Characteristic and sinterability of alumina-zirconia-yttria nanoparticles prepared by different chemical methods

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Abstract. The characteristics and sinterability of the Al_2O_3-ZrO_2(Y_2O_3) nanoparticles produced by simple and effective microwave and molten salts methods and processed by using spark plasma sintering were studied and compared. The crystalline powders with the specific surface area in the range of 72–108 m^2/g and crystallite size of 5–13 nm were obtained by calcination of samples prepared by both methods at 800 ºC. The content of t-ZrO_2 phase depends on concentration of Al_2O_3, Y_2O_3 and on calcination temperature but the impact of the preparation method is insignificant. The phase transition of tetragonal ZrO_2 to monoclinic for the samples without Y_2O_3 started at 1000 ºC though it was incomplete in the case of high content of Al_2O_3. The bulk materials with relative density of 86.1–98.7% were fabricated by the spark plasma sintering method at 1500–1600 ºC depending on the content of Al_2O_3 and Y_2O_3.

Introduction

Zirconia-alumina and yttria-alumina nanostructural nanocomposites find application as biomaterials, ball bearings, cutting tools and high-temperature structural materials due to combining mechanical and physical parameters of the components. However, the properties of sintered ceramics strongly depend on particle size, size distribution, phase composition and sinterability of the used powders, determined by their preparation and densification methods.

At present oxide nanoparticles are prepared mainly by liquid phase [1] such as hydrothermal [2], sol-gel [3], combustion synthesis [4], precipitation [5, 6] or by vapour phase processes using thermal plasma [7], laser beam [8] technique as well as by spray-drying mixed oxalate solutions [9]. The known synthesis methods ensure preparation of oxide nanoparticles with different morphology and size in the range of 5–10 nm, but they differ by the complexity, production rate and cost, and solvents used.

On the other hand the present trends in technology are directed to development of highly effective, economic and environment friendly preparations methods of nanoparticles.

From this point of view, fast microwave (MW) [10] and solvent free molten salts (MS) [11] synthesis successfully applied for preparation ZrO_2 nanoparticles will be very attractive for preparation of ZrO_2-Al_2O_3 nanocomposites

In the present work characteristics, phase composition and sintering behavior of the zirconia-alumina (ZA) and yttria-zirconia-alumina (YZA)nanoparticles prepared by microwave and molten salts methods have been studied in dependence of the content of alumina.

Materials and methods

The precursors used for preparation zirconia-alumina nanoparticles were reagent grade $ZrO(NO_3)_2 \cdot 2H_2O$, $ZrOCl_2 \cdot 8H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$. For MW synthesis separate solutions of the salts were prepared and mixed for 30 min at room temperature. The solution with

pH=9 was adjusted by adding NH_4OH. The synthesis was conducted in the commercial reactor Masterwave BTR (Anton Paar) at temperature 170 °C and pressure about 7.9 bar for 20 min. The obtained nanoparticles were extracted by filtration and washed with distilled water and ethanol followed by drying at 100 °C for 20 h.

For MS synthesis the definite amounts of the metal salts were mixed mechanically with KNO_3 and KCl at ratio MeO/salts = 1 : 4. The synthesis was performed in the furnace at temperature or 800 °C for 2 h. The nanoparticles prepared were separated by dissolving salts in distilled water and washing with ethanol.

In order to obtain well-crystalline powders and examine their phase transition the particles prepared were calcinated at 600–1300 °C.

The samples prepared by both method and calcinated at 800 °C were densified by using the spark plasma sintering technique (SPS-825 CE) in vacuum at 1400–1800 °C and pressure of 30 MPa.

The phase composition of powders and bulk materials was determined by X-ray diffraction (XRD) analysis at the room temperature (AdvanceD8, Bruker AXS). The crystallite size was calculated using X-ray diffractometer software EVA12 based on the Scherrer formula. The specific surface area (SSA) of powders was determined by the argon absorption-desorption method. Density of the bulk samples was determined by using the Archimede's method. The particle size was determined by high resolution transmission electron microscope (HRTEM).

