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## THERMOREACTIVE COMPACTION OF AN ALUMINA - POLYMETHYLSILOXANE COMPOSITION

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The ceramics used in conditions of sharp temperature fluctuations and exposure to the action of corrosive media must meet stringent requirements with respect to density, strength, and thermal-shock resistance.

These properties of ceramic products can be improved by the addition of an organosilicon binder to the starting material followed by forming the product by thermoreactive compaction.

The production of high-temperature organosilicon-bonded ceramic compositions is based on a chemical reaction which is influenced by the conditions of compaction and firing. The literature contains only limited information about organosilicon binding materials [1-3].\* Organosilicon polymers are used in combination with alumina for the production of ceramics with a stable structure and good mechanical, electrical, etc. properties [4, p. 243]. The polymer is added by mixing it mechanically with the refractory filler. The mix is subjected to a preliminary heat treatment at 800-900°C without a load.

The present authors investigated the thermoreactive compaction of  $Al_2O_3$  with an added organosilicon binder over a broad range of temperatures and pressures. The refractory filler was corundum produced by firing commercial alumina (GOST 6912 - 74) of grain-size fraction finer than  $60 \mu$  containing 99%  $Al_2O_3$  at 1400°C. The binder was an organosilicon polymer, viz., polymethylsiloxane (PMS), with the general formula  $R(SiO_{1.5})_p$ , where R is  $CH_3$  and R/Si is 1.0-1.6.

The choice fell on PMS because of its high heat resistance, which is due to the formation of oxygen bonds between the siloxane chains of the molecules and the complex polymeric structure of the silica  $(SiO)_p$ . At a high temperature, chemical centers form around the Si atoms which can react with the active centers of the refractory filler. Besides, PMS contains less carbon than other organosilicon polymers so that the porosity and carbonization of the product during the heat treatment are minimized; the complete oxidation of PMS gives silica.

Compositions were prepared of corundum with 10, 15, 20, 30, and 40% PMS after which specimens measuring  $40 \times 40 \times 5$  mm were formed from them at pressures of 300-600 kgf/cm<sup>2</sup> in a steel mold heated with Nichrome heaters (Fig. 1). The heating time to the compaction temperature (150-250°C) on the experimental apparatus was 30 min and the holding time 15 min in all cases.

The variation of the bending strength of the specimens with the compaction temperature is shown in Fig. 2. The maximum bending strength can be seen to shift into the region of lower compaction temperatures with an increase in the PMS content. An increase in the compaction pressure from 300 to 600 kgf/cm<sup>2</sup> results in a lower bending strength regardless of the PMS content of the specimen (Fig. 3) so that subsequently the specimens were compacted at a pressure of 300 kgf/cm<sup>2</sup> in order to bring to light the best indices. An investigation of the variation of the open porosity and cold-crushing strength of the specimens vs their composition and the compaction temperature (Figs. 4 and 5) showed that the open porosity was lowest (0.8%) and the cold-crushing strength highest (1070 kgf/cm<sup>2</sup>) for the specimens with 20% PMS compacted at 190°C.

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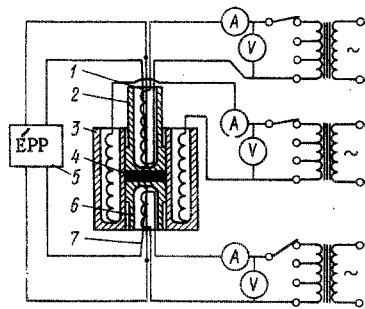


Fig. 1

Fig. 1. Apparatus for the thermoreactive compaction: 1, 7) Chromel — Alumel thermocouples; 2) top ram; 3) die; 4) specimen; 5) electronic potentiometer; 6) bottom ram.

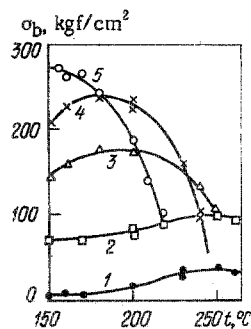


Fig. 2

Fig. 2. Bending strength  $\sigma_b$  of the specimens vs the compaction temperature  $t$ . The specimens contained 10% (1), 15% (2), 20% (3), 30% (4), and 40% (5) PMS. The compaction pressure was 300 kgf/cm<sup>2</sup>.

