EFFECT OF FINE ANDALUSITE ON THE PROPERTIES AND MICROSTRUCTURE OF LOW-CEMENT CORDIERITE-MULLITE CASTABLES

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Results are presented from the development and study of cordierite-mullite panels which are based on low-cement refractory castables (LCC) and can be used as kiln furniture. Cordierite powder was synthesized from talc, kaolin, and alumina. Synthetic cordierite aggregate was used as the main component in addition to andalusite, Kerphalite, cement Secar 71, calcined alumina, and microsilica. It was established that samples of the cordierite-based material with a mullite binder had a satisfactorily low CLTE (3.72×10^{-6} 1/K), which is indicative of their excellent thermal shock resistance.

Keywords: cordierite, andalusite, low-cement cordierite-mullite castables, kiln furniture, SEM-micrography, crack resistance.

Cordierite ($2Al_2O_3 \cdot 5SiO_2 \cdot 2MgO$) is a technically important ceramic material. Cordierite ceramics exhibit exceptional high-temperature properties, including excellent thermal shock resistance and chemical stability at elevated temperatures [1, 2]. While the superior thermal shock resistance of these ceramics make it possible to use them as kiln furniture [3], their relatively poor structural durability makes them unsuited for long-term use [4 – 6]. Since mullite ceramics ($Al_6Si_2O_{13}$) have a high melting point, good creep resistance, and a moderate coefficient of linear thermal expansion (CLTE), cordierite and mullite can be used in combination with one another to obtain advanced ceramics with high thermal shock resistance [7, 8].

Although kiln furniture is traditionally made by pressing, other ceramic-forming methods such as vibrocasting are also now being used. The production of kiln furniture by refractory-castables technology has certain advantages over conventional pressing. Refractory castables generally undergo little shrinkage during manufacture of the product, and this is especially true of large products. Since refractory castables are easily cast in complex molds, the restrictions on the shape of the finished product are negligible [9, 10]. Several studies have been made of the production and properties of cordierite-mullite refractory castables. Hipedinger, et al. [11, 12] developed cold-setting cordierite-mullite refractory castables with the use of magnesium phosphates as the binder. Chen, et al. [13 – 15] made several studies of the physical properties of cordierite castables — properties such as thermal shock resistance and hot modulus of rupture (HMOR). However, there have not been any comprehensive studies of the phase evolution and microstructural development of cordierite-mullite refractory castables with a hydraulic binder.

The results obtained in previous studies of the microstructure and properties of conventionally made cordierite ceramics with a mullite binder were included in our investigation [16]. The goal of the study being discussed in this article was to examine the physical and mechanical properties and microstructural changes of andalusite-based low-cement cordierite-mullite castables and the phase changes they undergo after sintering at different temperatures.

EXPERIMENTAL PART

First we synthesized cordierite powder by mixing talc, kaolin, and alumina. The mixture was then subjected to hydraulic pressing at a pressure of 40 MPa in a cylindrical die.

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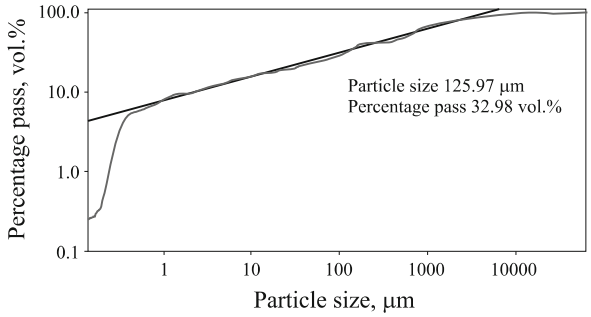

Fig. 1. Cumulative particle-size distribution in low-cement cordierite-mullite castables; straight line — Andreassen model with a distribution coefficient q equal to 0.30.

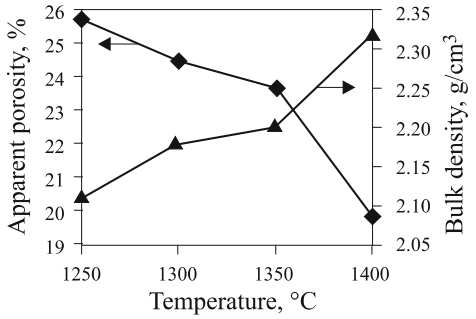

Fig. 2. Fluctuations of the values for bulk density and apparent porosity of samples of low-cement cordierite-mullite castables after sintering at different temperatures.

