

RIGA TECHNICAL UNIVERSITY

Alexey HMELOV

**SYNTHESIS OF CERAMIC POWDERS IN THE Al_2O_3 - SiO_2 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$
SYSTEM AND PRODUCTION OF MATERIALS**

Doctoral thesis summary

Riga 2011

RIGA TECHNICAL UNIVERSITY
FACULTY OF MATERIALS SCIENCE AND APPLIED CHEMISTRY
INSTITUTE OF SILICATE MATERIALS

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PhD student of the Doctoral Study Programme “Chemical technology”

**SYNTHESIS OF CERAMIC POWDERS IN THE Al_2O_3 - SiO_2 - $\text{ZrO}_2(\text{Y}_2\text{O}_3)$
SYSTEM AND PRODUCTION OF MATERIALS**

Doctoral Thesis Summary

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**DOCTORAL THESIS PROPOSED FOR OBTAINING THE DOCTORAL
DEGREE IN ENGINEERING CHEMISTRY SCIENCE IN RIGA
TECHNICAL UNIVERSITY**

The doctoral thesis for obtaining of doctoral degree in Engineering Chemistry Science will be publicly presented at the.....,2011, at Riga Technical university Faculty of Materials Science and Applied Chemistry, in room 272, in Azenes Street 14/24, in Riga.

The doctoral thesis can be reviewed in the Scientific Library of RTU in Kipsalas street 10, Riga, LV - 1048 or in Latvian National Library in Anglikanu street 5, Riga, LV - 1050.

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CONFIRMATION

I confirm that I have developed the present doctoral thesis that is submitted for consideration at Riga Technical university for obtaining the doctoral degree in Engineering Chemistry Science. The doctoral thesis hasn't been submitted in to some other university with the purpose of obtaining doctoral degree.

Alexey Hmelov.....

Date.....

The doctoral thesis is written in Latvian, contains an introduction, literature review (8 chapters), conclusions of literature review, methodological part (8 chapters), experimental part (9 chapters), conclusions and bibliography with 76 references. The doctoral thesis consists of 89 pages, 47 figures, 6 schemes, 8 tables.

Topicality of work. One of the tasks for development of high-temperature silicate materials is to ensure their production from ceramic powders by using specific ceramic technologies, that would be efficient in terms of energy consumption and guarantee production of high quality ceramic materials, int. al., by making use of Latvia's mineral resources, for instance, clays or clay minerals as the components that promote sintering process in the raw material compositions. However, nowadays due to increasingly higher requirements to ceramic materials applied in extreme conditions, for instance, at high temperatures, at rapid changes of temperature, in aggressive environments, etc., ceramic materials are expected to possess specific physical, chemical, mechanical and thermal properties characteristic of high-temperature resistant materials. One of such ceramic materials is mullite or mullite - ZrO_2 ceramics. These high-temperature ceramic materials are used in different areas, that include:

- internal lining in furnaces;
- supports for sintering of ceramic materials;
- acid and alkali resistant ceramics;
- crucibles and basins for melting and casting of metal/glass;
- plungers and moulds for molten metal/glasses;
- spades, nozzles, gas turbines;
- internal lining for synthesis chambers in plasma equipment;
- construction materials.

Wide application of mullite - ZrO_2 ceramic materials implies good thermal conductivity, resistance to oxidising environment, high fire and heat resistance, acid and alkali resistance and resistance to molten metals, as well as low thermal expansion coefficient.

Mullite ceramics has been well-known for years; it is traditionally obtained from high-temperature kaolin clays. Investigations about mullite - ZrO_2 ceramic materials appeared in middle of 20th century with the growing requirements to preservation of mechanical properties of the materials at high temperatures. At the same time, however, mullite - ZrO_2 ceramic materials possess certain specific qualities:

- mullite with the stoichiometry (3:2) during exploitation decompose at high temperatures;
- addition of ZrO_2 as a component in mullite ceramics is characterized by phase transformation under sintering/cooling conditions, which cause cracking or even crushing of ceramic materials.

Sintering of mullite ceramics proceeds sufficiently well at higher temperatures without any pressure supply. However, the introduction of ZrO_2 additive with Y_2O_3 as stabilized additive into mullite powder may deteriorate the sintering of mullite- ZrO_2 ceramics as a result of low diffusion coefficient of added additives. Therefore, for the purpose of obtaining dense ceramic material, new sintering methods, for example, spark plasma sintering is applied, which has also been used in this doctoral thesis.

The aim of work

Investigations and development of mullite- ZrO_2 ceramic materials dependence on the raw materials, int. al. with illite clay additive, preparation method of starting powders and sintering methods.

Assignments of work:

- ✓ processing of ceramic powders with different degree of dispersion, int. al. with illite clay additive by using of traditional milling of various duration as well as hydrothermal synthesis; the characterization and comparison of powders from the particle size and morphology viewpoint;
- ✓ development of ceramics: forming and sintering by conventional and spark plasma sintering methods in the maximum temperature (1100 - 1500 °C) range;
- ✓ determination of the most characteristic properties of ceramics: investigation of the process of formation of crystalline phases and microstructure (their comparison) depending on the ceramic powder composition and sintering methods;
- ✓ verification and comparison of ceramics mechanical properties - flexural strength and modulus of elasticity dependence on the thermal shock resistance and comparison of shrinkage, bulk density, densification, compression strength.

Scientific significance and novelty

- existence of certain relationships in the production of mullite - $ZrO_2(Y_2O_3)$ ceramics has been discovered that associated with the dispersity of ceramic powders, sintering types and conditions, crystalline phases and structure of ceramic materials with the properties of the materials (shrinkage, bulk density, compression strength, flexural strength and modulus of elasticity);
- the positive effect of milled powders during different periods of time and presence of illite clay additive on the compaction of ceramic materials during conventional and spark plasma sintering processes are demonstrated;
- spark plasma sintering process intensifies the densification of ceramic powders and provides development of dense, fine-crystalline mullite structure with regularly distributed crystalline grains of ZrO_2 .

Practical importance

- dense mullite - $ZrO_2(Y_2O_3)$ ceramic material with enhanced bulk density, compression strength is developed during spark plasma sintering conditions;
- production of ceramics with high thermal shock resistance at the temperature up to 1000/20 °C.

Practical application of work:

- The results of the research are used for development of the high-temperature ceramic material and evaluation of its sintering and mechanical properties within the framework of the project RTU - IZM, R - 7224;
- ceramic material production technologies that make use of the resources of Latvian earth entrails under the subproject “New ceramic materials and technologies”, within the framework of the National Research Programme (NRP) Nr. 2010.10-4/VPP- and 2011.10-4 VPP - 5.

Approbation of work

Scientific achievements and the main results of doctoral thesis have been presented: at 14 international, int. al. 6 regional scientific conferences; in 13 scientific publications, int. al. 9 scientific journals and 4 conference thesis as well as the results

of the doctoral thesis have been patented and has been proposed for practical application:

- Latvijas patents, Nr. 14238B, C04 B33/26; C04 B35/185; C04 B35/106; C04 B35/119; C04 B38/00. G. Sedmale, A. Hmeļovs, I. Šperberga. Termiski un mehāniski izturīga keramika. (02.09.2010.);
- G. Sedmale, A. Hmeļovs. High - temperature Ceramic Materials, High Tech in Latvia; 2008, p. 18 - 18;
- Publication: G. Sedmale, I. Sperberga, J. Grabis, A. Hmelov. „Phase development and mechanical properties of high - temperature ceramic in the system mullite - ZrO_2 ” results are inserted into data base „Industrial Gateway” in the September of 2011 year.

LITERATURE REVIEW

The literature review part provides analysis of the aspects of mullite and ZrO_2 phases formation in the binary and ternary Al_2O_3 - SiO_2 , Al_2O_3 - SiO_2 - ZrO_2 equilibrium phase diagrams. Transformation of crystalline phases in uni- and binary systems, accordingly, ZrO_2 and ZrO_2 - Y_2O_3 , depending on the temperature and pressure supply is considered.

Phase formation in the binary Al_2O_3 - SiO_2 system was studied by various authors [cited from 1 - 3]. The main findings of these studies proved that mullite is formed in the temperature range from 1850 °C to 1910 °C.

The results of research in the ternary equilibrium phase diagram of Al_2O_3 - SiO_2 - ZrO_2 system [cited from 4,5] display one ternary point eutectic at 1800 °C (with the composition of weight %): Al_2O_3 - 53; SiO_2 - 17; ZrO_2 - 30. In the diagram up to ~ 1800 °C there exist two crystalline phases: zircon ($ZrSiO_4$) and corundum (α - Al_2O_3). The formation of mullite phase with the stoichiometry 2:1 occurred in the solid state at the temperature near to 1800 °C with the Al_2O_3 and SiO_2 content of 68 and 42 mas %, respectively. Nearly the eutectic at 1900 °C mullite phase with the stoichiometry (3:2), corundum, tetragonal and monoclinic ZrO_2 phases are developed.

The binary ZrO_2 - Y_2O_3 system equilibrium phase diagrams were studied by Djuvetc, Braun and Odell as well as by Fan Fu-Kanu and Keler [cited from 6].

Formation of the following solid solution areas in the binary ZrO_2 - Y_2O_3 system equilibrium phase diagram has been established:

- solid solution based on the ZrO_2 ;
- solid solution based on the Y_2O_3 ;
- solid solution of cubic ZrO_2 located in the central part of equilibrium phase diagrams of the ZrO_2 - Y_2O_3 system.

Introduction of Y_2O_3 into crystalline lattice of ZrO_2 decreases the ZrO_2 transformation temperature. The transformation from the monoclinic to the tetragonal ZrO_2 , containing 1 mol % of Y_2O_3 occurs at 960 °C, which is shown by Fan Fu-Kanu and Keler. By increasing the Y_2O_3 content up to 4 mol % the transformation temperature of ZrO_2 is decreased to 550 °C.

The areas of formation of the cubic ZrO_2 solid solution are located nearly to concentration with Y_2O_3 content at 33,3 mol %. At the same time, the chemical compound is $Y_2Zr_2O_7$ with the considerable area of homogeneity expanding within the temperature range 1750 - 2150 °C is recognised as solid solution of cubic ZrO_2 . According to Fan Fu-Kanu and Keler, the compound of $Y_2Zr_2O_7$ melts without any decomposition at the temperature 2530 ± 30 °C.

The influence of transformations of ZrO_2 phases on development of compression stresses and resistance of ceramic materials to cracking is shown in Figure 1.

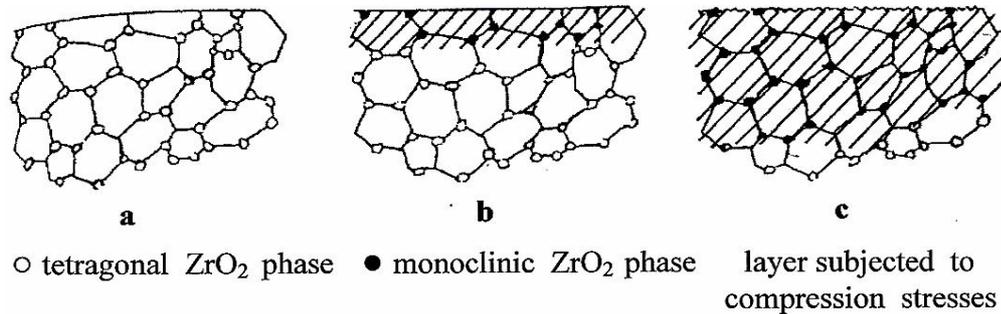


Fig. 1. Cross-section diagram of sample [7], where: (a) sintered sample; (b) sintered and cooled sample, where the transformation of ZrO_2 phases causes compression stresses; (c) mechanically scrubbed sample

The formation and development of compression stresses is a well-known [7] and vastly researched phenomenon occurring in the ceramic materials containing ZrO_2 . Compression stresses develop if transformation of ZrO_2 phases from tetragonal to monoclinic ZrO_2 occurs spontaneously at the surface or nearly to the surface of the sample.

Transformation of ZrO_2 phases resulting from the compression stress leads to development of cracks in the material. This process is further intensified as a result of tooling of the sample surface.

Mullite - ZrO_2 high-temperature ceramic materials [8] display high mechanical properties, high chemical and corrosion resistance also at high temperatures.

These properties are largely depending on main two factors:

- dispersity of ceramic powders [9 - 11]
- type of sintering and sintering temperatures [12,13].

Increase [9 - 11] of milling time (5 - 20 hours) of raw powders favours formation of the fine-grained and small-grained particles in ceramic powders and decreases the mullite formation temperature.

Mullite - ZrO_2 ceramics sintered by conventional method from the mixture of fine-dispersed Al_2O_3 and SiO_2 , ZrO_2 with 3 mol % Y_2O_3 powders show activation of mullite phase and transformation from the monoclinic to tetragonal ZrO_2 form in the temperature 1300 - 1400 °C range [12]. The mullite - ZrO_2/Y_2O_3 ceramics sintered at the temperature 1500 °C displays amplification of mechanical properties depending on the formed ZrO_2 phases (monoclinic and tetragonal forms).