Results and discussion

The samples containing 20 and 80 wt.% of alumina and 80 or 20 wt.% of unstabilized (ZA20 or ZA80) or stabilized ZrO_2 with 3 mol% Y_2O_3 (3YZA20 or 3YZA80) were prepared by both method.

As-received samples prepared using the molten salts (MS) synthesis had the specific surface area in the range of 98–110 m^2/g depending on the content of alumina.

The specific surface area of the as-prepared by microwave synthesis (MW) samples was in the range of 110–150 m^2/g due to lower synthesis temperature. All as-received MW samples were X-ray amorphous. Crystallization of t-ZrO_2 phase started at 600–800 °C (Fig. 1) depending on the content of alumina.
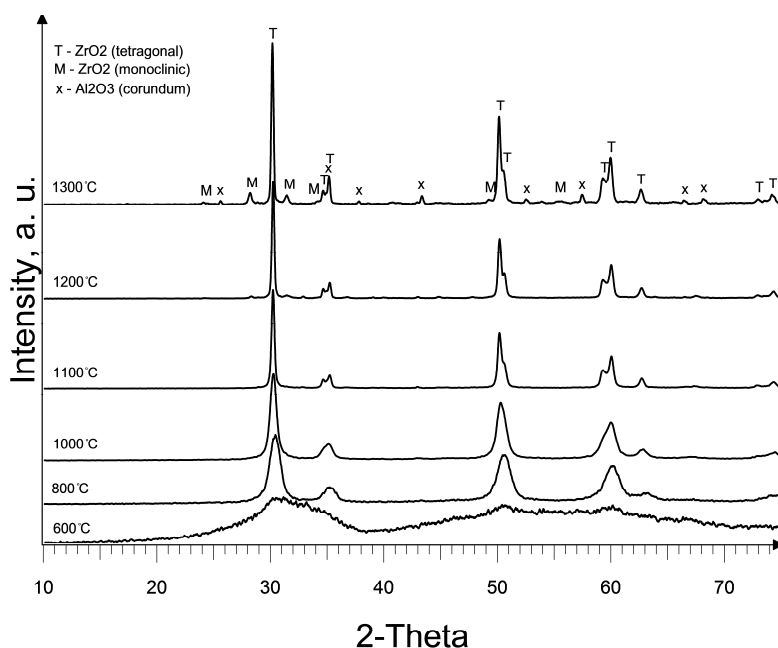

Figure 1. XRD patterns of calcinated 3YZA20 samples prepared by microwave synthesis

The XRD patterns of the as-prepared MS samples showed broad t-ZrO_2 maxima (Fig. 2) depending on the content of Al_2O_3. The increase of alumina content up to 80 wt.% decreases the crystallite size of zirconia from 7 nm to 5 nm. The crystallization of α-Al_2O_3 started at 1200–1300 °C for all samples.
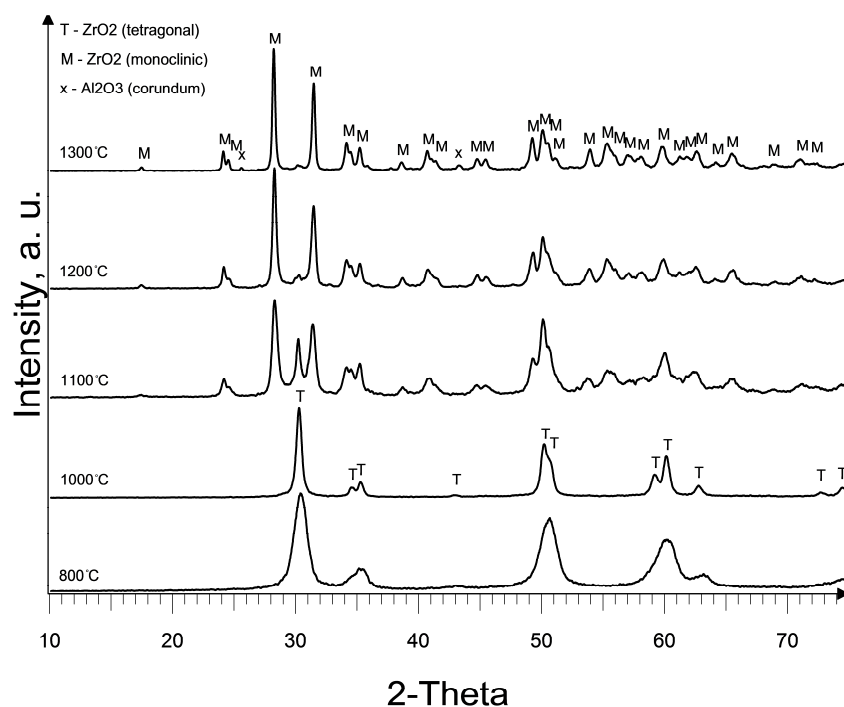
Figure 2. XRD patterns of calcinated ZA20 samples prepared by molten salts method.