This was followed by sintering at 1450°C for 5 h. The technology just described ensured the production of a high-density aggregates characterized by low water absorption during the casting operation. The formation of the cordierite was studied by means of x-ray diffraction.

The synthesized cordierite aggregate was subsequently crushed and screened to a particle size of 0.5 – 5.0 mm. The fractions were mixed with specified amounts of andalusite (<1 mm), Kerphalite, calcium aluminate refractory cement, microsilica, and calcined alumina. Table 1 shows the chemical and granulometric compositions of the raw materials. The castable was formulated in accordance with the Andreassen model (Fig. 1). Proceeding on the basis of this model, the CPFT parameter (cumulative percentage finer than a certain particle size), expressed as vol. %, was calculated from the equation

$$CPFT = d/D \quad (1)$$

where d is particle size and D is the maximum diameter of the particles.

The dry mixture was mixed for 4 min before the addition of 13 vol.% water and mixing for an additional 4 min. Flow measurements were made with the use of a flow cone in accordance with the standard ASTM C230. The samples were cast into steel molds with dimensions of 40 × 40 × 160 mm in accordance with the standard ASTM C862 and cured in the molds for 24 h before being dried at 110°C. Different sintering temperatures — 1250, 1300, 1350, and 1400°C — were chosen in order to assess the change in microstructure during the heat treatment. The samples were sintered in an electric furnace at a rate of 300°C/h and held at the maximum temperature for 3 h.

The density and porosity of the sintered samples were determined by the liquid immersion method, while cold compressive strength was determined in accordance with the standard ASTM C348. X-ray diffraction was used to evaluate the mullite phase in the matrix of the samples after sintering at different temperatures. The polished fracture surfaces of the samples that had been sintered at 1300 and 1400°C were studied on a scanning electron microscope (SEM VEGA TESCAN) equipped with an energy-dispersive spectrometer (EDS). Thermal shock resistance was determined by using a NETZSCH 402EP dilatometer to measure the CLTE of the samples sintered at 1300 and 1400°C.

RESULTS AND DISCUSSION

Figure 2 shows the bulk density and apparent porosity of the samples after drying and sintering at different temperatures. Due to the high sintering temperature and the stimulation of this process, the samples sintered at 1400°C exhibited the highest density and lowest porosity. They also had the

TABLE 1. Characteristics of the Raw Materials

Raw material	Chemical composition, wt.%							Particle size, mm
	$Na_2O + K_2O$	Fe_2O_3	TiO_2	MgO	CaO	Al_2O_3	SiO_2	
Cordierite	0.7	0.63	0.2	12.9	0.4	33.5	49.6	0.5 – 5.0
Andalusite	0.26	0.68	0.14	0.15	0.16	61.15	37.44	<1
Calcined alumina	0.06	0.03	—	—	0.02	99.8	0.05	F. p.*
Microsilica	1.3	0.78	—	0.97	0.49	1.32	93.6	Ditto
Cement Secar 71	0.5	0.2	0.4	0.5	28 – 29	69 – 70	0.4	Ditto

* F. p. — finely dispersed powder.

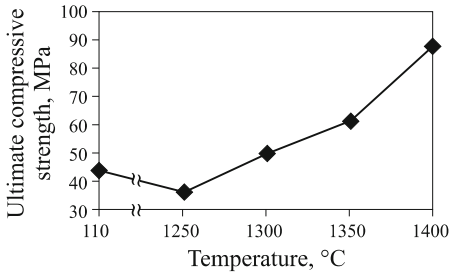

Fig. 3. Fluctuations of the values for the ultimate compressive strength of samples of low-cement cordierite-mullite castables after sintering at different temperatures.

highest ultimate compressive strength (Fig. 3), which was due to the large amount of mullite formed at this temperature. Comparison of these results and the results obtained for samples made by the usual method [16] shows that the cast samples were more than twice as strong as samples obtained by pressing.

