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CORUNDUM CERAMICS FOR MEDICAL PURPOSES

E. S. Lukin,¹ S. V. Tarasova,¹ N. A. Popova,¹ and N. A. Makarov¹Translated from *Steklo i Keramika*, No. 1, pp. 29–32, January, 2003.

The possibilities of using various kinds of aluminum oxide materials, modifying additives, and temporary technological binders for making bioinert ceramics based on aluminum oxide are considered. Regimes for heat treatment of intermediate pieces are developed. A ceramic material with a mean density of 4.01 g/cm³, three-point bending strength 380 ± 20 MPa, a size of corundum crystal equal to 4–6 μm, and zero open porosity is obtained, which can be used in endoprostheses caps for coxofemoral joints.

Among biologically inert materials, the most common are ceramics based on aluminum oxide due to their high chemical stability, mechanical strength, hardness, and wear resistance. Such ceramics preserve their biochemical properties during protracted stay in a human organism, which facilitates reaction-free ingrowth and lengthy service and makes them the most promising as bone implants [1].

The purpose of our study is to develop high-density ceramics for medical purposes based on aluminum oxide, namely, to use it as a coxofemoral joint endoprostheses cap.

Despite the fact that various materials have been developed based on Al₂O₃, the main problem in this case is to meet the requirements of standard ISO 6474 imposed on materials for medical purposes (Table 1). This primarily concerns the purity of initial aluminum oxide materials, in which the amount of impurities should be minimal. Consequently, the choice of additives ensuring the control of the microstructure and sintering temperature of corundum ceramics is limited as well.

Among the known modifying additives, only MgO and ZrO₂ satisfy the standard requirements, since after being introduced in minimum quantities they provide for obtaining ceramics with a uniform structure and high physicomachanical parameters. It is established that the best results in microstructure strength, density, and homogeneity were registered not so much due to ZrO₂ additive but due to introducing 1% additive (here and elsewhere wt.% unless otherwise specified) of a eutectic composition of the Al₂O₃–ZrO₂ system. Additives used in the present study were MgO and Al₂O₃–ZrO₂ [2, 3].

As ceramic pieces intended for making endoprostheses caps for coxofemoral joints are large enough, the process of drying and preliminary heat treatment of intermediate pieces to remove the temporary technological binder (TTB) is significant. Therefore, the selection of a TTB is one of essential problems in the technology of producing ceramic endoprostheses caps. Furthermore, the distribution of binder and the rate and temperature interval of its decomposition have a significant effect on microstructure and properties of ceramics.

The most significant stage is firing, in which it is necessary to obtain densely sintered ceramics with a homogeneous microstructure, a minimal possible crystal size, and high physicomachanical parameters.

Thus, the main technological problems include selection of aluminum oxide material satisfying the standard requirements for medical materials with respect to their chemical purity; selection of a TTB allowing for production of a high-quality intermediate piece, and development of temperature conditions for preliminary (air medium) and final (vacuum) heat treatment.

Before the experiments, chemical compositions of various types of aluminum oxide materials were studied by x-ray luminescence analysis: alumina of grade GN-1 and three different batches of grade GLMK designated as 1, 2, and 3, respectively, especially pure Al₂O₃ and aluminum oxide obtained from industrially produced aluminum hydroxide (Al₂O₃-H).

Alumina of various grades were milled for 24 h by wet grinding in a ball mill using corundum balls.

Material Al₂O₃-H was prepared as follows. Aluminum hydroxide was crushed by well milling in a ball mill, to which magnesium salt was added before milling to obtain 0.25% MgO doping in aluminum oxide. DTA data show that

¹ D. I. Mendeleev Russian Chemical Engineering University, Moscow, Russia.

