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MICROSTRUCTURE AND POROSITY OF 3YSZ SOLID ELECTROLYTE PREPARED USING ORGANIC POLYMERIC MATRIX

Two different complexing agents, namely citric acid and gelatin, were used for gel-combustion synthesis of yttria stabilized zirconia. The influence of synthesis conditions on properties of powders and sintered bodies was studied by X-ray Diffraction Analysis (XRD), Scanning Electron Microscope (SEM) and helium pycnometer measurements.

Keywords: yttria stabilized zirconia, gel-combustion synthesis, gelatin complexing agent.

1. Introduction

Zirconia (ZrO_2) is a well-known oxide ceramic, which crystallizes in monoclinic system in normal conditions. In temperatures above 1150°C ZrO_2 reveals phase transition to tetragonal crystallographic system and above 2370°C to cubic phase. The transition to cubic or tetragonal phase leads to significant improvement of zirconia electrical and mechanical properties [1].

The most popular method to stabilize the high-temperature tetragonal or cubic zirconia phase in standard conditions is by doping ZrO_2 with precisely adjusted amount of divalent or trivalent metal atoms. The following compounds have been reported as ZrO_2 dopants: MgO, CaO, Y_2O_3, Gd_2O_3, Sc_2O_3, Mg_3N_2, Si_3N_4, AlN [2]. Such modification has direct effect on considerable rise of material electrical conductivity.

High ionic electrical conductivity and temperature shock tolerance of the stabilized ZrO_2 make it suitable for application in electrochemical devices [3,4]. So far it was reported that the material can be applied in oxygen sensors [5], solid oxide fuel cells [4, 6], ceramic components and as catalyst or catalysts promoters in the synthesis of alcohol by hydrogenation of CO [7].

Among the group of the stabilized zirconia materials, yttria stabilised zirconia of the formula $0.97ZrO_2$-$0.03Y_2O_3$ (3YSZ), which crystallises in tetragonal system, is promising solid electrolyte in intermediate temperature fuel cells (IT-SOFC) [8]. For application as solid electrolyte the high density and gas tightness of the material is required. On the other hand, research presented in literature indicates that the 3YSZ material can be as well successfully used as anode material [9]. However, for this purpose it should be characterized by high open porosity and well developed microstructure of increased specific surface area. It is indispensable in order to provide satisfactory efficiency of the electrochemical processes taking place on the electrode.

Different wet synthesis routes of 3YSZ have been developed, so far. The most popular are coprecipitation method, sol-gel preparation method, hydrothermal method, polymerized complex processes and gel-combustion process. Among the above mentioned synthesis methods, gel-combustion method has many advantages. It is simple and low cost route allowing to produce products of desired composition. The prepared materials are characterized by high surface area and excellent sinterability [10].

The selected preparation conditions as well as type and amount of used organic agent impact on microstructure of the final product. The microstructure in turn determines many qualities of the ceramics, e.g. sinterability, gas-tightness, density, porosity, mechanical strength, electrical conductivity and chemical reactivity with gaseous phases. The mentioned properties are important in the point of view of possible application in specific electrochemical devices. It highlights, how important is investigation of the influence of synthesis modification on different properties of materials.

The organic substance that can be used as complexing agent for synthesis, besides the mentioned above compounds, is gelatin [11,12]. However up to now there are no reports about possible usage of this organic agent for zirconia-based materials synthesis.

The main aim of the studies was investigation of the influence of used organic agent kind and amount as well as preparation conditions on the selected properties of 3YSZ material. The gelatin was used for the first time as complexing agent for 3YSZ material synthesis. The qualities of materials prepared

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with citric acid and two different amounts of gelatin have been directly compared. Moreover, the effect of long-lasting grinding of the powder in vibrational ball mill on microstructure, density and porosity of the final samples was determined.

2. Experimental

Yttria stabilized zirconia of the formula $0.97ZrO_2$-$0.03Y_2O_3$ (3YSZ) was prepared by gel-combustion process from analytically pure reagents provided by Sigma-Aldrich. $ZrOCl_2 \times 8H_2O$ was dissolved in distilled water during 24 hours stirring process using magnetic stirrer. The liquid ammonia was added drop by drop resulting in precipitate of white $Zr(OH)_4$ intermediate product. The $Zr(OH)_4$ precipitate was washed several times with distilled water and dissolved in dilute nitrate acid during heating on a hot plate. Parallely the solution of $Y(NO_3)_3$ was prepared by dissolving Y_2O_3 powder in nitrate acid. The molar concentration of Y^{3+} and Zr^{4+} ions in the both solutions were determined by classical chemical weight method. The required amount of the yttrium and zirconium solutions were measured and mixed in order to obtain 150g of the $0.97ZrO_2$-$0.03Y_2O_3$ product. The solution was divided into three equal portions.

