DOI 10.1007/s11148-016-9931-8
Refractories and Industrial Ceramics *Vol. 57, No. 1, May, 2016*

VARYING THE GRANULOMETRIC COMPOSITION OF AN ELECTROFUSED-CORUNDUM-BASED CERAMIC WITH A PORCELAIN BINDER TO CONTROL ITS OPEN POROSITY AND STRENGTH

A. V. Belyakov,[1,2] Zaw Ye Maw Oo,[1] N. A. Popova,[1] Ye Aung Min,[1] and Kyaw Lwin Oo[1]

Translated from *Novye Ogneupory*, No. 2, pp. 34 – 37, February, 2016.

Original article submitted January 7, 2016.

A study is made of a strong porous ceramic based on granular mixes of a filler — electrofused corundum with particle sizes of 2 – 3 and 0.5 mm (95 wt.% of the mix) — and a porcelain binder (5 wt.%). Several mixes were prepared with different values for the 2 – 3 mm/0.5 mm ratio of filler-particle sizes: 0/95, 35/60, 40/55, 45/50, 50/45, and 95/0. The specimens were pressed at pressures of 25, 50 and 100 MPa and fired at temperatures of 1350 and 1450°C. The sintered specimens ranged from 19 to 143 MPa in ultimate flexural strength and 17 to 26% in open porosity. The results are attributed to the formation of a framework in the semifinished product along with regions outside the framework. The new porous permeable ceramic is promising for use in the form of filters and supports for ceramic membranes.

Keywords: ceramic, open porosity, strength, granular powders, electrofused corundum, ceramic filters.

Porous materials are widely used as catalyst supports in processes that involve oxidation, hydration, and dehydration at high temperatures, in the processing of raw materials in aggressive media, and in endothermic and exothermic reactions. In particular, various types of corundum-based materials that are characterized by a high degree of chemical inertness are used for these purposes. Thanks to the high porosity and unique structure of porous materials, they have specific properties that differ greatly from the properties of dense materials with a similar chemical composition [1 – 3].

The goal of the investigation being discussed in this article was to obtain a strong, porous, permeable ceramic based on electrofused corundum (EFC) for filters and membrane supports. Porous materials that have a narrow pore-size distribution and an average pore size of 4 – 6 μm are best suited for use as filtering elements [4].

Electrofused corundum F20 (0.5 mm) and F100 (2 – 3 mm) were used as the filler and porcelain powder (gel-like porcelain mass of grade LT, referred to below as porcelain LT) was used as the binder. The binder strongly bound the EFC grains to one another during the firing operation. All of the masses that were studied consisted of 95 wt.% granular filler and 5 wt.% binder. In order to obtain porous permeable ceramic products with adequate strength for their intended application and good filtering properties, the following values were used for the 2 – 3 mm/0.5 mm ratio of the content of coarse grains of the filler to fine grains of the filler: 0/95; 35/60; 40/55; 45/50; 50/45; 95/0. Pressing pressure in the experiment was 25, 50, and 100 MPa (pressures of 25 and 50 MPa were used for the compositions 0/95 and 95/0). The highest temperatures during the firing of the ceramic semifinished products were 1350 and 1450°C. The specimens that were obtained were used to study porosity, density, and mechanical strength in accordance with the methods described in [5].

Dried gel-like porcelain mass LT (5 wt.%) was mixed with the filler by the dry method for a certain period of time. The mixing operation was performed in a corundum drum with corundum grinding balls. The ratio grinding balls:material = 1:1. The total amount of time taken to mix the charge was 3 h. After mixing and the introduction of a temporary binder, we obtained a powder molding mix that was subsequently used to obtain test specimens by pressing. The temporary binder was an aqueous solution of polyvinyl alcohol

[1] Russian University of Chemical Technology, Moscow, Russia.
[2] av_bel@bk.ru

(5 wt.%). The amount of this binder that was used was equal to 10% of the weight of the charge.

The polyvinyl alcohol solution was added in small amounts to the dry mixture of components during continuous mixing. The moist, carefully mixed mass was then subjected to additional homogenizing by passing it through a No. 3 screen. The resulting molding mixes were pressed into disks 20 mm in diameter and 6 mm in height and were fired in air at 1350 and 1450°C inside a furnace equipped with lanthanum chromite heaters. The heating of the specimens was done in accordance with the regime depicted in Fig. 1.

Table 1 shows the results obtained from determining the average density of the products ρ and the ultimate flexural strength σ_{bnd} of the sintered specimens.

