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PREPARATION AND INVESTIGATION

OF MADDELEYITE - CORUNDUM ELECTROFUSED REFRACTORIES

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As a result of the increased output of glass tank furnaces and the higher melting temperatures used in order to improve the quality of the product, refractories of higher corrosion-resistance are required for those parts of the tank that are most subject to attack.

Investigations into the manufacture of electrofused zircon-mullite refractory have resulted in an improvement in its quality and in an increase in its resistance to corrosion in glass furnaces, but the fact that this refractory contains more than 20% of SiO_2 - a substance that is less resistant to the action of melts than ZrO_2 and Al_2O_3 - limits the further improvement of its stability.

In France and the U.S., a fused refractory containing 53% of ZrO_2 and not more than 12% of SiO_2 has recently been put into manufacture, imported zirconium are being used. This refractory is highly resistant to glass, but it has the disadvantage that, as a result of marked discontinuities in thermal expansion, the glass furnace must not be heated up rapidly.

For some years the Refractories Laboratory of the Glass Institute has been carrying out investigations on the preparation of zirconia-alumina refractories of high resistance to glass from native raw materials.

The compositions of the refractories in the system Al_2O_3 - ZrO_2 - SiO_2 which we studied in 1951-52 are indicated on the ternary diagram shown in Fig. 1. It will be seen from the diagram that in these refractories the concentrations of the components varied over the following ranges (%): Al_2O_3 45.7-35.4; ZrO_2 8.2-54.5; SiO_2 0.4-15. In further experimental fusions the SiO_2 content sometimes attained 15%.

The mixtures taken for fusion were generally compounded from technical alumina and zirconia concentrate of low iron content. For the preparation of experimental melts in the laboratory, the mixtures were briquetted. The fusions were carried out in graphite crucibles in an electric resistance furnace designed by the authors. In this furnace temperatures of up to 2000° could be attained, and the heating and cooling schedules could be accurately controlled.

R. Tatenlou, Verre et refractaire, No. 1, 1950.
E. A. Matveeva and M. P. Golubeva took part in the laboratory investigations.

Experiment showed that the optimum fusion temperature was generally in the range 2100-2250°. Such temperatures are readily attained in large-scale industrial electric furnaces.

In all, more than seventy fusions were carried out in the laboratory. After each fusion the melt was cooled down slowly in the furnace, the rate of cooling being controlled (with the aid of a brush autotransformer) so that the conditions under which the crystallization of the melt occurred would be similar to manufacturing conditions.

The crystallization products were investigated and tested in various ways. The following were determined: chemical composition (by a method developed under the direction of O. V. Krasnovsky in the chemical laboratory of the Institute), microstructure, phase composition, bulk density, true density, apparent porosity, true porosity, coefficient of expansion, deformation under load at high temperatures, resistance to corrosion by glass of the usual composition, stability to caustic alkali, and stability to sodium carbonate.

Petrographic investigations showed that, in fused refractories in the field of compositions studied, the main crystalline phases are corundum ($\alpha\text{-Al}_2\text{O}_3$) and baddeleyite (ZrO_2). Refractories of this type, therefore, may be termed baddeleyite-corundum refractories - or 'bacor', for short. In some of the microscopic sections, mullite and glass were also detected, though in smaller amount.

A peculiarity of fused refractories containing an appreciable amount of zirconia is the occurrence of anomalous points on the thermal expansion curve, the presence of which leads to some reduction in the thermal durability of the refractory. Most of the dilatometric curves of the laboratory samples showed two anomalous points.

One of these was the usual anomaly in the range 1100-1200°, which appears as a result of the rapid conversion of monoclinic ZrO_2 into the tetragonal form during heating and the reverse change during cooling, the change in volume being about 7%. The extent of this anomaly was found to be directly proportional to the zirconia content, and it is small for products containing less than 20% of ZrO_2 .

The second anomaly generally occurred in the range 560-700°. Preliminary experiments showed that this anomaly was associated with the presence of an appreciable amount of reduction products in the laboratory samples.

For samples prepared under laboratory conditions the temperature at which softening began under a load of 2 kg/sq.cm was in the range 1620-1810°. In particular, bacor No. 15 began to soften at 1710°. The beginning of softening was followed closely by melting. The samples were of high mechanical strength, the compressive strength of bacor No. 5, for example, being about 5000 kg/sq.cm.