Weighted amount of citric acid monohydrate ($C_6H_8O_7 \times H_2O$) was added to the first batch of nitrate solution in the molar ratio of 2:1 of citric acid particles to the Zr^{4+} and Y^{3+} cations sum. 0.5 of polyvinyl butyral was added in order to facilitate a polymerization process. The mixture was heated on a hot plate for 10 hours turning into a sol and subsequently into a white thick sol-gel. After drying for 24 hours at 250°C, the obtained dark grey powder was grinded in the agate mortar and calcinated at 600°C in the tubular furnace in atmospheric air. The mixture turned into white powder, which was further milled in ball mill (RETSCH PM 100) in the isopropyl alcohol for 6 hours with 300 rpm. After drying, the microstructure of the powder was visualized by scanning electron microscope (SEM). The bulk density of the powder was determined by simply weighting and measuring the volume of the powder. The phase composition of the final product was confirmed by X-ray diffraction analysis (XRD). The powder was pressed into 0,5g pellets of 10 mm diameter under 50 bar pressure and fired in the chamber furnace in 1200°C for 3 hours. The specific densities of the sintered bodies as well as open, closed and total porosities were determined by the mean of helium pycnometer.

Two batches of the material were prepared parallelly using two different amount of bovine gelatin. 50g (method I) and 25g (method II) of gelatin were separately dissolved in 500 ml of distilled water at 60°C followed by cooling the solutions to room temperature. Previously prepared portions of nitrate mixtures were poured drop by drop to gelatin water solutions while continuously stirring using magnetic stirrer. The obtained sol was dried at 250°C for 20 hours turning into grey porous solid material of significantly multiplied volume. The materials were crushed and milled on the agate mortar and calcinated in 600°C for 3 hours. The further studies on ball milled material were conducted analogously to the investigation of powders prepared by citric acid method.

The XRD measurements were done in air at room temperature using CuK_α radiation (Philips X' Pert) within the 2Q range 10-90° with the scan rate of 0.008°/s. Particle sizes were calculated from the line broadening of the X-ray diffraction peaks using the Scherrer formula. The observations of powders microstructure were performed by NovaNanoSEM 200 microscope using different magnifications. The specific densities as well as open, closed and total porosities were determined using helium pycnometer Accupuc 1340 provided by Micrometrics Instruments Corporation. The measurements of density and porosity were repeated a numerous of times in order to examine the reproducibility of the results.

3. Results and discussion

The XRD spectra coming from three powder samples prepared by different methods exhibit identical list of peaks characteristic for tetragonal crystallographic system. The obtained spectra are presented in Fig. 1.

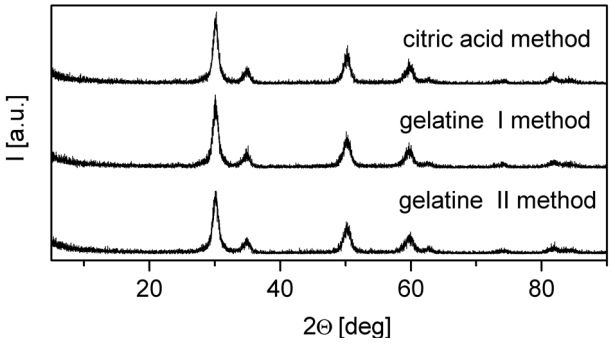

Fig. 1. XRD patterns of 3YSZ powders prepared by different methods

The spectra consist only from ZrO_2 phase peaks, showing that yttrium substituted zirconium in lattice sites and did not created additional phase in the material. Basing on the XRD data the mean sizes of the crystallites were determined. The crystallites in material prepared by citric acid are of 6,5 nm and 6,2 nm in materials derived in both gelatin methods.

In Fig. 2-5 the images of powders microstructure obtained by EIS technique with different magnifications are presented.

In Fig. 2A which presents microstructure of powders from I gelatin method before grinding the irregular, extended, sharp-edged structures with cave-like pores of diameters between 5-40 μm are visible. Fig. 4A, 5B and 5C contain images with higher magnifications of two different regions of the above mentioned sample. The apparent differences between the visualized fragments indicate significant inhomogeneity of the powder. In Fig. 4A smooth surface with few fractures is shown. In Fig. 5B round-edged, undulating extended structure with pores of a diameter about 0,5 μm is visible. In contrast, the region in Fig. 5C consists of irregular accreted aggregates of crystallites.