TABLE 1

Parameter	Requirement	
	Class A	Class B
Mean density, g/cm ³	Not less than 3.94	Not less than 3.90
Chemical composition, %:		
Al ₂ O ₃	Not less than 99.50	
MgO	Not more than 0.30	
impurities (R ₂ O + CaO + SiO ₂)	Not more than 0.10	
Microstructure, μm:		
mean crystal size	Not more than 4.5	Not more than 7.0
standard deviation	Not more than 2.6	Not more than 3.5
Mean four-point bending strength, MPa	Not less than 250	Not less than 150

phase transformation of γ -Al₂O₃ to α -Al₂O₃ occurs at a temperature of 1280°C. Therefore, Al(OH)₃ obtained after drying was ground through a No. 05 nylon sieve and then calcined at a temperature of 1350°C with a 3-h exposure at the maximum temperature. After calcination the material was milled in a ball mill and dried.

To prepare a eutectic composition of the Al₂O₃ – ZrO₂ system, AlCl₃ · 6H₂O and ZrOCl₂ · 8H₂O of the “analytically pure” grade were used. The salts were dissolved in distilled water in the required ratio taking into account their calcination losses, and the resulting solution was heated to about 100°C and then sprayed using compressed nitrogen at a pressure of $(1 - 2) \times 10^5$ Pa into a saturated ammonia solution at room temperature (20 – 25°C). The precipitate was transferred into a Buchner funnel and washed with distilled flowing water until pH ≈ 6.0. The filtrate was dried with acetone.

The material was milled by vibration milling in Teflon drums using corundum balls. Before the precipitated powder was milled, yttrium chloride was added to it in order to stabilize 3 mol.% Y₂O₃ formed in firing of zirconium dioxide. The obtained suspension was dried at a temperature of 80 – 100°C and the powder was ground through a No. 05 nylon sieve.

DTA data indicate that synthesis of all phases of the material end at a temperature of 1360°C. Accordingly, the powder was calcined at a temperature of 1400°C with a 3-h exposure. After calcination the material was ground by wet grinding in the same conditions as before calcination. The suspensions were dried at temperatures of 80 – 100°C, and the pow-

der was ground via a No. 05 nylon sieve and used as an additive.

The results of studying the chemical compositions of initial materials using the x-ray luminescence method are shown in Table 2. It can be seen that alumina GN-1 does not satisfy the standard requirement with respect to a content of aluminum oxide, alkaline oxides impurities, and SiO₂. Alumina GLMK of all batches approaches the standard regarding the aluminum oxide content and all batches satisfy the standard requirement of the magnesium oxide content. However, an elevated content of alkaline oxides and SiO₂ is registered in all batches. The material based on industrial aluminum hydroxide contains an increased content of MgO, since a certain quantity of magnesium oxide presumably exists in the initial aluminum hydroxide. Therefore, Al₂O₃-H can be used for other purposes, in particular, for the production of insulating ceramics.

The extra-pure aluminum oxide satisfies the requirements of ISO 6474 in all parameters (a satisfactory content of Al₂O₃ and MgO, alkali metal oxides, and SiO₂).

Based on the chemical analysis results, extra-pure (EP) aluminum oxide and the variety of alumina GLMK containing the least amount of impurities (GLMK-2) were selected for further studies.

TTBs in this study were wax and paraffin preliminarily dissolved in CCl₄, which were introduced into the mixture in the amount of 6%: polyvinyl alcohol (PVA) in the form of 5% aqueous solution that was added in the amount of 20% of the batch weight, and caoutchouc dissolved in benzene. The content of caoutchouc in intermediate pieces was 6%.

