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Hydrothermal synthesis of Al_2O_3–SiO_2–$ZrO_2(Y_2O_3)$ powder and their application for high-temperature ceramics

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Hydrothermal treatment of starting components was applied over the range of temperature 270–300 °C and at a pressure of 30 bars of the starting components for the synthesis of powders for mullite–zirconia ceramics. $Al(NO)_3 \cdot 9H_2O$, SiO_2-aeroc, $ZrO(NO_3) \cdot 2H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were used to obtain a mullite stoichiometric composition as well as to promote the transformation of ZrO_2 (monoclinic) into ZrO_2 (tetragonal). The mechanism and hydrothermal reactions are discussed.

The influence of the obtained nanosize powders on the sintering rate, phase composition and properties of mullite zirconia ceramics was studied and compared with the composition of traditionally obtained ceramics.

The pressed samples were sintered at temperatures from 1100 to 1500 °C. The effect of hydrothermal preparing process is emphasized.

It is shown that the densification of ceramic samples obtained from hydrothermally and traditionally prepared powders is greatly affected by the preparation methods used. XRD and SEM examinations showed the differences in mullite and ZrO_2 (tetr.) phase formation temperatures, as well as in the morphology and grain size of sintered ceramic samples.

The development of crystalline phases – mullite, ZrO_2 (tetragonal or monoclinic), as well as corundum (α-Al_2O_3) – in ceramic samples from conventionally obtained powders starts at 1300 °C, whereas from hydrothermal (in particular mullite phase) at1100 °C.

The values of compressive strength showed that they are greatly influenced by the preparation methods of starting powders – the compressive strength of samples prepared by the conventional method and sintered at 1400 °C reaches 160–170 MPa, whereas that of samples prepared by the hydrothermal method and sintered at 1500 °C reaches 100–105 MPa.

Introduction

Hydrothermal synthesis is a method mainly applied to produce oxide crystals from metal salt aqueous solutions by heating these solution. The reaction equilibrium of metal salt aqueous solution changes with temperature, which results in formation of metal hydroxides or oxides. The hydrothermal synthesis method is commonly conducted in an autoclave where the aqueous solution is heated slowly up to 270–290 °C and then aged for several hours [1]. During the heating period, reactions take place to produce monomers with subsequent nucleation and crystal growth. Because of the variation of the equilibrium with temperature, particles formed at lower temperatures dissolve to re-crystalize at higher temperatures during the heating up and aging period at the maximum temperature. Therefore, it takes a long time to obtain crystals of an equilibrium composition by this method.

Commonly, the hydrothermal synthesis method is used for the preparation of fine oxides, mainly of nanocrystallineZrO_2-tetragonal by addition of Ce^{3+}-, Nb^{5+}-, Y^{3+}- etc. oxides, SnO_2 [2–4]. Only a few studies are devoted to the synthesis of mullite – ZrO_2 nanoparticles, e.g., for applications in the field of monolitic / fibre reinforced ceramic composites [5].

In this study, the reactions of nanoparticle formation in the multicomponent system Al_2O_3–SiO_2–$ZrO_2(Y_2O_3)$ by hydrothermal synthesis with an emphasis on the influence of the obtained particle size and morfology on the development of crystaline phases and various properties of mullite – ZrO_2 ceramics are discussed and analysed.

Methods

Two mixes for hydrothermal preparation of the starting components were produced. In order to promote the formation reactions of desired crystalline phases by sintering and prospective by prevent the transition of t-ZrO_2, formed at higher temperatures, to m-ZrO_2 by cooling the samples, a small amount of a mineral raw material – illite-rich clay – was added to one part of the starting mixes (Table 1 and 2) [6].

The hydrothermal procedure was based on the method of Denkewic et al. [7], but several adjustments were made. The preparation of mixtures includes the following steps. In the first step aqueous solutions of aluminium nitrate hydrate $Al(NO)_3 \cdot 9H_2O$, zirconyl nitrate hydrate $ZrO(NO_3) \cdot 2H_2O$ and yttrium nitrate hydrate $Y(NO_3)_3 \cdot 6H_2O$ were prepared according to the composition given in Table 1.

Table 1. The starting mixtures (wt.sh.)

