

Formation of Pore Structure in Zirconia-Alumina Ceramics

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Abstract

In this research work different pore forming methods and sintering temperatures were applied to create micropores in zirconia (ZrO_2), alumina (Al_2O_3) and ZrO_2 -MgO composite ceramics in range from 4% up to 68%. The authors have found that the used different pore forming additives and sintering temperatures are influenced very strong not only the pore sizes and their distributions but on final compression strengths also. Using aluminum hydroxide for pore forming at sintering temperature of 1450-1650 °C 62% porosity can be obtained at more than 200MPa compressive strength.

Keywords: alumina, aluminum hydroxide, ceramics, composites, microstructure, pore forming, porosity, sintering, zirconia

1. Introduction

Porous ceramic materials have found wide application in various fields and it can be used as filter elements, catalyst carriers and heat-shielding elements. As compared to metals and polymers, ceramics have some advantages: high hardness, chemical inertness, wear resistance and thermal shock resistance, etc.

Operational properties of porous ceramic materials are largely determined by the parameters of the internal structure, such as pore volume, average pore size, shape and their contiguity. For example, a material with closed porosity and low thermal conductivity can be used as a thermal barrier, while open and connected polymodal porosity, combined with chemical inertness, is applicable to the filtration of liquids and gases.

Modern methods of pore structure formation make it possible to obtain porous ceramics with the necessary properties and characteristics by introducing various pore-forming additives into the initial powder compositions and sintering parameters changing. At present time there are several technologies for the production of porous ceramic materials: sintering of disperse systems at low temperatures, introduction of a pore-former or gas bubbles into a curable ceramic slurry. In [1] is described a method for obtaining a highly porous, up to 95%, ceramic, based on the rapid freezing and freeze-drying of a ceramic suspension. This makes it possible to obtain dendritic pore structures that can be good gas-filtering elements. The creation of macroporous structure described in [2] allows obtaining pores morphology similar to inorganic bone matrix. The choice of the method for creating the material pore structure

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is determined by the necessary morphology, functional properties and the corresponding application of the future product. Nevertheless, many of the technologies like additive technologies [3-5] for obtaining the necessary pore structure can be difficult or expensive, that prevents their wide use [6, 7].

One of the most common technologies for creating pore structure in ceramic materials is introduction of pore-forming particles into the initial powder composition followed by pressing and sintering. The selection of pore-former depends on the pores required average size and shape. The pore-forming material should be thermally removed particles, for example paraffin, rosin, ammonium carbonate and some types of polymers.

Another common method of porosity formation is the decomposition of hydroxides, for example, aluminum, zirconium, magnesium, etc. to their oxides with H_2O evaporation. This method of pore formation avoids the presence of impurities on the internal surfaces of the porous ceramic matrix [8].

Despite the fact that such studies devoted a considerable amount of work, comprehensive studies on the porosity formation laws in ceramics based on oxides using various methods of pore formation is not enough.

The purpose of this work is to study a pore structures formation in ceramics based on alumina and zirconia using organic pore-forming particles, hydroxides and variation in the sintering parameters.

2. Materials and methods

It have been studied ceramic composites ZrO_2 -MgO with 0-100 wt. % MgO, ZrO_2 - Al_2O_3 with 0-75 wt.% of $Al(OH)_3$ and Al_2O_3 with 0-100 wt.% of $Al(OH)_3$ in the initial powder compositions.

The mean size of particles of ZrO_2 powder stabilized with 3 mol. % MgO were 0.5-6 μm , magnesia were 7 μm . Alumina powder was obtained by annealing $Al(OH)_3$ at 1100 $^\circ C$, the particle size was 50-100 μm . The particle size of the alumina powder was 50-100 μm .

Powder mixtures were obtained by mechanical mixing of powder components and cold uniaxial pressing at 190 MPa using steel mould, followed by sintering in an air atmosphere with holding time one hour.

Materials with bimodal porosity were obtained by adding and burning out ultra-high molecular weight polyethylene (UHMWPE) particles with an average size of 50 μm , adding to the initial powder mixtures, followed by annealing at 300 $^\circ C$ for removing polyethylene particles and sintering at 1600 $^\circ C$ similar [9]. Two other methods of pore formation were used in ZrO_2 -MgO composite as changing of sintering temperature from 1200 $^\circ C$ to 1600 $^\circ C$ and decomposition of $Al(OH)_3$ with evaporation of H_2O sintering at temperatures 1450 - 1650 $^\circ C$ [10, 11].

