A.V. Pavlov^{1,2}, E.E. Aiymkhanov², Zh.B. Sagdoldina¹, A.B. Kassymov³, D.R. Baizhan^{1*}, M.S. Zhaparova¹

¹Sarsen Amanzholov East Kazakhstan University, Ust-Kamenogorsk, Kazakhstan; ²Ceramic plant, Ust-Kamenogorsk, Kazakhstan; ³Shakarim University of Semey, Kazakhstan (*E-mail: daryn.baizhan@mail.ru)

Research of methods for introducing TiO₂ nanoparticles into a micron matrix of BeO and TiO₂ powders and their effect on the rheological properties of a casting slip

This article presents the research results of methods for introducing nanodispersed TiO_2 powders into a micron matrix of beryllium and titanium oxides. It is shown that the presence of nanoparticles over 5.0 wt.% negatively affects the rheological properties of the casting slip and vice versa, the addition of nanoparticles in the range of 0.1-2.0 wt.% contributes to reducing the viscosity and increasing the casting ability of the slipping mass. Macrostructural analysis of the sintered billet indicates the complete absence of structural elements in the form of conglomerates of nanoparticles, or nano- and micro- TiO_2 particles. The developed method of introducing nanoparticles makes it possible to obtain products with their uniform distribution over the entire volume of the workpiece by slip casting under pressure. Further, the authors of the scientific work planned to research the effect of nanoparticles on the thermophysical and impedance characteristics of the obtained ceramics. Research into the effect of nanopawders on the electrophysical properties of beryllium ceramics is not known in the scientific world. The most important properties that the BeO+TiO₂ ceramics should possess is the ability to absorb ultrahigh frequency radiation, while it should heat up a little, i.e., conduct heat well. It is necessary to introduce the TiO₂ phase into the composition of the BeO ceramics as much as possible to obtain a high coefficient.

Keywords: TiO₂ nanoparticles, charge, casting slip, rheological properties, beryllium oxide, ceramics, macrostructure.

Introduction

Currently metals and alloys are increasingly being replaced by ceramic materials that have not only heat resistance and high strength, but also special electrical properties, for example, the ability to absorb electromagnetic radiation, which contributes to their widespread use in electronic engineering [1-2].

It is known that when TiO_2 microparticles are added to the composition of ceramics based on BeO, its dielectric constant and electrical conductivity with appropriate heat treatment in a reducing atmosphere can change significantly [3–4]. The main advantages of absorption (BeO + TiO₂) ceramics include the absence of magnetic properties and decomposing compounds, and the thermodynamic stability of properties in a wide temperature range [5]. It has been established that the addition of TiO₂ impurities to BeO of at least 30 wt % leads to a significant increase in the dielectric constant, and an increase in the degree of TiO₂ reduction is accompanied by an increase in the dielectric loss tangent [6].

Currently the most effective material is the composition BeO+30wt.% TiO₂. Improvement of the performance characteristics of such ceramics can be achieved by introducing TiO₂ nanoparticles into its composition, which will contribute to the expansion of the operating frequency range, increasing the stability of parameters during operation and the impact of external factors, expansion of the nomenclature in the field of special applications [7].

Radiation is absorbed by the entire volume of the particle with a decrease in the size of TiO_2 particles, down to nanoscale values [8].

A smaller crystal size leads to a larger specific surface area and, consequently, to an increase in the number of active centers, bulk and surface defects available for reactions. Reducing reactions proceed more efficiently and changing the electrical and chemical properties. As a result of the quantum size effect, the energy structure changes significantly, leading to optical absorption, photoluminescence, optical nonlinearity and other properties [9].

Thus, the questions of the influence of TiO₂ nanoparticles on the mechanisms of billet formation and the rheological properties of the casting slip of (BeO+TiO₂)-ceramic have not been studied. There is no clear

justification for the effect of TiO_2 nanoparticles on the phase composition and mechanisms of structure formation, structure of such ceramics during sintering [10].

Synthesis and research of nanophase high-temperature ceramics with increased density, thermal conductivity, special structural and electrophysical properties is useful for electronic engineering and instrument making in means of radar, navigation and long-distance communications. Interest in composite ceramics based on beryllium oxide with introduced impurities is caused by the needs of new areas of radio electronic engineering and special instrumentation, the development of modern long-distance communication systems, radar and navigation, and broadband systems for special purposes. Beryllium oxide in the process of sintering composite ceramics gives TiO₂ increased density, mechanical strength and thermal conductivity. Different ratios of TiO₂ components in ceramics and the degree of its reduction make it possible to control the amount of ultrahigh frequency absorption by such ceramics. In connection with the above, the development of a technology for obtaining a new material based on beryllium oxide modified with TiO₂ nanopowders is an important task. The aim of this work is to study the methods of introducing nanodispersed TiO₂ powders into the micron matrix of beryllium and titanium oxides.