Sample	$Al(NO)_3 \cdot 9H_2O$	SiO_2 (aeroc)	$ZrO(NO_3)_2 \cdot 2H_2O$	$Y(NO_3)_3 \cdot 6H_2O$	Illite clay
10h	421.75	22.20	10.20	9.95	–
10hi	411.95	21.80	10.00	10.10	8.00

Table 2. The chemical composition of illite clay (wt.%)

SiO_2	Al_2O_3	Fe_2O_3 / TiO_2	CaO / MgO	K_2O / Na_2O
55.95	23.00	8.30 / 0.90	2.10 / 3.95	5.60 / 0.20

After diffluence of these components, SiO_2-aeroc nanopowder, as well as an imputed amount of illite clay to one part of mixtures of this solution were added. After stirring for 20 min, 10% NH_4OH was added to reach a pH value up to 7. In these conditions, metal ions are present as hydroxides. The obtained emulsion was put into a pressure-vessel and hydrothermally treated in an autoclave at a temperature of 275–290 °C and pressure 27–29 bars for ~2 h. Then these processed sols were gradually treated up to a temperature of 650 °C. The particle size and morphology of the obtained powder were determined by scanning EM analysis and atom-force microscopy *CPII* (USA).

Hydrothermally as well as (for comparison) traditionaly prepared powders were pressed into 25 mm disks and cylinders with h = 25 mm and diameter 30 mm and subjected to different firing schedules in the air at temperatures from 1100 to 1500 °C. The degree of sintering after firing was characterized by the relative degree of densification and bulk density. The phase composition of sintered samples after each step of firing was analysed using XRD (model Rigaku, Japan, with CuK_α radiation at scanning interval from 2θ = 10–60 ° and speed 4 °/min). The morphology of powders and the microstructure of sintered samples were observed by the scanning EM analysis (model JSM-T200). The compressive strength was determined by using the Toni-technic (Baustoffprüfung) model 2020.

Results and discussion

The possible reactions that occurred in the aqueous starting batch (1st step) and were processed hydrothermally by heating in an autoclave (Fig. 1, 2nd step) can be described as follows:

1st step:

$$2Al^{3+} + H_2O \rightarrow AlO(OH) + NO^{3-};$$

$$Si^{4+}O^{2-} + H_2O \rightarrow SiO(OH)_2;$$

$$ZrO(NO_3)_2 + H_2O \rightarrow ZrO(OH)_2 + NO^{3-};$$

$Y(NO_3)_2 + H_2O \rightarrow YO(OH) + NO^{3-} + NH_4OH$ (pH ~7) → to form colloidal agregates + H_2O + illite clay → to form emulsion.

2nd step:

autoclave (~250 ml capacity), temperature 275 ±10 °C, pressure 27–30 bars for 2 h

$$2AlO(OH) + SiO(OH)_2 \rightarrow Al_2O_3 \cdot SiO_2 + 2H_2O;$$

$$ZrO(OH)_2 \rightarrow ZrO_2 + 2H_2O;$$

$$2YO(OH) \rightarrow Y_2O_3 + 2H_2O.$$

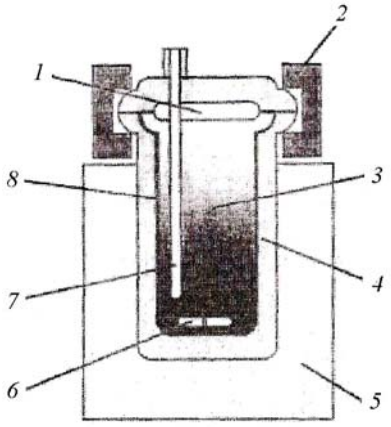


Fig. 1. Schematic representation of the autoclave used for synthesis of mullite + ZrO_2 powders: *1* – ring-like compression, *2* – pressure insurance, *3* – reaction medium, *4* – defence cover, *5* – external metal case, *6* – heating element, *7* – thermoelement

SEM photographs of the powder 10h heated at 1000 °C show amorphous particles or agglomerates less than 1 μm (Fig. 2). As is obvious from the AF-microscope picture of the hydrothermally prepared powder 10hi (Fig. 3), the particles have a round morphology with the size in a nanometer scale up to 100–150 nm.