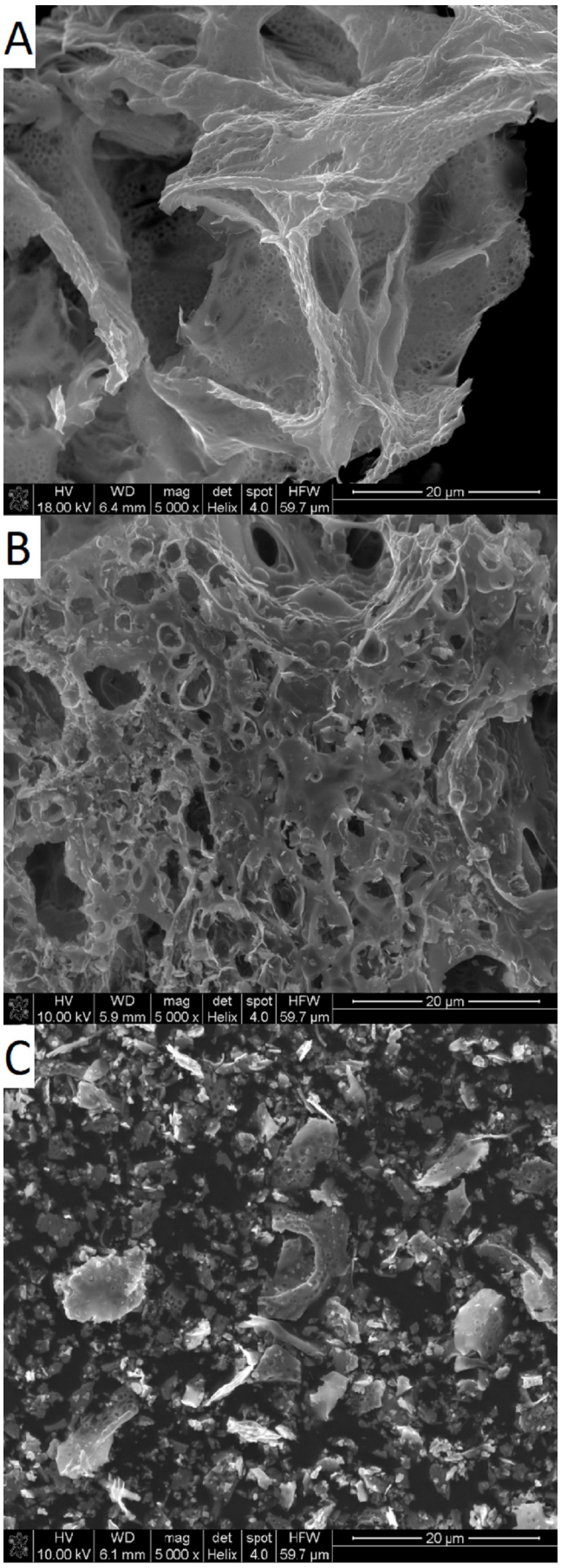

Fig. 2. SEM images of powders microstructure from samples prepared by: A-gelatin I method before grinding, B-gelatin II method before grinding, C-gelatin I method after grinding

The images of powder prepared by II gelatin method (using 25 g of gelatin) before grinding presented in Fig. 3D and 2B contain sponge like structures with 10 µm pores of different shapes. In case of powder prepared by citric acid method the microstructure is comprised of sharp-edged separated crystallites of size 2-5 µm.

The grinding process has direct effect on material microstructure. In fig. 2C, 3E and 4C sharp-edged irregular, separated particles of a diameter of 5-10 µm can be observed.

The open, closed and total porosity of sintered bodies was determined using helium pycnometer and the results are presented on histogram in Fig. 6.

The closed porosity in each case is of low value and do not exceed 5%. The highest value of open and total porosity show the samples prepared by methods using gelatin as organic agent without grinding in ball mill. Grinding of materials leads to significant decrease of open and total porosity. Therefore, the total porosity of grinded materials synthetized by gelatin method is even lower than the porosity of material prepared by citric acid method. The densities of the powders and sintered bodies were calculated and collected in Table 1. The powder prepared by citric acid method is characterized by much higher density than the powders prepared using gelatin method. Grinding the powders leads to significant increase of densities. There are slight differences between densities of the sintered bodies. The highest density exhibits specimen prepared by citric acid method. In case of specimens prepared by gelatin method grinding resulted in slight rise of densities.

