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Spark Plasma Sintering (SPS) to the Mullite-Zirconia Ceramics Development

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This research is devoted to the investigation comparison of effect of SPS (spark plasma sintering) and conventional sintering for the mullite-ZrO_2 ceramics development. Mullite-ZrO_2 ceramics were produced from different time ball-milled powders. The effect of illite nanoparticles on the powder sintering promotion process was investigated and evaluated. The density and compressive strength as well as microstructure and crystalline phase development of ceramics were investigated in order to show the impact of SPS by comparing with conventional sintering. It is shown that SPS at 1250 °C produces samples with densities that are to 1.6 – 2.2 times higher than densities of samples obtained with conventional sintering at 1300 °C. Both compressive strength and Vicker's microhardness increase correlate well with the increase of density. The microstructure of the SPS samples is dense and consists of well-textured mullite and cubic ZrO_2 particles, but conventionally sintered samples form mullite-corundum crystals with tetragonal ZrO_2 inclusion. It is shown that illite clay additive is effective to increase density and compressive strength only when using conventional sintering.

Keywords: Mullite-ZrO_2, SPS, structure, properties.

1. INTRODUCTION

Nowadays, due to increasingly high requirements for materials that are applicable in extreme conditions, like high- and rapidly changing temperature, aggressive environment etc., materials that possess excellent physical, chemical, mechanical and thermal properties are required. One of such materials is mullite or mullite-ZrO_2 ceramics.

Mullite-ZrO_2 composites can be prepared by various routes, such as reaction sintering of alumina (Al_2O_3) and zircon ($ZrSiO_4$) powders, sintering of "pre-mullite" powder mixed with ZrO_2 particles, or through a combination of process of reaction bonding of alumina and SiO_2 with addition of ZrO_2, as well as by using of sol-gel method and other colloidal mixing techniques [1 – 3]. Often both processes – powder synthesis and densification of ceramic product are coupled.

For acceleration of the mullitization, tetragonal ZrO_2 formation and also densification, initiated at lower temperatures, advanced sintering techniques are required, e. g. explosive shock consolidation, hot – pressing, high-pressure sintering, spark plasma or microwave sintering [4 – 7]. There is also a report on two steps transient viscous sintering where SiO_2 – coated Al_2O_3 composite powders were first sintered at 1300 °C to achieve almost full density (>99 %) and subsequently subjected to high temperature (~1500 °C) in order to obtain mullite with near theoretical density [8].

Spark plasma sintering (SPS) is used as one of the alternative sintering methods where lower synthesis temperatures can be applied in comparison with conventional sintering. It is known that in conventional process heat occurs in material from surface and then relatively slowly moves inside causing thermal gradient; this process also takes many hours. In the SPS spark discharge appears between particles of materials and localized high-temperature increase occurs in a moment of few minutes, causing melting of the powder surface particles thus fast sintering, resulting in a sintered compact of over 99 % density, is achieved [9].

The objective of this work is to evaluate SPS sintering in order to obtain high strength mullite-zirconia ceramics. Comparison of densification behaviour and mechanical properties, as well as phase and microstructure development are investigated in order to highlight the advantage of SPS processing over conventional reaction sintering.

To promote sintering and lower process temperature, the effect of illite clay nanoparticles on densification of mullite-ZrO_2 ceramic was also studied.

2. MATERIALS AND PROCEDURE

The mix of starting powders were produced from synthetic reagents of chemical grade γ Al_2O_3, silica-gel $SiO_2.nH_2O$ (85 % SiO_2), ZrO_2 (monoclinic), Y_2O_3. The weight ratio of reagents was chosen such us to form mullite. Illite clay was used as an additive for one part of mixes (Table 1). The chemical composition of illite clay consists from (wt.%): SiO_2 – 8.25; Al_2O_3 – 24.00; Fe_2O_3/TiO_2 – 4.85/1.05; CaO/MgO – 2.10/3.95; K_2O/Na_2O – 5.60/0.20.