Figure 4 shows the diffraction pattern of samples of the low-cement cordierite-mullite castables after sintering at different temperatures. Cordierite, mullite, andalusite, and anorthite were the main phases in the sintered samples. The amounts of these phases that were present varied in relation to the sintering temperature, as is apparent from the changes in the intensities of the peaks. A quantitative phase analysis performed on the D&ADVANCE x-ray diffractometer made by the "Bruker" company in Germany (tubular copper anode, wavelength 0.5406 nm, Cu *K*α-radiation, Ni filter) made it possible to determine the content of each crystalline phase in the samples. The results are shown in Table 2. It can be seen that the amount of mullite phase increased as a function of sintering temperature while the contents of the other phases decreased. The formation of a large amount of the mullite phase at the highest sintering temperature (~49% at 1400°C) ensured the formation of excellent thermomechanical properties for the samples. It was found that the formation of mullite in refractory castables depends on several factors [13]. A liquid phase was formed between 1200 and 1300°C as a result of a reaction between the cement and microsilica.

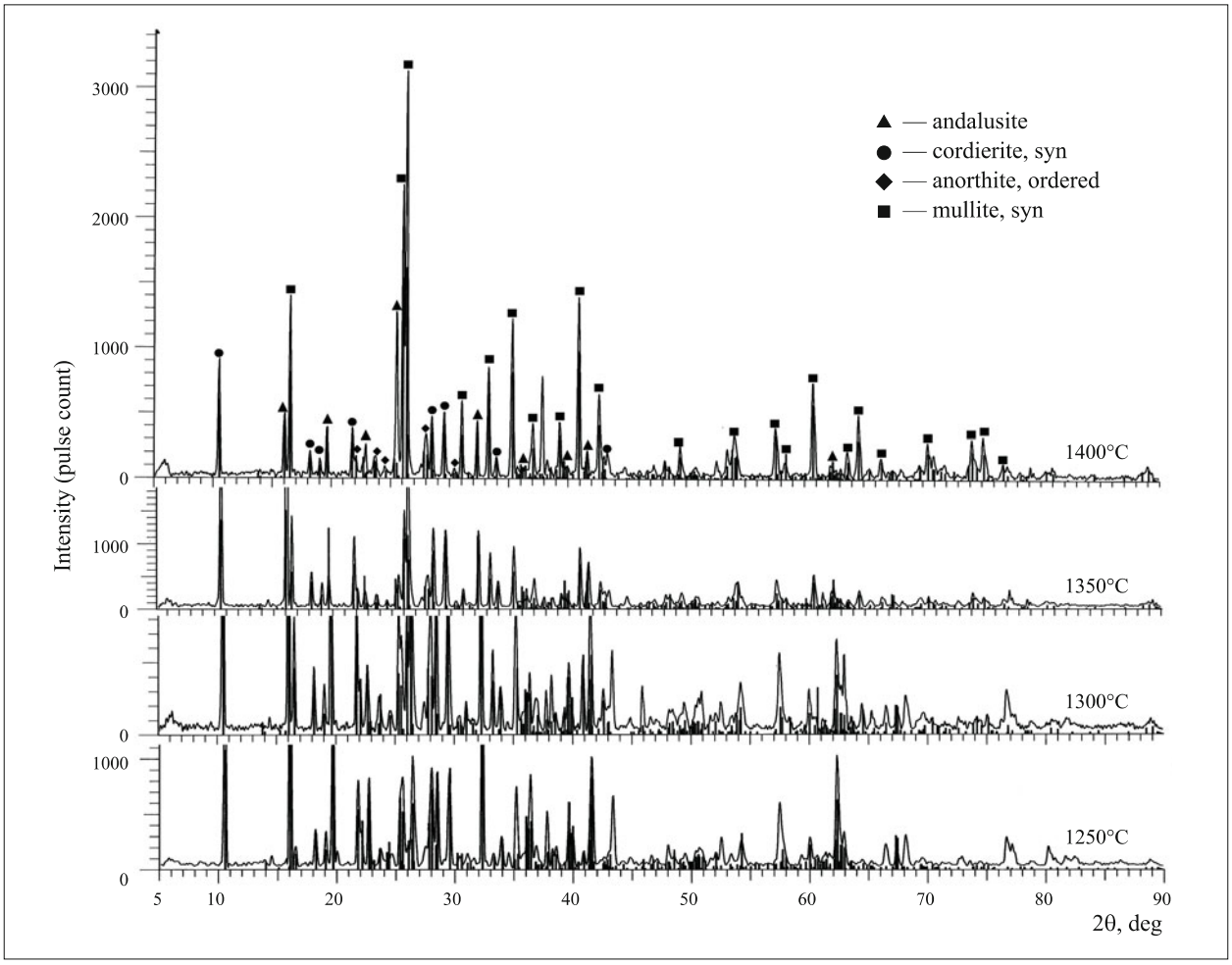

Fig. 4. Diffraction pattern of samples of low-cement cordierite-mullite castable after sintering at different temperatures (the temperatures are shown next to the curves).