In connection with the hydrothermal synthesis of mullite - ZrO_2 powders [14,15] silimanite-type aluminosilicates, impurities of corundum are developed. The crystallization of mullite and the transformation from monoclinic to tetragonal ZrO_2 phase occurred during the process of sintering at temperatures in the 1100 - 1300 °C range.

Mullite - ZrO_2 ceramics [16] compacted from the mixture of corundum ($\alpha - Al_2O_3$) and zircon ($ZrSiO_4$) by using of spark plasma sintering indicate at the activation of mullitization at 1200 °C by decomposing of zircon at 1100 °C. Mullite - ZrO_2 ceramics compacted by spark plasma sintering up to 1500 °C display the compression strength of 235,0 MPa and the bulk density of 3,10 g/cm³.

However, literature sources don't contain references of the research that would focus on:

- the influence of clay additive on the formation of crystalline phases, microstructure and properties of mullite - ZrO_2 ceramic materials, int. al. which sintered by spark plasma sintering;

- formation of crystalline phases and microstructure of mullite - ZrO_2 ceramic powders during hydrothermal synthesis and it's effect on the properties of ceramics as well as in the presence of illite clay additive.

PREPARATION OF SAMPLES AND METHODS OF RESEARCH

The studied compositions and characterization of used raw materials. Three various groups of compositions, which contain the components in the proportion that ensure the formation of mullite phase with the stoichiometry ($3Al_2O_3 \cdot 2SiO_2$) during the sintering process of ceramic materials have been studied. The ZrO_2 additive was used to enhance the mullite ceramics mechanical and thermal properties; at the same time, Y_2O_3 was used to ensure the transformation from monoclinic to tetragonal ZrO_2 and to facilitate formation of the mullite phase (Tables 1 - 3).

The first composition group

Table 1

Composition of component (wt. %) for conventional preparation of ceramic mixture					
Designation of compositions	$\gamma - Al_2O_3$	$SiO_2 \cdot nH_2O$ ($SiO_2 - 85\%$)	$ZrO_{2(mon.)}$	Y_2O_3	illite clay
4	61,10	27,20	3,34	-	8,36
5	60,80	27,15	3,35	0,35	8,35
6	60,65	27,30	3,00	0,60	8,45

The second composition group

Table 2

Composition of component (wt. %) for conventional preparation of ceramic mixture					
Designation of compositions	$\gamma - Al_2O_3$	$SiO_2 \cdot nH_2O$ ($SiO_2 - 85\%$)	$ZrO_{2(mon.)}$	Y_2O_3	illite clay
10	62,30	28,00	5,20	4,50	-
10i	57,30	25,85	4,70	4,15	8,00

The third composition group

Table 3

Composition of component (mass part) for hydrothermal synthesis					
Designation of compositions	Al(NO ₃) ₃ · 9H ₂ O	SiO ₂ - aerosile	ZrO(NO ₃) ₂ · 2H ₂ O	Y(NO ₃) ₃ · 6H ₂ O	illite clay
10h	421,75	22,20	10,20	9,95	-
10hi	411,95	21,80	10,00	10,10	8,00

Non-fractionated sage-green clays from Liepaja deposit (Latvia) is used as an illite clay additive. It's chemical, mineralogical composition as well as particle distribution are shown in Table 4. SiO₂ is introduced by using silica gel heated up to 1000 °C, whereas γ - Al₂O₃ is obtained by heating Al(OH)₃ at 550 °C during one hour.

The medium chemical and mineralogical composition of illite clay

Table 4

Chemical composition, mass %	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O/Na ₂ O
	50,5	20,8	7,5	1,2	1,9	3,6	6,0/0,1
Mineralogical composition, mas %	Illite - K _{0,5} (H ₃ O) _{0,5} Al ₂ [(OH) ₂ /AlSi ₂ H ₄ O ₁₀		Quartz SiO ₂	Calcite CaCO ₃	Getite α - FeOOH		Kaolinite Al ₂ (OH) ₄ [Si ₂ O ₅]
	65 - 70		18 - 20	5 - 6	7 - 8		5 - 7
Mean particle size, %	63 - 20 μm		20 - 6,3 μm		6,3 - 20 μm		< 2,0 μm
	20,5		21,5		28,5		29,5

Description of the chemical compounds applied for hydrothermal synthesis is provided in Table 5.

Description of the chemical compounds applied for hydrothermal synthesis

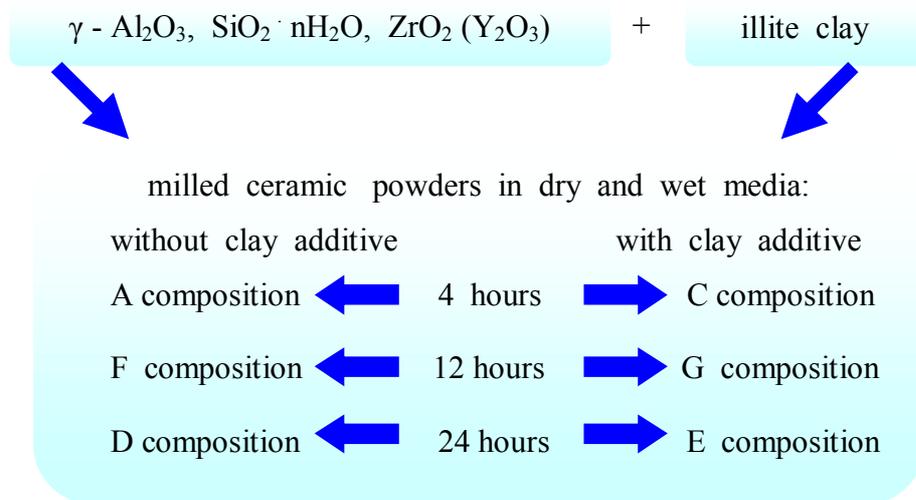
Table 5

Raw material	Manufacture	Pure degree, %
Al(NO ₃) ₃ · 9H ₂ O	Lach: ner	98
ZrO(NO ₃) ₂ · 2H ₂ O	ACROS Organics	99,9
Y(NO ₃) ₃ · 6H ₂ O	ACROS Organics	99,50
SiO ₂ - aerosile	Merck KGaA	99,0

Synthesis of ceramic powders

For preparation of ceramic powders conventional milling and hydrothermal synthesis were applied. Traditionally, for preparation of the second part of compositions different milling times, i.e., 4, 12 and 24 hours in dry and wet media are

used by using of a planetary ball mill (RETSCH PM 400) with the weight of 60 g of milled powders without illite clay (compositions **A**, **F** and **D**) and with illite clay additive (compositions **C**, **G** and **E**), Scheme 1.



Scheme 1. Description of ceramic powders traditionally milled for different periods of time

Hydrothermally synthesised suspension was prepared in accordance with the following method:

- dissolution/stirring of metal-containing salts for 1 hour (Table 5);
- adding of nano-sized SiO_2 - aerosol powder;
- adding illite clay to one part of the composition;
- stirring for ~ 20 minutes and adding ammonium hydroxide (NH_4OH) for the pH media to reach ~ 7 ;
- preparation of suspension.

The suspension prepared in the above described way was poured into quartz glass, which was placed in the autoclave that provide the necessary chemical processes run in the following synthesis conditions: maximum temperature ($T = 285 \pm 2$ °C), maximum pressure ($p = 30 - 32$ bar), the temperature rate - 10 °C per minute. The maximum temperature and the maximum pressure were reached within 2,5 hours, dwell time at the maximum temperature - 4 hours.

After hydrothermal synthesis the obtained suspension was treated during three temperature stages:

- drying: at temperatures of $100 - 120$ °C for 20 - 24 hours;
- first heating: at the temperatures of $600 - 650$ °C for 30 minutes;
- second heating: at the temperature of 1000 °C for 30 minutes.

Preparation of samples for sintering. The samples were produced by pressing of the powders with by hydraulic press “Sprut”, the mixture of dry powder and 3 % polivinyl alcohol was used. The maximum pressure applied: 150 MPa; samples of various forms were obtained: disks with the diameter of 30 mm and thickness of 3 mm; cylinders with the diameter 38 mm, height of 44 mm; bars with the length of 52 mm and thickness of 3 mm.

Methods of producing of ceramic samples

Conventional sintering. Ceramic samples were fired in conventional sintering conditions (Nabertherm GmbH HTO/08/14 and Nabertherm HT 16/17 type furnaces) in air environment at the maximum temperature ($1100 - 1200 - 1400(1500)$ °C, with the

isothermal holding time of 30 minutes at the temperature growth rate 5 - 6 °C per minute. The diameter of samples was 30 mm. The samples were cooled together with the furnace.

Spark plasma sintering (SPS). The ceramic samples prepared from the milled and hydrothermally synthesised powders with the weight (~50 grams) were compacted with the help of spark plasma sintering (SPS, Summimoto, Model SPS - 825. CE, Dr. Sinter, Japan) equipment in vacuum environment of 6 Pa with the pressing power on samples 30 MPa at the maximum temperature in the range of 1150 - 1400 °C, isothermal dwell time at the maximum temperature - 2 minutes, at the temperature growth rate of 100 °C per minute. The sample diameter - 30 mm. The samples were cooled together with the furnace.

Methods of research of the processed ceramic powders and ceramic samples

The *particle size* and *morphology* were determined with the help of the scanning electron microscope (SEM - analysis model JSM - T200); for examination of the *surface structure* of ceramic powders nuclear microscopy (VEECO CP II - USA) was used.

The *medium particle size distribution* of ceramic powders was defined by the photon-correlation spectrometer, in which was used strongly diluted 10^{-2} N KCl suspension as the medium.

The *crystallite size* of ceramic samples was determined by the X - Ray diffraction method (model Rigaku Ultimat, Japan, with CuK_α radiation, scanning interval $2\theta = 10 - 60^\circ$, goniometer rotation rate - 2 °C per minute).

The *transformation phases* of ceramic powders were determined at the temperatures in the 20 - 1400 °C range by the differential thermal analysis (DTA) and thermogravimetry (TG) methods by using of the SETARAM SETSYS - Evolution 1750 derivatograph.

The *phase composition* of ceramic samples was determined with the X - Ray diffraction method (model Rigaku Ultimat, Japan, with CuK_α radiation, scanning interval $2\theta = 10 - 60^\circ$, goniometer rotation rate - 2 °C per minute).

The *microstructure* of ceramic samples was analysed with the scanning electronic microscopy (SEM - analysis model JSM - T200).

Shrinkage and *bulk density* of ceramics were determined in accordance with the standard EN LVS 63 - 01: 2001. Shrinkage of ceramic samples is determined by the changes of linear dimensions before and after sintering. Bulk density is determined by the hydrostatic method (Archimede method), open porosity - by weighing of the samples that was impregnated with water, *densification* is determined by mathematical method based on the relation of real and bulk densities ($\rho_{\text{real}} = 3,56 \text{ g/cm}^3$).

Thermal shock resistance of the samples was determined on the basis of the standard LVS EN 993 - 11:2008. Thermal shock resistance was determined in the temperature 500/20 - 1000/20 °C range for each 100 °C.

Flexural strength was determined on the basis of the standard LVS EN 843 - 1:2006. The flexural strength of the samples sintered at 1300 °C and the samples subjected to thermal shock resistance was measured by three point method by using of ZWICK/ROEL BDO - FB020TN equipment.

Modulus of elasticity was determined on the basis of the standard ASTM EN 1876 - 01., by using Buzz - o - Sonic (BuzzMac International, LLC, USA) equipment. The modulus of elasticity was determined for the samples that were subjected to thermal shock resistance.

Compression strength was determined in accordance with the standard LVS EN 14617:2007. The compression strength of sintered ceramics was measured for cylinder

form samples in the temperature 1200 - 1500 °C range. To ensure the parallelity of planars, the surfaces of samples were polished before measuring. Determination of compression strength was performed with the TONI Technik equipment.

Initially, two parallel measurements of compression strength (5 results ($n_i = 5$) of each in two parallel measurements) of the samples sintered from the milled and the hydrothermally synthesized powders by conventional and spark plasma sintering methods performed and mathematical calculation of results done in accordance with [17,18].

The results of compression strength and dispersion of results around the arithmetic mean are shown in Figure 2. The standard deviation of results is from $\pm 0,30$ - 0,93 MPa.