Table 1. The starting powder compositions, wt.%

Sample	γ Al_2O_3	$SiO_2 \cdot nH_2O$	ZrO_2	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 starting mixtures of powders were prepared by ball-milling for different time (4, 10 or 12 and 24 hours) in planetary laboratory corundum mill with corundum balls and water media.

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Samples for conventional sintering were prepared as Ø = 25 mm disks and cylinders with h = 30 mm and 25 mm diameter and subjected to different firing schedules in air at max temperatures from 1200 °C to 1400 °C (with the heating rate (5 – 6) °C/min, holding time at maximum temperature 45 min.).

For the SPS the "Sumimoto, Model SPS-825.CE, Dr. Sinter, Japan" equipment was used. The powders were pressed as 25 mm high and 20 mm diameter cylindrical samples and subjected to temperatures varying between 500 °C and 1400 °C with a holding time of 4 minutes at ultimate temperature. The heating rate was 100 °C/min. under a pressure of 30 MPa. The vacuum level of 6 Pa was maintained during the SPS process.

The sintering degree after firing was characterized by the relative density. The density of sintered samples was measured by the Archimedes method with an accuracy of ±0.5 % using distilled water medium.

Microstructure and phase compositions of sintered samples were analysed using SEM (model JSM-T200, Japan) and XRD apparatus (model Rigaku, Japan, with CuK_α radiation at scanning interval from $2\theta = 10° - 60°$ and speed 4°/min), respectively.

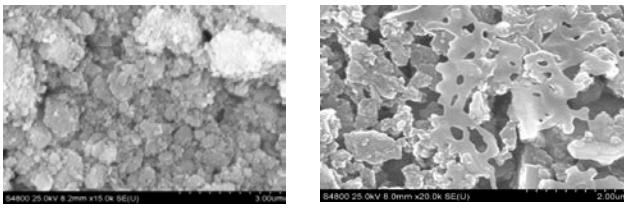
The compressive strength was determined by Toni-Technic (Baustoffprüfung) model 2020.

Vicker's microhardness (HV_s) testing method was based on the loading of polished surface of material under the test by diamond prism with regular tetragonal piramidal shape. Both diagonals were examined and measured in microscope after loading; afterwards, their mean size is calculated. Square of piramidal impression is calculated using this value. Vicker's hardness is relation between calculated square and applied load. In this case 49 N load was used for tests using equipment 2137 TU-UHL 4.2

3. RESULTS AND DISCUSSION

3.1. Starting powders and consolidation

SEM images of powders milled for 4 and 24 hours (Fig. 1) demonstrate agglomerates of particles with the mean size within ~(3 – 10) μm range. After 24 hour milling and addition of illite clay, agglomerates appear to be rounded and a little bit nebulous (Fig. 1, a and b). The mean size of particles in agglomerates is that of large scale nanometre range [10].



a b

Fig. 1. SEM image of ceramic powder milled during 4 hours (a) without clay additive; (b) powder milled during 24 hours with clay additive

Shrinkage of samples consolidated by both sintering methods is noticeably different. It grows gradually for the samples prepared by conventional sintering in all sintering temperature interval, reaching final shrinkage within 3.0 % – 5.5 % from theoretical values at 1300 °C. Size changes of ceramic samples prepared by SPS are amplified at the 500 °C and rapidly increase during SPS process (Fig. 2). As it is shown, main shrinkage in the specimens took place during the sintering between 700 °C and 1200 °C. Thereafter into final stage (until 1400 °C) shrinkage process becomes stable and specimens obtain their ultimate relative value of density. The effect of powder milling time on shrinkage is negligible. It could be observed a slightly greater shrinkage of samples from 4 h milled starting powder.

