Properties of $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ ceramics produced from different powder mixtures of zirconia and aluminum hydroxide

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Abstract

Porous $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ ceramics produced from powder mixtures of zirconia and aluminum hydroxide obtained by different methods is studied. The paper presents the data on the structure, phase composition, crystal structure and strength of the studied ceramics. It is found that the strength of the sintered $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ composites depends on the type of aluminum hydroxide used in the initial powder mixture. The pore size of the produced ceramics is shown to depend on sintering temperature. The crystallite size is determined at which the studied composites become solid.

Keywords: $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ composites, sintering, strength, crystallite size

1. Introduction

Composite materials on the basis of $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ have high strength, fracture toughness, corrosion and heat resistance. These properties allow the $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ ceramics to be used as materials for the production of bio-implants, catalyst carriers, membranes and filters [1, 2].

Porosity of the material and its porous structure determine the working characteristics of the ceramic products. Typically, required porosity and pore morphology in ceramic materials is attained by introducing and subsequent removal (by annealing) of an organic pore former. However, despite simplicity and accessibility, this method has a drawback, which is the presence of combustion products of the pore former (carbon and its compounds) in the porous material after annealing. The presence of compounds in the bulk of the material is inadmissible for bio-implants, catalyst carriers and filters. In order to avoid the presence of foreign compounds in a porous material, the required porosity is achieved through methods that imply the decomposition of powder mixture constituents into simpler compounds during sintering accompanied by gas release. An example of this kind of reaction is the decomposition of hydroxides to oxides. Although this method of producing porous materials has long been known, the literature provides no information on the structure and properties of ceramics produced by the given method. The aim of this paper is to study how the structure and properties of zirconia and aluminum hydroxide powders influence the structure and properties of $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ ceramics.

2. Materials and Experimental Procedure

Materials for the investigation were yttria-stabilized zirconia powders, aluminum hydroxide powders, and composites on their basis. Zirconia powders were produced by different methods, namely, chemical deposition of Zr and Y from nitrate salt solution, and decomposition of Zr and Y salt mixture solution in low-temperature plasma. Aluminum hydroxide powders were also obtained by different methods, such as decomposition of alumininate solution, and hydrolysis of ultrafine aluminum powder.

The structure of the initial powders and composite materials on their basis was analyzed by electron and optical microscopy. The X-ray structure and phase analysis of the initial powders and composites on their basis was carried out by X-ray diffraction with filtered CuKa radiation. Specimens of $\text{ZrO}_2$–$\text{Al}_2\text{O}_3$ ceramics were made by compaction of zirconia – aluminum hydroxide powder mixtures with 1, 5, 10, 25 and 50% volume fraction of aluminum hydroxide and by subsequent sintering of the compacts on air at temperatures 1400, 1500, 1550, 1600 and 1650 °C. The composite specimens were tested in compression with a universal Instron testing machine.

|                  | $<d>$ particle, μm | $S_{ts}$, m²/g | T-ZrO₂ content, % | CDD of t-ZrO₂, nm | a, Å | t-ZrO₂ | c, Å | t-ZrO₂ | Lattice microdistortion, ε |
|------------------|---------------------|----------------|-------------------|-------------------|------|--------|------|--------|--------------------------|
| Chemical deposition | 12                  | 7.6            | 65                | 20                | 5.0908 | 5.1849 | 2.37 $\times$ 10⁻³ |
| Plasma chemical synthesis | 1.5                | 7              | 90                | 20                | 5.1028 | 5.1749 | 2.42 $\times$ 10⁻³ |

Table 1. Properties of CD and PCS powders

I. tőblázat: CD és PCS porok tulajdonságai
3. Results and discussion

3.1 Powders

Examination of zirconia powders shows that the powder produced by chemical deposition (CD powder) consists of individual polycrystalline aggregates, and the powder produced by plasma chemical synthesis (PCS powder) consists of spherical particles and their aggregates. The average particle size, specific surface area, the content of the tetragonal zirconia phase, the size of the coherent diffracting domains of the tetragonal zirconia modification, microdistortion, and lattice parameters of the powders are given in Table 1.

Fig. 1 shows the SEM image of the aluminum hydroxide powder produced by aluminate solution decomposition (a), and X-ray diffraction pattern of this powder (b).

The high background at small diffraction angles suggests that the major part of the powder was in the X-ray amorphous state.

The aluminum hydroxide powder produced by hydrolysis of aluminum powder consists of spherical aggregates formed by individual particles (Fig. 2.a); the average particle size is 1.5 μm. According to X-ray analysis data, the powder has only one phase corresponding to bayerite Al(OH)₃ (Fig. 2.b).