The microstructure was studied by scanning electron microscope; pore volume was measured by the Archimedes method. The compressive strength was determined by using a universal testing machine with a constant strain rate $7 \cdot 10^{-4} s^{-1}$.

3. Results and discussion

On figure 1 are shown that ZrO_2 -MgO compacts with highest sintering temperature had a minimum porosity – 4%. Decreasing of sintering temperature was accompanied by a nonlinear increasing of pore volume up to 60%. The average pore size of ceramics sintered at 1600 $^\circ C$ were 8 μm , with standard deviation, σ , is 6 μm , these data are illustrated by microphotography on figure 2. Decreasing of sintering temperature leads to increasing of the pore sizes from 14 μm and $\sigma = 11 \mu m$ for 1500 $^\circ C$ and 17 μm and $\sigma = 10 \mu m$ for 1400 $^\circ C$.

Figures 3 shows a scanning electron microscopy image of the ZrO_2 - Al_2O_3 - $Al(OH)_3$ fracture surface, and figure 4 shows a polished surface of Al_2O_3 - $Al(OH)_3$ ceramic material after sintering at 1600 $^\circ C$. During the sintering alumina one can observed a decomposition of hydroxide and formation of irregular shape pores. Estimation of pore size distribution are shown that the average pore size is 2.1 μm in ZrO_2 - Al_2O_3 ceramic and 4 μm in Al_2O_3 .

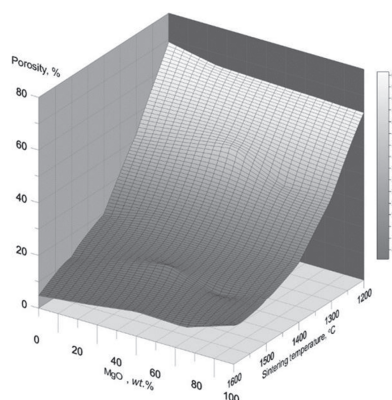


Fig. 1. Porosity of ZrO_2 -MgO vs. composition and sintering temperature
1. ábra A porózus ZrO_2 -MgO összetétele és szinterelési hőmérséklete

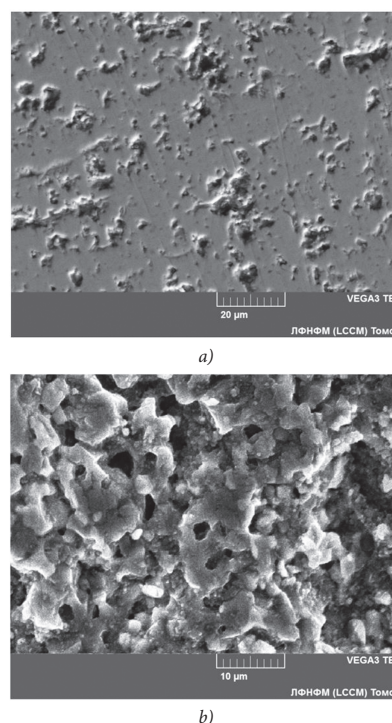


Fig. 2. The microstructure of the polished surface (a) and the fracture surface (b) of the ZrO_2 -50wt. %MgO ceramic sintered at 1400 $^\circ C$.
2. ábra Az 1400 $^\circ C$ -on szinterelt ZrO_2 - 50m% MgO kerámia csiszolat (a) és töretfelületének (b) mikrostruktúrája

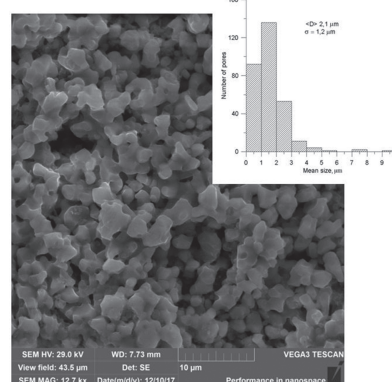


Fig. 3. a) Microstructure of the ceramic fracture surface, based on ZrO_2 with the 75% addition of aluminum hydroxide. Sintering temperature 1600 $^\circ C$ and pore size distribution
3. ábra Az 1600 $^\circ C$ -on szinterelt 75% alumínium-hidroxid adalékkal készült ZrO_2 kerámia töretfelületének a szerkezete és a pórusméret eloszlása