Material and methods of research

The measurement of the specific surface area was determined on a device for dispersive analysis of the PSC series, the principle of operation of which is based on the method of gas permeability of Kozeny and Karman [11].

The determination of the bulk density of the researched powders was carried out according to the approved factory methodology based on the determination of the bulk density of a unit volume of free bulk powder. The bulk density of the powder with this measurement method is determined by the formula:

$$\gamma = \frac{P_2 - P_1}{V} \tag{1}$$

where, γ — bulk density of powder, g/cm³; P_2 — powder cylinder weight, g; P_1 — empty cylinder weight, g; ν — calibrated cylinder volume (25 cm³) [12].

The microstructure, granulometric structure, and phase analysis of powders and sintered samples were studied by using a scanning electron microscope with a JSM-6390LV, 2007 energy dispersive microanalysis, with a resolution in high vacuum up to 3 nm and the possibility of obtaining images in secondary and reflected electrons.

X-ray phase analysis of the powders and the obtained samples was carried out by using an X'PertPRO X-ray diffractometer of thr PANanalytical firm, 2005.

The main parameter of the slip mass «casting ability» was determined on a special factory-made installation PLC-1, which is designed to determine the casting ability of hot thermoplastic slips prepared from ceramic mixes under conditions close to the operation of injection molding machines [13].

Determination of viscosity η in the temperature range 55–80 °C was carried out by using a rotational viscometer RV-8.

The measurement sequence was in accordance with the recommendations of the factory instructions, where the viscosity value was calculated by the formula:

$$\eta = K \frac{P + m - F}{\omega} \tag{2}$$

where η — experiment of material viscosity, poise; *P* — the total weight of the load installed on two cups, g; *m* — weight of cups with hooks, g; *F* — friction loss in bearings, g; ω — inner cylinder rotation speed, sec⁻¹, which is calculated by the formula:

$$\omega = \frac{5}{\tau} \tag{3}$$

where τ — time of five revolutions of the inner cylinder; *K* — device constant, which depends on the dimensions of the working cylinders and the height of the material loading, cm⁻¹·s⁻², is calculated by the formula:

$$K = \frac{R \cdot g}{8\pi^2 [r_1^2 \cdot r_2^2 \cdot h/(r_2^2 - r_1^2) + r_1^3 \cdot r_2^3/(r_2^3 - r_1^3)]}$$
(4)

where R — the radius of the pulley on which the thread is wound, cm; r_1 - radius of the inner cylinder and hemisphere, cm; r_2 — radius of the outer cylinder, cm; h — immersion height of the inner cylinder into the material, cm; g — acceleration of gravity 981 cm/s² [14].

The value of apparent density was determined according to [15].

Results and discussions

It is necessary to carry out complex physicochemical and mechanical studies of the feedstock and sintered products obtained on its basis to predict and correctly interpret the mechanisms of structure formation in ceramics based on BeO with the addition of micro- and nanocrystalline TiO_2 powders, the formation of a structure with specified parametric characteristics and properties.

The highly sintered beryllium oxide powder used in this work was obtained by grinding sintered ceramic scrap in vibrating mills. The characteristics of the powder meet the requirements of TU 95–143–79, for grade «B2» (Table 1).

Table 1

Characteristic, № of batch	p 67		
Bulk weight $\rho_0 \times 10^3$ kg/m ³	0.77		
Specific surface area S, cm ² /g	Specific surface area S, cm ² /g		
Moisture % weight	Moisture % weight		
Average crystal size, µm		5	
	boron	1.7.10-5	
	silicon	$7.3 \cdot 10^{-3}$	
	manganese	8.2.10-4	
	iron	5.1.10-2	
	magnesium	5.2.10-3	
	chrom	1.0.10-2	
Elemental content	nickel	1.1.10-2	
efimpurities 9/ wt	aluminum	$3.2 \cdot 10^{-2}$	
of impurities, 76 wi	copper	8.0.10-4	
	zinc	$7.5 \cdot 10^{-3}$	
	calcium	$4.2 \cdot 10^{-3}$	
	silver	1.1.10-5	
	cadmium	1.2.10-5	
	lithium	6.7.10-4	
	sodium	8.7·10– ³	
The amount of impurities, % wt	· · · · · · · · · · · · · · · · · · ·	0.14	

The main characteristics of the used powder of beryllium oxide grade «B2»

The main characteristics of the used micron TiO_2 powder of the rutile modification in terms of quality and chemical composition, according to the passport data, are given in Table 2.