In their resistance to glass melts, the experimental samples were found to be better than electrofused zircon-mullite and thermite-corundum.

From the formulations that did not require the addition of artificial ZrO_2 , bacor No. 15 was selected for large-scale trials on account of its all-round properties. On the basis of this formulation, two experimental batches of bacor blocks were prepared in 1955 with the aid of workers of the Erevan Mullite Works, including the chief engineer, M. B. Sulkhanov,

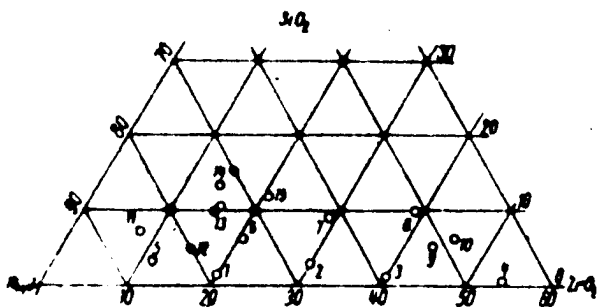


Fig. 1. Ternary system $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{SiO}_2$: compositions of refractories investigated.

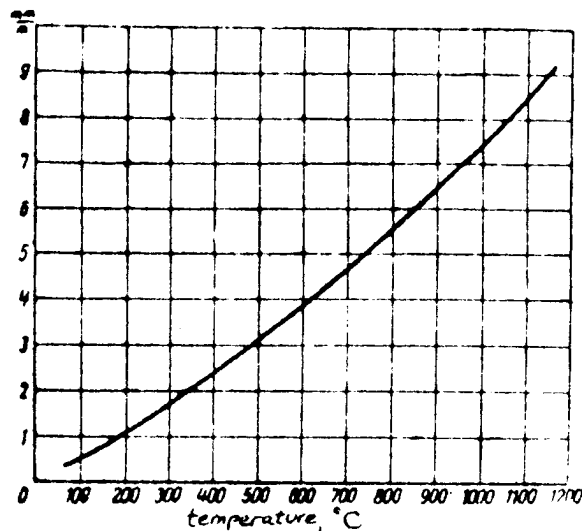


Fig. 2. Thermal expansion of bacor (first trial batch)

the director of the laboratory, S. F. Rustambekov, and one of the foremen, V. M. Srmoyan. In one batch of blocks, measuring 600 X 400 X 250 mm, there were many failures due to cracking (the diatomite was not technically satisfactory). A 100 % yield of satisfactory blocks measuring 600 X 300 X 250 mm was obtained from mixture No. 4.

Details of the chemical compositions, bulk densities, and apparent porosities of the bacor blocks are given in Table 1. The thermal expansion curve for the refractory is shown in Fig. 2, from which it can be seen that, unlike the laboratory bacor, the bacor prepared on the large scale gives a smooth curve. In the temperature range 20-1100°, the mean coefficient of linear expansion is $76 \cdot 10^{-7}$, i.e. almost the same as that of electrofused mullite and zircon-mullite.

Figures 3-6 show photomicrographs of samples taken from bacor blocks (we carried out the petrographic investigations under the direction of V. V. Lapin, Doc. Mineralogical and Geological Sci.). The samples taken for petrographic investigation were taken from the working face and from the center of the block. The photomicrographs show that bacor contains an appreciable amount of dendrite formations composed of baddeleyite crystals (ZrO_2). No natural minerals could be detected in the sections.

The following refractories were selected for submission to comparative measurements of resistance to glass: the first large-scale trial batch of bacor, prepared in 1953; improved zircon-mullite, block No. 2403, made on the works in 1952; improved zircon-mullite, of low iron content, block No. 7076, made in 1953 under manufacturing conditions.

In tests on the resistance of the fused refractories to glass, test samples were taken at a distance of 100 mm below the working face of the block so as to obtain more reliable results.

The chemical compositions of the refractories tested are given together with some of their properties in Table 1.

In the tests on resistance to glass, a glass melt of the following composition was used (%): SiO_2 —73.00; SO_3 —0.55; Al_2O_3 —0.37; Fe_2O_3 —0.06;



Fig. 3. Microstructure of bacor from working part of block. (Transmitted light; magnification 90; parallel nicols.)