TABLE 1

Density of powders and sintered bodies prepared by different methods

Specimen kind	Density [g/cm^3]				
	Citric acid method	I gelatin method before grinding	II gelatin method before grinding	I gelatin method after grinding	II gelatin method after grinding
Powder	1,243	0,101	0,553	0,157	0,529
Sintered body	5,951	5,616	5,628	5,733	5,799

4. Conclusion

The 3YSZ material was synthetized by gel-combustion process using two different organic media, namely citric acid and two different amounts of gelatin. Moreover, in case of material prepared with gelatin, the effect of long-lasting grinding in ball mill on microstructure, density and porosity was investigated. Basing on XRD data in each case one phase material crystalizing in tetragonal system was obtained. Crystallites sizes in all the samples determined by XRD method are of similar value. Basing on SEM observations, grinding process plays significant role on modification of microstructure of the 3YSZ powders. Before grinding the powders prepared by gelatin method con-

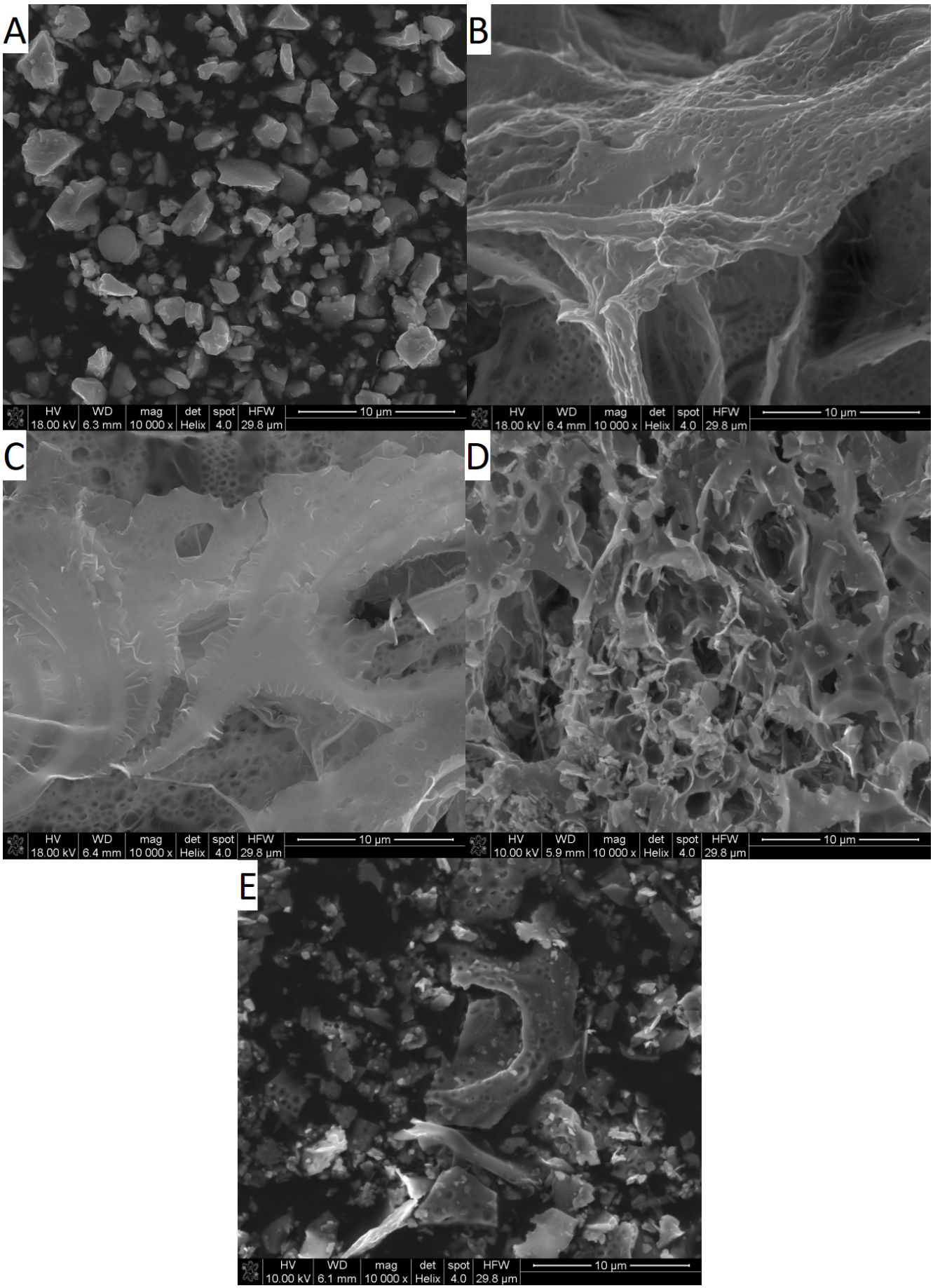

Fig. 3. SEM images of powders microstructure from samples prepared by: A-citric acid method, B&C-gelatin I method before grinding, D-gelatin II method before grinding, E-gelatin I method after grinding