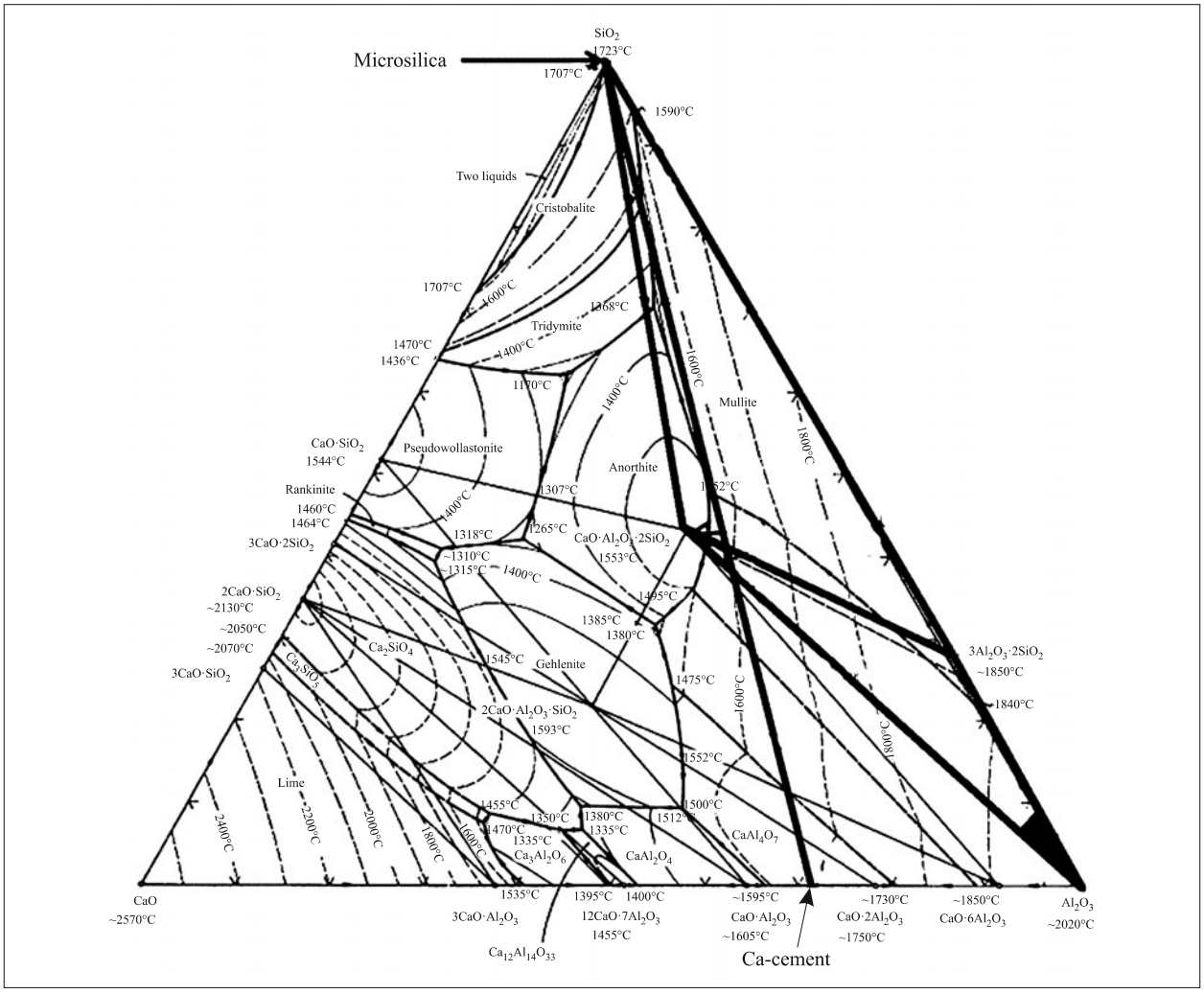

Fig. 5. Phase diagram of the ternary system Al_2O_3–SiO_2–CaO [5].

The strength of the material was relatively low in this case; roughly 10% of the samples consisted of a glassy liquid phase. However, mullite was subsequently precipitated from the liquid and strengthened the matrix, which ultimately led to a reduction in the amount of liquid phase in the samples. Furthermore, a certain amount of silica diffused into the solution together with fluxing oxides and helped form other silica-bearing phases that were similar to anorthite. The amount of the anorthite phase formed at 1400°C shows that the quantity of this phase in low-cement mullite-cordierite castables can be reduced to a minimum. Thus, the physical and mechanical properties of the material can be improved by the formation of a large amount of mullite. On the other hand, heating of the samples converts about 80% of the andalusite phase to mullite, while the other 20% forms a glassy phase rich in silica [14, 15].