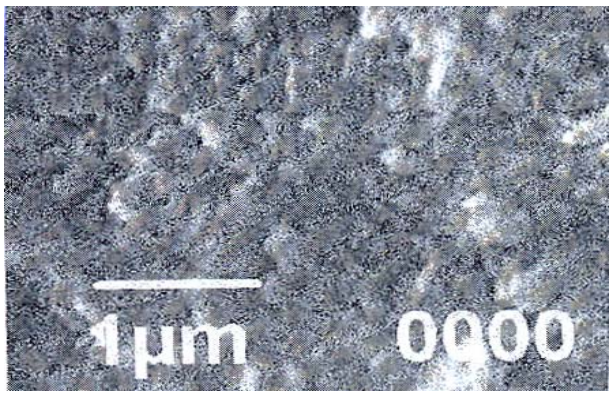
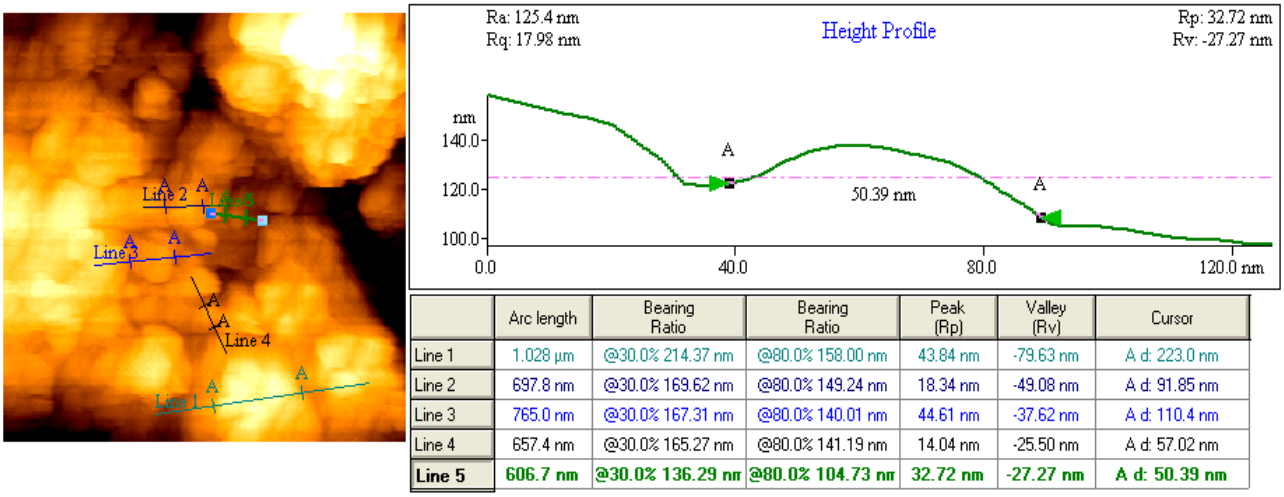


Fig. 2. SEM photographs of particles of hydrothermally prepared powders for sample 10 h



	Arc length	Bearing Ratio	Bearing Ratio	Peak (Rp)	Valley (Rv)	Cursor
Line 1	1.028 µm	@30.0% 214.37 nm	@80.0% 158.00 nm	43.84 nm	-79.63 nm	A d: 223.0 nm
Line 2	697.8 nm	@30.0% 169.62 nm	@80.0% 149.24 nm	18.34 nm	-49.08 nm	A d: 91.85 nm
Line 3	765.0 nm	@30.0% 167.31 nm	@80.0% 140.01 nm	44.61 nm	-37.62 nm	A d: 110.4 nm
Line 4	657.4 nm	@30.0% 165.27 nm	@80.0% 141.19 nm	14.04 nm	-25.50 nm	A d: 57.02 nm
Line 5	**606.7 nm**	**@30.0% 136.29 nm**	**@80.0% 104.73 nm**	**32.72 nm**	**-27.27 nm**	**A d: 50.39 nm**

Fig. 3. AFM images of the powder 10hi and particle height profile

The data on the bulk density and densification of samples obtained from the milled starting powder (24 hours in planetary mill) and sintered at a temperature ranging from 1250 to 1500 °C and for samples from hydrothermally prepared powder are plotted in Figure 4. Comparing both results it is obvious that generally densification and also bulk density are affected by the used method of preparation of the starting powder, i.e., by the particle size and morphology. Also, noted can be the influence of additional illite-rich clay on the mentioned properties of both samples.