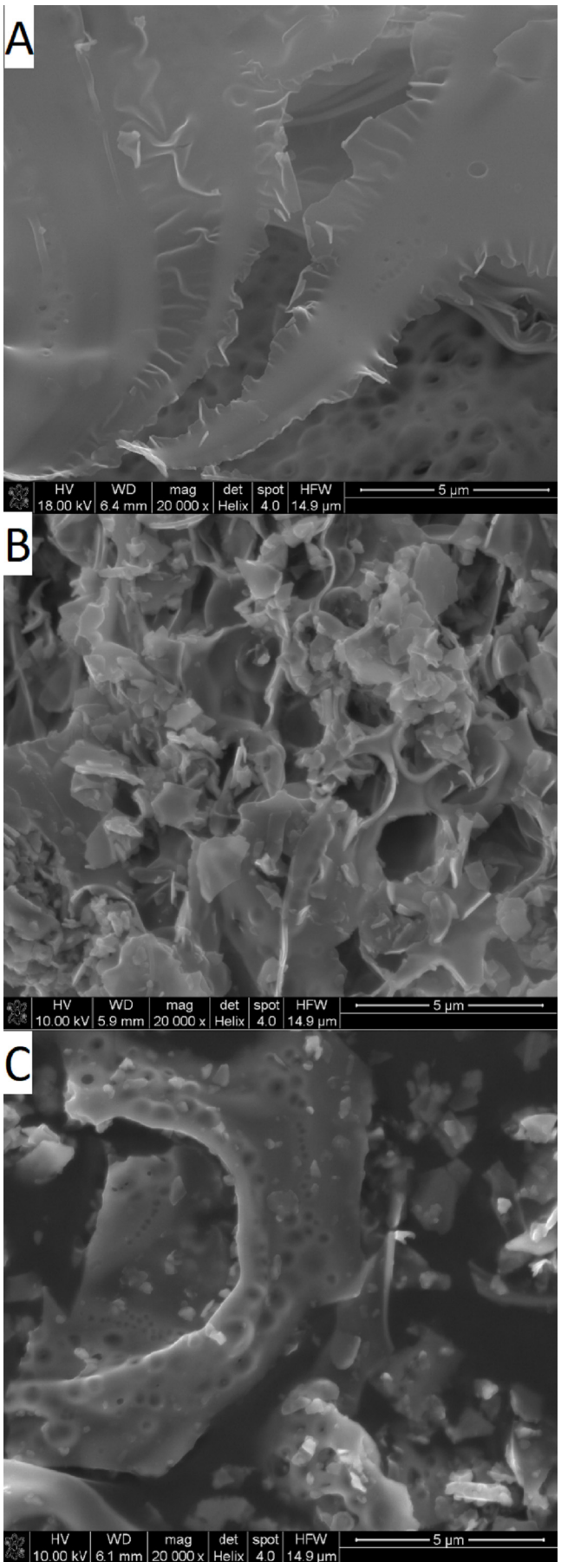

Fig. 4. SEM images of powders microstructure from samples prepared by: A-gelatin I method before grinding, B-gelatin II method before grinding, C-gelatin I method after grinding