3.2 Sintered ZrO₂–Al₂O₃ ceramics

The structure of the obtained composite materials is represented by light and dark regions and by pores. According to elemental analysis data, the light regions correspond to zirconia, and the dark regions correspond to alumina (Fig. 3.a).

Analysis of the influence of the aluminum hydroxide volume fraction in the initial powder mixture on the average pore size of the composites shows that the dependences are different for composites obtained at different sintering temperatures. The average pore size of the composites sintered at temperature 1400 °C increases with the growing volume fraction of aluminum hydroxide in the initial mixture (Fig. 3.b). In this case, the type of aluminum hydroxide used in the initial mixture exerts almost no effect on the average pore size.

An increase in the average pore size is also observed for the composites sintered at 1500 °C, though only for those made from the CD zirconia powder. The average pore size of the PCS zirconia powder composites does not change (Fig. 3.c). Similarly, the average pore size of all composites sintered at 1650 °C does not vary depending on the aluminum hydroxide volume fraction (Fig. 3.d).

Analysis of the phase composition of the obtained ceramics shows that independently of the content of aluminum hydroxide in the initial mixture and its production method the sintering temperature growth is accompanied by a decrease of the tetragonal zirconia phase content in the porous.
ZrO₂–Al₂O₃ composites. In the sintering temperature range 1400–1550 °C of the composites the tetragonal zirconia phase content decreases from 70 to 25% and does not change up to a sintering temperature of 1650 °C. In the PCS ZrO₂(Y) powder composites with 1, 5 and 10 m% of aluminum hydroxide in the initial mixture, independently of its production method, the tetragonal ZrO₂ phase content remains at 90% up to a sintering temperature of 1600 °C. For the ceramics with 25 and 50% Al₂O₃×4H₂O in the initial mixture the tetragonal ZrO₂ phase content decreases from 90 to 40% at sintering temperatures 1500 and 1650 °C, respectively. For the composites with 25 and 50% Al(OH)₃ in the initial mixture the tetragonal ZrO₂ phase content decreases to 50% at sintering temperature 1500 °C and higher. At sintering temperature 1400 °C, independently of the aluminum hydroxide content in the initial mixture and its production method, the tetragonal zirconia phase content in the ZrO₂–Al₂O₃ composites made from the PCS ZrO₂(Y₂O₃) powder is 100%. It is known [1, 3, 4] that there is the notion of the critical grain size for the tetragonal modification of zirconia at which the tetragonal-to-monoclinic transformation takes place; this value is equal to 1.2 μm. The correlation between the zirconia grain size and its tetragonal phase content in the composites shows that in the CD powder ceramics the tetragonal zirconia phase content rapidly decreases in the average grain size interval from 0.4 to 0.8 μm. As for the PCS powder composites, the most rapid decrease in the tetragonal ZrO₂ phase content is observed at an average grain size ranging from 0.6 to 0.8 μm. It is also known [5] that the critical grain size of the tetragonal modification of zirconia can decrease with porosity growth in the material. This is related to a decrease in the level of the elastic stresses induced by neighboring grains and suppressing the tetragonal-to-monoclinic transformation occurring with an increase of the unit cell volume. The porosity of the studied ceramics varied from 10 to 60%, due to which, probably, the value of the critical grain size in them was lower as compared to [3, 4]. It is also probable that, along with the ZrO₂ grain size, the presence of Al₂O₃ could also influence the ratio of the tetragonal and monoclinic ZrO₂ phases in the ZrO₂–Al₂O₃ composites. As has been shown above, the ZrO₂(Y) powder composites with 25 and 50% of aluminum hydroxide in the initial mixture, which respectively corresponds to 21 and 42% of Al₂O₃ in the sintered ceramics, the tetragonal zirconia phase content decreases drastically at sintering temperature above 1500 °C. This effect can also be caused by the formation of the chemical compound Y₃Al₅O₁₂, or yttrium aluminum garnet. As is shown in [6], independently of the mixture composition, the interaction of yttria and alumina begins at temperature 900–950 °C with the formation of the Y₂Al₂O₇ compound, YAlO₃ is formed at 1100 °C, and starting from 1300 °C the yttrium aluminum garnet Y₃Al₅O₁₂ is crystallized. So, a stable Y₃Al₅O₁₂ compound can be formed in the Y₂O₃–Al₂O₃ system at temperature above
1300 °C independently of the mixture composition [6, 7]. Apparently, the formation of yttrium aluminum garnet in the ZrO$_2$–Al$_2$O$_3$ composite materials could lead to destabilization of the tetragonal zirconia phase. However, the X-ray diffraction patterns of the ZrO$_2$–Al$_2$O$_3$ composites had no reflections from Y$_2$Al$_5$O$_{12}$ owing to a small amount of yttria in the system.