The highest value of the index σ_{bnd} for the compositions shown in Table 1 was obtained for the specimens pressed at 50 MPa from coarse-grained (2 – 3 mm) powder after firing at 1450°C (115 MPa). The ultimate flexural strength of specimens pressed at 50 MPa from fine-grained (0.5 mm) powder after firing at 1450°C was also high and was 106 MPa. The density of the specimens decreased substantially with a decrease in pressing pressure. A decrease in this pressure for the fine-grained (0.5 mm) mix from 50 to 25 MPa with a firing temperature of 1450°C led to a larger reduction in ultimate flexural strength — from 106 to 40 MPa — than for the coarse-grained (2 – 3 mm) mix — from 125 to 59 MPa. Strength was somewhat higher for the coarse-grained specimens (115 MPa) than for the fine-grained specimens (106 MPa) with a pressing pressure of 50 MPa and a sintering temperature of 1450°C. However, the same specimens sintered at 1450°C had similar values of σ_{bnd} (100 MPa for the coarse-grained specimens and 102 MPa for the fine-grained specimens).

Firing the same mixes at a lower temperature (1350°C) led to a decrease in σ_{bnd}, although firing temperature had less of an effect than pressing pressure. For specimens that had an EFC filler of the 0.5 mm fraction and were pressed at 50 MPa, a decrease in firing temperature from 1450 to 1350°C was accompanied by a decrease in σ_{bnd} from 106 to 102 MPa. Ultimate flexural strength decreased from 115 to 100 MPa for the specimens with a coarser (2 – 3 mm) filler. The sintering temperatures (1350 and 1450°C) had less of an effect on σ_{bnd} for the fine-grained mix than the coarse-grained mix: 102 and 106 MPa, respectively, for specimens pressed at 50 MPa. With a pressing pressure of 25 MPa, an increase in

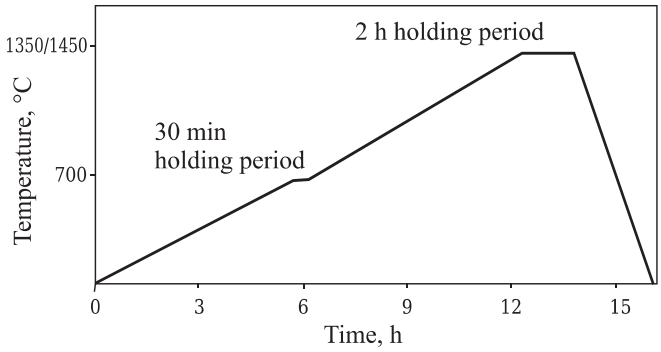

Fig. 1. Specimen firing regime, maximum temperatures 1350 and 1450°.

TABLE 1. Ceramic Properties of Specimens Formed with Pressing Pressures of 25 and 50 MPa and Fired at Temperatures of 1350 and 1450°C

Specimen composition		Pressing pressure, MPa	Firing temperature, °C	Open porosity, %	ρ, g/cm^3	σ_{bnd}, MPa
component	content of component, %					
EFC of the 2 – 3 mm fraction	95	50	1350	19	3.10	100
2 – 3 mm		25	1350	17	3.15	50
Porcelain LT	5	50	1450	17	3.21	115
		25	1450	17	3.23	59
EFC of the 0.5 mm fraction	95	50	1350	23	3.02	102
0.5 mm		25	1350	21	3.05	40
Porcelain LT	5	50	1450	21	3.02	106
		25	1450	18	3.06	40

TABLE 2. Ceramic Properties of Specimens of Dual-Fraction Compositions Fired at 1350°C

Content of the 2 – 3 mm/0.5 mm fractions of EFC in the specimen, %	Pressing pressure, MPa	Open porosity, %	ρ, g/cm^3	σ_{bnd}, MPa
35/60	100	23	2.95	98
	50	26	2.87	66
	25	23	2.97	19
40/55	100	23	2.97	122
	50	24	2.94	76
	25	22	3.03	24
45/50	100	22	3.03	129
	50	22	3.04	93
	25	19	3.15	48
50/45	100	20	3.13	135
	50	21	3.06	115
	25	17	3.18	61

* The content of porcelain LT was 5% in all of the specimens.

temperature did not lead to an increase in ultimate flexural strength. The strength value was 40 MPa in this case (see Table 1).

Table 2 shows the results obtained from determining the ceramic properties and ultimate flexural strength of specimens of dual-fraction compositions pressed at 25, 50, and 100 MPa and fired at 1350°C. An increase in the content of the 2 – 3-mm fraction was accompanied by a decrease in open porosity P_{opn} from 26 – 23 to 21 – 17%. The density of the material increased with an increase in the content of the 2 – 3-mm fraction of EFC regardless of the pressing pressure. After firing at 1350°C, the average value of porosity was 23%.