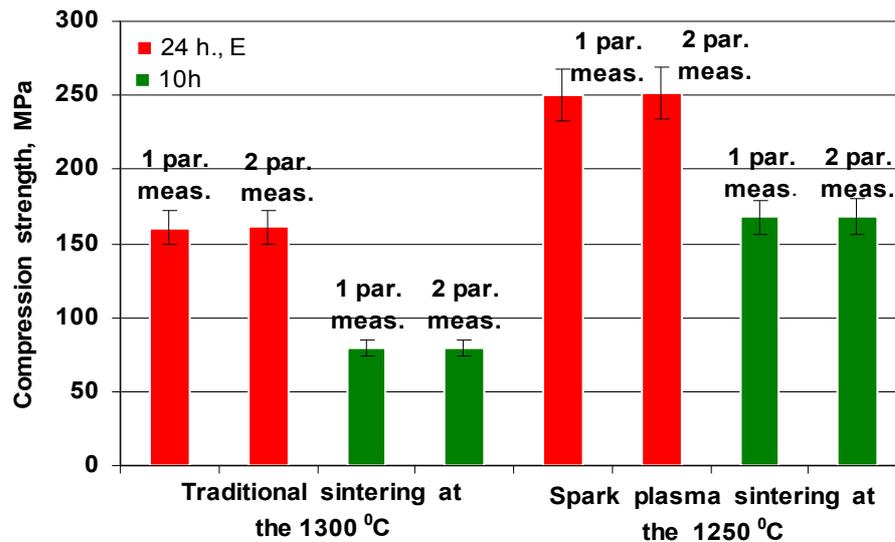


Fig. 2. Results of compression strength and dispersion of results around the arithmetic mean of the samples (compositions **E** and **10h**)

RESULTS AND EVALUATION OF RESULTS

1. Investigations of particle size and morphology

SEM microphotographs of ceramic powders milled during 4 and 24 hours without and with clay additive are shown in Figure 3.

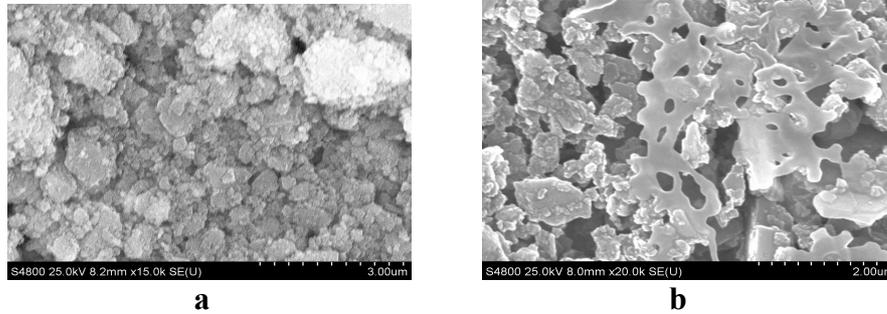


Fig. 3. SEM microphotographs of ceramic powders (compositions A and E):
(a) composition A (powder milled during 4 hours) without clay additive;
(b) composition E (powder milled during 24 hours) with clay additive

SEM microphotograph of powder (Fig. 3a) milled during 4 hours demonstrates closely packed mainly spherically shaped particles. The particle size is in the ~ 3 - 10 μm range. Isolated particles and agglomerates are visible. As a result of 24 hour milling of ceramic powders with clay additive “amorphous” agglomerates with the size of 5 - 10 μm (Fig. 3b) are formed.

AFM microscopy of hydrothermally synthesized powder (composition 10h) (Fig. 4) shows formation of densely packed fine particles with the size ~ 50 - 60 nm.

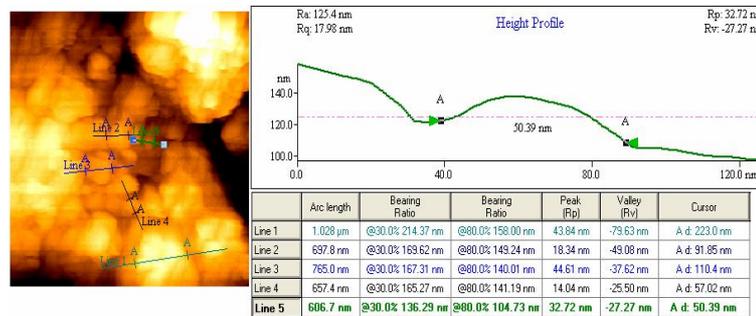


Fig. 4. AFM microscopy of the hydrothermally synthesized powder (composition 10h) heated at 600 $^{\circ}\text{C}$

Particle size distribution (Fig. 5) using of photon correlation spectrometer suggests that the investigated powders (~ 50 - 60 %) consist mainly of the particles and agglomerates with the size in the 200 - 520 nm range. There is also a small quantity of particles (6 - 8 %) with the size in the 500 - 700 nm range.

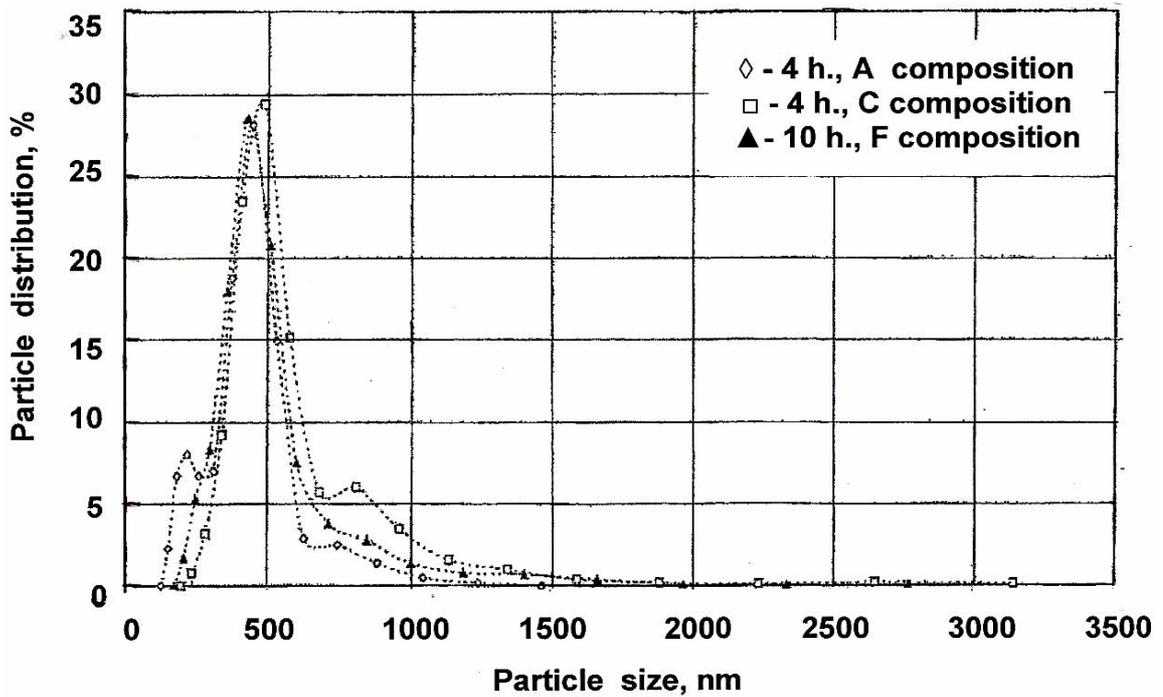


Fig. 5. Distribution of the size of particles and aggregates in ceramic powders without clays (compositions A, F) and with clays (composition C) after 4 and 12 hour milling

Based on the X - Ray analysis phase the calculated size of Al_2O_3 , SiO_2 , ZrO_2 and Y_2O_3 crystallites in ceramic powders milled (during 4 - 24 hours) without and with clay additive is shown in Figure 6.

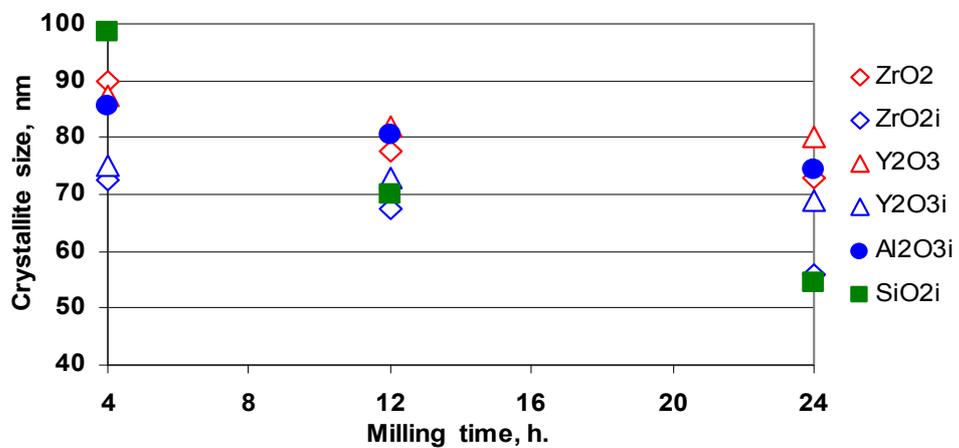


Fig. 6. Changes in crystallite size of ceramic powders milled (during 4 - 24 hours) without and with clay additive. Desig: i - illite clay additive

As can be seen, presence of clay additive favours decrease of the crystalline particle size. The crystallite size is in the 73 - 90 nm range in the compositions without clays and from 72,5 to 85,5 nm in the compositions with clays.

2. Formation of mullite - ZrO₂ ceramics from powders of the first composition group

The main feature of the first composition group (Table 1) is the increased content of Y₂O₃ in the compositions, which purpose is to promote transition from the monoclinic to tetragonal ZrO₂ phase and formation of mullite phase during the sintering process. Formation of crystalline phases in the composition 6 with Y₂O₃ of 0,60 wt. % in the temperature 1200 - 1500 °C range is shown in Figure 7.

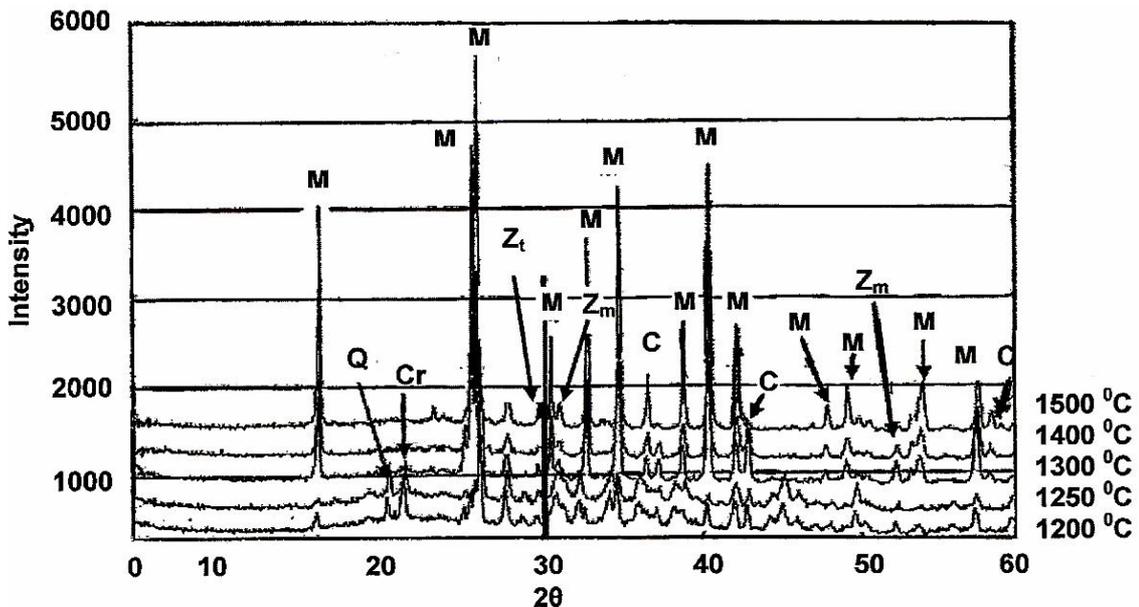


Fig. 7. X-Ray of the formation of crystalline phases of the composition 6 in the temperature 1200 - 1500 °C range. Desig: M - mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), C - corundum ($\alpha - \text{Al}_2\text{O}_3$), Q - quartz (SiO_2), Cr - cristobalite (SiO_2), Z_m - monoclinic ZrO₂, Z_t - tetragonal ZrO₂

As can be seen, crystallization of mullite phase is intensified with the increase of temperature from 1200 to 1500 °C.

As shown in X-Ray patterns - with the temperature increase the formation of tetragonal ZrO₂ is started in samples with Y₂O₃ additive (0,60 wt. %), at the same time, diffraction intensity of monoclinic ZrO₂ phase is decreased, which indicate at partial stabilization of ZrO₂ due to the diffusion of Y³⁺ ions into the crystalline lattice of ZrO₂ during sintering. To ensure more complete transformation of ZrO₂ from monoclinic to tetragonal ZrO₂ as well as achieve formation of mullite, the amount of further stabilised Y₂O₃ additive is increased (see Table 2).

3. Effect of powder processing on the formation of phase composition and microstructure of mullite - ZrO₂ ceramics

3.1. Effect of powders milling time and illite clay additive

Investigations of the milling time and the effect of illite clay additive on the formation of mullite - ZrO₂ ceramic phase composition demonstrated, that the increase of the milling time and presence of clay additive have considerable influence on

on the crystallization of mullite and considering by the intensity of diffraction patterns lead to formation of less tetragonal ZrO_2 .

For example, the X-Ray patterns in Figure 8 show significant difference between the diffraction patterns of the ceramics based on powders that subjected to similar milling times with clay additive (E) and without clay additive (D).