Fig. 4. Dependence of porosity on the crystallite size of the tetragonal zirconia phase in composite powders on the basis of different zirconia. Dependence corresponds to ceramics based on zirconia powders: 1 – CD; 2 – PCS.

4. ábra A tetragonális cirkónium-oxid fázis porozitása és a krisztallit méret közötti összefüggés különböző cirkónium-oxid kompozit porokban. Jelmagyarázat: 1 – CD; 2 – PCS.

Fig. 4 illustrates the dependence between porosity of ZrO$_2$–Al$_2$O$_3$ composites and the size of coherent diffracting domains of the tetragonal zirconia phase. It is evident from the figure that with the size reduction of coherent diffracting domains of the tetragonal ZrO$_2$ phase, the porosity of the composites decreases. Extrapolating the approximation function to the non-porous state gives the size of the coherent diffracting domains of the tetragonal ZrO$_2$ phase equal to 65 nm for the CD zirconia powder composites, and 20 nm for the PCS zirconia powder composites.

Fig. 5 illustrates the porosity dependence of the tensile strength of the ZrO$_2$–Al$_2$O$_3$ composites. The PCS zirconia powder composites have the highest tensile strength 1100 MPa at 7% porosity (Fig. 5.a). For the CD zirconia powder composites, the highest tensile strength is 350 MPa at 20% porosity (Fig. 5.b). As is seen from Fig. 5, the dependences are exponential. Extrapolation to the non-porous state gives the tensile strength values equal to 1300–2400 MPa, which is in agreement with the data provided in [1, 8, 9]. It is remarkable that the type of aluminum hydroxide used in the initial powder mixture had no effect on the strength of the ZrO$_2$–Al$_2$O$_3$ ceramics made from the PCS ZrO$_2$(Y$_2$O$_3$) powder. Contrarily, the tensile strength of the CD ZrO$_2$(Y$_2$O$_3$) powder composites was higher in composites whose initial powder mixture contained Al$_2$O$_3$×4H$_2$O.

4. Conclusions

1. The critical grain size of the tetragonal modification of ZrO$_2$ in porous ZrO$_2$–Al$_2$O$_3$ ceramics is found to be 0.8 μm, in contrast to 1.2 μm for non-porous ZrO$_2$.

2. The sintering temperature determines the average pore size in the composites. An increase in the aluminum hydroxide content at low sintering temperatures causes a significant (more than threefold) growth of the average pore size, while at temperature growth the pore size is independent of the aluminum hydroxide content. As for the PCS zirconia powder composites, this effect is observed at lower temperatures.

3. The strength of the ZrO$_2$–Al$_2$O$_3$ composites made from the PCS ZrO$_2$ powder is higher than the strength of the CD ZrO$_2$ powder composites; it is independent of the type of aluminum hydroxide in the initial mixture. The strength of the ZrO$_2$–Al$_2$O$_3$ composites made from the CD ZrO$_2$ powder does depend on the type of aluminum hydroxide: the composites on the basis of the zirconia – hydrated alumina powder mixture have higher strength than the composites on the basis of the zirconia – bayerite powder mixture.

4. The crystallite size of the tetragonal zirconia phase determines the sintered material porosity: for the PCS zirconia powder composites the non-porous state is attained at the average crystallite size of the tetragonal ZrO$_2$ phase equal to 20 nm, and for the CD zirconia powder composites it is about 65 nm.

5. Acknowledgements

This work has received partial financial support by Tomsk State University Competitiveness Improvement Program and RF President Grant MK-5681.2014.8.
Különböző összetételű cirkónium- és alumínium-hidroxid keverékekőből szintetizált ZrO$_2$-Al$_2$O$_3$ kerámiák tulajdonságai

A cikk különféle eljárással előállított ZrO$_2$-Al$_2$O$_3$ porózus porkerámiák tulajdonságait ismerteti. A vizsgált területek felölelik többek között a szerkezet, a fázisösszetétel, a kristályfelszín és a szilárdság kérdéseit. Az eredmények rávilágítanak, hogy a szinterelt ZrO$_2$-Al$_2$O$_3$ porózus kerámiák szilárdsága függ attól, hogy milyen típusú alumínium-hidroxidot tartalmaz a kezdeti keverék. A szinterelés hőmérséklete meghatározza a porkerámiák porozitását.

Kulcsszavak: ZrO$_2$–Al$_2$O$_3$ kompozitok, szinterelés, szilárdság, kristális méret

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Ref:
Zhukov, I. – Buyakova, Svetlana P. – Kulkov, Sergei S.: Properties of ZrO$_2$–Al$_2$O$_3$ ceramics produced from different powder mixtures of zirconia and aluminum hydroxide
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 68, No. 3 (2016), 74–78. p.
http://dx.doi.org/10.14382/epitoanyag-jsbcm.2016.13

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