NANOSTRUCTURED ZIRCONIA COMPOSITES STABILIZED WITH CeO₂ FOR BIOMEDICAL APPLICATIONS

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Received May 28, 2004

The paper presents the influence of additives on the stabilization of ZrO₂ powders, with the main objective of obtaining ceramics-ceramics composites with improved thermo-mechanical and biocompatibility properties. Comparative analyses were made on zirconia powders in the ternary system ZrO₂-CeO₂-SrO. Investigations of microstructure and surface morphology were performed using scanning electron microscopy and atomic force microscopy.

Key words: composite materials, zirconia, stabilising oxides, biomaterials, biocompatibility.

1. INTRODUCTION

The researchers became very interested in zirconia based ceramics in the last decades, due to the wide range of applications of these oxide materials and their exceptional properties: electrical, mechanical and thermal properties – ionic conductors (oxygen sensors, heating elements), structural and refractory ceramics (component of thermal motors, gas turbines); biocompatibility properties – bioinert ceramics used in medicine.

Zirconia as a pure oxide does not occur in nature but it is found in baddeleyite and zircon (ZrSiO₄), which form the main sources for the material. Zirconia has three polymorphic forms, corresponding to crystalline structures with cubic, tetragonal and monoclinic symmetry. The polymorphic transitions can be represented as follows:

\[
\text{liquid (melt) } \xrightarrow{2680^\circ C} \text{cubic } \xrightarrow{2370^\circ C} \text{tetragonal } \xrightarrow{1170^\circ C, 950^\circ C} \text{monoclinic}
\]

The transformation of monoclinic to cubic zirconia is accompanied by a large change in lattice size, determined by the volume shrinkage. Due to the rapid phase change and the effects of contraction at heating and expansion at
cooling, the cracking of material can occur. In order to reduce this risk, it is necessary to partially or totally stabilize the cubic form of zirconium dioxide by using additives or stabilizing agents.

The most common method used to stabilize zirconium dioxide consists in addition of oxides, which lead to the formation of solid solutions by solid state reactions at high temperature. Zr$^{4+}$ is replaced by metallic cations with medium valence – Ca$^{2+}$, Mg$^{2+}$, Y$^{3+}$ and the equilibrium of charges is re-established by the presence of anionic holes, resulting a sub-stoichiometry in oxygen. Even if the details of stabilization are not perfectly elucidated, it may be easily explained by the decomposition of the anionic lattice, caused by the oxygen deficit.

Materials based on partially stabilized zirconia (PSZ) (with low quantities of stabilizers) for thermo-mechanical applications are generally characterized by a three-phase structure – the cubic matrix, the dispersed tetragonal precipitates and the monoclinic polymorph. As long as the sizes of precipitate particles remain very small (< 0.5 µm), they will not be in the monoclinic state, but in the metastable tetragonal one.

The stabilization of zirconia powders represents a challenge for the researchers in the domain, of a great importance being the stabilizing oxides used in the process and the compositional domain. The impressive number of paperwork dedicated to this subject in the last decade illustrates this fact [1–4]. A large transition zone characterizes ceramic powders partially stabilized with CeO$_2$, as compared to samples stabilized with MgO or Y$_2$O$_3$.

From the phase equilibria diagram of the binary system ZrO$_2$-CeO$_2$ [5], [6], elaborated by Duvez and Odell, the presence of three solid solutions domains can be observed. At less than 10 mol.% CeO$_2$ and temperatures lower than 1000°C, the monoclinic solid solution is stable. At maximum 20 mol.% CeO$_2$ and temperatures higher than 1000°C, the existence of a tetragonal solid solution is evidenced. For bigger amounts of CeO$_2$, two solid solutions are possible to be formed simultaneously, one with tetragonal structure and another with cubic one.

A diagram of phase equilibria of the system ZrO$_2$-CeO$_2$ elaborated by Negas et al. [7] shows the existence of a domain of tetragonal solid solutions, with maximum 15 mol.% CeO$_2$ and a domain of cubic solid solutions on a wide range of compositions, at high temperatures.