The 3YZA samples calcinated at 700–800 °C contained only the t-ZrO$_2$ phase but the ZA samples prepared by MW and MS synthesis besides t-ZrO$_2$ contained about 3–15% and 6–18% m-ZrO$_2$, respectively, depending on the content of Al$_2$O$_3$. The phase transition of ZrO$_2$ phases according to the calcination temperature depends mainly on the content of Y$_2$O$_3$ and Al$_2$O$_3$ but the impact of the preparation method is limited (Fig. 3).
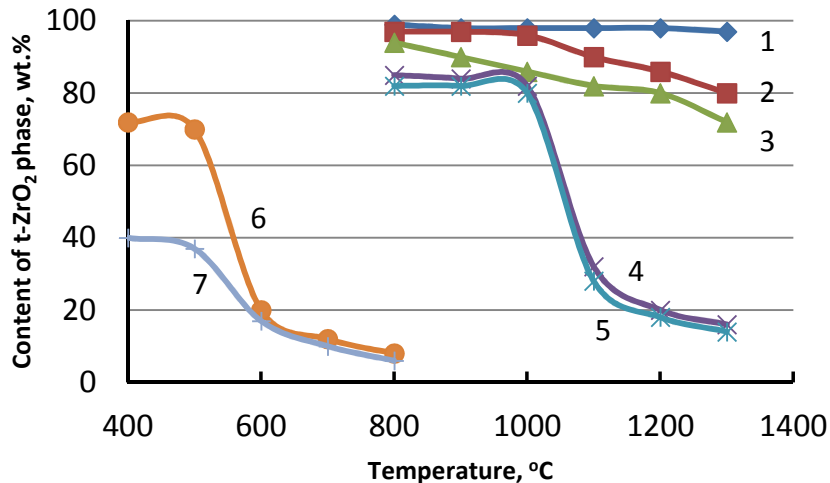

Fig. 3. Content of t-ZrO$_2$ phase in 3YZA20 (1), ZA80 (2,3), ZA20 (4,5) and ZrO$_2$ (6,7) prepared by molten salts (1,3,5,6) and microwave synthesis (2,4,7).

The phase transformation in the 3YZA samples calcinated up to 1300 °C was negligible. Only about 3% of t-ZrO$_2$ was transformed in m-ZrO$_2$. The phase change in the calcinated ZA samples started at temperature of 1000 °C which was two times higher as that for pure ZrO$_2$ nanoparticles prepared by the same methods. The intensity of the phase transition is strongly affected by the content of Al$_2$O$_3$. It means that the t-ZrO$_2$ phase was at least partially stabilized by alumina and due to limited crystallite growth of ZrO$_2$ in the presence of Al$_2$O$_3$ particles.