Table 2

Main characteristics of the used micron TiO₂ powder, RK grade, rutile modification

The name of indicators	TI requirements, %	Analysis results
Mass fraction of titanium dioxide, %, not less	99	99.5
Mass fraction of rutile form, %, not less	97	100
Mass fraction of iron compounds in terms of Fe ₂ O ₃ , %, no more	0.08	0.05
Mass fraction of phosphorus compounds in terms of P_2O_5 , %, no more	0.03	0.03
Mass fraction of sulfur compounds in terms of SiO ₃ , %, no more	0.03	0.01
Mass fraction for silicon compounds in terms of SiO ₂ , %, no more	0.15	0.15
Mass fraction of «metallic iron», %, no more	0.02	0.01
Specific surface, cm ² /g, within	3300-4600	4060

Micron titanium dioxide powder was additionally sieved with a vibrating sieve through a metal mesh N_{0} 0045. Powders with a specific surface area of at least 4500 cm²/g were selected. The average particle size was 5–10 µm. Surface morphology and particle size distribution of micron TiO₂ powder after sieving is shown in Figure 1 (a, b).



a) — magnification of 5k, b) — magnification of 20k

Figure 1. Micrographs of micron titanium dioxide powders

The X-ray diffraction pattern of a micron TiO₂ powder is shown in Figure 2, small peaks indicate the presence of permissible admixtures (Fe₂O₃, P₂O₅, SiO₂).



Figure 2. X-ray diffraction pattern from a titanium dioxide sample for 2 θ values in the range from 0° to 120°. Deciphering the values of the angles (2 θ =27,4; 2 θ =36,0; 2 θ =39,1 etc.) and peak intensities in the «Quantax 70» program indicates the complete compliance of the sample with the rutile modification of TiO₂

Thus, the micro-powder used in the research contains 99.53 wt%, which corresponds to TI 301-10-020-90. The element-wise content of impurities is also within the permissible values. The results of X-ray structural analysis indicate its full compliance with the rutile modification, which confirms the conditionality and the possibility of manufacturing serial ceramic products using factory technology.

Titanium dioxide nanopowder obtained by the method of electric explosion of a conductor (Fig. 3 a, b.) was used to manufacture experimental samples in order to study the methods of introduction and the effect of nanoparticles on the rheological properties of the foundry slip, their uniformity of distribution in the volume of the micron matrix. A nanopowder is a mixture of irregularly shaped particles ranging in size from 5 to 10 nm.



a) magnification 400k, b) magnification 100k

Figure 3. Micrograph of TiO_2 nanoparticles obtained by the method of electrical explosion of a conductor

Along with nanoparticles ≥ 10 nm, there are formations up to 15 nm in size, which, apparently, are agglomerates of smaller particles. As a rule, the shape of all particles is close to spherical. The research of the particle size distribution showed that the nanopowder has a logarithmically normal distribution with an average particle size of 10 nm. Deviation from the average size is no more than 20 %.

The research results by the XRF method are shown in Figure 4.



Figure 4. X-ray diffraction pattern from a TiO₂ nanopowder sample for 2 θ values in the range from 0° to 120°. Deciphering the values of the angles (2 θ = 25,3; 2 θ = 31,0; 2 θ = 37,8,0 and etc.) and peak intensities in the «Quantax 70» program indicates the complete compliance of the sample with the anatase modification of TiO₂

The insertion of nanoparticles into the composition of the charge is one of the most difficult tasks from the technological point of view [16]. Nanoparticles must be evenly distributed over the entire volume of the charge, to exclude their possible coagulation and agglomeration. The problem was solved in several ways: mixed dry and in a liquid medium in a roller mill; in a liquid medium in a specially designed impeller-type reactor with continuous bubbling with compressed air.

The dry mixing method failed to achieve a uniform distribution of particles in the volume of micron powders, due to the fact that the components of the charge are distributed mainly along the perimeter of the working chamber, under the action of centrifugal force, while mixing occurs only in the direction of rotation of the drum. The slip mass from the charge obtained by this technology was not prepared.

The method of introducing nanoparticles in which mixing of the charge components was carried out in a specially designed impeller-type reactor was the most effective. The installation is a cylindrical vertically

located stainless steel tank on a rigid base, inside which a shaft with blades is installed, during the rotation of which the charge is mixed, and compressed air is continuously supplied in the lower part (Fig. 5).



1 — electric motor; 2 — compressed air supply channel; 3 — shaft with blades; 4 — charge; 5 — supply of compressed air for bubbling the charge; 6 — drain hole.

Figure 5. Schematic diagram of the P-60 reactor operation

Air bubbles, rising up according to the Archimedes law through the entire volume of the charge, allow the movement of flows in the liquid not only in the horizontal, but also in the vertical direction.