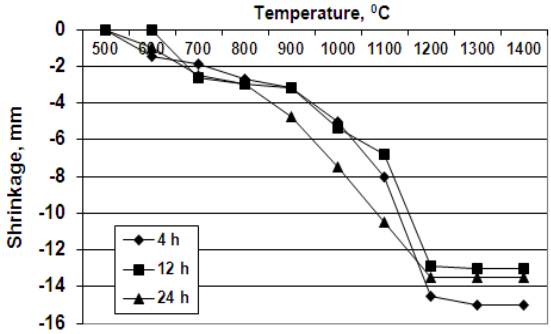


Fig. 2. Changes of shrinkage of ceramic samples 10 compacted from differently (4, 12 and 24 hours) milled powders by using SPS

3.2. Mechanical properties

Comparative compressive strength and density measurement results of samples prepared by conventional sintering (at 1300 °C) and SPS (at 1250 °C) in dependence of milling time of starting powders is evaluated and shown in Fig. 3 and Fig. 4.

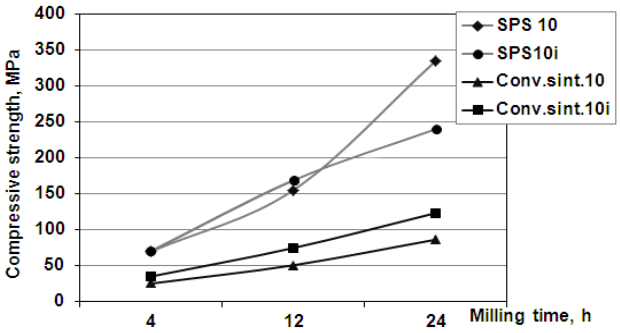


Fig. 3. Compressive strength of samples 10 and 10i sintered conventional and by SPS as function on milling time of starting powders: i – the samples with illite clay addition

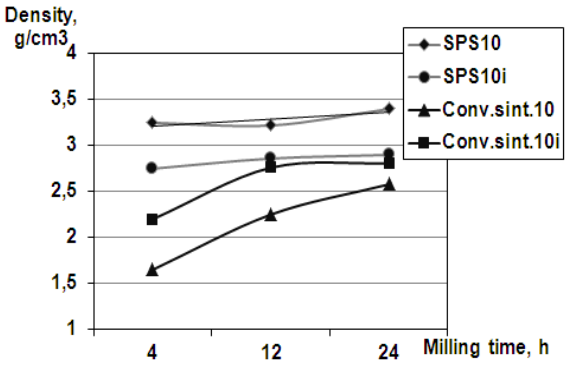


Fig. 4. Density of samples 10 and 10i sintered conventional and by SPS as function on milling time of starting powders: i – the samples with illite clay addition

It can be seen that composites 10 by SPS at 1250 °C achieve densities for up to 1.6 – 2.2 times higher than achievable using conventional sintering at 1300 °C. Both of the addition of illite clay additive and milling time increase enhance the values of density and compressive strength for the samples prepared by conventional sintering. On the contrary, for SPS samples illite additive lowers density values, especially for 24 h milled sample. It can be also seen that illite additive for conventionally sintered samples improves density and compressive strength values except for ceramic samples from 24 h milled powder that also contains illite additive. Obviously, in this case, simultaneous development of somewhat amorphous and gassy phases has started, which causes formation of closed pores in the samples during the cooling.

The continuous increase of Vicker's microhardness of SPS ceramic samples was consistent with increase in the milling time of starting powder, i. e., with the reduction of particle size in powders. These values (Fig. 5) correlate well with the density results of the SPS samples, except for samples with illite additive.

