

## STRUCTURE AND PHYSICOMECHANICAL PROPERTIES OF POROUS CERAMIC BASED ON $\text{Al}_2\text{O}_3$ PREPARED USING A FILTRATION COMBUSTION METHOD

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A technological approach is proposed making it possible to prepare highly porous ceramic based on  $\text{Al}_2\text{O}_3$  using a method of filtration combustion (FC). The method is based on an exothermic oxidation reaction (in an FC regime) of aluminum powder PAP-2 particles mixed with spherulites of commercial alumina (type 1 material) or kaolin fibers (type 2 material). Depending on the volume fraction of PAP-2 open porosity for sintered type 1 material is from 38 to 50%, and ultimate strength in bending is from 10 to 50 MPa. Good material thermal shock resistance, evaluated from the relative loss of crack resistance after thermal cycling by a regime of heating to 850°C and cooling in an air stream (18°C), comprises 12 – 15% and is unchanged after five successive thermal cycles. Material of type 2 is an ultra-lightweight heat insulator with density of 0.25 – 0.50 g/cm<sup>3</sup>. The bearing strength is 0.10 – 0.15 MPa, and thermal conductivity in the range 20 to 1000°C is 0.06 – 0.17 W/(m·K).

**Keywords:** porous aluminum oxide ceramic, self-propagating high-temperature syntheses (SHS), filtration combustion (FC) method, powder workpiece (PW), ultra-lightweight heat insulation.

### INTRODUCTION

Porous ceramic materials based on  $\text{Al}_2\text{O}_3$  are used extensively in high-temperature engineering, for example as thermally stable structural elements, heat insulation, and gas and liquid media filters [1 – 4]. Creation of a pore space in material may be achieved by normal methods, for example use of additions that burn-off, implementation of a foam method, and also due to forming objects from fibers or hollow spherical particles, i.e., micro-balloons [5].

The possibility has been demonstrated in [6] of creating significant porosity in aluminum oxide material as a result of using the effect of zonal compaction during powder workpiece (PW) sintering consisting of particles of a nanosize range. In addition, in order to prepare porous refractory materials and heat insulation new technology has been developed combining cold swelling and self-propaga-

tion high-temperature synthesis (SHS), providing so-called “thermochemical synthesis”, and sintering of the phases formed due to the heat of exothermic reactions [7]. A method is also well known of reaction sintering in a filtration combustion (FC) regime in air of aluminum-magnesium alloy for preparing MgO–Al cermet [8], making it possible to prep[are highly porous objects. This technological approach may be considered as a variety of the SHS method in which combustion of a PW is achieved as a result of surrounding its surface with hot (550 – 600°C) air carrier within the volume of a furnace space. In this case FC is supported as a result of a drop in air oxygen partial pressure, contained within a system of communicating PW pores and flowing round a PW. In this case pumping (filtration) of air is realized within the volume of a workpiece. It should be noted that within the material a significant proportion of unoxidized aluminum is retained due to the protective action of dense aluminum oxide films at its surface.

Features of the structure and physicomechanical properties of porous ceramic based on  $\text{Al}_2\text{O}_3$  prepared using the FC method were studied within the scope of the present work.

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## EXPERIMENTAL PROCEDURE AND RESEARCH

The starting materials used were commercial alumina powder grade G-00 (GOST 30558) whose particles have a spherulitic structure and also kaolin fibers (GOST 23619), and aluminum powder grade PAP-2 (GOST 5494) with a flaky shape of particles of sub-micron thickness. Previously spherulites of commercial alumina were heat treated in air for 1 h in order to complete modification transition  $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ , accompanied by a reduction in volume by about 14%.

In order to prepare specimens aluminum powder in an amount of 37 – 70 vol.% was mixed with spherulites and the mixture obtained was compacted under a pressure of 200 MPa (PW type 1). Also from kaolin fibers an aqueous suspension was prepared within which with continuous mixing aluminum powder was added (10 – 30 vol.%). Then water was extracted from the mixture obtained by vacuum filtration and the workpiece obtained was dried in air (PW type 2). Both PW types were heated in air to 500 – 550°C with which the FC process was initiated. After its completion heating continued to 1500°C with subsequent isothermal exposure for 1 h providing total oxidation of the metal component. In this case two types of sintered materials were prepared containing spherulites (type 1) and kaolin fibers (type 2).