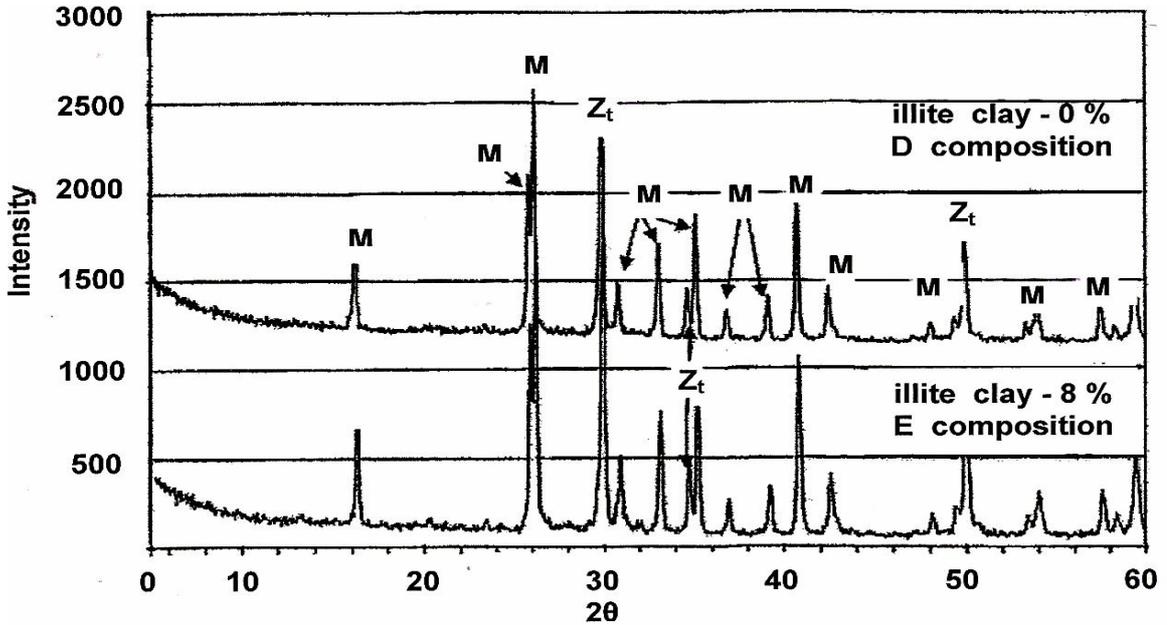


Fig. 8. Formation of crystalline phases in ceramics sintered at $1300\text{ }^{\circ}\text{C}$ depending on the illite clay additive: compositions D and E. Desig: M - mullite ($3Al_2O_3 \cdot 2SiO_2$), Z_t - tetragonal ZrO_2

The influence of clay additive on the intensity of mullite crystallization and, especially on tetragonal ZrO_2 form in the samples sintered at $1300\text{ }^{\circ}\text{C}$, in turn, as shown in the X-Ray diffraction pattern, increases with the increase of the milling time.

SEM microstructures of mullite - ZrO_2 ceramic samples from powders milled during different time and sintered at $1300\text{ }^{\circ}\text{C}$ are shown in Figure 9.

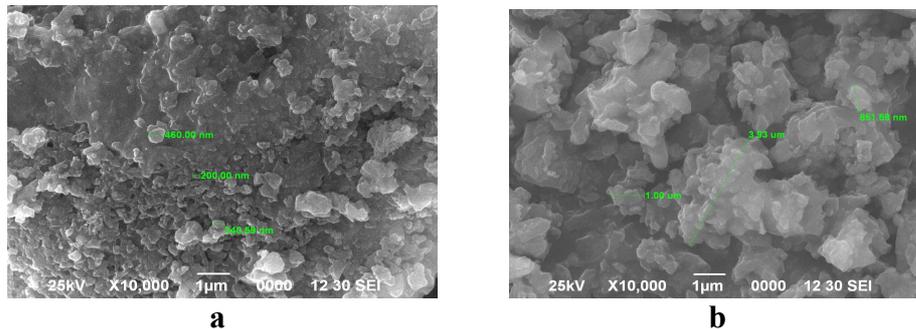


Fig. 9. SEM images of ceramic samples sintered at $1300\text{ }^{\circ}\text{C}$:
(a) composition A (powder milled during 4 hours) without clay additive;
(b) composition D (powder milled during 24 hours) without clay additive

The microstructure of the ceramic sample (Fig. 9a) sintered from the powder milled during 4 hours shows the crystalline structure with irregular distribution of the particles. Particle size is in the $\sim 200 - 460\text{ nm}$ range.

The microstructure of the sample sintered from the powder milled during 24 hours (Fig. 9b) shows uniform clusters of prismatic and pseudoprismatic mullite crystals. Individual crystals size is 850 nm, while clusters of the grain size varies from 1 to 7 μm .

Coarse crystalline microstructure with the crystals sized between 1 - 10 μm is developed in the ceramic samples sintered from the powders with clay additive, for example, in composition C (Fig. 10a).

At the same time, the microstructure of the ceramic sample sintered from the powder milled during 24 hours with clay additive (Fig. 10b) consists of densely packed crystalline grains, mainly of mullite crystals of prismatic and pseudoprismatic habitus. It can be assumed that increase of the milling time especially promotes growth of mullite crystals in the powders with clay additive, which is associated with the formation of liquid phase during the sintering process, thus contributing the development of homogeneous, fine - crystalline structure of mullite - ZrO_2 samples.

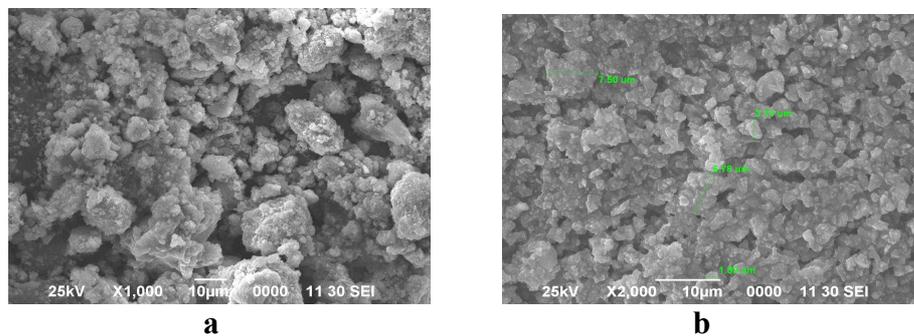


Fig. 10. SEM images of ceramic samples sintered at 1300 $^{\circ}\text{C}$:
(a) composition C (powder milled during 4 hours) with clay additive;
(b) composition E (powder milled during 24 hours) with clay additive

3.2. Influence of hydrothermally synthesized powder

Dependence of formation of the crystalline phase in the ceramic materials sintered from hydrothermally synthesized powder at the maximum sintering temperatures are shown in Figure 11.

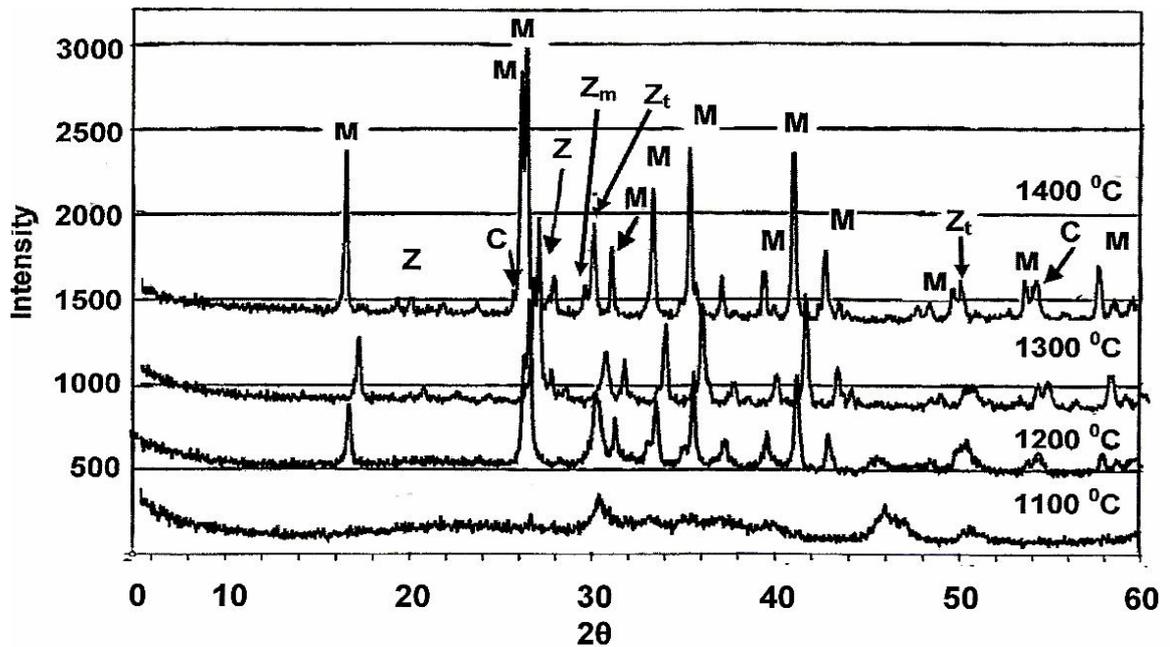


Fig. 11. X-Ray diagrams of ceramic samples sintered from hydrothermally synthesized powders dependence on sintering temperatures (1100 - 1400 °C). Desig: M - mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), C - corundum ($\alpha - \text{Al}_2\text{O}_3$), Z_m - monoclinic ZrO_2 , Z_t - tetragonal ZrO_2 , Z - ZrSiO_4 (zircon)

Results of X-Ray analysis indicate that the crystallization of mullite and tetragonal ZrO_2 phases occur at temperatures, starting at 1200 °C. Its crystallization (especially, mullite) is associated with the decomposition of formed during hydrothermal synthesis pseudocrystalline aluminosilicate - silimanite, which favour the crystallization of mullite at lower temperatures. Unreacted Al_2O_3 that is present in mullite forms the corundum ($\alpha - \text{Al}_2\text{O}_3$) phase.

In turn, crystallization of the ZrSiO_4 phase (diffraction patterns at $2\theta - 20$ and $28,6^\circ$) occurs as a result of decomposition of the weakly bonded aluminosilicate (silimanite), which liberate SiO_2 reacting with ZrO_2 at temperatures in the 1300 - 1400 °C range. Higher sintering temperatures (1300 - 1400 °C) promote further development of mullite phase and the formation of zircon (ZrSiO_4) phase.

It can be assumed that the development of tetragonal ZrO_2 form in ceramics is facilitated by the diffusion of Y^{3+} ions into crystalline lattice of ZrO_2 during hydrothermal synthesis with subsequent stabilization of this phase during sintering of the samples.

SEM microstructure of mullite - ZrO_2 ceramic sample sintered from the hydrothermally synthesized powders at 1300 °C is shown in Figure 12.

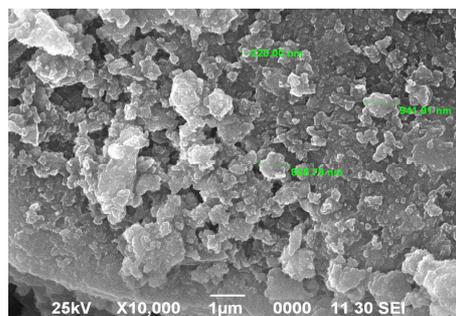


Fig. 12. SEM microstructure of ceramic sample sintered from composition 10h at 1300 °C

The microstructure is non-homogeneous and consists of xenomorphic crystalline mullite clusters with the size (100 - 200 nm) and densely packed crystalline agglomerates with the size of 800 - 900 nm as well as of pores.

3.3. The bulk density - densification

Changes of the bulk density - densification of the ceramic samples sintered from milled and hydrothermally synthesized powders in the temperature 1250 - 1500 °C range are shown in Figure 13.

The bulk density and densification of ceramic samples (Fig. 13) without and with clay additive differs significantly. Clay additive leads to an increase of bulk density. For example, the bulk density of the samples sintered at 1500 °C without clay additive is 2,86 g/cm³, whereas in the presence of clay additive is 3,35 g/cm³. This is explained by the compactness of particles in the presence of liquid phase (mainly, during decomposing and melting of clays), which promotes more active diffusion of the particles. As a result, the particles during sintering process become more active, which leads to increase of densification.

At the same time, ceramic samples without clay additive demonstrate lower bulk density and densification. This is explained by the fact that the sintering process without or with insignificant presence of the liquid phase is occurred; wherewith the diffusion process occurs more slowly.