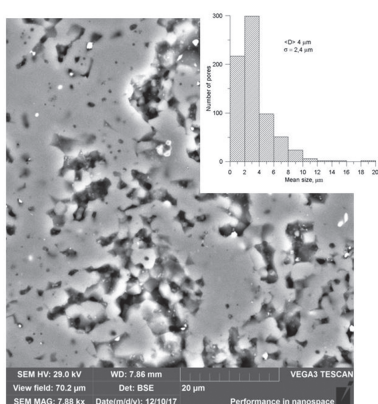


Fig. 4. a) Microstructure of the polished surface of ceramics alumina-75% aluminum hydroxide; Sintering temperature 1600 °C and pore size distribution

4. ábra Az 1600°C-on szinterelt 75% alumínium-hidroxid adalékkal készült Al₂O₃ kerámia csiszolat felületének szerkezete és a pórusméret eloszlása

On figures 5 are shown the dependences of pore volume in ZrO₂-Al₂O₃ and Al₂O₃ ceramics after sintering vs. aluminum hydroxide content and sintering temperature. It can be seen that in ZrO₂-Al₂O₃ ceramics the pore volume increases with increasing of hydroxide concentration and almost does not changes with sintering temperature. Alumina ceramic, obtained with an aluminum hydroxide addition showed an increasing of porosity with increasing of Al(OH)₃ concentration, but decreasing with increasing of sintering temperature, figure 6.

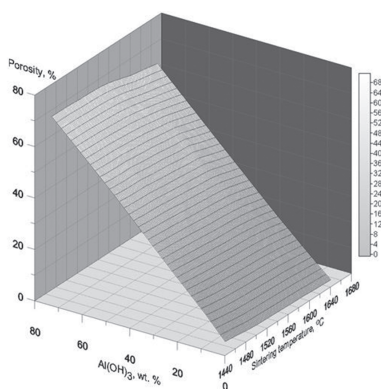


Fig. 5. Dependence of pore volume in ceramics based on ZrO₂ vs. aluminum hydroxide content and sintering temperature

5. ábra A ZrO₂ alapú kerámia pórustérfogatának változása az alumínium-hidroxid tartalom és a szinterelési hőmérséklet szerint

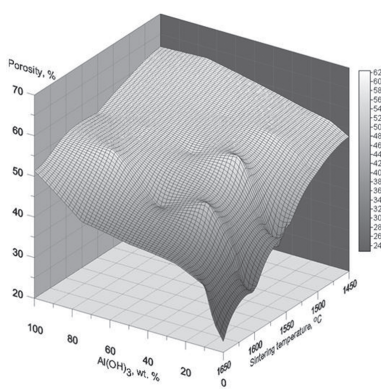


Fig. 6. Dependence of pore volume in ceramics based on Al₂O₃ from the concentration of aluminum hydroxide and the sintering temperature

6. ábra Az Al₂O₃ alapú kerámia pórustérfogatának változása az alumínium-hidroxid tartalom és a szinterelési hőmérséklet szerint

Addition of UHMWPE to the ZrO₂-MgO composite leads to creation a bimodal pore structure and increases the average micropores size up to 30 μm without a dependence on the MgO concentration. As one can see from figure 7 that in sintered ZrO₂-MgO ceramic there are two pore types - with average size about 100 and 10 μm. The large pores have the morphology of the pore-forming particles - spherical-shape which can be both isolated and connected. Pores of smaller sizes are formed by the compacting of powder particles parameters and its mean size is 29 μm. The pore size distributions are shown on Figure 8 and as one can conclude from Table 1 its does not depends on MgO content.

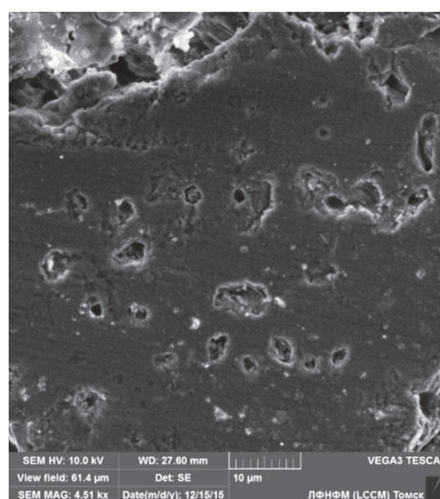
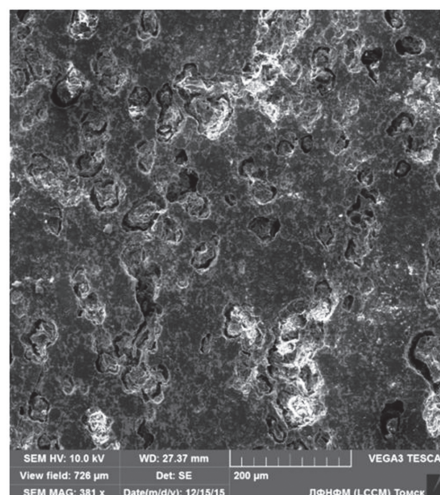