Material of type 1 was tested for thermal shock resistance, and the value of relative loss of notched specimen crack resistance was evaluated after the action of thermal stresses [9], using a device for local thermal shock [10]. In this case thermal stresses at a notch tip were created by thermal cycling by a regime of heating in air at 850°C, and air stream cooling (18°C). The relative loss of crack resistance was calculated by an by a formula  $(1 - K_{1c}^T/K_{1c}) \cdot 100\%$ , where  $K_{1c}$  and  $K_{1c}^T$  are values of critical stress intensity factor for specimens before and after thermal cycling respectively. Ultimate strength in bending was determined in prismatic specimens with a size of 8 × 8 × 50 mm, using a three-point loading scheme with a deformation rate of 1 mm/min. For type 2 material the collapsing stress was determined in compression for cylindrical specimens 20 mm in diameter and 50 mm long with a deformation rate of 0.1 mm/min. In addition, the index of effective thermal conductivity in the range 20 to 1000°C was determined by a hot wire method under conditions of steady state heat flow using a measuring bridge (ISO 8894-1).

The material phase composition was studied using x-ray phase analysis (XPA) in a DRON-3 unit (Cu K<sub>α</sub> radiation) by a standard procedure, and the structure was studied in a Hitachi-F405A electron microscope from a specimen fracture surface obtained after mechanical tests. The density  $\rho$  of sintered specimens was calculated as the ratio of their weight to volume. Overall porosity was calculated from a relationship  $(1 - \rho/\gamma) \cdot 100\%$ , where  $\gamma = 3.99 \text{ g/cm}^3$ . Open porosity was determined by hydrostatic weighing.

## DISCUSSION OF RESULTS

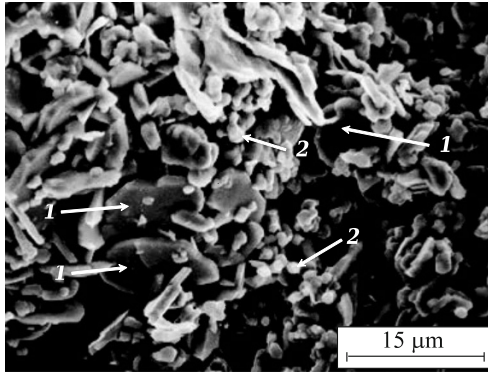
Porous ceramic materials were prepared by the FC method. It duration for specimens of material type 1 was 7 – 10 min, and for materials of type 2 it was 3 – 5 min. in the first case maximum brightness temperature was 1200°C, and in the second it was 1500°C.

In the initial stage of the FC process there is synthesis of Al<sub>2</sub>O<sub>3</sub>-phase as a result of exothermic reaction in the system melt (a) – gas (O<sub>2</sub>) as a result of oxygen diffusion through aluminum oxide surface films of flaky particles towards aluminum melt. The strength of these films is sufficient in order to maintain overheated aluminum melt at the FC temperature. Completion of specimen FC is apparently connected with formation of a dense network of nanosize aluminum oxide crystals at the surface of aluminum flaky particles, which it passivates, making them inactive and impermeable for the gaseous oxidizing agent, i.e., air oxygen. In this case aluminum flakes appear within dense aluminum oxide capsules.