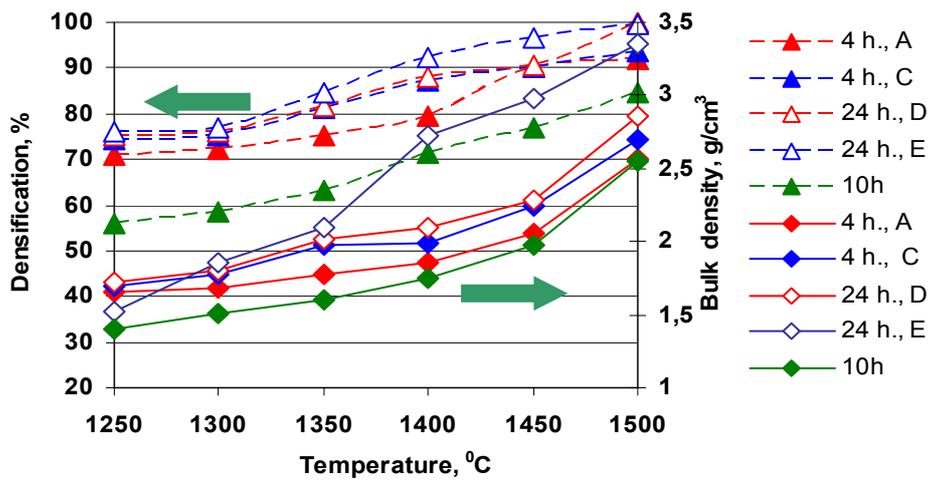


Fig. 13. Changes of the bulk density (—) and densification (---) of the ceramic samples from the powders sintered by various methods depending on the maximum sintering temperatures (1250 - 1500 °C)

As seen above, the ceramic sample sintered from hydrothermally synthesised powder at 1500 °C demonstrates lower bulk density and densification - 2,55 g/cm³ and 84,7% accordingly. Despite the dimensions of the hydrothermally synthesized powder particles being in the nano-size range, the activity of diffusion of these particles is lower than of the particles in the milled powders.

3.4. Mechanical and thermal properties of mullite - ZrO₂ ceramic samples

The comparative results of bulk density and compression strength of the ceramic samples sintered from milled and hydrothermally synthesized powders are given in Figure 14.

The compression strength and bulk density (Fig.14a) of conventionally sintered ceramic samples, depending on the powder milling time, grows more rapidly of the ceramic samples sintered from the powders, which milled up to 12 hours. Further increase of the milling time up to 24 hours additional promote the increase of compression strength and bulk density, especially of the samples with clay additive.

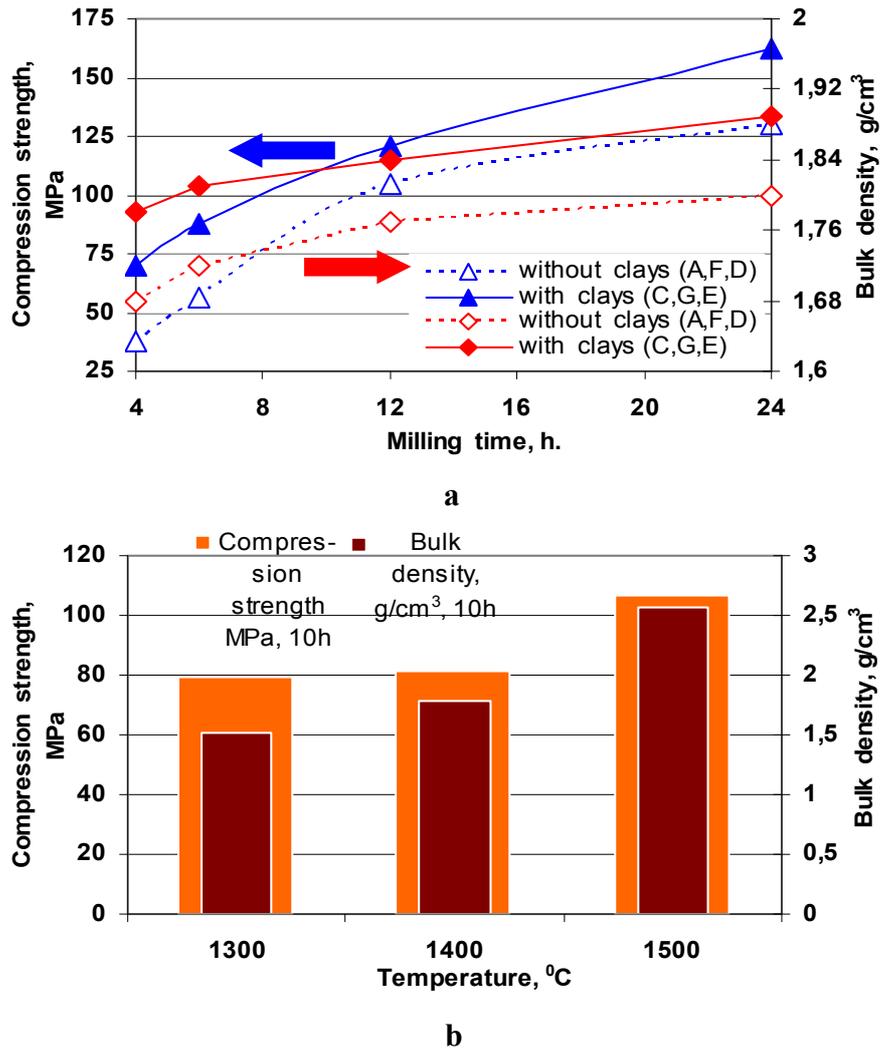


Fig. 14. Changes of compression strength and bulk density of ceramic samples depending on the:
(a) milling time of the powders sintered at 1300 °C;
(b) maximum sintering temperatures of hydrothermally synthesized powders in the temperature 1300 - 1500 °C range

If the maximum compression strength of ceramic samples without clay additive is 130,3 MPa, then the maximum compression strength of ceramic samples with clay additive is 162,0 MPa. This is explained by a more effective compactness of particles and disappearance of pores in the presence of liquid phase.

Our results suggest that the recommended milling time is in the 12 - 24 hours range; however the increase of the milling time from 12 to 24 hours results in relatively insignificant improvement of these properties. Therefore, the optimal duration of the milling time in the listed range may be chosen not only in view of the ceramics properties, but also of the expenses of process.

The compression strength (Fig. 14b) of ceramic samples sintered from the hydrothermally synthesized powders is increased at the temperatures in the 1300 - 1500 °C range. At the same time, the values of compression strength are lower compared to the samples sintered conventionally from the milled powders, for example at the temperature of 1300 °C. This is associated with the presence of pores in sintered ceramics sintered from hydrothermally synthesized powders. It is also evident by lower bulk density of the samples sintered from the hydrothermally synthesized powders compared to the samples sintered conventionally at 1300 °C - 1,51 g/cm³.

The thermal shock resistance of ceramic samples is defined by flexural strength and modulus of elasticity subjected to thermal shock resistance in the temperature 500/20 - 1000/20 °C range. This phenomenon is discussed below within the context of Figure 15.

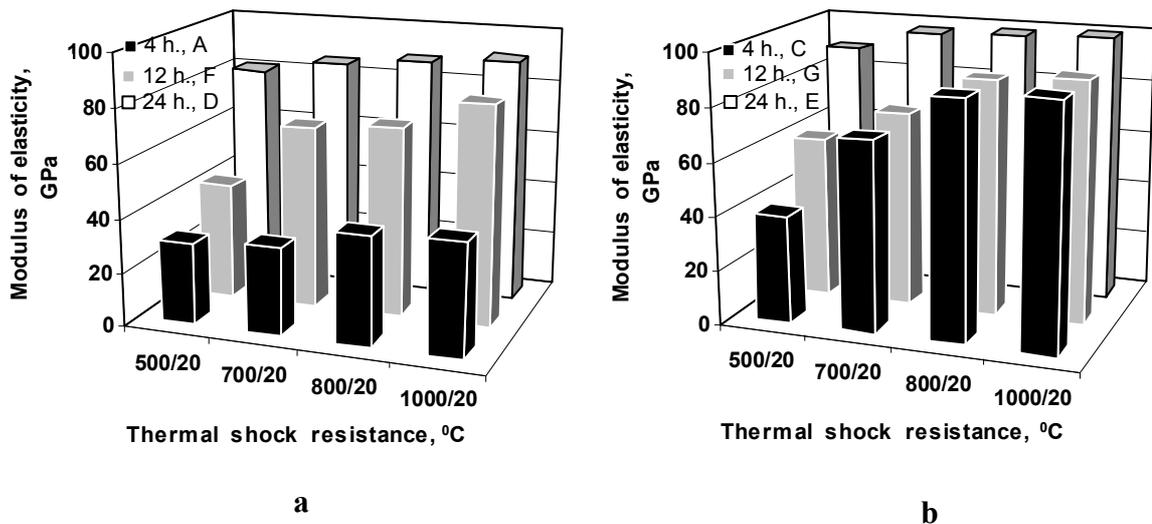
In general, the moduli of elasticity of the samples increase depending on the thermal shock resistance (500/20 - 1000/20 °C) and the dispersity of powders.

The modulus of elasticity increased rapidly, especially at higher thermal shock resistance – 800/20 - 1000/20 °C for the samples without clay additive (Fig. 15a).

As a result, the increase of the modulus of elasticity of ceramic samples (Fig. 15b) with clay additive is uniform, especially at higher thermal shock resistance - 800/20 - 1000/20 °C. These values are in the 88,3 - 99,5 GPa range.

Increase of the modulus of elasticity along with the increase of thermal shock resistance is associated with the ZrO₂ form transformation from the monoclinic ZrO₂ to tetragonal as well as with the development of mullite crystalline forms and the growth of prismatic “needles” [19].

Increase of the modulus of elasticity of the ceramic samples sintered from hydrothermally synthesized powders is shown in Figure 15c. In general, modulus of elasticity are increased together with the increase of thermal shock resistance in the temperature 500/20 - 1000/20 °C range and in the presence of clay additive.



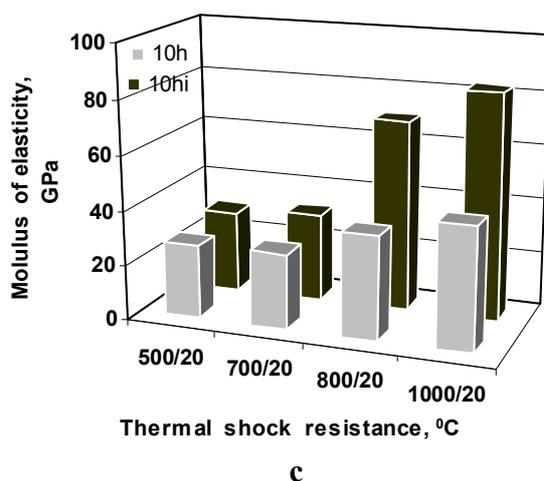


Fig. 15. Changes of the modulus of elasticity of ceramic samples depending on the thermal shock resistance 500/20 - 1000/20 °C:

- (a) samples sintered from the milled powders without clay additive at 1300 °C;
- (b) samples sintered from the milled powders with clay additive at 1300 °C;
- (c) samples sintered from the hydrothermally synthesized powders at 1500 °C.

The resistance of ceramic samples to rapid treatment and cooling, i.e., to thermal shock, is characterised not only by the modulus of elasticity, but also by resistance of sintered samples to cracking/crashing [19]. As our results show, the samples subjected to thermal shock resistance at 1000/20 °C retain the homogeneity in volume and on the surface. This is proved by uniform propagation of the sound via the tested sample, through experimental setting of the modulus of elasticity, by using the (Buzz - o - Sonic) equipment.

Increase of the flexural strength of ceramic samples demonstrate behaviour similar to the samples, for which the modulus of elasticity is increased depending on the thermal shock resistance. However, certain differences for determining flexural strength of the samples are evident.

Flexural strength of ceramic samples without clay additive increases more rapidly with the increase of thermal shock resistance and the dispersity of the ceramic powders. For example, the flexural strength of the samples sintered from the powder that milled during 4 hours is 15,9 MPa, while for these sintered from the powder milled during 24 hours the flexural strength is 42,6 MPa (Fig. 16a). This is associated with the considerable or even complete transformation of ZrO₂ modification from monoclinic to tetragonal ZrO₂ at the maximum thermal shock resistance - 1000/20 °C.

