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SYNTHESIS AND CHARACTERIZATION OF ALUMINA- AND ZIRCONIA-BASED POWDERS OBTAINED BY THE ULTRASONIC SPRAY PYROLYSIS

W. Kucza[1*], *J. Obłąkowski*[1], *R. Gajerski*[1], *S. Łabuś*[1], *M. Danielewski*[1], *A. Małecki*[1], *J. Morgiel*[2] *and A. Michalski*[3]

[1]Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Al. Mickiewicza 30 Cracow 30-059, Poland
[2]Polish Academy of Sciences, Institute of Metallurgy and Materials Sciences, Reymonta 25, Cracow 30-059, Poland
[3]Warsaw University of Technology, Faculty of Materials Science and Engineering, Wołoska 141, Warsaw 02-507, Poland

The ultrasonic spray pyrolysis (USP) technique was used for synthesis of alumina- and zirconia-based powders. The starting agents were aqueous solutions, atomized by the ultrasonic spray generator and pyrolized in the furnace under the open-air conditions. The powders prepared by USP were in the form of solid and hollow aggregates (spheres) consisted of nanosize amorphous grains as determined by the microscopy and the X-ray diffraction techniques. The alumina-based powders were consolidated by the pulse plasma sintering resulting in single-phase materials. Different behavior of solid and hollow particles during the isostatic sintering is found; a higher degree of deformation of spheres is observed in the second case.

Keywords: *alumina, plasma sintering, SEM, spray pyrolysis, TEM, zirconia*

Introduction

Ceramic powders found many applications in modern industry as catalysts, adsorbents, abrasives, biomaterials, solid electrolytes or ionic barriers, thermal barriers, etc. In this aspect alumina- and zirconia-based materials, in the form of dense or porous materials, are considered to be very important because of their strength, thermal stability, high chemical resistance [1] and catalytic properties [2]. Spray pyrolysis-based techniques become more and more popular route for ceramic powder fabrication as a result of its simplicity, high homogeneity of obtained materials, versatility, low cost and applicability at the open atmosphere condition [3–7]. Moreover, such techniques offer obtaining of metastable phases [4] and/or nanomaterials [4, 6] in one-step process. Spray pyrolysis involves liquid precursor atomization, its transport by a carrier gas and a reaction in a furnace. In order to reduce powder loss a system of electrostatic filters are used. Key parameters influencing morphology of powders obtained by spray pyrolysis (porosity, grain size, particles shapes) are: the precursors [3, 6, 7], operating temperature [6], carrier gas [3] (neutral gas or its mixture with hydrogen), its flow rate, etc.

It is well known that mechanical properties of alumina can be increased by producing homogenous and fine-grained materials [8]. Therefore additives are used for preventing the grain growth during a thermal treatment. The oxide Cr_2O_3 is isostructural to Al_2O_3, forms solid solutions with alumina above 1400°C [8, 9] what eventually results in better mechanical and thermal performances. The same strategy is adopted in the case of zirconia, where additives of Y_2O_3 and CeO_2 stabilize the structure and improve thermal shock resistance [10].

The first target of the present study was to combine advantages offered by ceramic materials and by the spray pyrolysis technique. As a result, synthesis and characterization of alumina-based powders (pure Al_2O_3 and Al_2O_3–2%Cr_2O_3) and zirconia-based powders (ZrO_2–10%Y_2O_3 and ZrO_2–15%CeO_2) are presented. The second one was manufacturing of materials by the pulse plasma sintering of the obtained powders and their preliminary characterization. The influence of sintering conditions on morphology of these materials is presented.

Experimental

Powders preparation

Alumina- and zirconia-based powders were synthesized by the ultrasonic spray pyrolysis method. Aque-

* Author for correspondence: witek@agh.edu.pl

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Table 1 Solution concentrations and pyrolysis conditions

Nominal composition/mol%	Solution concentration/M	Temperature/°C	Air flow/m^3 h^{-1}
Al_2O_3	0.08 $Al(NO_3)_3 \cdot 9H_2O$	800	0.20
Al_2O_3–2%Cr_2O_3	0.08 $Al(NO_3)_3 \cdot 9H_2O$+$Cr(NO_3)_3 \cdot 9H_2O$ (2%)	800	0.30
ZrO_2–10%Y_2O_3	0.08 $ZrO(NO_3)_3 \cdot nH_2O$+Y_2O_3 (5%)	860	0.45
ZrO_2–15%CeO_2	0.08 $ZrO(NO_3)_3 \cdot H_2O$+$NH_4[Ce(NO_3)_5] \cdot 4H_2O$ (15%)	900	0.15