TABLE 2

Material	Weight content, %							
	Al ₂ O ₃	SiO ₂	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	ZnO	ZrO ₂
Alumina:								
GN-1	98.92	0.59	0.19	0.09	0.035	0.031	–	–
GLMK-1	99.30	0.23	0.25	0.10	0.035	0.032	0.002	–
GLMK-2	99.35	0.12	0.26	0.10	0.031	0.023	–	0.001
GLMK-3	99.38	0.14	0.27	0.15	0.032	0.024	0.001	0.002
Al ₂ O ₃ -H	99.28	0.10	0.48	0.06	0.036	0.032	0.002	–
Al ₂ O ₃ (EP)	99.76	0.01	0.18	0.02	0.019	–	–	–

TABLE 3

Binder	Density of molded piece, g/cm ³	Mean density, g/cm ³	Open porosity, %	Linear shrinkage, %	Three-point bending strength, MPa
Wax	2.18	2.28	43.2	2.5	35 ± 8
PVA	2.10	2.24	44.1	2.9	25 ± 7
Paraffin	2.27	2.35	41.3	1.9	32 ± 7
Caoutchouc	2.00	2.20	45.0	5.8	30 ± 9

The most dangerous temperature interval for preliminary heat treatment is the one in which chemical destruction of the binder or transformation of its components from a liquid to a gaseous state proceeds at the maximum velocity. Let us name this interval the dangerous temperature interval. We will also conventionally name the velocity of the physicochemical processes occurring within this interval the decomposition rate. The DTA method was used in this study to determine this rate.

Analyzing the DTA results, it should be noted that the maximum decomposition rate in the dangerous interval is registered in caoutchouc: it is 3–5 times higher than that of other binders.

The lowest rate of decomposition in this interval is exhibited by PVA. The decomposition interval for various binders varies over wide limits and constitutes 300–500°C, and complete destruction of all types of TTB ends at 500–600°C. The dangerous temperature interval for wax, PVA, and paraffin starts at 200–250°C and ends at 350–450°C.

Consequently, preliminary heat treatment of samples molded using the specified binders has to include a slow temperature rise up to 600°C. In our case the following regime of preliminary heat treatment of samples was used: heating up to 600°C at a rate of 1 K/min and then heating to a final temperature at a rate of 3 K/min. The exposure at the final temperature was 1 h.

The preliminary heat treatment temperature was selected to ensure, on the one hand, mechanical strength of the intermediate piece subsequent for subsequent technological operations and, on the other hand, to provide for minimum recrystallization and agglomeration of particles in preliminary firing.

The samples were fired at temperatures of 1300–1450°C with an interval of 50°C. The initial materials were composites containing Al₂O₃ (EP) without additives, Al₂O₃ (EP) with 0.25% MgO additive, Al₂O₃ (EP) with additives of 0.25% MgO and 0.30% ZrO₂, as well as alumina GLMK with a eutectic additive of the Al₂O₃–ZrO₂ system. The binder was PVA that has the minimum decomposition rate in the dangerous temperature interval.

The studies show that the minimum size of corundum crystals persists in all types of materials at any firing temperature. However, with increasing pretreatment temperature, agglomeration of particles intensifies, and in all cases ag-

TABLE 4

Initial mixture*	Mean density, g/cm ³	Three-point bending strength, MPa
Al ₂ O ₃ (EP)	3.75	330 ± 18
Al ₂ O ₃ (EP) + 0.25% MgO	3.76	340 ± 22
Al ₂ O ₃ (EP) + 0.25% MgO + 0.3% ZrO ₂	3.91	380 ± 18
GLMK-2 + 1% Al ₂ O ₃ – ZrO ₂	4.01	380 ± 20

* In all cases open porosity was equal to zero.

glomerates reach 6–8 μm. In final heat treatment this will produce local sintering of materials, intense recrystallization and, consequently, a nonuniform granular microstructure. The latter will have an adverse effect on the mechanical strength and density of samples due to the virtually inevitable formation of coarse sealed intracrystalline porosity. Therefore, the optimum temperature for preliminary heat treatment should be taken equal to 1300°C.

To select the optimum binder, the density, ceramic properties, and three-point bending strength of samples molded with different TTB and heat-treated at 1300°C (Table 3) were determined. Besides, samples were studied using a scanning electron microscope to identify the mean pore size, the mean the pore shape factor, the mean surface area of an individual pore, the total surface area of pores in the particular section of the sample, and the total perimeter of pores. The petrography analysis method was used to study the distribution of the binder in molded pieces.