The grains of the mullitized andalusite have a specific microstructure. The grains retain their original form and chemical composition, but single crystals of andalusite are converted to a structure composed of single crystals of mullite and a capillary network filled with a glassy phase [13].

A more complete analysis of the results was performed by examining the ternary phase diagram of Al_2O_3–SiO_2–CaO. Figure 5 shows the ternary diagram with the additives studied in this investigation. When a mullite binder is formed in refractory castables, it is extremely important that the mullite

TABLE 2. Results of Quantitative Phase Analysis of Samples of Low-Cement Cordierite-Mullite Castable

Phase	Mass content of phase at the temperature, °C			
	1250	1300	1350	1400
Cordierite $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	42.8	41.5	40.1	32.3
Mullite $3Al_2O_3{\cdot}2SiO_2$	9.0	21.1	28.9	48.7
Andalusite $Al_2O_3{\cdot}SiO_2$	32.1	26.8	23.4	12.1
Anorthite $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	16.1	10.6	7.6	6.9

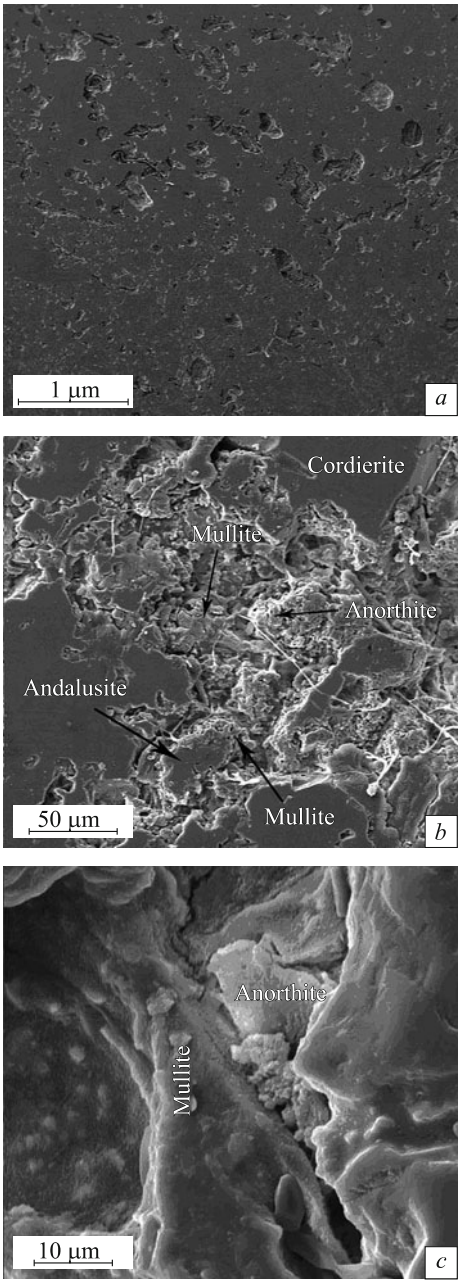

Fig. 6. SEM micrograph of the polished surface of samples sintered at 1400°C: *a*) ×40; *b*) ×600; *c*) ×4000.

