specimen breaks. The difference in the readings of the previously graduated micrometer also determines the load which breaks the specimen.

The fragment of filamentary crystal attached to the lower quartz filament is studied under a microscope and its diameter is measured in different planes. The area of the cross section is calculated as the area of a circle with the average diameter of these measurements. The diameter is measured to an accuracy of ± 0.5 μm which is 17, 10, and 7%, respectively, for diameters of 3, 5, and 7 μm. Consequently, the area of the cross section is determined to an accuracy of 34, 20, and 14%, respectively.

The measurement of the areas of the cross section of the filamentary crystals involves a fundamental error in the determination of their strength since the load is measured to an accuracy of ± 10 mg which is 0.2-0.3%. The achievable accuracy of the determination of the strength of an MgO FC can be regarded as completely satisfactory since the majority of crystals are 5-7 μm and the large number of the measurements makes it possible when treating the results to use statistical methods with adequate reliability.

The ultimate extensive strength of the crystals varied from 500 to 1500 MPa depending on their diameter.

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A REFRACTORY CERAMIC WITH ETHYL SILICATE BINDER

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The technique of casting articles made of thixotropic self-hardening grainy masses with ethyl silicate binder (ESB) [1-3] ensures the production of contructional ceramic elements of any complicated shape. Many articles of this type cannot be manufactured by pressing and the traditional slip casting does not permit a

TABLE 1. Properties of Corundum Refractories

Characteristics	Characteristics of refractories manufactured by		
	casting with ESB	casting from aqueous slips	semidry pressing
Before firing:			
open porosity, %	20—26	30—38	20—28
apparent density, g/cm^3	2,46—2,65	2,55—2,85	2,85—2,98
ultimate compressive strength, MPa	17,5—26,0	2,5—3,0	2,0—2,5
After firing at 1730 °C:			
open porosity, %	5—7	0,5—4	18—25
apparent density, g/cm^3	3,10—3,40	3,60—3,90	2,96—3,15
ultimate compressive strength, MPa	300—450	350—540	65—80
elastic modulus, GPA	62—80	200—350	105—140
thermal-shock resistance before destruction of specimens (1200 °C — water), heat cycles	10	2	5—7

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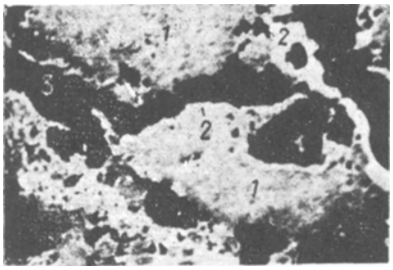

Fig. 1. Microstructure of a refractory made from seawater MgO with ESB: 1) periclase; 2) forsterite; 3) magnesium ferrite; magnification × 250; reflected light.

coarsely dispersed mass to be used. Using ESB it is possible to create articles with a specified distribution of the existing phases in various directions and also to produce polyceramic multilayer constructions in which layers of a transitional composition are formed as a result of the difference in the thermal expansions of the neighboring layers of the polyceramic article.

Refractories with ESB have important properties, the combination of which cannot easily be provided in pressed goods. The high wetting tendency of ESB makes it possible to obtain materials with a fragmentary structure consisting of grains of filler surrounded by a film of highly active SiO_2 (in the unfired article) or silicates (synthesized when the articles are fired). The thickness of the silicate films covering the filler grains is controlled by the compositions of the binder and mass. It is well known that dense refractories of a fragmentary structure have great strength and thermal-shock resistance [4-6]. Such a combination of properties is most desirable for several constructional materials [5, 7].

The application of this technique of manufacturing refractory ceramic with ESB has been indicated in [9-11]. The ethyl silicate binder is obtained by hydrolyzing ethyl silicate in the presence of reaction catalysts. The hydrolyzate-binder is mixed with the powder fillers. The grain size of the powdered filler is not limited and is determined only by technological feasibility. Depending on the concentration of binder in the mass, a slip of fairly uniform mass can be obtained for the vibrocompaction of the articles.

Ethyl silicate binders can be used for manufacturing nonmolded articles and also mortar, adhesives, tamping masses, and coatings. The articles are molded in metal, plastic, or other demountable molds. The mass solidifies as a result of gel-formation and the condensation of the products of hydrolysis of the ethyl silicate and this is accompanied by the removal of ethyl alcohol and water. The duration of the solidifying process (from several minutes to 2-3 days) is controlled by the composition of the binder and by additives which activate the hardening; PAV, e.g., can be used for this purpose. The hardened casts of the refractories have a strength of 15 MPa or more and this enables them to be used without firing. As a result of the hydrophobicity of the products of the polycondensation of the ESB, the casts are adequately water-resistant.

The characteristics of refractories made by casting from masses with ESB indicate the advantages of using this particular process.