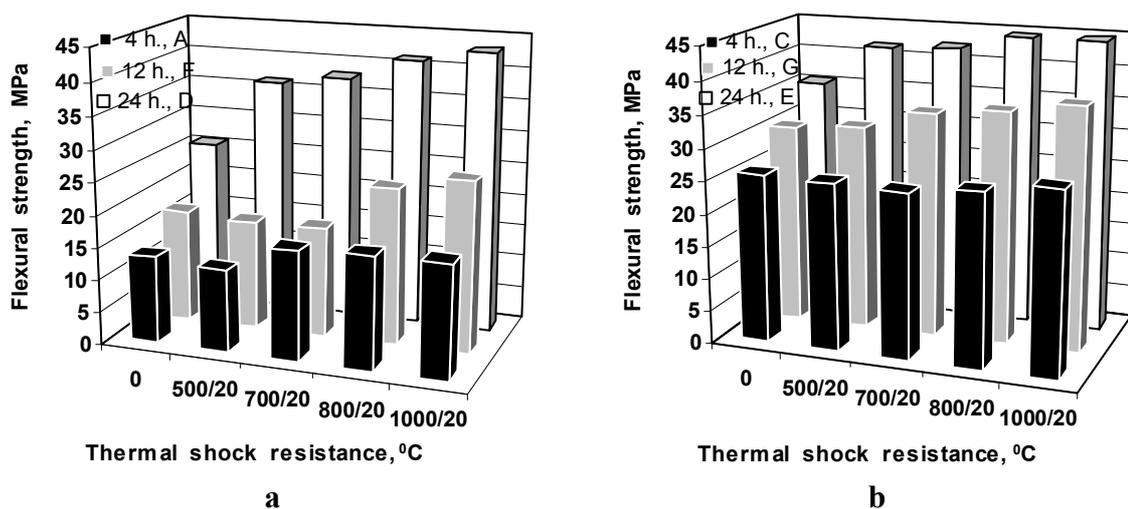


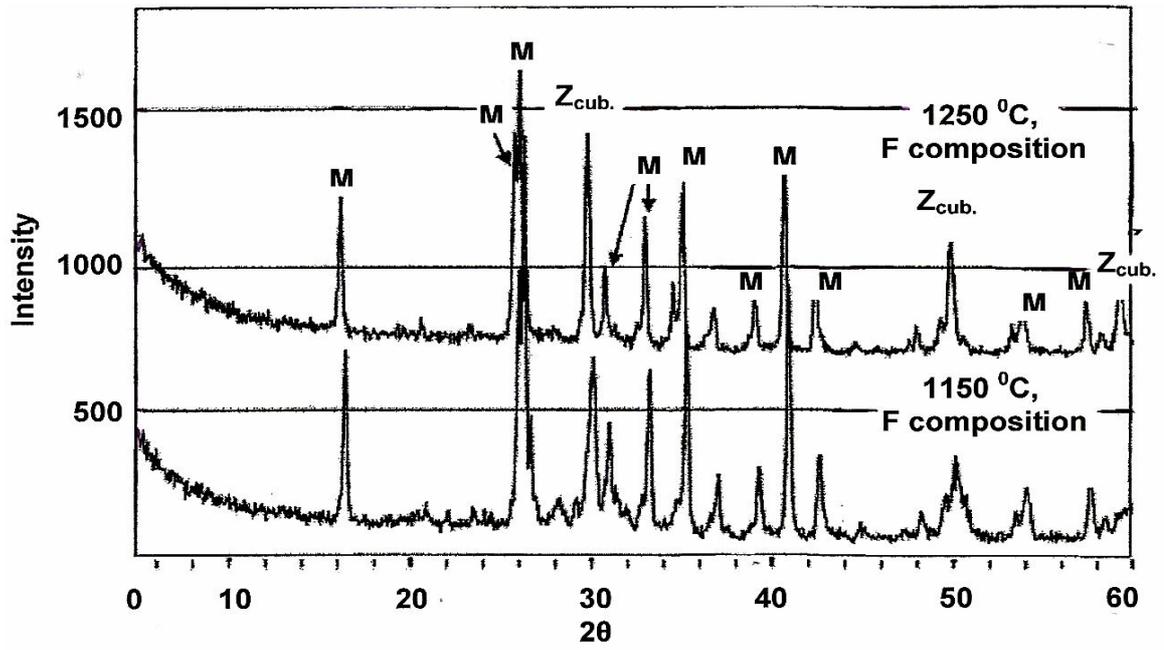
Fig. 16. The changes of flexural strength of ceramic samples sintered at 1300 °C depending on the thermal shock resistance in the 500/20 - 1000/20 °C range: **(a)** without clay additive; **(b)** with clay additive

The increase of flexural strength of the ceramic samples sintered from the milled powders (compositions **C**, **G**, **E**) with clay additive (Fig. **16b**) is similar to the increase of modulus of elasticity. The flexural strength of ceramic samples increases uniformly and gradually. Increase of the flexural strength is also determined by the dispersity of the powders. With the increase of thermal shock resistance the flexural strength of the samples sintered from more dispersed powders (milled during 24 hours) compared to the samples sintered from less dispersed powders (milled during 4 hours) are increased gradually.

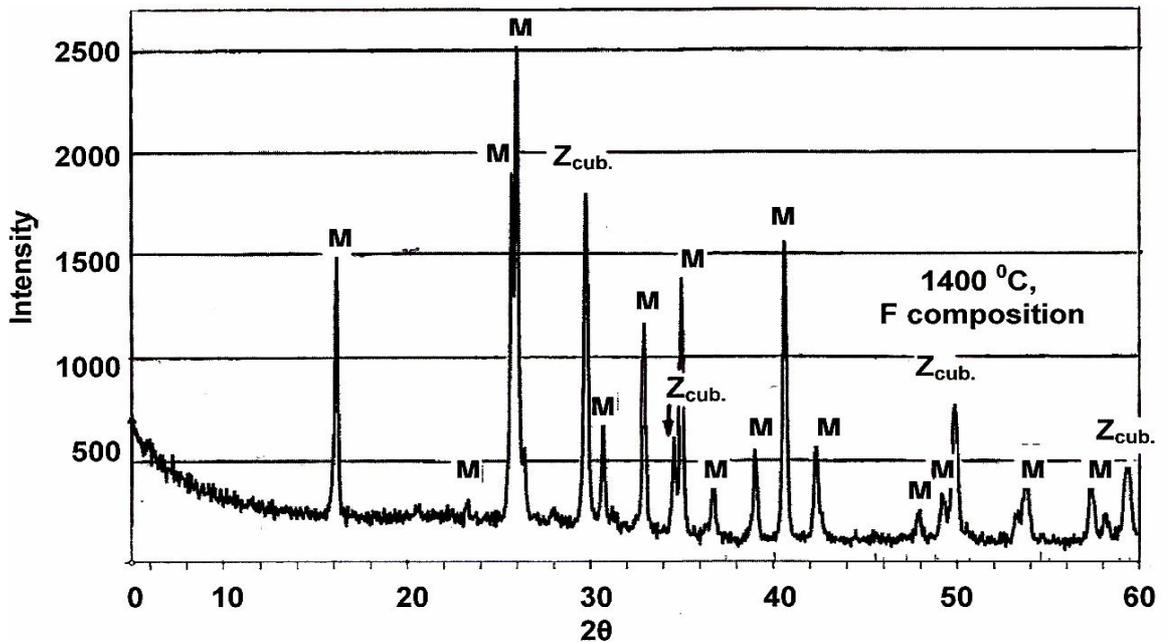
The flexural strength of sintered ceramic samples (Fig. **16**) that haven't subject to the verification of thermal shock resistance is considerably lower. For example, the flexural strength of the samples without clay additive is 13,5 - 15,9 MPa and of the samples with clay additive is in the 26,0 - 28,1 MPa range with the increase of the dispersity of powders. This is explained by partial stabilization of tetragonal ZrO₂ phase in these samples unlike the samples that subjected to the verification of thermal shock resistance.

5. Influence of spark plasma sintering (SPS) on the phase composition, structure and properties of mullite - ZrO₂ ceramic samples

Formation of crystalline phases in the ceramic samples compacted from the milled and hydrothermally synthesized powders sintered by spark plasma in the temperature 1150 - 1400 °C range is shown in Figure **17**.



a



b

Fig. 17. X-Ray diffraction patterns of the compacted ceramic sample (composition F) sintered by spark plasma sintering: **(a)** sintered in the temperature 1150 - 1250 °C range; **(b)** sintered at 1400 °C. Desig: M - mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), $Z_{\text{cub.}}$ - solid solution of cubic ZrO_2

As shown in the X-Ray diffraction patterns in Figure 17, formation of the mullite phase and the stable solid solution of cubic ZrO_2 are intensified at the maximum temperatures of 1150 - 1400 °C. Not only changes in the sintering technologies, but also presence of Y_2O_3 additive contribute to active formation of mullite and the solid solution of cubic ZrO_2 during spark plasma sintering process, which is the result of active particle diffusion.

As indicated in the work [6], the transformation from tetragonal ZrO_2 to cubic ZrO_2 form at the atmospheric pressure and in the presence of (MgO , CaO , Y_2O_3 etc.) additives occurs at the temperatures approximately $2100\text{ }^\circ\text{C}$. Obviously, formation of solid solution of cubic ZrO_2 in vacuum occurs at lower temperatures during spark plasma sintering process.

During spark plasma sintering of the samples compacted from the hydrothermally synthesized powders zircon ($ZrSiO_4$) is crystallized as well (Fig. 18), which diffraction intensity at these temperatures is increased, especially at the temperature $1400\text{ }^\circ\text{C}$.

The formation of zircon phase is associated with the decomposition of non-stoichiometric mullite, forming SiO_2 , which reacts with ZrO_2 during spark plasma sintering process [13].

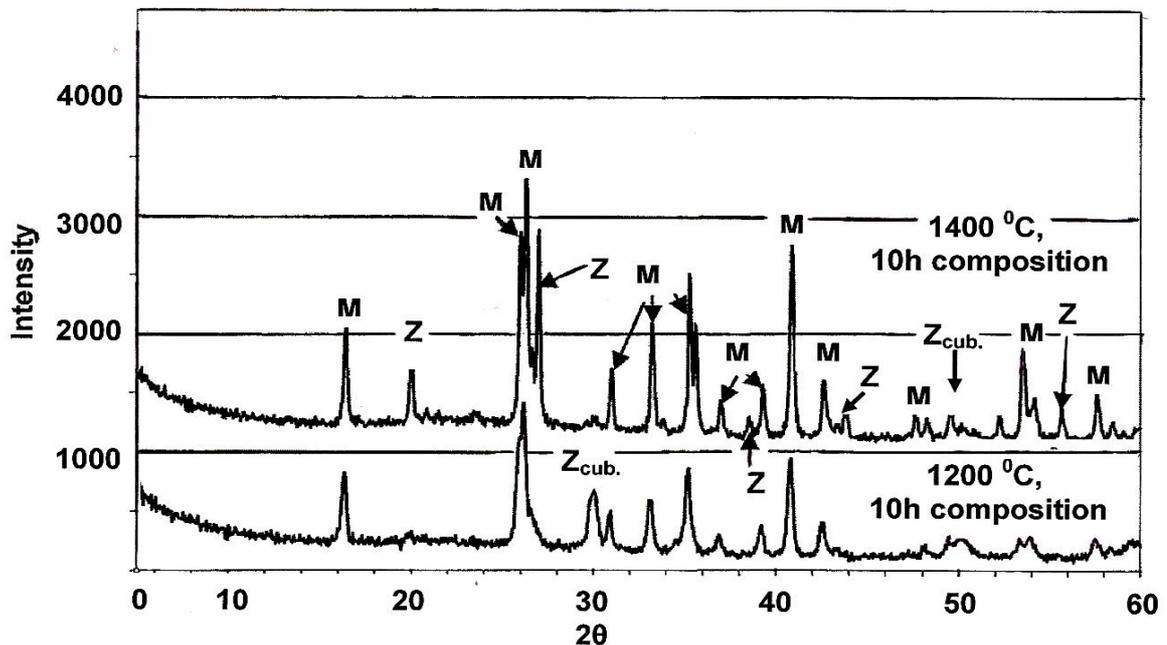


Fig. 18. X-Ray diffraction patterns of compacted ceramic samples compacted from the hydrothermally synthesized powders by the spark plasma sintering at 1200 and $1400\text{ }^\circ\text{C}$ (composition **10h**). Desig: M - mullite ($3Al_2O_3 \cdot 2SiO_2$), $Z_{cub.}$ - solid solution of cubic ZrO_2 , Z - zircon ($ZrSiO_4$)

The comparative SEM microstructures of ceramic samples sintered by conventional method and by spark plasma sintering are shown in Figure 19.

Ceramic samples compacted by spark plasma sintering have fine-grained, uniform, dense and crystalline microstructure (Fig. 19b). The microstructure consists of fine, crystalline mullite crystals with the size of $1 - 2\text{ }\mu\text{m}$ and regularly distributed solid solution of the cubic ZrO_2 phase. The microstructure of the traditionally sintered ceramic sample (Fig. 19a) displays well developed mullite crystals with the size in the $5 - 6\text{ }\mu\text{m}$ range.

The microstructure of the ceramic sample (Fig. 19c) sintered from hydrothermally synthesized powders is uniform, dense, equally amorphous, consists of xenomorphic mullite crystals and regularly distributed solid solution of cubic ZrO_2 in the mullite matrix.