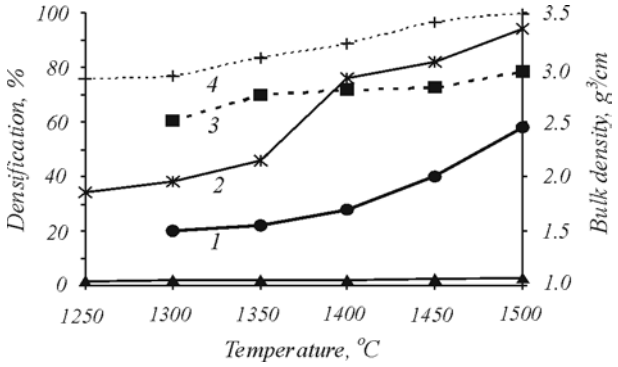


Fig. 4. Densification (—) and bulk density (**…**) of samples 10i milled for 24 h and hydrothermally synthesized samples 10h, sintered at temperatures from 1250 to 1500 °C: *1* – 10 h, *2* – 10 i, 24 h, *3* – 10 h, *4* – 10 i, 24 h

A sharp decrease in bulk density / densification (the bold lines in Fig. 4) was observed for the sample 10h sintered from hydrothermally prepared powder. It could be caused by changes in the phase composition due to the elimination of the liquid phase by sintering and the development of pores. This is confirmed also by the microstructure (Fig. 5). One can see a xenomorphic structure of mullite crystalls and close packed crystalline platelets of various size, as well as pores. Nano-sized grains of mullite with the size up to 100–200 nm and platelets sized up to 800–900 nm can be seen in the sintered sample.

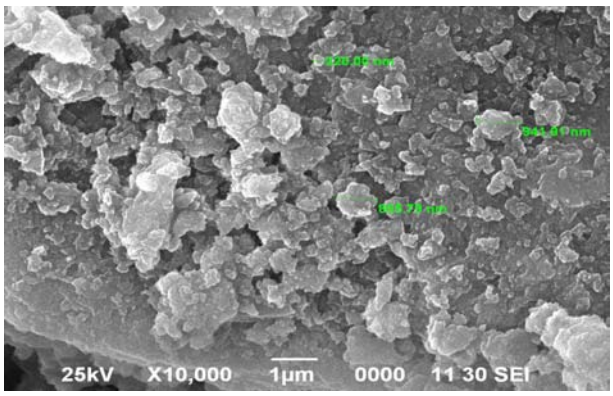


Fig. 5. SEM images of the samples 10h sintered at 1300 °C

Figure 6 shows the XRD patterns of samples 10h sintered at 1100–1400 °C obtained from hydrothermally prepared starting powders. Due to the grain / particle reduction and more active particles in starting powders, the chemical reactions proceed more actively starting from temperature of 1100 °C to pattern the mullite nuclei and increase starting from 1200 °C to form mullite and ZrO_2 (tetragonal) and $ZrSiO_4$ phases.

Although the formation of mullite phase in sintered ceramic samples 10h from hydrothermally synthesized powder is more active (Fig. 4) than from conventionally milled powder, the densification process is less pronounced. It is one of the reasons for the lower strength values of the respective samples. As is obvious (Fig. 7), the value of compressive strength for ceramic samples from hydrothermal powder sintered at 1500 °C reaches 105 MPa, whereas from conventionally milled powder sintered at 1400 °C it reaches up to 170 MPa [7].