ous precursors were obtained by dissolution of the inorganic salts $Al(NO_3)_3 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, $NH_4[Ce(NO_3)_5] \cdot 4H_2O$ and the oxide Y_2O_3 (a.p., POCH, Poland) in appropriate ratios in distilled water. The obtained solutions were atomized by the ultrasonic nebulizer (frequency: 2.6 MHz) and then transported by a carrier gas into the furnace where pyrolysis occurred. In order to reduce costs, the open atmosphere condition was selected in the present study. For collecting of the obtained ceramic powders an electrostatic filter at the outlet of the furnace was used. More detailed description of the applied experimental set is given in [11]. Several experiments were carried out prior to this study in order to optimize the process parameters such as solution concentrations, furnace temperature and the carrier gas flow. The final compositions of aqueous solutions and synthesis conditions are collected in Table 1.

Sintering

The powders received by spray pyrolysis were consolidated using the pulse plasma sintering. The sintering was carried out under a load of 600 kg cm^{-2} and the air pressure of 10^{-2} Pa. The whole process was divided into three steps: (1) in order to eliminate adsorbed gases samples were preheated at 150°C for 100–150 s, (2) pulse sintering was carried out at the temperature range 1000–1200°C for 100–300 s, and (3) cooling to a temperature 100°C, for about 250 s.

Materials characterization

Thermal studies of the obtained powders (TG and DTA) were carried out using TG-DTA thermobalance (2960 SDT, TA Instruments). Evolving gas analysis (EGA) was made by means of the quadrupole mass spectrometer (QMD 300 ThermoStar, Balzers). Phase characterization was carried out using powder X-ray diffractometer (Co lamp). Powders and sinters morphologies were analyzed by Scanning Electron Microscopy (SEM, Hitachi S3500N) and Transmission Electron Microscopy (TEM, Philips CM20, 200 kV).

Results and discussion

Powders

The powders obtained by spray pyrolysis of the nominal compositions of Al_2O_3 and Al_2O_3–2%Cr_2O_3 were thermally analyzed. These results as well as those of evolving gases analyses are presented in Figs 1a and b, respectively. For both compositions mass losses are observed pointing at significant nonstoichiometry of the as-received powders, however in the case of Al_2O_3–2%Cr_2O_3 the mass loss is twice lower. Quadrupole mass spectrometry measurements show that nonstoichiometry of Al_2O_3 is related to decomposition of residual nitrate used in synthesis (200–500°C) and oxygen release (800–1000°C), whereas for Al_2O_3–2%Cr_2O_3 to oxygen release only (800–1000°C). In both cases mass losses are diminished for temperatures higher than 1000°C, therefore this value was taken as a down limit for the pulse plasma sintering process.

XRD spectra of as-received alumina-based powders are shown in Fig. 2. The obtained patterns are characteristic for amorphous materials (background reflections are present only). Scanning electron micrographs of the ceramic powders are presented in Figs 3–5; for the nominal compositions: Al_2O_3–2%Cr_2O_3, ZrO_2–10%Y_2O_3 and ZrO_2–15%CeO_2, respectively. The obtained powders consist of spherical particles with a diameter between 20 nm–10 microns, depending on precursor and sintering conditions. The spherical geometry is related to the drying of droplets produced by the ultrasonic atomizer. These particles are solid or hollow spheres built from nanocrystallites, as can be seen in Fig. 6, where TEM micrographs of zirconia based powder are presented.