Fig. 7. Microstructure of ZrO₂-MgO porous ceramics

7. ábra A porózus ZrO₂-MgO kerámia mikroszerkezete

MgO, mass %	The average size of micropores, μm; Standard deviation, μm	The average size of macropores, μm; Standard deviation, μm	Porosity, vol. %
0	29; σ=19	98; σ=31	45
25	30; σ=23	104; σ=21	43
50	27; σ=17	94; σ=27	45
75	26; σ=17	101; σ=30	49
100	28; σ=20	105; σ=27	47

Table 1. The average pore size of ZrO₂-MgO ceramics
1. táblázat A ZrO₂-MgO kerámiák átlagos pórusmérete

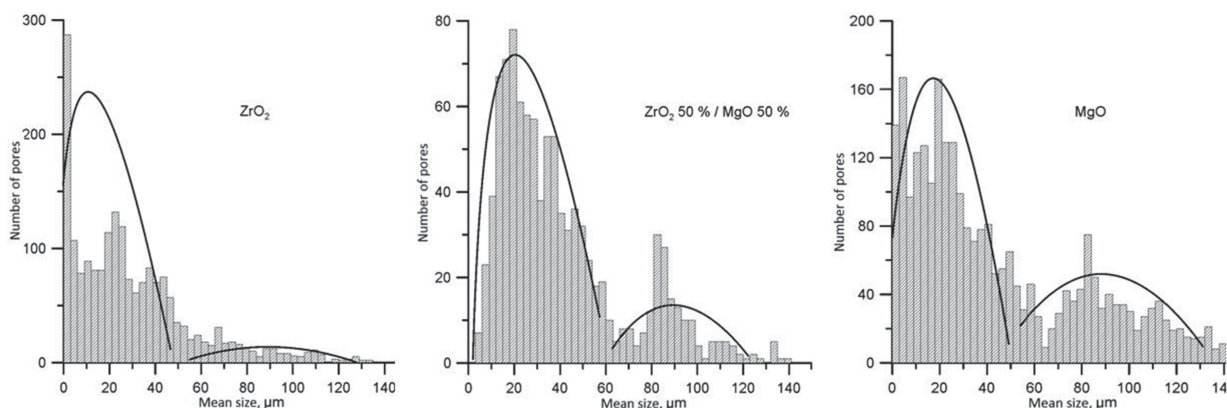


Fig. 8. Pore size distribution according to composition
 8. ábra A pórusméret-eloszlás az összetétel szerint

Pore-forming technologies, based on the changes of sintering temperature and $Al(OH)_3$ and UHMWPE addition, makes it possible to obtain micropores with an average size up to $17 \mu m$. Average pore size of ceramic obtained with $Al(OH)_3$ addition in initial powders were $2.1 \mu m$ in $ZrO_2-Al_2O_3$ ceramic and $4 \mu m$ for Al_2O_3 ceramic.

Increasing of ZrO_2 -MgO composite sintering temperature from 1200 to $1600 \text{ }^\circ C$ leads to a decrease in porosity from 68 to 4% . The average size of micropores decreases from 17 to $8 \mu m$ without significant dependence of components in the initial powder composition.

Determination of compression strength of a ZrO_2 -MgO composite, sintered without adding pore-forming particles are shown, that strength increases with sintering temperature increasing, the maximum strength is 230 MPa can be achieved after sintering at highest temperature $1600 \text{ }^\circ C$, figure 9.

Figures 10 and 11 are shown the compression strength of $ZrO_2-Al_2O_3$ and Al_2O_3 ceramics. Both ceramics showed the increasing of strength with increasing of sintering temperature and decreasing of aluminum hydroxide concentration in initial

powder composition. Ceramics based on ZrO_2 has maximum compressive strength 64 MPa after sintering at $1650 \text{ }^\circ C$ without the aluminum hydroxide addition. The minimum compressive strength was 8 MPa after sintering at $1450 \text{ }^\circ C$ and with aluminum hydroxide addition 75% . At the maximum sintering temperature and the minimum content of aluminum hydroxide the Al_2O_3 -based ceramic had compressive strength 165 MPa . The minimum compressive strength was 10 MPa for ceramic sintered as aluminum hydroxide content with a sintering temperature $1450 \text{ }^\circ C$. The compression strength of the ZrO_2 -MgO composite with bimodal porosity increases with an increasing of MgO content in the composition from 18 to 33 MPa .