Samples molded using wax, paraffin, and PVA as a TTB have approximately equal pore size and porosity. The optimum distribution of the binder is observed in samples molded with wax and paraffin. Samples molded using caoutchouc have the least homogeneous binder distribution. The latter correlates with data on mean density (see Table 3): the most homogeneous distribution of TTB makes it possible to mold samples with the highest density, which produces the densest ceramics. For instance, a sample molded with introduction of paraffin has the highest density. Similarly, after preliminary treatment, the highest mean density is registered in samples molded with paraffin.

Sample molded using caoutchouc have the minimum density and the lowest density after preliminary heat treatment. These samples have the highest porosity and the largest pore size.

However, all samples have approximately equal mechanical strength, which is sufficient for subsequent technological operations.

Thus, the use of caoutchouc in the considered technological scheme is unacceptable, and its introduction does not ensure the production of articles with high parameters

Despite the fact that PVA has the minimum rate of decomposition in the dangerous temperature interval, the distribution of this binder over the sample volume is unsatisfac-

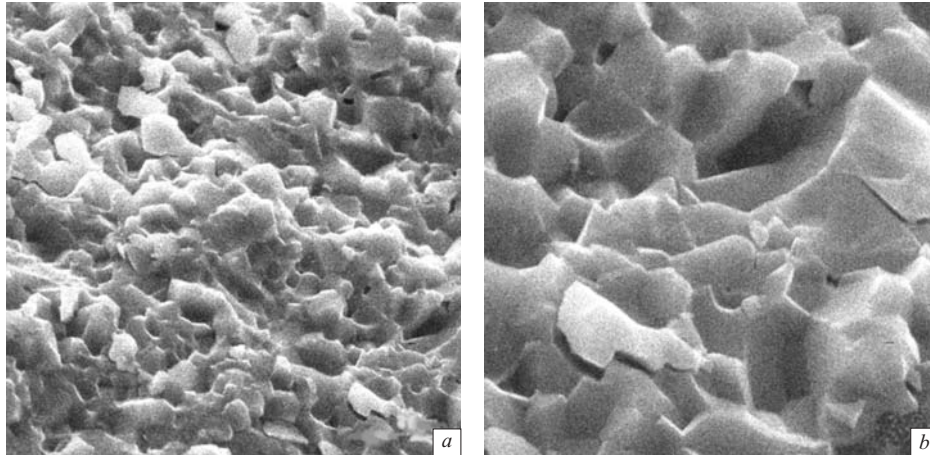


Fig. 1. Electron microscopic photos of corundum ceramic fracture at magnification $\times 2000$ (a) and $\times 5000$ (b).

tory, accordingly, its use as well does not allow for making ceramics with high physicomechanical parameters.

Since samples molded with paraffin have higher density and lower porosity than samples using other binders, this TTB best satisfies the given purposes.

Based on the results of studies, cylindrical samples 40 mm in diameter and 40 mm high were prepared based on especially pure Al_2O_3 and alumina GLMK-2. The TTB was paraffin. After preliminary heat treatment, ceramic samples intended for coxofemoral joint caps were fired in vacuum at a temperature of 1600°C . The ceramic properties and mechanical strength of samples are listed in Table 4. It can be seen that the highest density and strength are registered in ceramics based on alumina GLMK-2. This material is characterized by corundum grains sized $4 - 6 \mu\text{m}$, the size of sealed pores is less than $2 \mu\text{m}$, and the pore content is about 0.5%. According to luminescence chemical analysis, this ceramic contains (%): 99.25 Al_2O_3 , 0.25 MgO , and 0.33 ZrO_2 . The microstructure of obtained ceramics is shown in Fig. 1.

Thus, the performed study established the technological specifics of making bioceramics based on aluminum oxide, which fully satisfies the requirements of ISO 6474 standard imposed on bioinert ceramics. Such ceramics can be used for various implants and, in particular, as caps for coxofemoral joint endoprostheses.

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