Among the dual-fraction materials sintered at 1350°C, the maximum open porosity of 26%, with 66 MPa for σ_{bnd}, was exhibited by the specimens which had a 35/60 ratio of coarse to fine EFC fractions and were pressed at 50 MPa (Table 2).

An analysis of the data in Table 3 for specimens that had the same composition as in Table 2 but were fired at 1450°C showed that with a pressing pressure of 25 MPa (40% content of the 2 – 3-mm EFC fraction and 55% content of the 0.5-mm EFC fraction) the sintered porous specimens had an open porosity of 21% but relatively low flexural strength (38 MPa). A better set of properties was displayed by the composition that had a 40/55 coarse-to-fine ratio for EFC content and was pressed at 50 MPa (open porosity was 22%, but flexural strength was 97 MPa). This composition proved to be 2.5 times stronger in this case than when it was pressed at 25 MPa (97 MPa versus 38 MPa) (Table 3).

The tendencies of the properties of the specimens to change as the ratio of the EFC fractions 2 – 3 mm/0.5 mm was varied in the order 35/60, 40/55, 45/50, and 50/45 show that an increase in the content of the coarse fraction at the expense of the fine fraction did not produce any significant changes in open porosity but had a marked effect on average density and, in particular, on strength. This is in contradiction to the well-known fact that an increase in the strength of a ceramic is usually accompanied by a decrease in its porosity. The tendencies just referred to were also manifest with an increase in pressing pressure in the order 25, 50, and 100 MPa and an increase in the maximum firing temperature from 1350 to 1450°C (see Tables 2 and 3).

In accordance with the Le Chatelier — Braun principle, a structure that prevents compression of the ceramic semifinished product is formed as it is pressed [6, 7]. Such a structure is formed most readily and most rapidly when a three-dimensional framework comprised of denser regions (local compactions) [8] is formed inside the semifinished product. This framework begins to resist the pressing force and transmits it to the walls of the mold and the dies. In fact, it is the structure and properties of the framework that determines the strength of the specimens after pressing and sintering. In mixes with filler particles of 2 – 3 and 0.5 mm, an increase in the pressing pressure from 25 to 50 MPa increases strength after firing at 1350 and 1450°C by factors of 2.5 and 2, respectively (see Table 1). At the same time, the framework also prevents consolidation of the regions of the semifinished product located between the framework's dense elements. As a result, the material which is not part of the framework is compacted to a lesser extent and ends up making the main contribution to the open porosity of the sintered specimens. With an increase in pressing pressure, open porosity increased for mixes with a particle size of 0.5 mm (Table 1). For mixes with a particle size of 2 – 3 mm, the value of P_{opn} increased only after firing at 1350°C and did not change when the firing temperature was 1450°C.

The structure of the framework and the regions that are not part of it depends not only on the pressing pressure but also on its redistribution in the semifinished product, which is determined by the internal frictional forces (between the particles of the mix) and the external frictional forces (between the particles and the walls of the mold). In the general case, the smaller the particles, the greater the friction. Also, mixes which contain 2 – 3-mm particles in sections that are perpendicular to the direction of the applied force have fewer contacts than a mix with 0.5-mm particles. This helps form a stronger framework and a dense semifinished product from a coarse-grained mix. Thus, the average density of the sintered specimens obtained from mixes with a particle size of 2 – 3 mm is higher than that of the specimens obtained from mixes with a particle size of 0.5 mm (Table 1).

During sintering — especially sintering that is conducted in the presence of the liquid

TABLE 3. Ceramic Properties of Specimens of Dual-Fraction Compositions Fired at 1450°C

Content of the 2 – 3 mm/0.5 mm fractions of EFC in the specimen, %	Pressing pressure, MPa	Open porosity, %	ρ, g/cm^3	σ_{bnd}, MPa
35/60	100	23	2.97	107
	50	24	2.87	84
	25	22	2.78	32
40/55	100	22	2.99	131
	50	22	2.87	97
	25	21	2.79	38
45/50	100	22	3.02	143
	50	21	2.91	111
	25	19	2.90	43
50/45	100	21	3.02	151
	50	21	2.90	141
	25	18	2.92	53

* The content of porcelain LT was 5% in all of the specimens.

phase which is formed in a porcelain binder — changes take place in the structure of the framework and the regions that are not part of it. The higher the sintering temperature, the greater these changes. For specimens obtained from a mix with 2 – 3-mm particles, the differences between the structure of the framework and the structure of the regions outside it remain more the same when the material is fired at 1350°C than when it is fired at 1450°C. For example, after firing at 1350°C the specimens' open porosity increased from 17 to 19% with an increase in pressing pressure from 25 to 50 MPa. The structures of the framework and the regions that are not part of the framework change to a greater extent when the firing temperature is 1450°C. When the specimens are pressed at 25 MPa and 50 MPa, their open porosity is the same (see Table 1) but the structure of the framework may be different from the structure of the non-framework material.