The crystallite size of the ZA80 samples prepared by MW and MS synthesis and calcinated at 1000 °C are in the range of 9–11 nm and 12–14 nm and correspondingly the content of t-ZrO$_2$ phase is about 97% and 88%, respectively.

The intensive crystallite growth in the ZA20 samples was observed at temperature above 1000°C. As the result, the ZA20 samples calcinated at 1200 °C had the crystallite size in the range of 35–46 nm and they contained only 18% of t-ZrO_2 phase..

The additional calcination of all samples had a significant impact on SSA (Fig. 4) due to the particle growth and their partial sintering. However, just a slight increase of the crystallite size in the range of 5–14 nm was observed at calcination temperature in the range of 800–1000 °C.
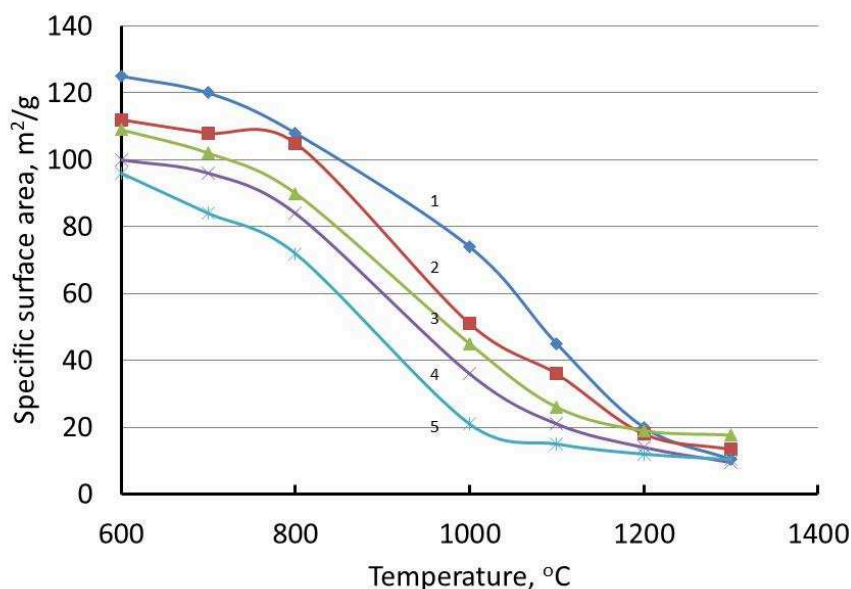

Fig. 4. Specific surface area of 3YZA80 (1,2), 3YZA20 (4,5), Al_2O_3 (3) prepared by molten salts (2,5) and microwave synthesis (1,3,4).

According to the results of HRTEM studies, the prepared zirconia-alumina powders contained aggregates of elementary particles (Fig. 5). The shape of the elementary particles was close to spherical. The particle size of powders prepared by MW and MS synthesis was in the range of 20–40 nm and 20–70 nm, respectively.
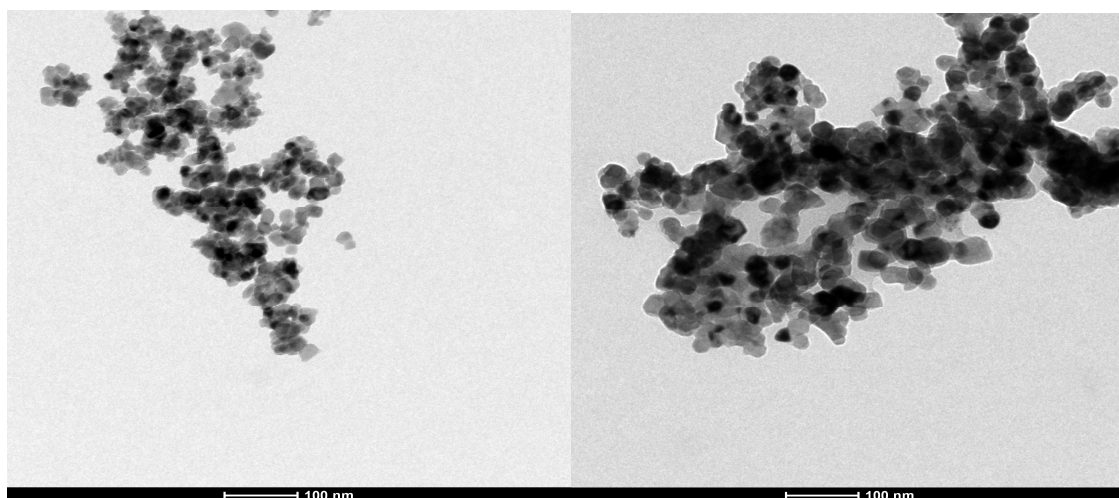