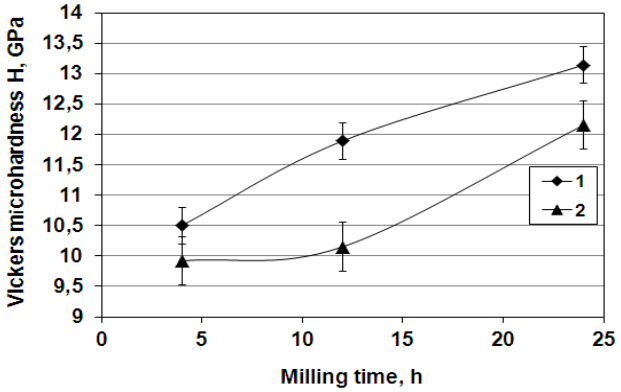
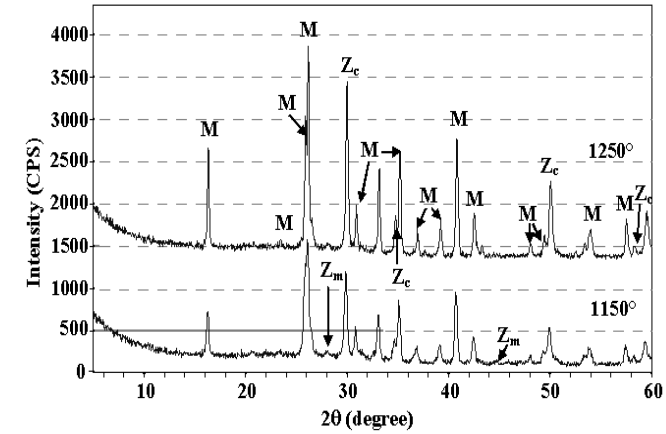


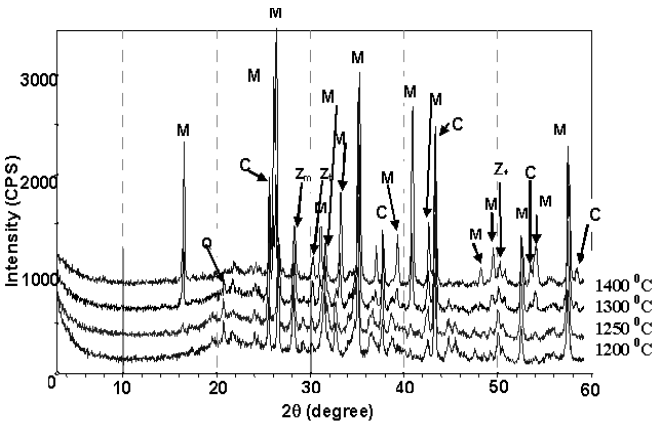
Fig. 5. Effect of milling time on Vicker's microhardness for SPS ceramic samples: 1 – ceramic sample 10 without illite additive, 2 – 10i with illite additive

3.3. Phase evolution and microstructure characterization

Crystalline phase development of ceramic sample 10, sintered by SPS at two temperatures and conventionally in temperature range from 1200 °C to 1400 °C are shown in XRD spectra, Fig. 6, a and b. The main difference between both X-ray diffraction patterns is related to the formation of stable cubic ZrO_2 when SPS is used and intensive mullite phase formation at already 1150 °C, whereas for conventionally sintered samples formation of tetragonal ZrO_2 takes place and mullite phase forms at higher temperatures. Intensity of mullite phase crystallization grows with an increase of temperature by conventional sintering and formation of corundum phase can be observed as well. Presence of monoclinic ZrO_2 phase in conventionally sintered sample 10 (without illite additive) obviously indicates that tetragonal ZrO_2 modification forms at higher temperatures and is unstable during the cooling of samples transforming into monoclinic ZrO_2. As it can be seen in X-ray diffraction patterns (Fig. 7), in the presence of illite clay additive it was not observed. Therefore, there is a probability that illite stimulates transformation of monoclinic ZrO_2 to stable tetragonal ZrO_2 phase.



a



b

Fig. 6. X-ray diffraction patterns of ceramic sample 10 sintered by SPS at 1150 °C and 1250 °C temperatures (a) and the same sintered conventionally at temperatures ranges from 1200 °C to 1400 °C (b) : M – mullite $Al_4[Al_4(Si_3Al)O_{20}]$, C – corundum α-Al_2O_3, Z_t – ZrO_2 tetragonal, Z_c – ZrO_2 cubic, Z_m – ZrO_2 monoclinic, Q – SiO_2 cristobalite