4. Conclusion

Thus, the methods of pore volume formation in ceramics allow to obtain the pore volume in ZrO_2 and Al_2O_3 ceramics in the range from 4% to 68% and sintering temperature increasing leads to decreasing of the average pore size and pore volume.

It have been found that the introduction of pore-forming

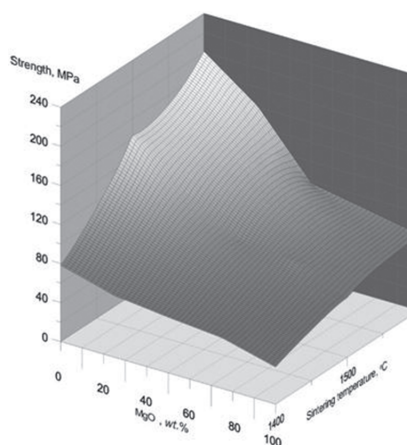


Fig. 9. Dependence of compressive strength of ZrO_2 -MgO vs. composition and sintering temperature

9. ábra A ZrO_2 -MgO kerámia nyomószilárdságának változása az összetétel és a sinterelési hőmérséklet függvényében

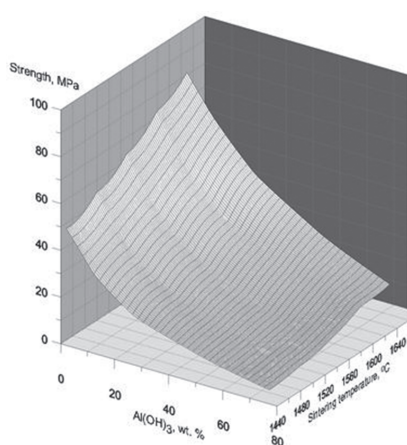


Fig. 10. Dependence of the compressive strength of ZrO_2 -based ceramics vs. the sintering temperature and aluminum hydroxide content

10. ábra A ZrO_2 alapú kerámia nyomószilárdságának változása az alumínium-hidroxid tartalom és a sinterelési hőmérséklet szerint

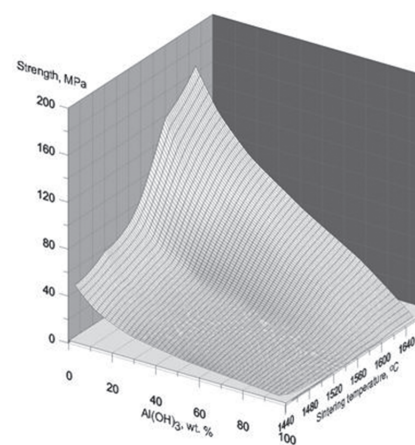


Fig. 11. Dependence of the compressive strength of Al_2O_3 -based ceramics vs. the sintering temperature and aluminum hydroxide content

11. ábra Az Al_2O_3 alapú kerámia nyomószilárdságának változása az alumínium-hidroxid tartalom és a sinterelési hőmérséklet szerint

particles into the ZrO₂-MgO initial powder composition and sintering at 1600 °C makes it possible to obtain a pore structure inheriting the morphology of the pore-forming particles. The maximum compressive strength was 33 MPa. The compression strength of ZrO₂-MgO ceramic obtained without the introduction of pore-forming particles reaches up to 200 MPa.

Addition of aluminum hydroxide to Al₂O₃ with sintering at temperatures 1450–1650 °C allows to achieve a porosity of up to 62%, while the compressive strength is 220 MPa.

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Póruszerkezetek létrehozása cirkónium-oxid – alumínium-oxid kerámiákban

Jelen kutatómunkában különböző pórusképző módszerek és szinterelési hőmérsékletek alkalmazásával cirkónium-oxid, alumínium-oxid és ZrO₂-MgO kerámia kompozitokban 4-68%-os mikropórus szerkezetet hoztak létre. A szerzők megállapították, hogy az alkalmazott különböző pórusképző adalékoknak és szinterelési hőmérsékleteknek nem csak a pórusok méretére és elhelyezkedésére van jelentős hatása, hanem a nyomószilárdságra is. Pórusképző adalékként alumínium-hidroxidot és 1450-1650°C-os szinterelési hőmérsékletet alkalmazva 62%-os porozitás érhető el több mint 200MPa-os nyomószilárdsággal.

Kulcsszavak: alumínium-oxid, alumínium-hidroxid, kerámiák, kompozitok, mikroszerkezet, pórusképzés, porozitás, szinterelés, cirkón-dioxid

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