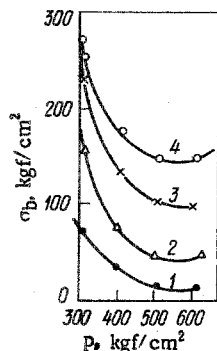


Fig. 3

Fig. 3. Bending strength  $\sigma_b$  of the specimens vs the compaction pressure  $p$ . The specimens contained 10 and 15% (1), 20% (2), 30% (3), and 40% (4) PMS. The compaction temperature was 190°C.

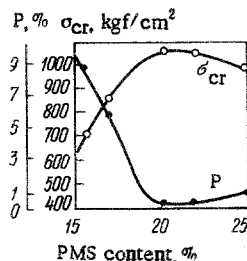


Fig. 4

Fig. 4. PMS content as a factor in the open porosity  $P$  and cold-crushing strength  $\sigma_{cr}$  of the specimens. The compaction temperature was 190°C and the pressure 300 kgf/cm<sup>2</sup>.

A deviation of the compaction temperature from the optimum resulted in an increase in the porosity of the specimen. It follows that the PMS content of the mix determines the compaction temperature (see Fig. 2) which will give specimens of optimal strength and density.

Moreover, the compaction temperature and pressure also influence the rate and degree of the setting of the polymer. A higher temperature results in a more rapid formation of a dense and firm structure but a temperature above the optimum weakens the structure. An increase in the compaction pressure increases the residual microstresses in the specimen and the rate of the decomposition of the organic component at the compaction temperature owing to the catalytic effect of the compaction pressure on the degradation processes, the natural consequence being a decrease in the strength of the specimen. For example, specimens with 20% PMS compacted at a pressure of 500 kgf/cm<sup>2</sup> were found to contain overpressure cracks oriented perpendicularly to the direction of the compaction pressure which subsequently caused the destruction of the specimens in the firing process.

The high strength and low open porosity of specimens produced in optimal compaction conditions enables them to be used without further heat treatment.

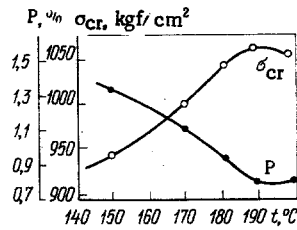


Fig. 5

Fig. 5. Compaction temperature  $t$  as a factor in the cold-crushing strength  $\sigma_{cr}$  and open porosity  $P$  of specimens with 20% PMS. The compaction pressure was 300 kgf/cm<sup>2</sup>.

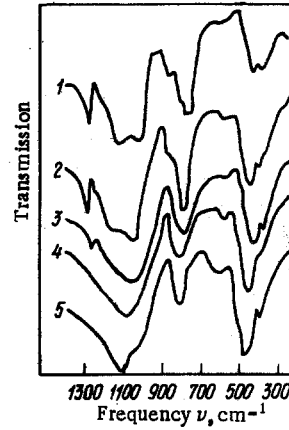


Fig. 6

Fig. 6. IR spectra of PMS heated at 3.3 deg C/min to 200°C (1), 500°C (2), 600°C (3), 700°C (4), and 900°C (5).

The processes developing during the heat treatment of compacted specimens of the Al<sub>2</sub>O<sub>3</sub> – PMS compositions were investigated from their IR absorption spectra and the results of differential-thermal and x-ray phase analyses. Heating produces structural changes in PMS, i.e., the methyl groups break away from the silicon atom as demonstrated by the decrease in the intensity of the absorption band at 1270 cm<sup>-1</sup> which characterizes the valence fluctuation of the Si – CH<sub>3</sub> bonds (Fig. 6). The results of an ultimate analysis showed that the rate at which the methyl groups break away and are destroyed is highest up to 600°C (Table 1).

A comparison of the results of a differential-thermal analysis of the compositions and the PMS (Fig. 7) showed that in the presence of corundum the onset of the thermooxidative degradation of PMS (355-440°C) is shifted by 80-100°C towards higher temperatures. At 500°C the IR spectrum contains absorption bands at 550-700 cm<sup>-1</sup>, which are connected with the deformational vibration of the Si – O bonds and the intensity of which increases with the compaction temperature (see Fig. 6). The end product of the thermooxidative degradation of PMS consists predominantly of cristobalite.