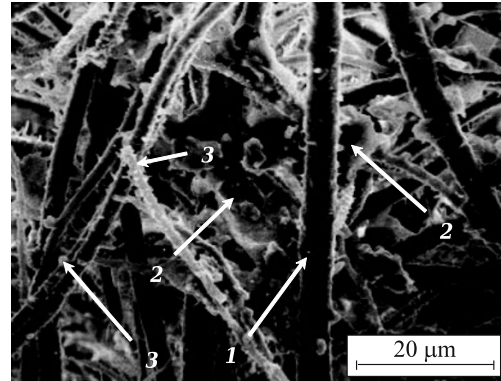
As is seen from XPA results (Table 1), it was only possible to provide total aluminum oxidation within the composition of type 1 material after additional heat treatment in air (for completion of FC) at 1500°C for 1 h. Under these conditions the diffusion activity of atomic oxygen becomes adequate for penetration through aluminum oxide capsules of flaky particles and total metal oxidation. Lamellar aluminum oxide particles ( $\alpha\text{-Al}_2\text{O}_3$ ) are shown in Fig. 1 within the structure of the material obtained, which inherits the shape of the original flaky particles of PAP-2 powder. The material with significant porosity ( $\Pi_{\text{open}} = 38 - 50\%$ ) has quite good strength ( $\sigma_{\text{ben}} = 10 - 50 \text{ MPa}$ ), which increases with an increase in volume fraction ( $V$ , %) of aluminum powder in the original mixture with spherulites (Table 2). This feature is explained by the reinforcing action of lamellar aluminum oxide particles forming a continuous framework, receiving the applied load. In this case a significant loss of crack resistance is observed after thermal shock due to rapid elimination of a temperature gradient within structural elements having micron cross section. It should be noted that the index for loss of crack resistance for material type 1 does not change after five successive thermal cycles, whereas for dense aluminum oxide material (No. 4, see Table 2) a marked reduction was observed in crack resistance after repeated thermal cycling as

**TABLE 1.** Phase Composition of Type 1 Material ( $V = 70 \text{ vol.}\%$ ) in Relation to Heat Treatment Regime in Air

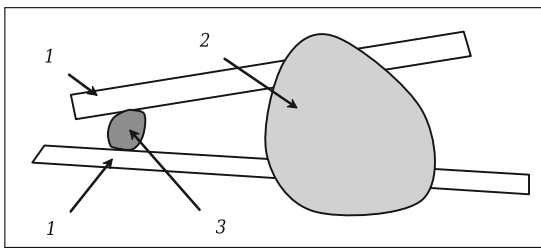
Heat treatment regime	Crystalline phase content, vol.%	Amorphous phase content, vol.%				
		Al	$\gamma\text{-Al}_2\text{O}_3$	$\theta\text{-Al}_2\text{O}_3$	$\alpha\text{-Al}_2\text{O}_3$	
temperature, °C	time, h					
800	1	50	40	6	—	4
1200	1	4	—	—	96	—
1500	1	—	—	—	100	—



**Fig. 1.** Fracture surface type 1 material: 1) lamellar aluminum oxide particles; 2) aluminum oxide crystals within spherulite composition.



**Fig. 3.** Fracture surface of type 2 material: 1) kaolin fibers; 2) aluminum oxide lamellar particles covering fibers; 3) aluminum oxide droplet-like particles covering fibers.



**Fig. 2.** Schematic image of kaolin fiber bonding within heat insulation specimen: 1) kaolin fibers; 2) lamellar aluminum oxide particle; 3) aluminum oxide droplet-like particle.

**TABLE 2.** Dependence of Material Physicomechanical Properties on Volume Content ( $V$ , %) of Aluminum Powder in Mixture with Kaolin Fibers (Type 2 Material)

Material number	$V$ , vol. %	$\rho$ , g/cm <sup>3</sup>	$\Pi_{open}$ , %	$\sigma_{ben}$ , MPa	$K_{1c}^T / K_{1c}^{rel. un.}$	$(1 - K_{1c}^T / K_{1c}^{rel. un.}) \cdot 100$ , %
1	30	1.9	50	10 – 20	0.7 / 0.8	12.5
2	50	2.1	42	22 – 28	1.3 / 1.5	14.0
3	70	2.3	38	30 – 50	1.7 / 2.0	15.0
4*	—	3.8	0	250 – 300	1.5 / 4.0	62.5

\* Dense Al<sub>2</sub>O<sub>3</sub> ceramic sintered from micropowder (Al<sub>2</sub>O<sub>3</sub> + 0.5% MgO) in air (1700°C, 1 h). Given for comparison.