Fig. 4. Microstructure of bacor from working part of block. (Reflected light; magnification 86; parallel nicols.)



Fig. 5. Microstructure of bacor from center of block. (Transmitted light; magnification 90; parallel nicols.)



Fig. 6. Microstructure of bacor from center of block. (Reflected light; magnification 165; parallel nicols.)

TABLE 1

REFRACTORY	COMPOSITION (% by weight)										Bulk Density (g/cc)	Apparent porosity (%)
	SiO ₂	TiO ₂	ZrO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	Other Components	Total		
Bacor; first trial batch, 1953	14.42	0.32	15.20	66.97	0.63	0.33	0.85	1.14	0.14	100.0	3.09	10.2
Bacor; third trial batch	15.05	0.41	22.57	60.54	0.43	0.24	0.31	0.73	-	100.28	3.23	7.6
Improved experimental zircon-mullite of low iron content block No. 7076	21.69	0.54	6.98	69.89	0.56	Traces	0.20	0.69	0.16	100.71	3.23	0.5
Improved zircon-mullite; block No. 2403	23.00	1.34	5.50	66.44	1.88	1.22	1.01	1.01	0.18	100.57	3.00	1.3
High-alumina ceramic block	27.43	0.71	-	66.90	0.92	1.68	1.60	1.38	-	100.56	2.68	10.8
Ceramic corundum refractory	3.5	TiO ₂ +Al ₂ O ₃ 95.9			0.6	-	-	-	-	-	3.15- 3.20	10-12

CaO—5.47; MgO—3.4; Na₂O—16.55. Three crucibles were placed simultaneously in a furnace, and each of these crucibles contained two like test samples of each of two different refractories.

The results of these tests are given in Table 2, in which each figure is the mean of two determined values.

The bacor produced on the large scale was found to be less resistant to glass than the laboratory bacor, but Table 2 shows that the first experimental batch of bacor, which was prepared under manufacturing conditions, suffers considerably less corrosion by melted glasses (both at the glass surface and also below the surface) than improved electrofused zircon-mullite.

A batch of eleven bacor blocks was tested under normal conditions of use, for which purpose they were incorporated in the maximum-temperature zone of the melting section of the tank of a glass tank furnace at the Pioneer Glass Works, Mishoron. This trial showed that bacor is a more resistant refractory than electrofused zircon-mullite.

With our assistance, a third batch of 145 bacor blocks was manufactured in 1954 at the State Mullite Works, Erevan, and for testing purposes these blocks were built into the walls of the tank of a glass furnace at the Stalin Glass Works in Gomei. The chemical composition of a sample of bacor from this batch is given

TABLE 2

Refractory	Crucible	Rate of corrosion (mm in 24 hr.)	
		at 35 mm from the upper end of sample	at the surface of the glass.
Bacor, first trial batch	1	0.45	1.91
Improved zir- con-mullite; block No. 2403	1	1.28	3.19
Bacor, first trial batch	2	0.52	1.70
Improved zir- con-mullite of low iron con- tent; block No. 7076	2	0.64	1.84

TABLE 3

Refractory	Rate of corrosion (mm in 24 hr.)	
	at 35 mm from the upper end of sample	at the surface of the glass
Bacor; third batch	0.36	0.38
High-alumina vitreous cera- mic block	0.32	0.45
Ceramic corun- dum refractory	0.56	1.24
	0.38	0.62

in Table 1. The bulk density of the blocks was 2.91-3.32 g/cc. The density of the bacor was 3.7 g/cc.

Samples sawn from bacor blocks of the third batch at 100 mm below the surface of the block were compared with a high-alumina vitreous ceramic block and a ceramic corundum refractory¹ for resistance to glass. The chemical compositions, bulk densities, and porosities of these refractories are given in Table 1, and the results of the comparative test for resistance to glass are given in Table 3 (each figure in Table 3 is the mean for two samples).

The results presented in Tables 2 and 3 show that bacor has a higher stability to glass than other refractories used for building the tanks of glass furnaces.

¹D. S. Rutman, D. N. Poluboyarinov, and L. V. Vinogradov, Refractories, No. 4 1954.