phase be stable [14]. This means that the compositions of the castable and the binding phase must be located in one of the two compatibility triangles in Fig. 5, the corundum-anorthite-mullite triangle or the mullite-anorthite-silica triangle. The mullite phase is unstable if the composition is outside these triangles, and in this case even if a mullite phase is formed it will dissolve over time. Taking the CaO content of the castable into account, we calculated the composition of the matrix of samples that were inside the corundum-anorthite-mullite triangle of the phase diagram and thus had a stable mullite phase. It is apparent from Table 2 that there was a

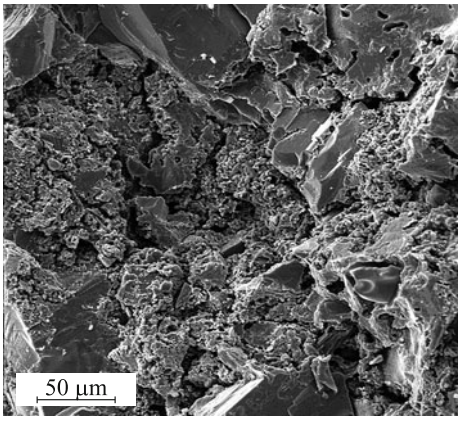

Fig. 7. SEM micrograph of the fracture surface of samples sintered at 1300°C, ×500.

certain amount (~12%) of untransformed andalusite in the samples sintered at 1400°C, i.e. the soaking time for the samples during the sintering operation should be lengthened in order to convert all of the andalusite to mullite.

Figure 6*a* shows a low-magnification SEM micrograph obtained for a sample that underwent sintering at 1400°C. The high sintering temperature in this case helped form a structure which was uniform enough so that it was difficult to identify cordierite grains and the mullite phase without the use of energy-dispersive x-ray spectroscopy (EDS). The uniformity of the structure accounts for the high mechanical strength of the samples in this case. Figure 6*b* shows the SEM micrograph obtained at high magnification for the sample sintered at 1400°C. The microstructure includes cordierite grains and a matrix composed of the phases mullite, andalusite, and anorthite. This microstructure can be obtained by using the fracture surface instead of a polished surface. The mullite binder is readily seen in Fig. 6*c* at an even higher magnification, although a certain amount of the anorthite phase is also present. Figure 7 shows the SEM micrograph of the fracture surface of samples sintered at 1300°C. The surface includes different phases.

Measurements of the CLTE of samples sintered at 1300 and 1400°C yielded values of 3.72×10^{-6} and 4.40×10^{-6} 1/K within the range 25 – 600°C. Compared to the CLTE values for cordierite and mullite — equal to 1.7×10^{-6} and 5.3×10^{-6} 1/K, respectively — the cordierite-mullite samples have a relatively low CLTE. This ensures that the products will have excellent resistance to thermal shock during service.

CONCLUSION

Cordierite aggregates were synthesized for use in making low-cement cordierite-mullite refractory castables based on andalusite. The low-cement cordierite-mullite castable developed as part of this investigation has properties superior

to those of conventional castables and can be used to make kiln furniture. The optimum temperature for sintering the material was determined to be 1400°C, which ensures that the product will have good physical and mechanical properties. However, the soak performed during the sintering operation should be lengthened to minimize the amount of residual untransformed andalusite. The amount of anorthite will also be minimized in the preparation of samples based on the low-cement castable, which will improve the product's physical and mechanical properties by forming a larger amount of the mullite phase. The mullite-bonded cordierite-based material has a CLTE of 3.72×10^{-6} 1/K after sintering at 1400°C, which gives products made from this material excellent thermal shock resistance. In addition, studies performed by scanning electron microscopy showed that the structure includes a matrix composed of mullite, andalusite, and anorthite together with cordierite grains. This dense-sintered structure ensures that the finished products will have excellent physical and thermomechanical properties.

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