**TABLE 3.** Dependence of Material Physicomechanical Properties on Volume Fraction of Aluminum Powder in Mixture with Spherulites (Type 1 Material)

Material number	$V$ , vol. %	$\rho$ , g/cm <sup>3</sup>	$\Pi_{open}$ , %	$\sigma_{ben}$ , MPa
1	10	0.25	93	0.10
2	20	0.40	90	0.12
3	30	0.50	88	0.15

a result of the action of thermal stresses leading to formation of macrocracks within the structure.

Material of type 2 with density of 0.25 – 0.50 g/cm<sup>3</sup> is classified as ultra-light weight heat insulation (Table 3). Stresses corresponding to the initial instant of collapse increase with an increase in volume fraction of aluminum powder in a mixture with kaolin fibers. In this case an effect is also observed of structural reinforcement by lamellar aluminum oxide particles (similar to type 1 material). Within the material structure bonding of kaolin fibers is achieved by covering them with aluminum oxide lamellar and droplet shaped particles as a result of sintering over contact areas (Fig. 2). It should be noted that formation of particles 3 (see Fig. 2) occurs in the FC stage: agglomerates of nanoparticles of dusty fraction, contained in powder type PAP-2, during heating above the aluminum melting temperature form “sessile” droplets with a typical shape due to limited wetting of the kaolin fiber surface. This mechanism of bonding kaolin fibers within the volume of a specimen is confirmed with consideration of their fracture surface after mechanical tests (Fig. 3).

The ultra-lightweight heat insulation developed is demonstrated by the relatively low thermal conductivity, i.e., 0.06 – 0.17 W/(m·K) in the range from 20 to 1000°C, which may be explained by the screening action of lamellar Al<sub>2</sub>O<sub>3</sub> particles arranged normal with respect to the heat flow. The dependence of thermal conductivity  $\lambda$  for type 2 material ( $V = 20$  vol.%) on temperature  $T$  is given below.

$T$ , °C	20	200	400	600	800	1000
$\lambda$ , W/(m·K)	0.06	0.08	0.09	0.10	0.12	0.17

### CONCLUSION

In order to prepare porous ceramic materials based on Al<sub>2</sub>O<sub>3</sub> an FC method is used for a PW in air in air consisting of a mixture of aluminum powder PAP-2 with spherulites of

commercial alumina (material type 1) and with kaolin fibers (material type 2). After the end of FC specimens are additionally treated in air at 1500°C for 1 h in order to complete aluminum oxidation. In this case from aluminum flaky particles lamellar aluminum oxide ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) particles are synthesized, inheriting the shape of the original aluminum flakes.

It has been established that for type 1 material with variation of the volume fraction of PAP-2 powder from 30 to 70% in a mixture with spherulites the open porosity is reduced from 50 to 38% and ultimate strength in bending increases from 10 – 20 to 30 – 50 MPa. This is connected with the reinforcing action of lamellar aluminum oxide particles that form a continuous framework withstanding an applied load. For type 1 material an insignificant loss of crack resistance (12 – 155) is recorded after thermal cycling by regime of heating at 850°C – air stream cooling at 18°C (this index did not change after five subsequent thermal cycles). This fact is possible due to rapid avoidance of a temperature gradient in structural elements having a micron cross section.

Type 2 material, with density of 0.25 – 0.50 g/cm<sup>3</sup>, is classified as ultra-lightweight heat insulation. Its density increases with an increase in volume fraction of aluminum powder (10 – 30%) in a mixture with kaolin fibers, and the collapsing strength with action of a compressive load is 0.10 – 0.15 MPa. The low thermal conductivity of the heat insulation obtained, i.e., 0.06 – 0.17 W/(m·K) in the range to 1000°C is explained by the screening action of lamellar Al<sub>2</sub>O<sub>3</sub> particles arranged normal with respect to heat flow.

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