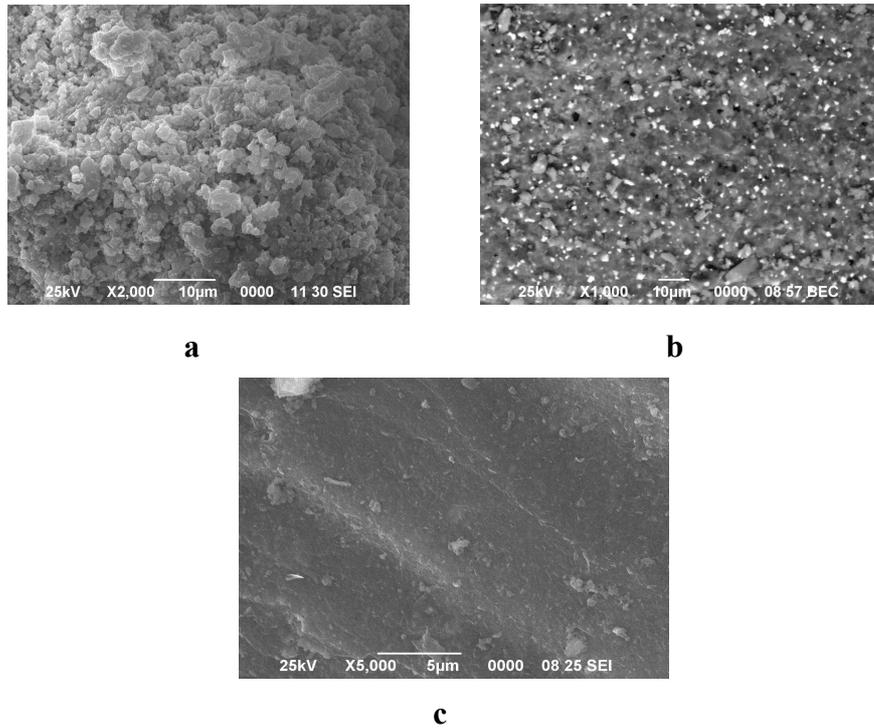


Fig. 19. SEM microstructures of the ceramic samples:
(a) sintered by conventional method at 1300 °C from milled powder;
(b) sintered by spark plasma sintering at 1250 °C from milled powder;
(c) compacted by spark plasma sintering at 1250 °C from hydrothermally synthesized powder. Mullite crystals (dark phase), corundum crystals (grey phase) and solid solution of cubic ZrO₂ phase (white grains)

Changes of sample size compacted from the milled and hydrothermally synthesized powders by spark plasma sintering in the temperature 500 - 1200 °C range are shown in Figure 20.

The changes of size of ceramic samples are amplified at the temperature, starting at 500 °C and rapidly increased during spark plasma sintering process in the temperature 900 - 1200 °C range.

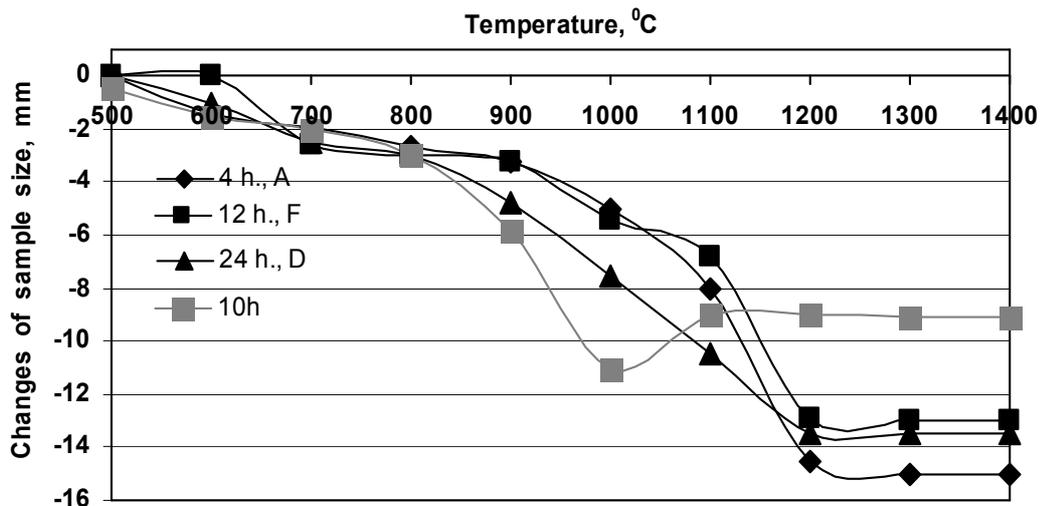


Fig. 20. Changes of size of ceramic samples compacted from milled and hydrothermally synthesized powders by using of spark plasma sintering in the temperature 500 - 1200 °C range

Changes of size of ceramic samples compacted from the milled powders demonstrate the similar behaviour, with the exception of ceramic sample compacted from the powder milled during 24 hours (composition **D**) showing the changes of size at temperature up to 1200 °C, that is more faster compared to the samples compacted from the compositions **A** and **F** during densification process. Total shrinkage of the samples compacted from the composition **D** powder at 1400 °C is 46,7 % compared to the samples sintered from the compositions **A** and **F**, that demonstrate the shrinkage of 43,3 % and 45,6 % respectively.

Shrinkage of the samples (considering to the acquired changes of size) doesn't changed in the temperature 1200(1250) - 1400 °C range. Dense ceramics structure of the mullite - ZrO₂ is formed at 1250 °C (see Fig. **19b**).

Various changes of size are displayed the sample compacted from the hydrothermally synthesized powder (composition **10h**), which develop extreme shrinkage of 36,7 % at the temperature 1000 °C. This can be explained by the assumption that the agglomerates “collapsed” in powder at the temperatures in the 900 - 1000 °C range, thus forming new fine-dispersed and active particles promoting rapid compaction of the hydrothermally synthesized powders up to 1000 °C. Shrinkage have retarded in the temperature 1000 - 1100 °C range, because agglomeration process is occurred. No change in compaction of the samples was noticed at higher temperatures of 1100 - 1400 °C.

Comparative changes in the bulk density of the ceramic samples prepared by conventional and spark plasma sintering and dependence on the milling time and hydrothermally synthesized powders are shown in Figure **21**.

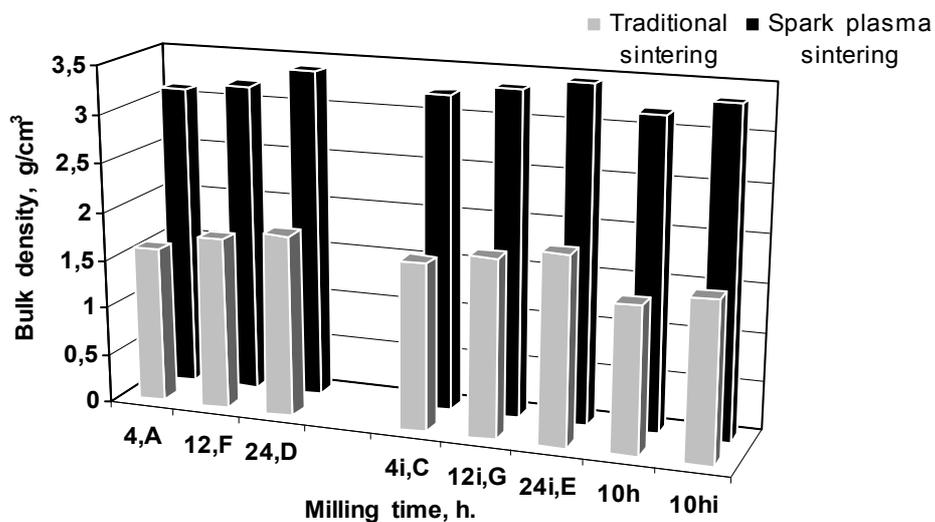


Fig. 21. Changes of the bulk density of ceramic samples compacted from milled and hydrothermally synthesized powders by using of spark plasma sintering at 1250 °C and by conventional sintering at 1300 °C. Desig: i - illite clay additive

The bulk density of sintered samples differs significantly. The bulk density of ceramic samples compacted by spark plasma sintering is in the 3,12 - 3,45 g/cm³ range. The bulk density of the samples sintered by conventional method and by spark plasma sintering without and with the clay additive gradually increase with the increase of the milling time, including increase of powder dispersity.

It should be noted, that ceramics without clay additive that sintered traditionally from hydrothermally synthesized powder has lower bulk density ($1,51 \text{ g/cm}^3$) compared to the samples compacted from milled powder (composition E - $1,87 \text{ g/cm}^3$) without clay additive.

Changes of compression strength of mullite - ZrO_2 ceramic samples depending on the dispersity of powders and sintering methods are shown in Figure 22.

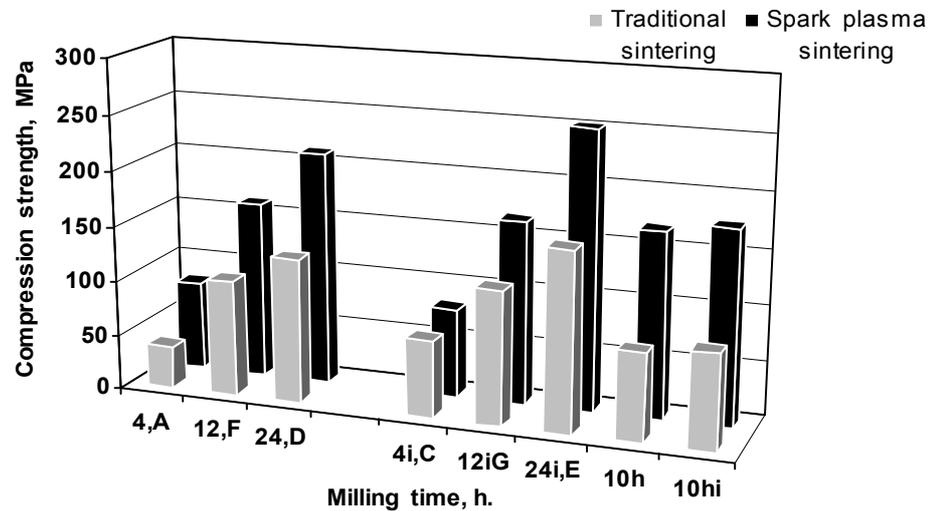


Fig. 22. Changes in compression strength of ceramic samples sintered from milled and hydrothermally synthesized powders by using of spark plasma sintering at $1250 \text{ }^\circ\text{C}$ and compacted by using conventional sintering at $1300 \text{ }^\circ\text{C}$. Desig: i - illite clay additive

The compression strength of ceramic samples sintered by traditional method (Fig. 22) dependence on the dispersity of powders and illite clay additive correlates with the corresponding bulk densities of the samples and increased from $38,0$ to $162,0 \text{ MPa}$.

The ceramic sample with clay additive (composition E) exhibits the compression strength of up to $252,0 \text{ MPa}$ during spark plasma sintering. This sample is characterized by uniform and dense microstructure with the prevailing of mullite crystals with regularly distributed crystalline grains of solid solution of cubic ZrO_2 (See Fig. 19b).

The ceramic samples sintered by traditional method from hydrothermally synthesized powders at the temperature $1300 \text{ }^\circ\text{C}$ demonstrate the compression strength that is not less than $79,5 \text{ MPa}$. The compression strength of the samples sintered from hydrothermally synthesized powders without clay additive at $1250 \text{ }^\circ\text{C}$ during spark plasma sintering increased up to $168,0 \text{ MPa}$, while with clay additive - $176,0 \text{ MPa}$.

CONCLUSIONS

- Development of mullite - ZrO_2 ceramic powders processed by conventional milling technique and hydrothermal synthesis was performed in this research work. Particle size/distribution and morphology, their influence on the sintering process (in the conditions of conventional and spark plasma sintering) as well as crystalline phases, structure, properties (shrinkage, bulk density/densification), flexural strength, modulus of elasticity, including their dependence on the thermal shock and compression strength of sintered mullite - ZrO_2 ceramic materials were determined;

- increase of milling time (4 - 24 hours) favours development of “amorphous” particles in the raw powders. Clay additives promote decrease of the particle size as well as formation of agglomerates. Ceramic powder synthesized by hydrothermal method consists of the fine particles with the size $\sim 50 - 60$ nm. Particle size distribution consists mainly of the particles ($\sim 50 - 60$ %) with the size in the 200 - 520 nm range. There is also a small quantity of particles (6 - 8 %) with the size in the 500 - 700 nm range;
- The crystalline particle size in the compositions of powders without clay additive is 73 - 90 nm, while in the compositions with clay is in the 72,5 - 85,5 nm range;
- the milled powders with clay additive compared to the hydrothermally synthesized powders promote development of dense, more uniform crystalline microstructure of the ceramics. The optimal milling time is in the 12 - 24 hours range;
- crystalline phases – mullite, corundum, tetragonal ZrO_2 are formed in the mullite - $ZrO_2(Y_2O_3)$ ceramic materials that are sintered traditionally from the milled powders at the maximum temperatures 1200 - 1500 °C. Formation of the mullite phase starts at 1200 °C, while at the temperature of 1400 °C the zircon ($ZrSiO_4$) is formed in the ceramic samples sintered from the hydrothermally synthesized powders;
- increase of the milling time of raw powders up to 24 hours and presence of the clay additive lead to the increase of the bulk density, densification, higher compression strength of up to 3,35 g/cm³, 99,7 % and 162,0 MPa, respectively, in the ceramic samples sintered at the temperature 1500 °C. The ceramic samples sintered from hydrothermally synthesized powders demonstrate lower value of the bulk density (2,55 g/cm³), densification (84,7%) and compression strength (106,5 MPa);
- values of modulus of elasticity (89,5 - 99,5 GPa) and flexural strength (41,8 - 44,7 MPa) show increase of the samples with clay additive subjected to the thermal shock resistance in the 500/20 - 1000/20 °C range. Samples sintered from hydrothermally synthesized powders with clay additive are characterized by lower values of modulus of elasticity (30,0 - 82,7 GPa) at the thermal shock resistance in the 500/20 - 1000/20 °C range;
- spark plasma sintering method promotes formation of the uniform, dense, crystalline microstructure of the samples sintered from milled powders consisting of fine-crystalline mullite grains with the regularly distributed solid solution of cubic ZrO_2 particles. Similar to amorphous microstructure consisting of xenomorphic mullite crystals is developed in the ceramic samples compacted from hydrothermally synthesized powders;
- the value of compression strength of the sample produced by spark plasma sintering is approximately by 90 MPa is higher than the value of traditionally sintered samples. The ceramic samples with the bulk density and compression strength of 3,45 g/cm³ and 252,0 MPa, respectively, are obtained from the powder milled during 24 hours with clay additive that was sintered by spark plasma sintering method at the temperature 1250 °C.

