass-furnace regenerators.

During operation in a regenerator, the parts are subject to vigorous attack by corrosive components present in the flue gases. This produces a vitrified layer up to 10 mm thick. It consists of corrosion products enriched in alkalis (up to 22%) and alkaline earths (up to 15%), and these components include newly formed phases of various alkali aluminosilicates, in particular albite, nepheline, and nosean [1].

Forsterite-zircon bonding layers are formed around the periclase grains, which have high corrosion resistance to attack by alkali components and corrosive dust components from the charge.

Alkali resistance. To test components for alkali resistance, we prepared specimens of dimensions 150 × 25 × 25 mm. The rods were fired in a mixture consisting of coke powder and potassium carbonate at 1100°C, hold time 2 h. The resistance to alkali attack was evaluated from the changes in mass and volume (Table 3).

Energy-dispersive electron microscopy gave maps of the major components after the tests for alkali resistance (Fig. 2). A periclase-zircon component on test for alkali resistance becomes impregnated with potassium carbonate, which opens up the structure somewhat. It is not found that the alkali components attack the periclase matrix and the forsterite-zircon binder.

TABLE 3. Alkali Resistance of PTs-1 Periclase-Zircon Components Made by Bakor Company

Specimen number	Open porosity*[1], %	Apparent density*[1], g/cm^3	Change, %, in	
			mass	volume
1	10.2/10.9	3.36/3.31	–0.4	–1.0
2	11.0/12.2	3.33/3.28	–0.5	–1.2

*[1] The first item is before firing and the second after it.

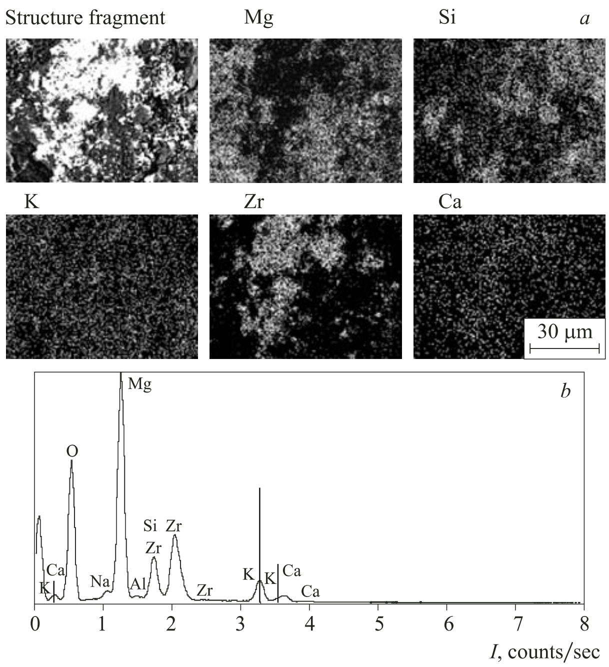

Fig. 2. Energy-dispersive electron microscopy of periclase-zircon specimen after test for alkali resistance: *a*) part of structure, distributions of basic elements; *b*) spectrum with element peak identification.

Glass resistance. This was examined by the crucible method by the use of container brown glass made by the Center-Glass-Gas Company. Composition of the glass in wt.%: Al_2O_3 1.19, SiO_2 81.0, Fe_2O_3 0.69, CaO 10.2, Na_2O 4.21, K_2O 0.77, TiO_2 0.075.

Glass powder in the fractions 0.5 – 0 mm was used to prepare disks of diameter 12 mm and height 15 mm. They were placed in previously fired periclase-zircon crucible cubes with edge 50 mm and hole of diameter 12 mm. Figure 3 shows a crucible after test. The attack by the glass liquid produces slight corrosion of the periclase grains and impregnation of the specimen by the glass liquid.

The degree of impregnation can be estimated from the relative percentage content of SiO_2 in relation to depth in the refractory. Spectral analysis of the upper zone (at the base of the hole), the middle, and lower zone showed the SiO_2 contents decreasing from the upper to the lower zones, in %: 16.96 → 10.20 → 8.34.

These periclase-zircon PTs-1 components thus have high resistance to attack by a glass liquid.

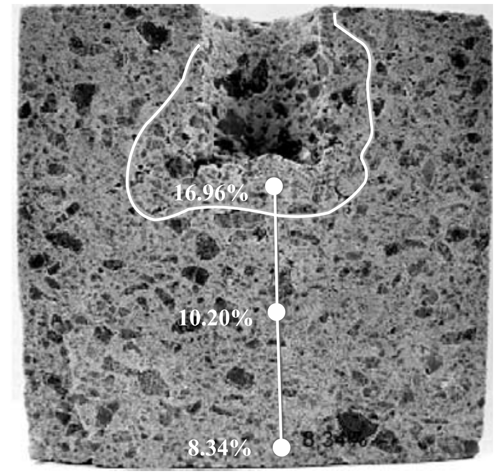

Fig. 3. Periclase-zircon crucible (in section) after test for glass resistance with impregnation boundary shown.

The porosity has a large effect on the dissolution of refractories. With porosity 20 ± 8%, the corrosion was much more influenced by the characteristics of the pores such as the structure and size than it was by the open porosity (pp. 145 and 146 of [4]).

Petrography showed that the pores in the binder are small, with diameters up to 20 μm, isolated, and of closed type. Mercury porometric analysis was used to estimate the size distribution of the pores, and the results are as follows:

Total porosity, % 11.07
Apparent density, g/cm^3 . . . . 3.31
Mean pore diameter, μm 12.75
% of pores by sizes, μm:
< 5 . . . . 10.03
5 – 20. . . . . 66.12
> 20 . . . . 23.19

The high density of the PTs-1 specimens provides for only slight infiltration of alkali components on use in regenerative glass industry furnaces, which greatly increases the working life of the liner under conditions of attack by corrosive volatile components.

CONCLUSIONS

The Borovichi Refractories Company has developed periclase-zircon components of grade PTs-1 for lining glass-industry furnace regenerators. The components have good physicochemical characteristics together with good thermomechanical and thermophysical properties, and corrosion resistance, which provides for long technical life. These highly resistant periclase-zircon components can be used in regenerative chambers to provide fault-free and reliable operation for the furnace throughout the working period.

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