Samples were obtained with additives 5; 10; 15; 20; 25; 30 wt.%.%Ti O_2^{nano} rest of BeO and 0.1; 0.5; 1.0; 1.5; 2.0 wt.%Ti $O_2^{nano}+TiO_2^{\mu m}$ +70 wt% BeO to study the effect of the method of introducing nanoparticles into the micron matrix of beryllium and titanium oxides, on the uniformity of their distribution and the effect on the rheological properties of the casting slip.

The mixtures of the following composition $(1-x)BeO+xTiO_2$ were obtained by using the developed technology for introducing nanoparticles, Table 3.

Table 3

(1-)BeO+xTiO ₂	x=0.05 (5 %)	x=0.1 (10 %)	x=0.15 (15 %)	x=0.2 (20 %)	x=0.25 (25 %)	x=0.3 (30 %)
Ssp., cm^2/g	16200	17000	17700	18000	18100	18400
Nat. weight., g/cm ³	0.76	0.74	0.70	0.67	0.63	0.60

Values of the main parameters of the charge with the addition of TiO_2^{nano} nanoparticles

As can be seen from the data in Table 3, the specific surface area predictably increases with an increase in the concentration of TiO_2 nanoparticles. It should be noted that the specific surface area of the beryllium oxide powder BeO used in this study was 11000 cm²/g.

The indicator of the flowability of the charge is the bulk density, that is, its density in the unconsolidated state, which takes into account not only the volume of the material particles themselves, but also the space between them, also decreases with an increase in the concentration of nanoadditives. For both physical characteristics, there are tendencies of change inherent in the presence of nanoparticles.

Further, slip masses were prepared for each percentage composition on the basis of an organic binder — wax, paraffin, oleic acid at the rate of LOI (loss on ignition) — 9.5 %. The rheological properties of the obtained slip batches are presented in Table 4.

Table 4

(1-x)BeO+xTiO ₂	x=0.05 (5 %)	x=0.1 (10%)	x=0.15 (15%)	x=0.2 (20 %)	x=0.25 (25 %)	x=0.3 (30 %)
LOI, %	9,5	9,3	9,4	9,2	9,3	9,3
Viscosity, Pa·s	45	59	72	88	93	107
Casting capacity, mm	76	62	41	33	27	16

Rheological properties of thermoplastic slips based on beryllium oxide with the addition of nanoparticles 5–30 wt.% TiO_2^{nano}

In the process of casting blanks using TiO_2 nanopowders it was noted that the rheological properties of the slip mass strongly changed with an increase in their concentration: the slip became viscous and difficult to mix (Table 4). This is due to the fact that nanoparticles, having a highly active surface, require the introduction of a much larger amount of organic binder, compared with micron-sized TiO_2 powders, which negatively affects the properties of slips (viscosity and castability) and the quality of sintered products in the form of the presence of shells, impurities and excessive porosity.

As it is known, the casting ability of a slip characterizes its suitability for casting articles of a given configuration. It is a conditional complex characteristic that depends on the viscosity and the rate of solidification. The lower the viscosity and speed of solidification of the slip, the higher its casting ability. In turn, the viscosity determines the ability of the foundry mass to continuously fill the mold during the casting process. It is possible to increase the casting ability indicator by adding a binder to the slip mass, however, the more binder in the slip, the worse the quality of the sintered product, since after the operation of burning the binder, the evaporated organic matter leaves behind defects in the form of various cavities and pores. Thus, for the purity of the experiment, it was decided not to increase the castability of the slip by adding a binder. Forming a billet by slip casting is possible by increasing the pressure applied to the slip in the case of a low casting capacity.

Work on forming the blanks was carried out on a micro-casting unit for casting thermoplastic slips of factory design (Fig. 6).



1 — slip mass in the evacuation reactor; 2 — shaft with blades; 3 — evacuation channel;
4 — electric motor; 5 — steering wheel for pressing the casting mold; 6 — formed blank; 7 — casting mold;
8 — heating circuit; 9 — compressed air supply channel; 10 — slip mass in a casting reactor.

Figure 6. Photo and schematic diagram of the micro-casting installation

The pressure on the slip was proportionally increased with an increase in the concentration of nanoparticles to maintain the required pouring rate, according to the graph shown in Figure 7.



Figure 7. Graph of the dependence of the pressure change on the slip from the concentration of nanoparticles in the range of 5–30 wt.% TiO₂^{nano}, batches 1–6, respectively

Next, samples were obtained, the composition of which is shown in Table 5. In order to improve the rheological properties of the casting slip the amount of added nanoadditives was limited from 0.1 to 2.0 wt.% TiO_2^{nano} .