PUBLICATIONS REVIEW

1. G. Sedmale, I. Sperberga, A. Hmelov, U. Sedmalis, A. Actins. Phase formation and structure of mullite - alumina - zirconia and spinel - enstatite ceramics from synthesis ingredients and mineral raw materials. *Mat. Sci. Forum*, 2008, vol. 575 - 578, Switzerland, pp. 953 - 958;
2. Г. П. Седмале, И. Э. Шперберга, А. В. Хмелёв, А. Патмалниекс. Образование керамики в системе $Al_2O_3 - SiO_2 - ZrO_2$ в присутствии минерализаторов. - *Огнеупоры и техническая керамика*. - 2008, Москва, Россия, т. 5, с. 18 - 23;
3. G. Sedmale, I. Sperberga, J. Grabis, A. Hmelov, L. Lindina. Characterization of mullite-zirconia ceramics produced from different synthesized powders. *Processing of the 2nd International Congress on Ceramics - Global Roadmap for Ceramics* (Edited by A. Bellosi & G.N. Babini), Verona, Italija, 2008, pp. 1 - 6;
4. G. Sedmale, A. Hmeļovs High - temperature Ceramic Materials, *High Tech in Latvia*; 2008, p. 18 - 18.
5. G. Sedmale, I. Sperberga, A. Hmeļovs. Dabas aizsardzības motivēti keramikas materiāli, pielietojot Latvijas minerālās izejvielas. *Materiālzinātne un lietišķā ķīmija*, 2009, Rīga, Latvija, lpp. 78. - 87.;
6. G. Sedmale, A. Hmelov, I. Sperberga, A. Pludons, J. Grabis. Hydrothermal synthesis of $Al_2O_3 - SiO_2 - ZrO_2(Y_2O_3)$ powder and their application for high - temperature ceramics. *Chemine Technologija*, Kaunos, Lietuva, 2009, pp. 56 - 61;
7. I. Sperberga, G. Sedmale, A. Pludons, A. Hmelov, I. Steins. Contribution of spark plasma sintering to the development of mullite - ZrO_2 ceramics. *Chemine Technologija*, Kaunos, Lietuva, 2009, pp. 61 - 65;
8. G. Sedmale, I. Sperberga, J. Grabis, A. Hmelov. Phase development and mechanical properties of high - temperature ceramic in the system mullite - ZrO_2 . *Processing of symposium „Functional and structural ceramic and ceramic matrix composites (CCMC)”* (edited by V. Skorokhod), Kiev, Ukraine, 2009, pp. 237 - 243;
9. Latvijas patenti. Nr. 14238B, C04 B33/26; C04 B35/185; C04 B35/106; C04B35/119; C04 B38/00. G. Sedmale, A. Hmeļovs, I. Šperberga. Termiski un mehāniski izturīga keramika. (02.09.2010.);
10. Г. П. Седмале, А. В. Хмелёв, И. Э. Шперберга. Влияние дисперсности керамических порошков на свойства муллитциркониевой керамики. *Новые огнеупоры*, Москва, Россия, 2011, с. 41 - 46;
11. Г. П. Седмале, А. В. Хмелёв. Характеристика муллит-циркониевой керамики, полученной из порошков, синтезированных гидротермальным способом. *Стекло и керамика*, Москва, Россия, 2011, с. 23 - 27;
12. G. P. Sedmale, A. V. Khmelev. Characteristic of mullite - zirconium ceramic obtained from powders synthesized by the hydrothermal method. *Glass and Ceramics*, Moscow, Russia (Russian Original), 2011, vol. 68, No 3-4, pp. 123 - 127.
13. G. Sedmale, I. Sperberga, A. Hmelov, I. Steins. Characterization of mullite - ZrO_2 ceramics prepared by various methods. *Mat. Sci. and Eng.*, Osaka, Japan, 2011, pp. 1 - 4.

CONFERENCE REVIEW

1. G. Sedmale, L. Lindiņa, I. Apsitis, A. Hmelov, I. Sperberga. Influence of mineralizers on high - temperature phases formation. The 3rd Baltic Conference of Silicate Materials, Riga, Latvia: RTU, 24 - 25 may, 2007;
2. I. Sperberga, A. Hmelov, A. Patmalnieks, G. Sedmale. Formation of ceramics in alumina - zirconia - silica system by presence of mineralizers. ECERS, Berlin, Germany: Estrel Convention Center, 17 - 21 june, 2007;
3. A. Hmeļovs, G. Sedmale, J. Grabis. Keramikas izejas pulvera ieguves veida ietekme uz mullīta - ZrO₂ keramikas fāžu sastāvu un īpašībām. 49. Studentu Zinātniskā un tehniskā konference, Rīga, Latvija: RTU, 27. - 30. aprīlis, 2008;
4. G. Sedmale, I. Sperberga, J. Grabis, A. Hmelov, L. Lindina. Characterization of mullite - zirconia ceramics produced from different synthesized powders. The 2nd International Congress on Ceramics, Verona, Italy: Gran Guardia Palace - Venue Centre, 29 june - 4 july, 2008;
5. G. Sedmale, I. Sperberga, J. Grabis, A. Hmelov. Phase development and properties of high - temperature ceramics in the system mullite - ZrO₂. E - MRS Fall Meeting Conference, Warsaw, Poland: Warsaw university of Technology, 15 - 19 september, 2008;
6. A. Hmelov, G. Sedmale, I. Sperberga, J. Grabis, A. Pludons. Hydrothermal synthesis of Al₂O₃ - SiO₂ - ZrO₂(Y₂O₃) powder and their application for high - temperature ceramics. The 4th Baltic Conference on Silicate Materials, Kaunos, Lietuva: Kaunos university of Technology, 7 - 8 may, 2009;
7. G. Sedmale, I. Sperberga, I. Steins, A. Pludons, A. Hmelov. Contribution of spark plasma sintering to the development of mullite - ZrO₂ ceramics. The 4th Baltic Conference on Silicate Materials, Kaunos, Lietuva: Kaunos university of Technology, 7 - 8 may, 2009;
8. I. Sperberga, G. Sedmale, U. Sedmalis, A. Hmelov, I. Steins. Spark plasma sintering of differently synthesized ceramic powders. The 11th International Conference and exhibition of the European Ceramic Society, Krakov, Poland: Auditorium Maximum of Jagiellonian university, 21 - 25 june, 2009;
9. G. Sedmale, A. Hmeļovs, I. Šperberga. Differencēti iegūtu pulveru ietekme uz mullīta - ZrO₂ keramikas īpašībām. 50. Starptautiskā Zinātniskā konference, Rīga, Latvija: RTU, 12. - 16. oktobris, 2009;
10. G. Sedmale, A. Hmelov, I. Sperberga, J. Grabis. Phase development and mechanical properties of high - temperature ceramic in the system mullite - ZrO₂. International Conference - HighMatTech, Kiev, Ukraine: Frantsevich Institute for Problems of Materials Science of NASU, 19 - 23 oktober, 2009;
11. G. Sedmale, A. Hmeļovs, I. Šteins, I. Šperberga. The use of SPS method for sintering of mullite - ZrO₂ ceramics. The 51th International Conference, Riga, Latvia: RTU, 11 - 15 oktober, 2010;
12. G. Sedmale, I. Sperberga, A. Hmelov, I. Steins. Contribution of various preparing methods of starting powders and sintering to the development of mullite - ZrO₂ ceramics. The 3rd International Congress on Ceramics, Osaka, Japan: Osaka International Convention Centre, 14 - 18 november, 2010;

13. A. Hmelov, G. Sedmale, I. Šperberga, J. Grabis. Mullite - ZrO₂ ceramics prepared by various methods. The 5th Baltic Conference on Silicate Materials - BaltSilica, Riga, Latvia: RTU, 23 - 25 may, 2011.

CITATED LITERATURE REVIEW

1. I. Šperberga, U. Sedmalis, G. Sedmale. Silikātu un grūti kustošo savienojumu nemetālisku materiālu fizikālā ķīmija //RTU. - 2010, lpp. 170.
2. Торопов Н. А., Барзаковский В. П., Лапин В. В. Диаграммы состояния силикатных систем - двойные системы (справочник) // „Наука”. - 1969, т. 1, с. 821.
3. P. Boch, J. - C. Niepce. Ceramic materials: processes, properties and applications // Kluwer Publishers. - 2007, p. 213 - 126.
4. T. Chraska, K. Neufutt, J. P. Ctibor, P. Rohan. Fabrication of bulk nanocrystalline alumina - zirconia materials // Ceramics International. - 2008. - vol. 34. - p. 1229 - 1236.
5. C. Zaneli, M. Dondi, M. Raimondo, G. Guarini. Phase composition of alumina - mullite - zirconia - refractory materials // J. Eur. Ceram. Soc. - 2010. - vol. 30. - p. 29 - 35.
6. Торопов Н. А., Барзаковский В. П., Лапин В. В. Диаграммы состояния силикатных систем (справочник) // „Наука”. - 1979, т. 1, с. 437 - 439.
7. J. Shackelford, F. Doremus. Ceramics and glass materials: Structure, properties and processing // Materials Information Society. - 2008, p. 201.
8. F. Aldinger, V. A. Weber. Advanced ceramics and future materials: an introduction to structures, properties, technologies, methods // Kluwer Publishers. - 2010, p. 178 - 179.
9. Yu. E. Pivinskii, P. V. Dyakin, S. V. Vikhman. A study and comparison of the properties of bauxite treated by dry and wet grinding technologies // Refractories and Industrial Ceramics. - 2003. - vol. 44. - No 6. - p. 399 - 404.
10. Yu. E. Pivinskii, P. V. Dyakin, S. V. Vikhman. Press - molding of high - alumina ceramic castables. Part 1. Compaction and properties of matrix system based on mixed HCBS compositions; bauxite, quartz and commercial alumina // Refractories and Industrial Ceramics. - 2005. - vol. 46. - No 3. - p. 220 - 224.
11. Yu. E. Pivinskii, P. V. Dyakin. Preparation and properties of corundum HCBS ceramics. Part 1. Mixed HCBS in the system corundum - very fine quartz glass // Refractories and Industrial Ceramics. - 2010. - vol. 51. - No 1. - p. 25 - 31.
12. H. C. Park, T. Y. Yang, S. Y. Yoon. Preparation of zirconia - mullite composites by an infiltration route // Mat. Sci. Eng. A. - 2005. - vol. 405. - p. 2333 - 2338.
13. K. A. Khor, L. G. Yu, Y. Li, Z. L. Dong, Z. A. Munir. Spark plasma reaction sintering of mullite - ZrO₂ composites from plasma spheroidized zircon/ alumina powders // Mat. Sci. Eng. - 2003. - vol. 339. - p. 286 - 296.
14. S. Hartmut, S. Komarneni. Mullite // Technology and Engineering. - 2006, p. 509.
15. C. Kaya, X. Gu, E. G. Butler. Nanostructured ceramic powder by hydrothermal synthesis and their application // Microporous and Mesoporous materials. - 2002. - vol. 54. - No 1-2. - p. 37 - 49.

16. E. Rocha - Rongel, H. Miyamoto. Zirconia - mullite composites consolidated by spark plasma reaction sintering from zircon and alumina // J. Am. Ceram. Soc. - 2005. - vol. 88. - No 5. - p. 1150 - 1157.
17. Абрамс И. А. Математическая обработка результатов измерений - лабораторный практикум // РТУ. - 1980, с. 41.
18. M. Jansone, I. Klincāre, A. Ķiploka, M. Knite, V. Novikovs. Fizikas praktikums studentiem // RTU. - 2003, лр. 6 - 8, 12 - 14.
19. N. M. Rendtorff, L. B. Garrido, E. F. Aglietti. Thermal shock behaviour of dense mullite - zirconia composites obtained by two processing routes // Ceramics International. - 2008. - vol. 34. - p. 2017 - 2024.