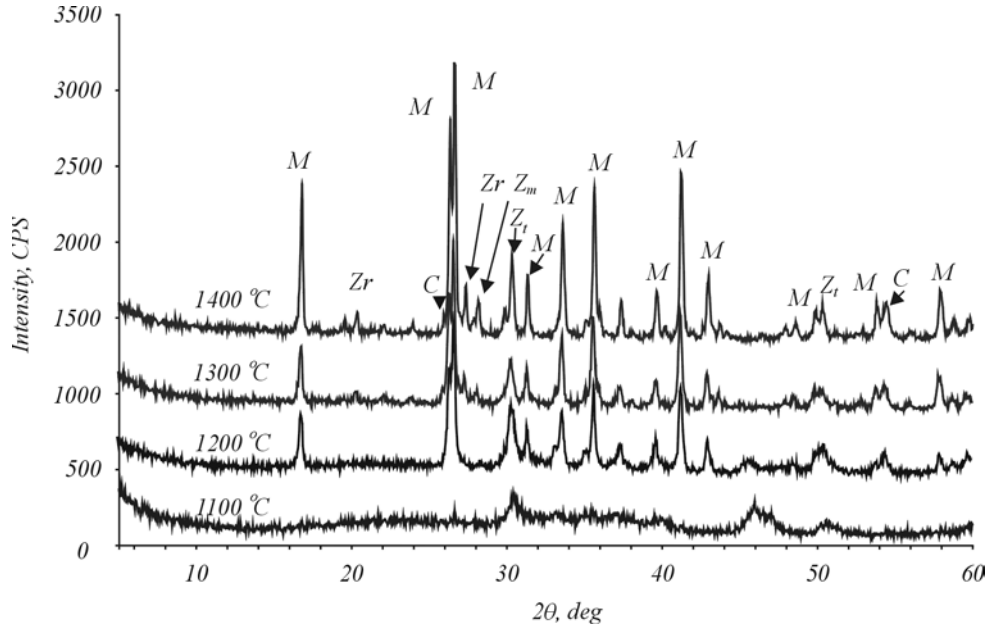


Fig. 6. Development of crystalline phases in ceramics from hydrothemally synthesized powders sintered at temperatures ranging from 1100 to 1400 °C: M – mullite $3Al_2O_3{\cdot}2SiO_2$, C – corundum α-Al_2O_3, Z_t – ZrO_2 (tetr.), Z_m – ZrO_2 (mon.), Zr – zircon $ZrSiO_4$

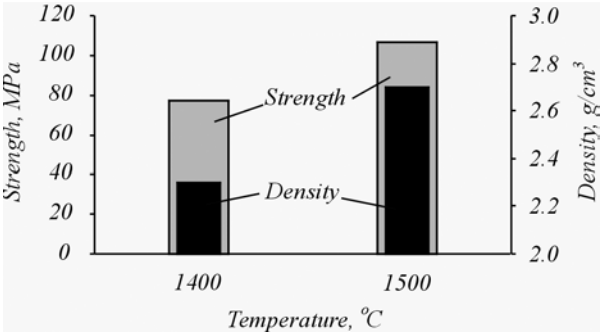


Fig. 7. Strengh / density relation of sample 10 h sintered at 1400 and 1500 °C

Conclusions

The reactions of nanoparticle formation by the hydrothermal preparation method in the multicomponent system Al_2O_3–SiO_2–$ZrO_2(Y_2O_3)$ were investigated.

The influence of particle size and morfology on the development of crystaline phases and various properties of mullite–ZrO_2 ceramics sintered at temperatures ranging from1100 to 1500 °C is shown.

SEM and XRD results show (accordingly) the effect of the hydrothermal preparation process on the development of mullite, ZrO_2 (tetragonal) and zircon $ZrSiO_4$ phases in sintered samples starting from a temperature of 1200 °C.

Examination of the bulk density and densification by sintering indicate that the densification of ceramic samples from hydrothermally prepared powder in comparison with conventially prepared one is lower and consequently their compressive strength is also lower.

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G. Sedmale, A. Hmelov, I. Sperberga, A. Pludons, J. Grabis

HIDROTERMINĖ Al_2O_3-SiO_2-$ZrO_2(Y_2O_3)$ MILTELIŲ SINTEZĖ IR JŲ PRITAIKYMAS AUKŠTATEMPERATŪRĖJE KERAMIKOJE

S a n t r a u k a

Mulito-cirkonio keramikos sintezei naudojamos pradinės žaliavos buvo termiškai apdorotos 270–300 °C temperatūroje ir 30 bar slėgyje. Mulito stechiometriniam oksidų santykiui gauti ir monokliniinio ZrO_2 virsmui į tetragoninį ZrO_2 naudoti $Al(NO_3)_3{\cdot}9H_2O$, SiO_2-aeroc, $ZrO(NO_3){\cdot}2H_2O$ ir $Y(NO_3)_3{\cdot}6H_2O$ mineralai. Aptartos hidroterminės reakcijos ir jų mechanizmas.

Išanalizuota sukepimo greičio įtaka susidariusioms nanodalelėms, mulito cirkonio keramikos mineralinė sudėtis, savybės ir palyginta su tradicinės keramikos mineraline sudėtimi.

Supresuoti bandiniai degti 1100–1500 °C temperatūroje. Nustatyta, kad keramikos bandinių tankumas labai priklauso nuo pradinių miltelių paruošimo metodo: tradicinio ir hidroterminio. XRD ir SEM analizių metodais nustatyti mulito ir ZrO_2 (tetr.) fazės susidarymo temperatūrų, keramikos morfologijos ir dalelių dydžių skirtumai.

Mulitas, ZrO_2 (tetragoninis ir monoklininis), kaip ir korundas (α-Al_2O_3) keramikoje pradeda susidaryti: įprastai paruošus mišinį – 1300 °C temperatūroje; hidrotermiškai – 1100 °C temperatūroje.

Stiprio gniuždant duomenys labai priklauso nuo pradinio mišinio paruošimo metodo: naudojant įprastinį ir išdegus 1400 °C temperatūroje, jis siekia 160–170 MPa, tuo tarpu hidrotermiškai apdorojus 1500 °C temperatūroje pasiekiamas 100–105 MPa stipris gniuždant.