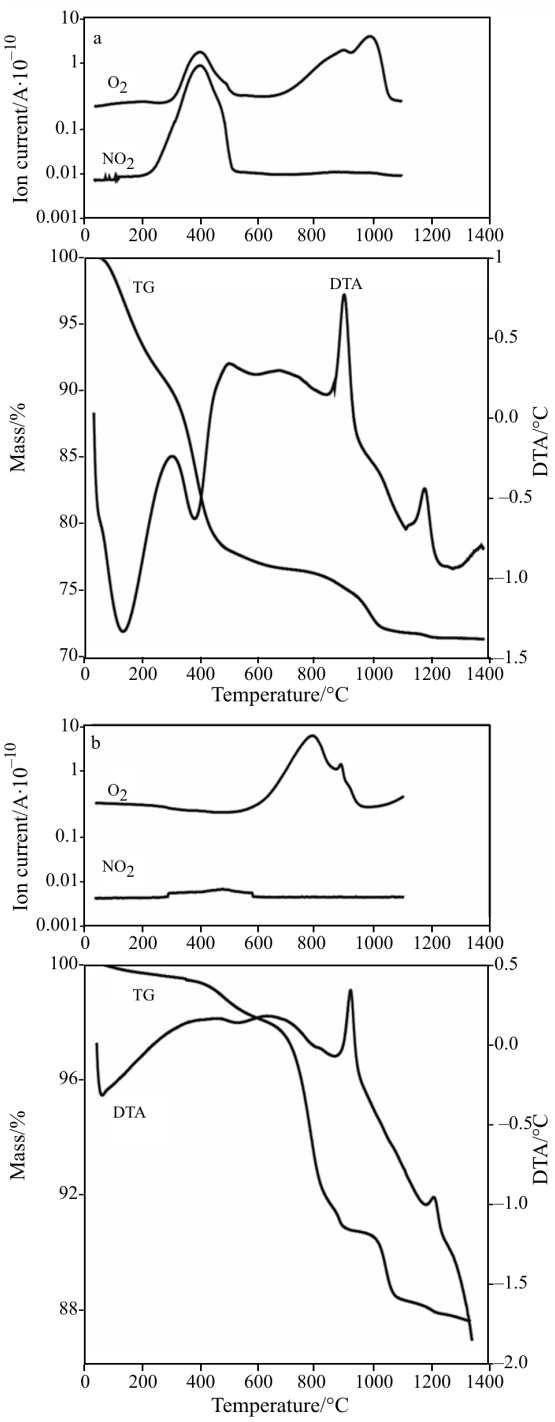

Fig. 1 DTA/TG and QMS measurements for powders of nominal compositions: a – Al_2O_3 and b – Al_2O_3–2%Cr_2O_3

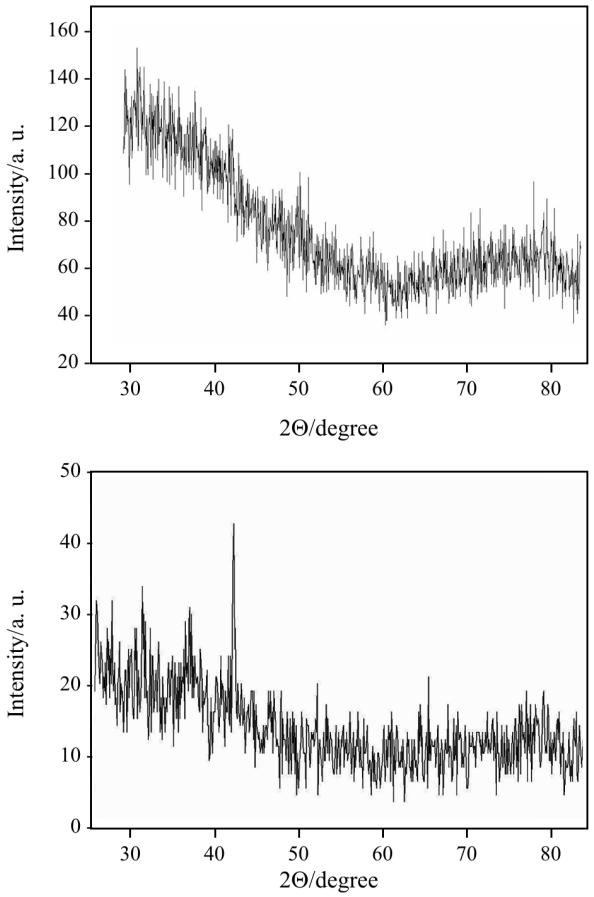

Fig. 2 XRD patterns of as-received powders of nominal compositions: a – Al_2O_3 and b – Al_2O_3–2%Cr_2O_3

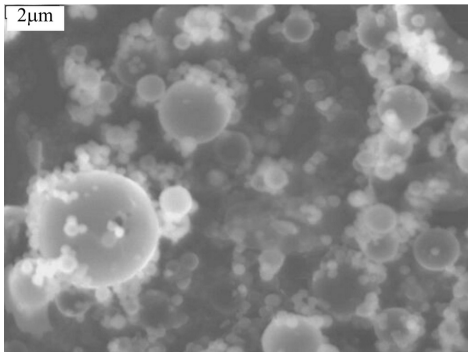

Fig. 3 SEM micrograph of the alumina-based powder of the nominal composition Al_2O_3–2%Cr_2O_3