Table 5

N₀ batches	The composition of the charge	S _{sp} ., cm ² /g	Nat. weight., g/cm ³
P1	BeO + 29.9 wt.%TiO ₂ ^{μm} + 0.1 wt.%TiO ₂ ^{$nano$}	12700	1.07
P 2	BeO + 29.5 wt.%TiO ₂ ^{μm} + 0.5 wt.%TiO ₂ ^{$nano$}	13800	1.03
P 3	BeO + 29.0 wt.%TiO ₂ ^{μm} + 1.0 wt.%TiO ₂ ^{$nano$}	14600	0.97
P 4	BeO + 28.5 wt.%TiO ₂ ^{μm} + 1.5 wt.%TiO ₂ ^{$nano$}	15700	0.93
P 5	BeO + 28.0 wt.%TiO ₂ ^{μm} + 2.0 wt.%TiO ₂ ^{$nano$}	16200	0.90

Values of the main parameters of the charge with the addition of nanoparticles 0.1–2.0 wt%

The specific surface area also increases with the introduction of nanoparticles up to 2.0 wt% into the volume of the charge. The specific surface area of the beryllium oxide powder BeO used in this study was also $11000 \text{ cm}^2/\text{g}$, and the specific surface area of the titanium dioxide powder was $10000 \text{ cm}^2/\text{g}$. The indicator of the flowability of the charge, the bulk density, also does not significantly decrease with an increase in the concentration of nanoadditives, remaining in the permissible range of values.

Further, slip masses were prepared for each percentage composition on the basis of an organic binder — wax, paraffin, oleic acid at the rate of LOI (loss on ignition) — 9.5 %. The composition of the wax paraffin components and the slips preparation technology are identical.

The rheological properties of the obtained slips batches are presented in Table 6.

Table 6

Rheological properties of thermoplastic slips with the addition of nanoparticles 0.1-2.0 wt.%

Characteristics	P1	P2	P3	P4	P5
LOI, %	9.6	9.4	9.2	9.2	9.2
Viscosity, Pa·s	49	48	44	43	40
Casting capacity, mm	63	65	71	78	83

As can be seen from Table 6, the rheological properties of slips with the introduction of nanoparticles in the range of 0.1–2.0 wt.% remain at an acceptable level. The casting ability of the slip increases with an increase in the concentration of nanoparticles, it becomes less viscous. Thus, a relatively small number of introduced nanoparticles allows maintaining a minimum volume of organic binder while maintaining the casting properties of the slip mass at an acceptable level.

Due to the increase in casting capacity, the pressure on the slip was decreased in proportion to the increase in the concentration of nanoparticles, according to the graph shown in Figure 8.



Figure 8. Graph of the dependence of the pressure change on the slip from the concentration of nanoparticles in the range from 0.1 to 2.0 wt.%, batches 1–5, respectively

The observed effect is explained by the filling of voids between solid and larger powder particles with particles of smaller fractions, as a result of which the density of the charge increases, and the reorientation of large grains contributes to a decrease in friction against the walls of the tooling.

On the obtained samples there are many fragments of the TiO_2 phase and pores after sintering, predominantly round form with the size up to 3 mm, indicating the processes of conglomeration of nanoparticles. The number of fragments increases in proportion to the introduced amount of TiO_2^{nano} in the case of the introduction of nanoparticles 5.0–30.0 wt.% (Fig. 9).



The figure signature number corresponds to the batch number according to: P1– 5wt.%Ti O_2^{nano} ; P2 — 10wt.%Ti O_2^{nano} ; P3 — 15wt.%Ti O_2^{nano} ; P4 – 20wt.%Ti O_2^{nano} ; P5 – 25wt.%Ti O_2^{nano} and P6 — 30wt.%Ti O_2^{nano} .

Figure 9. Macrostructure of samples containing TiO_2 nanoparticles. Magnification \times 16

Thus, it is not possible to obtain a completely homogeneous sample without pores and impurities containing nanoparticles from 5 to 30 wt% TiO₂.

Figure 10 shows the macrostructure of samples containing nanoparticles of 0.5–2.0 wt%.



The figure signature number corresponds to the batch number according to: P2 - 0.5wt.%TiO₂^{nano}; P4 - 1.5wt%TiO₂^{nano} and P5 - 2.0wt%TiO₂^{nano}

Figure 10. The macrostructure of samples with containing nanoparticles of TiO₂. Magnification \times 16

As can be seen, the macrostructure of the samples with a nanoparticle content of up to 2.0 wt% is rather uniform with this method of introducing nanoparticles, there are practically no grouped fragments of the TiO_2 phase. Thus, it is not possible to obtain a homogeneous, dense sample with the introduction of nanoparticles in excess of 5 wt%.

Conclusions

1. In this work an effective method is proposed for introducing nanodispersed TiO_2 powders into a micron matrix of beryllium and titanium oxides, in which air bubbles, rising upward according to the Archimedes law through the entire volume of the charge, allow the movement of flows in the liquid not only horizon-tally, but also in the vertical direction.