The strength of the unfired refractories (Table 1) with ESB is several times greater than that of articles of an analogous composition but made using traditional methods; this increase is mainly due to the composition

TABLE 2. Properties of the Magnesial Ceramic with Ethyl Silicate Binder

Specimen No.	Open porosity, %	Ultimate strength, MPa		Elastic modulus, GPa	Thermal-shock resistance	
		on extension	on compression		destructive temp. gradient in wall of hollow cylinder, °C/cm	No. of heat changes (1300 °C – water) before destruction
ÉP-1	3,0	27,5	No data	180	150	15—20
ÉP-2	13,0	8,0	98,5	24	520	60—80
SP-3	2,4	17,0	210,0	196	350	30—35
AM-5	60,0	2,2	20,5	98	No data	120—150
ŠP-4	8,8	No data	135,0	No data	No data	40—45
ÉP-4	12,9	» »	90,0	»	»	30

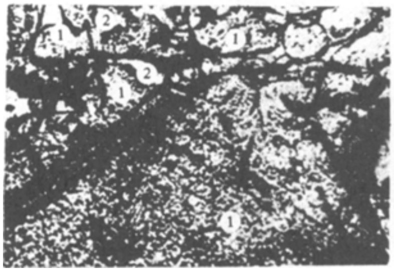

Fig. 2

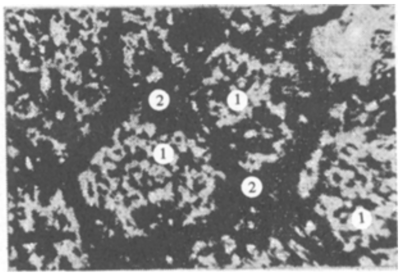

Fig. 3

Fig. 2. Microstructure of refractory made from fused periclase with ESB: 1) periclase; 2) silicates; magnification × 250; transmitted light; no analyzer.

Fig. 3. Microstructure of a pressed refractory made from seawater MgO in a spinel binder: 1) periclase; 2) spinel; magnification × 250; reflected light.

of the binder and the concentration of the latter in the mass. Thus, the ultimate compressive strength of the casts of a corundum ceramic with ESB made from a mixture containing 70% ethyl silicate is 17-18 MPa; with 90% ethyl silicate, up to 28 MPa; and with 95%, 12 MPa. This can be explained by the difference in the properties of the binders obtained with different concentrations of ethyl silicate in the mixture [8, 10, 11] and it also depends on the uniformity of the distribution of the binder between the grains of filler.

After firing, the corundum ceramic with ESB has an ultimate compressive strength of 250-300 MPa and an open porosity of 7-15%. The structure of such a ceramic consists of grains of corundum surrounded by interlayers of mullite and this provides the improved thermal-shock resistance of the material (Table 1) in accordance with the data in [4-6, 12]. The amount of mullite is determined by the 2-4% SiO_2 in the cast articles. The corundum ceramic with ESB can be recommended for use as the nozzle of an air-heater up to temperatures of 1750°C.

The ceramic made of MgO [13-16] with ESB was prepared from powdered electrosmelted periclase (ÉP), seawater MgO (SP), and acicular single crystals of MgO (AM). The properties of the specimens are given in Table 2.

Specimens of ÉP-1, ÉP-2, and SP-3 were prepared from masses containing filler with fractions of 2-1 mm and finer than 60 μm; specimens of SP-4 and ÉP-4 were made from finely milled powders of fractions < 60 μm. A spinel-forming additive (alumina powder) was added to the composition of the SP-3 and ÉP-2 specimens in amounts of 4%; and to the ÉP-4 and SP-4 compositions, in amounts of 0.4%. For the preparation of the ÉP-4 specimens we used a combined ethyl silicate and $MgCl_2$ binder [17].

The use of seawater MgO makes it possible to more than double the strength of the magnesial—spinel ceramic with the ethyl silicate but the thermal-shock resistance of the material in this case is lowered. The excellent thermal-shock resistance of the magnesial ceramic with ESB is clearly not so much the result of the spinel-forming additive as of the presence of forsterite which is synthesized in the form of a shell around the periclase grains (Figs. 1 and 2). The recommended [4-6, 12] ratio of the thermomechanical properties of components of a two-phase refractory in order to improve its thermal shock-resistance is fulfilled in this case both for the magnesial spinel and the forsterite. However, a significant contribution to the increased thermal-shock resistance of the magnesial ceramic with ESB is made by the forsterite shells which are uniformly distributed in the structure of the ceramic as a result of the above-mentioned uniform distribution of the SiO_2 from the ethyl silicate around the grains of filler.