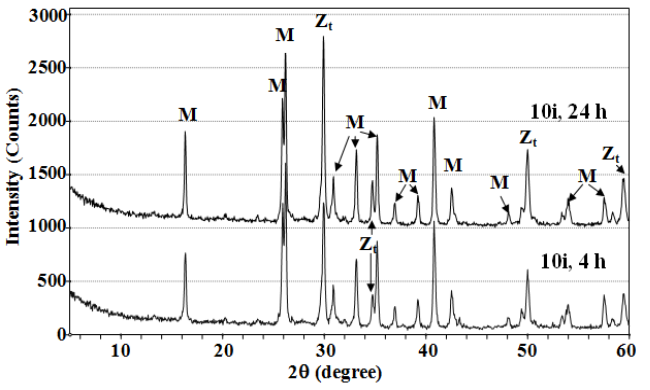
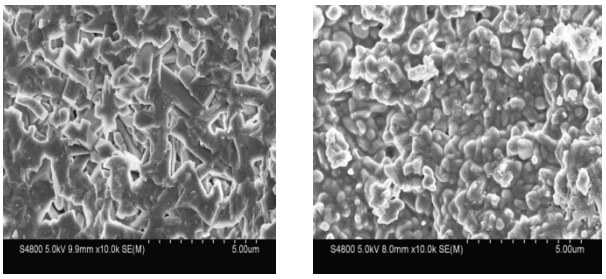


Fig. 7. XRD patterns of ceramic sample 10i from different times milled powder with illite additive and sintered at 1300 °C

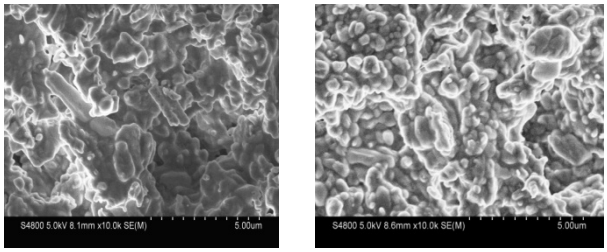
SEM images (Figures 8 and 9) show the fracture surface microstructure of mullite-ZrO_2 ceramic samples 10 and 10i, sintered by SPS at 1250 °C and conventionally at 1300 °C.

It can be seen that prismatic mullite crystals in sample 10 (Fig. 8) are more compressed and their morphology is not formed as good as for conventionally sintered sample 10i (Fig. 9). Addition of illite to both SP and conventionally sintered sample leads to the development of rounded forms as well as, obviously, enhanced formation of closed pores.



a b

Fig. 8. SEM images of mullite-ZrO_2 ceramic samples sintered by SPS at 1250 °C: a – sample 10, b – sample 10i



a b

Fig. 9. SEM images of mullite-ZrO_2 ceramic samples sintered conventionally at 1300 °C: a – sample 10, b – sample 10i

4. CONCLUSIONS

The reaction sintering of dense mullite – zirconia ceramics from different time milled powder mixtures of γ Al_2O_3, silica-gel $SiO_2 \cdot nH_2O$ (SiO_2 – 85 %), Y_2O_3 both with and without the 8 wt.% illite clay addition as a sintering aid was achieved by the use of SPS and conventional sintering. Both techniques were used to compare the densification, phase and microstructure development, as well as mechanical properties.

The formation of mullite starts for SPS at temperature of about 1150 °C and is completed at designated temperature of about 1250 °C, whereas by sintering conventionally, a weak start of crystallization is achieved at 1200 °C and doesn't fully develop until 1400 °C. It is shown that by both sintering techniques ZrO_2 transforms into more stable forms – partly in tetragonal ZrO_2 when sintering conventionally and cubic ZrO_2 when using SPS.

Effect of increase of milling time for starting powder is effective for both density and compressive strength. Impact of illite additive is, however, different – it lowers the sintering temperature, phase formation and promotes densification along with an increase of compressive strength for conventionally sintered samples, but an opposite influence can be observed for SPS samples.

Comparison of the characteristics of the mullite-ZrO_2 ceramic samples with and without illite clay additive as well as advantage of SPS when sintering by both techniques has been shown.

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