2. It has been experimentally shown that the addition of nanoparticles from 5 to 30 wt% TiO_2^{nano} negatively affects the casting properties of slips (viscosity and casting ability) and, consequently to the quality of sintered products in the form of cavities, impurities and excessive porosity.

3. As a result of research, the effect of the concentration of nanoparticles on the main technological parameters, such as specific surface area, bulk density, viscosity, casting ability, pressure on the slip during billet molding, the optimal concentration of nanopowder of TiO_2 , — 0.1 — 2.0 wt. % was established, providing normal indicators of technological parameters.

Acknowledgments

The work was carried out within the framework of grant funding for scientific research on 2021–2023 years by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (AP09058686).

References

1 Кийко В.С. Керамика на основе оксида бериллия: получение, физико-химические свойства и применение / В.С. Кийко, Ю.Н. Макурин, А.Л. Ивановский. — Екатеринбург: УрО РАН, 2006. — 440 с.

2 Кийко В.С. Получение, физико-химические свойства и пропускание СВЧ-излучения керамикой на основе ВеО / В.С. Кийко, С.Н. Шабунин, Ю.Н. Макурин // Огнеупоры и техническая керамика. — 2004. — № 10. — С. 8–17.

3 Kiiko V.S. Microstructure and electrical conductivity of compositing (BeO+TiO₂) ceramics / V.S. Kiiko, M.A. Gorbunova, Y.N. Makurin, A.D. Neuimin, A.L. Ivanovskii // Refractories and Industrial Ceramics. — 2007. — Vol. 48, No. 6. — P. 429–434.

4 Кийко В.С. Композиционная (BeO+TiO₂)-керамика для электронной и других областей техники / В.С. Кийко, А.В. Павлов // Новые огнеупоры. — 2017. — № 12. — С. 64–70.

5 Кийко В.С. Влияние добавок диоксида титана на физико-химические и люминесцентные свойства бериллиевой керамики / В.С. Кийко // Неорган. материалы. — 1994. — Т. 30, № 5. — С. 688–693.

6 Дрокин Н.А. Электрофизические свойства керамики БТ-30 / Н.А. Дрокин, В.С. Кийко, А.В. Павлов, А.И Малкин // Новые огнеупоры. — 2020. — № 6. — С. 56–63.

7 Мальцев П. СВЧ-технологии — основа электроники будущего / П. Мальцев, И. Шахнович // Электроника наука /технология /бизнес. — 2015. — № 8 (00148). — С. 72–84.

8 Морозов А.Н. Синтез и каталитические свойства наноструктурированных покрытий диоксида титана: дис. ... канд. хим. наук: 05.17.01 / Морозов Александр Николаевич; Рос. хим.-техн. ун-т им. Д.И. Менделеева. — М., 2014. — 160 с.

9 Serpone N. Size effects on the photophysical properties of colloidal anatase TiO₂ particles: size quantization versus direct transitions in this indirect semiconductor / N. Serpone, D. Lawless, R. Khairutdinov // J. Phys. Chem. — 1995. — Vol. 99, No. 45. — 1995. — P. 16646–16654.

10 Sagdoldina Zh.B. Structural evolution of ceramic coatings by mechanical alloying / Zh.B. Sagdoldina, B.K. Rakhadilov, M.K. Skakov, O. Stepanova // Materials testing. — 2019. — Vol 61, No 4. — P. 304–308.

11 ГОСТ 23401-90. Порошки металлические. Катализаторы и носители. Определение удельной поверхности. — М.: Изд-во стандартов, 1991. — С. 10.

12 ГОСТ 19440-94. Металлические порошки. Определение насыпной плотности. — М. Изд-во стандартов, 1997. — С. 41.

13 Rakhadilov, B.K. Development of air-plasma technology for hardening cutting tools by applying wear-resistant coatings / B.K. Rakhadilov, A.B. Kenesbekov, P. Kowalevski, Y.A. Ocheredko, Zh.B. Sagdoldina // News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences. — 2020. — No 3(441). — P. 54–62.

14 Rakhadilov B.K. Preparation of powder coatings on the surface of steel balls by mechanochemical synthesis / B.K. Rakhadilov, D.B. Buitkenov, Zh.B. Sagdoldina, L.G. Zhurerova, W. Wieleba // Bulletin of the university of Karaganda-Physics. — 2020. — Vol. 4 (100). — P. 8–13.

15 ГОСТ 2409-95. Огнеупоры. Способ определения кажущейся плотности, открытой, полной и закрытой пористости, водопоглощения. — М.: Изд-во стандартов, 2004. — С. 5.