A petrographic study of sections of fired periclase specimens established that the dense specimens of SP-4 of a pale-brown color are characterized by a grainy structure. In transparent sections, periclase (basic mass), forsterite, and opaque clusters of magnesium ferrite are observed. The grain size of the periclase varies from 36 to 162 μm; the silicates make up < 5%. Magnesioferrite in the form of very small grains (< 9 μm) forms accumulations which are coordinated exclusively with the contacts between grains. In reflected light (Fig. 1) the main mass of the specimen, the combined periclase and forsterite, and forsterite with a higher reflective capacity and forming borders around the periclase grains, can be distinguished.

TABLE 3. Properties of Unfired Articles Obtained by Various Methods

Preparation method	Binder	Moisture content of mass, %	Ultimate compressive stress, MPa, of articles made from				
			magnesium oxide	yttrium oxide	zircon	corundum	quartz sand
Casting	Ethylsilicate	—	14	13,0	17,0	18,5	15,0
Pressing	The same	4—6	5,5	4,0	5,0	6,0	4,5
The same	SDW	6	2,0	2,5	2,0	1,5	2,0

Specimens of EP-4 based on fused periclase and the ESB plus $MgCl_2$ are also characterized by a grainy structure. The periclase grains are broken up by cleavage cracks in the finer regions. Irregularly shaped pores around the periphery are framed by yellow glass (3-5%). Silicates (5-7%) are arranged around the cleavage cracks of the periclase and between the grains in the bonding mass. The silicates are mainly forsterite (Fig. 2).

The thermal-shock resistance of the refractory ceramic obtained by semidry pressing from fused corundum and fused periclase in sulfite distillery waste (SDW), the ÉP-2, and SP-3 (Table 2) specimens was studied under strictly controlled conditions of intermittent heating (1600°C — air) by light radiation in an arc furnace with a parabolic mirror. The thermal-shock resistance was 1-2, 1-2, > 5, and 3-4 heat changes, respectively, before the destruction of the specimen. The heat flow into the specimen was $9.2 \cdot 10^5$ W/m^2. The grain composition of all the specimens was the same. The pressed articles contained identical amounts of spinel (8%). The structure of the specimens obtained by semidry pressing at 150 MPa consists of sintered periclase grains surrounded by shells of aluminomagnesial spinel (Fig. 3). The most thermal-shock resistant were the ÉP-2 and SP-3 ceramics.

The casting technology with ESB makes it possible to obtain materials with fibrous fillers without the destruction or deformation of the fibers as normally occurs under pressing. The acicular single crystals of MgO obtained at the High-Temperatures Institute [14] had a length of 10 μm to 5 mm and a diameter from 0.2 to 200 μm. On being pressed, a significant proportion of the crystals were destroyed and the reinforcing effect reduced. By casting masses with ESB with a filler of single crystal MgO, specimens were obtained [15] with a porosity of 55-70% and a strength sufficient for the exploitation of the material in construction work (Table 2). The grid structure formed by the acicular filler without the destruction of the crystals produced the good thermal-shock resistance of the material. The thermal-conductivity coefficient of the material at 800°C is 0.46-0.53 W/m · K.

Refractories made from yttrium oxide and zircon, chamotte, and fused mullite, with or without the addition of zircon [18, 19] and some other materials [20], were prepared by casting with ESB. These materials have an adequate ultimate compressive strength before firing (> 13 MPa) as is clear from Table 3.

The masses with ESB with refractory fillers were used as unfired adhesives for making a strong joint of parts of the sliding steel-casting gates. The joints were moisture-resistant, very strong [21], and required no impregnation with bakelite lacquer before the working surface was ground. The sliding gates based on periclase stuck with ethyl silicate refractory adhesive were tested at the Novolipetsk Metallurgical Plant. The tests demonstrated the high efficiency of the adhesive compound.

The use of ethyl silicate in semidry pressing makes it possible to increase the strength of the pressings by 1.5-3 times more than with articles of an analogous composition plasticized with SDW (Table 3).

We prepared current-conducting and electrical-insulation films of coating layers from masses with ESB with fillers made from silver, palladium, platinum—rhodium, aluminum, silicon, quartz, and silicides of various metals. Tests showed the possibility of using such masses for the manufacture of film thermocouples, elements of electrical and radio circuits, and high-temperature protective coatings on high-melting metals. Such thermocouples and coatings are operational up to 1650-1700°C.

The use of the ESB makes it possible to obtain thermal and electrical insulating materials and articles and protective coatings with an improved thermal-shock resistance for use in constructional work. Refractory adhesives can also be made.

The technology for the production of thixotropic masses with ESB with powder fillers makes it possible to produce articles of a complex shape and with accurate dimensions. Such articles can also be used without firing. Refractory adhesives with ESB give a strong joint for ceramic details in constructions which have to operate at temperatures up to 1800°C and they are also moisture-resistant at normal temperatures.

In each actual instance of choosing the mass, it is necessary to take into account the physicochemical processes which occur during the interaction between the SiO_2 of the binder and filler in order to develop refractory materials with specified properties.

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