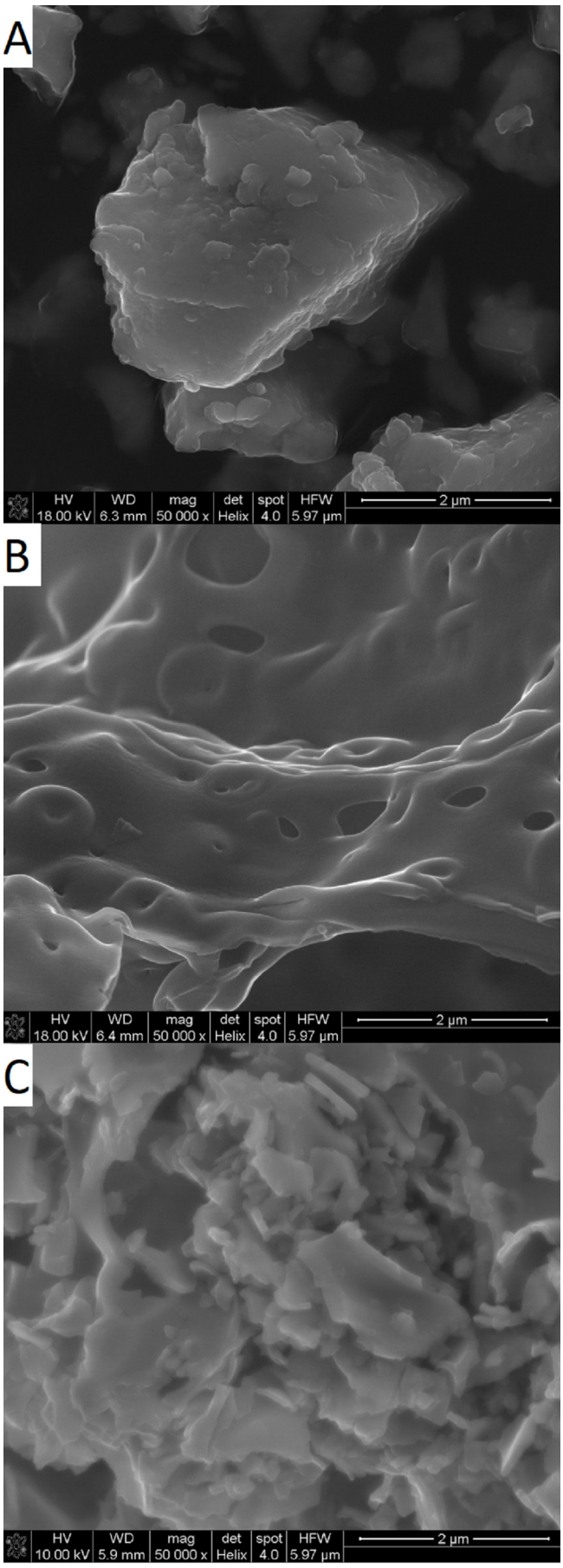

Fig. 5. SEM images of powders microstructure from samples prepared by: A-citric acid method, B-gelatin I method before grinding, C-gelatin II method after grinding

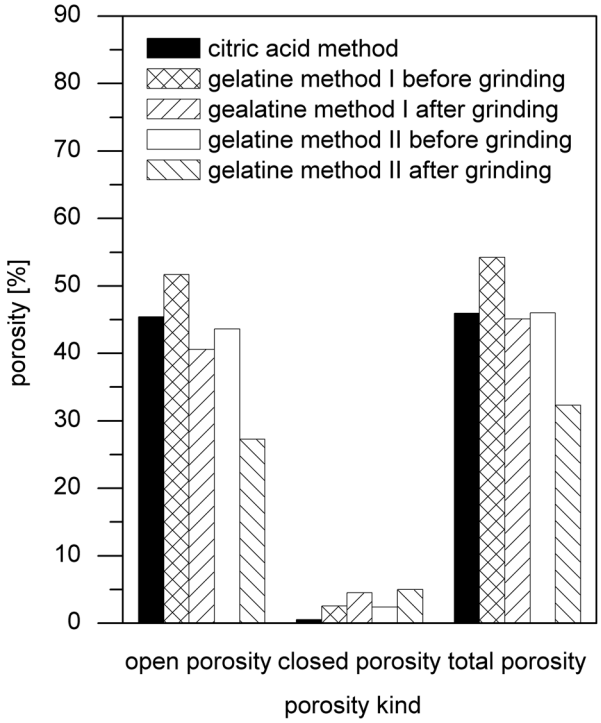

Fig. 6. Porosity of sintered bodies prepared by different methods

sisted of inhomogeneous structures of different sizes and shapes. After grinding the separated irregular crystallites were visible. The preparation conditions have direct effect on the density of prepared powders. The density of powder prepared by citric acid method was about 12 times higher than in case of powder prepared using higher content of gelatin. The highest density demonstrate specimen from citric acid method and the lowest from material derived from I gelatin method without grinding. It turned out that sintered samples of highest open and total porosities were obtained from powders derived with higher content of gelatin without grinding. In contrast, using ball milled powders produced by lower content of gelatin, sintered bodies of decreased open and total porosity were prepared.

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