The structures of the framework and the non-framework regions change appreciably in the case of the use of mixes with 0.5-mm particles. The average density of the resulting specimens is lower due to the increase in friction between the particles (Table 1). For specimens fired at either of the above two temperatures, an increase in pressing pressure led to an increase in open porosity. As was the case for the specimens obtained from a mix with 2 – 3-mm particles, P_{opn} was higher (from 21 to 23%) when firing temperature was 1350°C than when it was 1450°C (from 18 to 21%).

Changing over to a dual-fraction mix made it possible to optimize open porosity while also obtaining satisfactorily high strength. High gas permeability is important for ceramics that are used as filters, and this parameter depends on open porosity [9]. An increase in the content of the coarse fraction in mixes containing particles of both fractions (2 – 3 mm and 0.5 mm) facilitates consolidation of the framework and the semifinished product as a whole (Tables 2 and 3). The strength and average density of the sintered specimens increase in this case, which is consistent with the data in Table 1. Both the fine fraction and the coarse fraction participate in the formation of the framework during the pressing operation. The increased content of the coarse fraction helps form a dense, strong framework, which ensures the formation of a strong ceramic. An increase in the content of the fine fraction helps increase open porosity mainly in the regions that are not part of the framework.

The reason for this may be that the framework is formed by internal and external friction forces during the shaping of the semifinished product. The porosity of the regions that are part of the framework decreases during consolidation, but open porosity in the non-framework regions decreases to a considerably lesser extent in this process. The difference between the porosities of these two types of regions may increase during the sintering operation. The main contribution to the value of P_{opn} of the sintered specimens is made by the porosity of the regions located in the cavities of the framework. The properties of the framework and the regions located in its cavities determine the change in the open porosity and strength of the sintered specimens. The presence of a strong, dense framework in the semifinished product increases the strength of the sintered product as well [10]. This explains why an increase in the content of the coarse fraction (2 – 3 mm) relative to the fine fraction (0.5 m) increases both the porosity and the strength of the sintered porous products. The relationship just mentioned holds over a fairly wide range of values for the coarse fraction/fine fraction ratio.

Thus, by changing the proportions of the coarse (2 – 3 mm) and fine (0.5 mm) fractions of electrofused corundum, it is possible to increase the strength of a porous ceramic while retaining adequate open porosity. The formation of the framework is affected by the field of internal and external friction forces that exists during the pressing of the semifinished product. It is known that the properties of a ceramic semifinished product which is being pressed are strongly influenced by the granulometric composition of the mix, the rate of increase in pressing pressure, the final pressing pressure, and the type and amount of the temporary binder that is used. These factors affect the distribution of the frictional forces in the semifinished product during pressing, the structure of the framework which is formed, and the structure of the regions outside the framework.

REFERENCES

1. I. Ya. Guzman, *Porous High-Refractory Ceramics* [in Russian], Metallurgiya, Moscow (1971).
2. A. S. Berkman, *Porous Permeable Ceramics* [in Russian], Stroizdat, Moscow (1969).
3. N. T. Andrianov, V. L. Balkevich, A. V. Belyakov, et al., *Chemical Engineering of Ceramics: Text for Higher Educational Institutions* [in Russian], OOO RIF "Stroimaterialy," Moscow (2011).
4. G. Bruno, A. M. Pozdnyakova, A. M. Efremov, et al., "Thermal and mechanical response of industrial porous ceramics," *Mater. Sci. Forum*, **652**, 191 – 196 (2010).
5. N. T. Andrianov, *Practicum on the Chemical Engineering of Ceramics: Text for Higher Educational Institutions* [in Russian], OOO RIF "Stroimaterialy," Moscow (2005).
6. A. V. Belyakov and V. S. Bakunov, "Structural evolution in ceramic technology and processing," Refractories and Industrial Ceramics, **47**(1), 48 – 52 (2006).
7. A. V. Belyakov and V. S. Bakunov, "Structural evolution in ceramic technology and processing," Refractories and Industrial Ceramics, **47**(2), 110 – 115 (2006).
8. A. V. Belyakov and A. S. Yen'ko, "Identification of local compactions in ceramics," Glass and Ceramics, **56**(11/12), 389 – 392 (2000).
9. E. S. Lukin, O. V. Gorshkova, O. V. Logina, et al., "Strong porous ceramic based on alumina," Refractories and Industrial Ceramics, **30**(9/10), 621 – 623 (1989).
10. E. Hammel, O. L.-R. Ighodaro, and O. I. Okoli, "Processing and properties of advanced porous ceramics: an application based review," *Ceram. Int.*, **40**(10), 15351 – 15370 (2014).