Fig. 5. Micrographs of 3YZA nanoparticles prepared by microwave synthesis (left) and 3YZA nanoparticles prepared by molten salts synthesis (right)

The determined particle size exceeded the calculated crystallite size remarkably. Detailed studies of the elementary particles showed that there were small clusters with size about 8–10 nm (Fig. 6) what corresponds to the crystallite size calculated from the broadening of XRD maxima.

Fig. 6. High resolution image of
ZA20 nanoparticles (bar 5 nm)

Solidification of the samples by SPS was performed by using well crystalline powders calcinated at 800 °C. Shrinkage of all samples during the SPS process started at 800 °C and became negligible at temperature in the range of 1450–1560 °C depending on the content of alumina and yttria. Maximal relative density of the bulk materials was reached at 1600 °C within 2 minutes (Table 1). It indicated that additives of alumina to zirconia increased the sintering temperature of the samples with respect to that of 3YSZA prepared by similar methods [12].

Table 1. Characteristics of the samples calcinated at 800 °C and sintered at 1600 °C

Samples	Specific surface area [m^2/g]	Bulk materials	
		Relative density [%]	Phase composition of sample and content of t-ZrO_2 [%]
MS ZA20	69.2	86.1	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (2.3)
MW ZA20	77.3	98.6	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (2.7)
MS YZA20	73.7	98.4	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (94.0)
MW YZA20	67.7	98.7	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (90.0)
MS ZA80	94.2	97.6	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (68.0)
MW ZA80	95.5	96.2	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (65.0)
MS YZA80	102.0	98.3	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (97.0)
MW YZA80	110.0	98.6	m-ZrO_2, α-Al_2O_3, t-ZrO_2 (98.0)

The results showed that density of the samples depended strongly on the content of yttria and alumina what also influenced phase composition of zirconia. All samples stabilized with yttria had high density independently on the content of alumina because the phase transition t→m-ZrO_2 was small during the sintering process with respect to that in precursors. Similar behavior was characteristic for the samples containing 80% Al_2O_3 limiting the phase transformation of ZrO_2.

Smaller content of Al_2O_3 (20%) and absence of Y_2O_3 promoted formation of m-ZrO_2 during sintering and the density of the bulk material was low.

The bulk materials had fine-grained microstructure with the grain size in the range of 0.4–1.5 µm. Obviously, high sintering temperature and presence of agglomerates stimulated fast grain growth.

The obtained results provided evidence that molten salts and microwave synthesis combined with calcination at 800 °C allowed to prepare zirconia-alumina nanoparticles with similar crystallite size, phase composition and sinterability. However, the molten salts synthesis method is simpler and economically more effective.

Summary

The developed molten salts and microwave synthesis combined with calcination at 800 ºC ensure preparation of crystalline zirconia-alumina nanoparticles with specific surface area in the range of 72–108 m^2/g and crystallite size in the range of 5–13 nm with similar phase composition and sinterability.

The phase composition of zirconia-alumina powders and bulk materials depends strongly on the content of alumina and yttria.

The limited phase transformation of ZrO_2 in presence of Y_2O_3 or Al_2O_3 results in higher density of bulk materials sintered by SPS. Additives of Al_2O_3 demand higher sintering temperature with respect to zirconia stabilized with yttria.

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