Sinters

In this paper consolidation of alumina-based powders by the pulse plasma sintering is presented. XRD patterns of sintered materials are shown in Figs 7a and b, for compositions Al_2O_3 and Al_2O_3–2%Cr_2O_3, respectively. The main phase in both cases was the hexagonal alumina (JCPDS-ICDD file no. 046-1212). It is worth to note a thorough evolution of XRD patterns after relatively short time of the thermal treatment (sintering lasted up to 300 s). SEM micrographs of fractures of alumina samples sintered at 1100 and 1200°C are presented in Figs 8a and b, respectively. The higher degree of consolidation was found for the higher temperature, the density measurements carried out by the Archimedes' method showed densities: 2.70 and 3.10 g cm^{-3}, respectively. Similar studies were carried out for the powder of the nominal composition

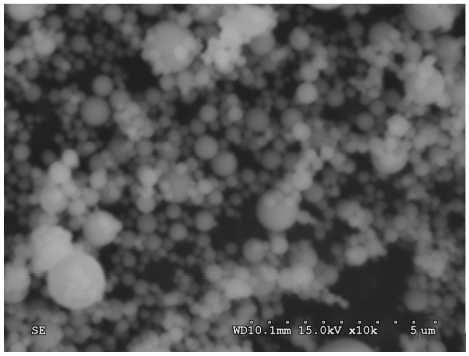

Fig. 4 SEM micrograph of the zirconia-based powder of the nominal composition ZrO_2–10%Y_2O_3

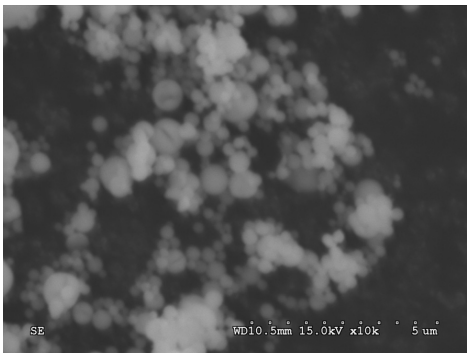

Fig. 5 SEM micrograph of the zirconia-based powder of the nominal composition ZrO_2–15%CeO_2

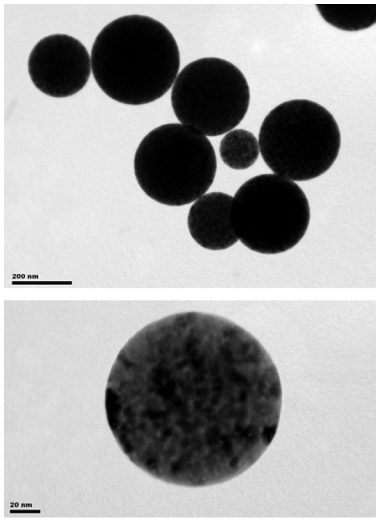

Fig. 6 TEM micrographs of the zirconia-based powder of the nominal composition ZrO_2–15%CeO_2

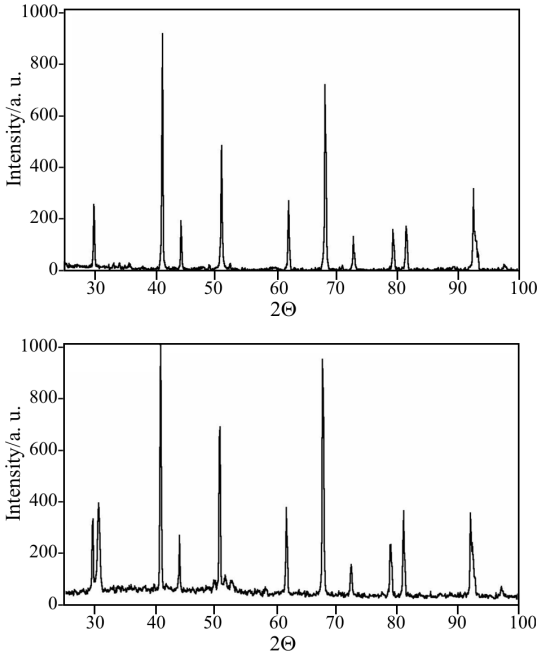

Fig. 7 XRD patterns of alumina based materials obtained by pulse plasma sintering of powders: a – Al_2O_3 and b – Al_2O_3–2%Cr_2O_3