16 Погожев Ю.С. Дисперсно-упрочненные наночастицами электродные материалы и покрытия на основе карбида титана: дис. ... канд.ист. наук. техн.: 05.16.06 / Погожев Юрий Сергеевич; Моск. гос. ин-т стали и сплавов. — М., 2006. — 184 с.

А.В. Павлов, Е.Е. Айымханов, Ж.Б. Сагдолдина, А.Б. Касымов, Д.Р. Байжан, М.С. Жапарова

ТіО₂ нанобөлшектерін BeO және ТіО₂ ұнтақтарының микрондық матрицасына енгізу әдістерін және олардың құю шликерінің реологиялық қасиеттеріне әсерін зерттеу

Мақалада нанодисперсті титан оксиді TiO₂ ұнтақтарын бериллий мен титан оксидтерінің микрон матрицасына енгізу әдістерінің зерттеу нәтижелері көрсетілген. 5 %-дан жоғары нанобөлшектердің болуы құю шликерінің реологиялық қасиеттеріне теріс әсер етеді және керісінше, 0,1–2,0 мас. % аралығында нанобөлшектердің қосылуы тұтқырлықты төмендетуге және жылжымалы массаның құю қабілетін арттыруға ықпал етеді. Агрегатталған дайындаманы макроқұрылымдық талдау нанобөлшектердің конгломераттары немесе нано- және микро- TiO₂ бөлшектері түрінде құрылымдық талдау нанобөлшектердің конгломераттары немесе нано- және микро- TiO₂ бөлшектері түрінде құрылымдық талдау нанобөлшектердің конгломераттары немесе нано- және микро- TiO₂ бөлшектері түрінде құрылымдық элементтердің толық болмауын көрсетеді. Нанобөлшектерді енгізудің дамыған әдісі өнімді шликерді құю арқылы дайындаманың бүкіл көлеміне біркелкі таратуға мүмкіндік береді. Ғылыми жұмыстың авторлары болашақта алынған нанобөлшектері бар керамиканың жылу физикалық және импеданс сипаттамаларына нанобөлшектердің әсерін зерттеуді жоспарлады. Ғылыми әлемде наноұнтақтардың бериллий керамикасының электрофизикалық қасиеттеріне әсерін зерттеу туралы белгісіз. Бериллий оксиді және титан оксидтері қоспасы BeO+TiO₂ керамикасының ең маңызды қасиеттерінің бірі — аса жоғарғы жиілікте сәулеленуді сіңіру қабілеті, ол аз қызуы керек, яғни жылуды жақсы өткізеді. Жоғары коэффициентті алу үшін BeO керамика құрамына TiO₂ фазасын мүмкіндігінше көп енгізу керек.

Кілт сөздер: TiO₂ нанобөлшектері, шихта, құю шликері, реологиялық қасиеттері, берилий оксиді, керамика, макроқұрылым.

А.В. Павлов, Е.Е. Айымханов, Ж.Б. Сагдолдина, А.Б. Касымов, Д.Р. Байжан, М.С. Жапарова

Исследование методов введения наночастиц TiO₂ в микронную матрицу порошков BeO и TiO₂ и их влияния на реологические свойства литейного шликера

В статье представлены результаты исследований методов введения нанодисперсных порошков TiO_2 в микронную матрицу оксидов бериллия и титана. Показано, что наличие наночастиц свыше 5,0 мас. % отрицательно влияет на реологические свойства литейного шликера, и, наоборот, добавление наночастиц в диапазоне 0,1–2,0 мас. % способствует снижению вязкости и повышению литейной способности шликерной массы. Макроструктурный анализ спеченной заготовки свидетельствует о полном отсутствии структурных элементов в виде конгломератов наночастиц или частиц нано- и микро-TiO₂. Разработанный способ введения наночастиц позволяет получать изделия с их равномерным распределением по всему объему заготовки методом шликерного литья под давлением. В дальнейшем авторы научной работы планировали исследовать влияние наночастиц на теплофизические и импедансные характеристики полученной керамики. Об исследованиях влияния нанопорошков на электрофизические свойства бериллиевой керамики в научном мире не известно. Самыми важными свойствами, которыми должна обладать керамика BeO+TiO₂, это способность поглощать CBЧ-излучение, при этом она должна мало нагреваться, т.е. хорошо проводить тепло. Для получения высокого коэффициента необходимо как можно больше вводить в состав керамики BeO фазу TiO₂.

Ключевые слова: наночастицы TiO₂, шихта, шликер, реологические свойства, оксид бериллия, керамика, макроструктура.

References

1 Kiiko, V.S., Makurin, Iu.N., & Ivanovskii, A.L. (2006). Keramika na osnove oksida berilliia: poluchenie, fizikokhimicheskie svoistva i primenenie [Beryllium oxide-based ceramics: preparation, physical and chemical properties and application]. *Ekaterinburg: UrO RAN*, 440 [in Russian].