The x-ray phase analyses showed that at 1300°C the Al<sub>2</sub>O<sub>3</sub> interacts with the cristobalite until mullite is formed. A specimen fired at 1500°C consists of α-Al<sub>2</sub>O<sub>3</sub> and small amounts of γ-Al<sub>2</sub>O<sub>3</sub>, mullite, cristobalite,

TABLE 1. Carbon and Hydrogen Content of PMS vs the Heat Treatment Temperature

Element	Proportion, %, of element vs heat-treatment temperature, °C								
	200	300	400	600	700	800	900	1000	1100
C	17,84	14,69	8,09	7,29	6,98	5,50	3,69	Traces	
H	5,68	5,33	4,09	2,49	2,17	1,34	0,87	0,72	—

TABLE 2. Some Properties of the Specimens vs the Firing Temperature

Properties	Indices of properties of specimens fired at temp., °C								
	of								
	700	1100	1200	1300	1400	1500	1600	1700	
Open porosity, %	6-8	12-14	12-14	10-11	10-11	4-6	2-4	2	
Linear shrinkage, %	0,6	0,6	0,6	1,0	1,2	1,6	1,7	2,0	
Cold-crushing strength $\sigma_{cr} \cdot 10^{-2}$ , kgf/cm <sup>2</sup>	10-13	13-14	13-14	13-18	15-20	17-20	25-40	35-50	

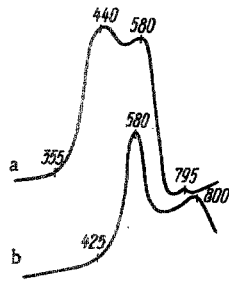


Fig. 7

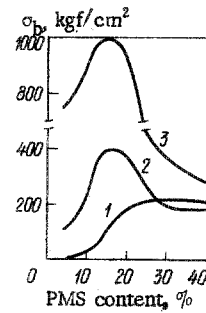


Fig. 8

Fig. 7. Results of a differential-thermal analysis of PMS (a) and of a specimen containing 20% PMS (b). The temperature, °C, is stated against the curves.

Fig. 8. PMS content as a factor in the bending strength  $\sigma_b$  of specimens heat-treated at 190°C (1), 1400°C (2), and 1700°C (3).

and glass phase. The proportion of mullite, cristobalite, and glass phase increases with the PMS content.

The total content of  $\text{SiO}_2$  is lower in a heat-treated than in an unfired specimen. For example, a specimen with 20% PMS contains 18%  $\text{SiO}_2$  before firing and 17% after firing. The decrease in the  $\text{SiO}_2$  content is evidently attributable to the volatilization of  $\text{SiO}_{1-x}$  during the rupture of the Si—O—Si bonds. This assumption is supported by the results of the ultimate analysis.

Some of the properties of specimens with 20% PMS heat-treated at various temperatures are given in Table 2 and Fig. 8.

The thermal-shock resistance was determined by heating specimens measuring  $40 \times 5 \times 5$  mm and containing 20% PMS to 1300°C followed by cooling in running water. The thermal-shock resistance was 64 reversals for specimens fired at 1400°C and 14–20 reversals for specimens fired at 1700°C.

Bricks measuring  $200 \times 105 \times 25$  mm were produced by the above technology from a composition containing 20% PMS. The bricks were formed at a pressure of 300 kgf/cm<sup>2</sup> and a temperature of 190°C with a holding time of 30 min and then fired for 8 h at 1700°C. The linear shrinkage of the finished bricks was 1.8% and the thermal-shock resistance six to eight reversals.

## CONCLUSIONS

An investigation was carried out of the thermoreactive compaction of a composition of alumina with polymethylsiloxane, the technological parameters being varied. Before a heat treatment the open porosity of specimens containing 20% PMS is 0.8%, the bending strength 260 kgf/cm<sup>2</sup>, and the cold-crushing strength 1070 kgf/cm<sup>2</sup>.

Firing at 1700°C gave a high-alumina composition ceramic with an open porosity of 2%, a bending strength of 1000 kgf/cm<sup>2</sup>, a cold-crushing strength up to 5000 kgf/cm<sup>2</sup>, and a thermal-shock resistance of 14–20 reversals from 1300°C into water (in tests with specimens).

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