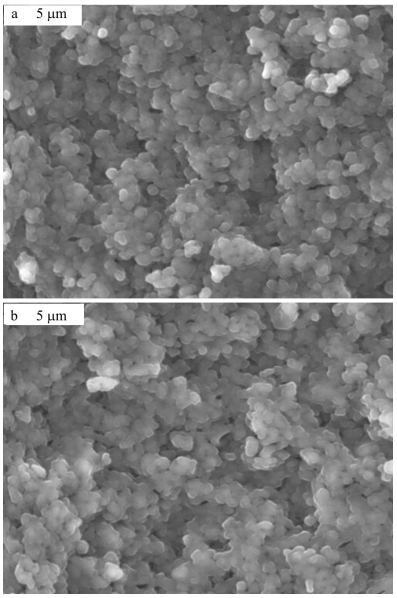

Fig. 8 SEM micrographs of fractures of alumina powder (nominal composition: Al_2O_3) sintered for 300 s at a – 1100°C and b – 1200°C

Al_2O_3–2%Cr_2O_3. In this case the sintering temperature remained constant (1100°C) whereas times were varied: (a) 100 and (b) 300 s. The morphology of these samples are presented in Figs 9a and b. The determined density for the sample sintered at 1100°C was even higher that that for the pure Al_2O_3 sintered at 1200°C that is related to chromia additive. It is worth to note that the pulse plasma sintering prevents particle growth for the times applied in this study.

Additionally TEM micrographs of Al_2O_3 material sintered at the lowest temperature of 1000°C for 300 s are shown in Figs 10a and b. The samples were prepared using FIB technique prior to microscope observations. The growth of necks between neighboring spheres (Fig. 10a) and their deformation (Fig. 10b) as results of the isostatic sintering are observed. The de-

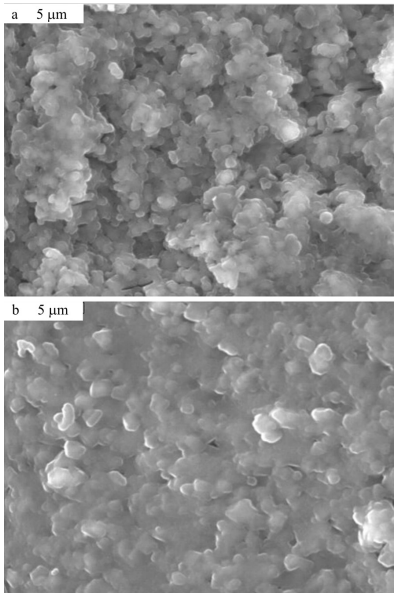

Fig. 9 SEM micrographs of fractures of chromia doped alumina of (Al_2O_3–2%Cr_2O_3) powders sintered at 1100°C for a – 100 and b – 300 s

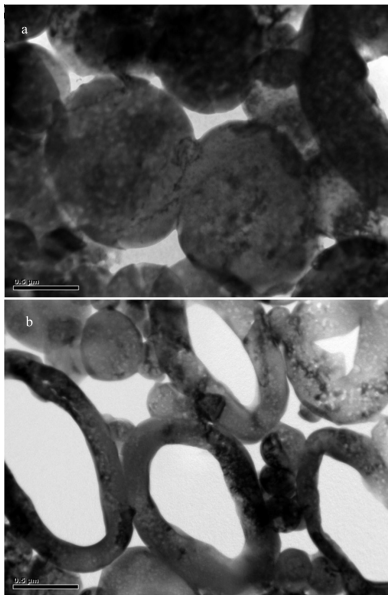

Fig. 10 TEM micrographs of Al_2O_3–2%Cr_2O_3 sample obtained by sintering at 1000°C for 300 s, prior to microscope observations, samples were prepared using FIB technique

formation of hollow spheres was quite extensive, whilst solid spheres barely changed their shape in the same conditions: Fig. 10b presents remains of agglomerated hollow particles that were distorted during the isostatic sintering (the same direction and degree of the deformation excludes occurrence of this phenomenon during the synthesis). It is observed that hollow particles of alumina are plastic even at moderate temperatures (1000°C) suggesting improved performances of these particles under the thermal shocks and erosion.

Conclusions

Alumina- and zirconia-based powders were synthesized by spray pyrolysis. Alumina-based powders were sintered by means of the pulse plasma sintering. After the sintering, XRD patters show evolution from the amorphous type to the well-crystallized one. Morphologies of powders and sinters were studied by SEM and TEM techniques; powders were in the form of full or hollow spherical particles consisted of nano-grains. These particles were distorted during the sintering with degree of deformation depending on whether particles were hollow or not. Sintering studies show that alumina powders obtained by spray pyrolysis are good starting precursors for obtaining both porous and dense materials by varying the processing conditions, e.g. for catalysis or biomaterial applications, respectively.

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