2 Kiiko, V.S., Shabunin, S.N., & Makurin, Yu.N. (2004). Poluchenie, fiziko-khimicheskie svoistva i propuskanie SVChizlucheniia keramikoi na osnove BeO [Production, physical and chemical properties and transmission of microwave radiation by BeO-based ceramics]. *Ogneupory i tekhnicheskaia keramika — Refractories and technical ceramics*, 10, 8–17 [in Russian].

3 Kiiko, V.S., Gorbunova, M.A., Makurin, Y.N., Neuimin, A.D., & Ivanovskii, A.L. (2007). Microstructure and electrical conductivity of compositing (BeO+TiO₂) ceramics, *Refractories and Industrial Ceramics*, 48(6), 429–434. 4 Kiiko, V.S., & Pavlov, A.V. (2017). Kompozitsionnaia (BeO+TiO₂)-keramika dlia elektronnoi i drugikh oblastei tekhniki [Composite (BeO+TiO₂)-ceramics for electronic and other fields of technology]. *Novye ogneupory* — *New refractories*, 12, 64–70 [in Russian].

5 Kiiko, V.S. (1994). Vliianie dobavok dioksida titana na fiziko-khimicheskie i liuminestsentnye svoistva berillievoi keramiki [Effect of titanium dioxide additives on the physicochemical and luminescent properties of beryllium ceramics]. *Neorganicheskie materialy — Inorganic Materials*, 30(5), 688–693 [in Russian].

6 Drokin, N.A., Kiiko, V.S., Pavlov, A.V., & Malkin, A.I (2020). Elektrofizicheskie svoistva keramiki BT-30 [Electrophysical properties of BT-30 ceramics]. *Novye ogneupory-New refractories*, 6, 56–63 [in Russian].

7 Maltsev, P., & Shakhnovich, I. (2015). SVCh-tekhnologii — osnova elektroniki budushchego [Microwave technologies-the basis of electronics of the future]. *Elektronika nauka /tekhnologiia /biznes* — *Electronics science /technology /business*, 8 (00148), 72–84 [in Russian].

8 Morozov, A.N. (2014). Sintez i kataliticheskie svoistva nanostrukturirovannykh pokrytii dioksida titana [Synthesis and catalytic properties of nanostructured titanium dioxide coatings]. *Candidate's thesis*. Moscow [in Russian].

9 Serpone, N., Lawless, D., & Khairutdinov, R. (1995). Size effects on the photophysical properties of colloidal anatase TiO₂ particles: size quantization versus direct transitions in this indirect semiconductor, *J. Phys. Chem.*, 99(45), 16646–16654.

10 Sagdoldina, Zh.B., Rakhadilov, B.K., Skakov, M.K., & Stepanova, O. (2019). Structural evolution of ceramic coatings by mechanical alloying, *Materials testing*, 61(4), 304–308.

11 GOST 23401–90. Poroshki metallicheskie. Katalizatory i nositeli. Opredelenie udelnoi poverkhnosti [State Standard 23401– 90 Metal powders. Catalysts and carriers. Determination of the specific surface area]. (1991). Moscow: Izdatelstvo standartov [in Russian].

12 GOST 19440–94. Metallicheskie poroshki. Opredelenie nasypnoi plotnosti [State Standard 19440–94 Metal powders. Determination of bulk density]. (1997). Moscow: Izdatelstvo standartov [in Russian].

13 Rakhadilov, B.K., Kenesbekov, A.B., Kowalevski, P., Ocheredko, Y.A., & Sagdoldina, Zh.B. (2020). Development of airplasma technology for hardening cutting tools by applying wear-resistant coatings, *News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences*, 3(441), 54–62.

14 Rakhadilov, B.K., Buitkenov, D.B., Sagdoldina, Zh.B., Zhurerova, L.G., & Wieleba, W. (2020). Preparation of powder coatings on the surface of steel balls by mechanochemical synthesis, *Bulletin of the university of Karaganda-Physics*, 4 (100), 8–13.

15 GOST 2409–95. Ogneupory. Sposob opredeleniia kazhushcheisia plotnosti, otkrytoi, polnoi i zakrytoi poristosti, vodopogloshcheniia [State Standard 2409–95 Refractories. Method for determining the apparent density, open, full and closed porosity, water absorption]. (2004). Moscow: Izdatelstvo standartov [in Russian].

16 Pogozhev, Yu.S. (2006). Dispersno-uprochnennye nanochastitsami elektrodnye materialy i pokrytiia na osnove karbida titana [Nanoparticle-reinforced electrode materials and coatings based on titanium carbide]. *Candidate's thesis. Moskovskii gosudarstvennyi institut stali i splavov. Moscow* [in Russian].