This paper presents the influence of additives on the stabilization of ZrO$_2$ powders and also the delimitation of optimum compositional domains for obtaining stabilized zirconia powders. Stabilization in binary systems usually requires high temperatures and sometimes, even if the tetragonal solid solution is formed, it becomes unstable by cooling and transforms into the monoclinic form. Due to these reasons the research is focused towards the ternary systems, in this case ZrO$_2$-CeO$_2$-SrO.
2. EXPERIMENTAL DETAILS

2.1. MATERIALS AND METHODS

- Zirconium dioxide

The powder consisted in non-stabilized (monoclinic) high purity zirconia. The average diameters of the zirconia powders were determined using Fischer methods and TEM (Transmission Electron Microscopy).

In order to increase the accuracy for determining the grinding fineness of the powders, the grain-size distribution using a laser granulometer was performed, as shown in Table 2.1. This method is especially used for fine particles \( (d < 100 \, \mu m) \) and its principle is based on measuring the diffraction rings formed by the laser fascicle when meeting a particle.

<table>
<thead>
<tr>
<th>Grain size (µm)</th>
<th>&lt; 1</th>
<th>&lt; 1.5</th>
<th>&lt; 2</th>
<th>&lt; 3</th>
<th>&lt; 4</th>
<th>&lt; 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain-size fraction (%)</td>
<td>62</td>
<td>75</td>
<td>78</td>
<td>86</td>
<td>93</td>
<td>100</td>
</tr>
</tbody>
</table>

The chemical composition of ZrO\(_2\) powder was determined by spectral analysis, by qualitative measurements of the main impurities. The ZrO\(_2\) powder was characterized by X-rays diffraction and the results show that it corresponds to the monoclinic ZrO\(_2\).

- The stabilizing oxides

The analytically pure CeO\(_2\) had an advanced dispersion degree, with BET surface area higher than 36,000 cm\(^2\)/g. SrO was also analytically pure, with advanced dispersion level, its BET surface area being higher than 30,200 cm\(^2\)/g. The high purity materials forming the ternary mixture were homogenized in isopropyl alcohol (solid:liquid ratio = 1:2) and the resulting slurry was dried at constant mass. The samples were shaped in cylinder forms with \( d = h = 18 \, \text{mm} \), at 15 MPa, burned in an electrical furnace at 1400–1750°C and then were slowly cooled. Structural and phase analyses have been carried out using the X-ray diffraction method.

2.2. COMPOSITIONAL DOMAINS

The ternary mixture was gravimetrically dosed as shown in Table 2.2.
Table 2.2

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZrO₂ (wt.% )</th>
<th>CeO₂ (wt.% )</th>
<th>SrO (wt.% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>96Z-3Ce-Sr</td>
<td>96</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>94Z-5Ce-Sr</td>
<td>94</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>89Z-10Ce-Sr</td>
<td>89</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>84Z-15Ce-Sr</td>
<td>84</td>
<td>15</td>
<td>1</td>
</tr>
<tr>
<td>79Z-20Ce-Sr</td>
<td>79</td>
<td>20</td>
<td>1</td>
</tr>
</tbody>
</table>

where: Ce = CeO₂, Sr = SrO₂, Z = ZrO₂.

3. RESULTS AND DISCUSSION

Comparative analyses were made between the ceramic and structural characteristics of some zirconia powders stabilized with CeO₂ and doped with 1 wt.% SrO and the characteristics of the same type of masses not doped with SrO, after thermal treatment at 1610°C in vacuum. The doped samples were subsequently burned at 1550°C and respectively 1750°C in oxidizing atmosphere.

A good densification of the non-doped compositions is observed for the samples treated in vacuum at 1610°C. The better densification at this temperature was obtained for compositions with 3 wt.% CeO₂ and 1 wt.% SrO.

In contrast, for the doped samples burned at 1550°C and 1750°C, a better densification is observed when the quantity of the stabilizing oxide increases (from 3 to 20 wt.%) and the quantity of doping oxide is maintained constant (1 wt.% SrO). The better densification in oxidizing atmosphere is thus obtained for the samples with 20 wt.% CeO₂ +1 wt.% SrO (Figs. 3.1, 3.2).

Fig. 3.1. – Evolution of the apparent density of ceramic samples in the system ZrO₂-CeO₂-SrO after thermal treatment in oxidizing atmosphere at 1550°C, and 1750°C, respectively.
Fig. 3.2. – Evolution of the apparent porosity of ceramic samples in the system ZrO$_2$-CeO$_2$-SrO after thermal treatment in oxidizing atmosphere at 1550°C and 1750°C, respectively.

The samples containing 3–20 wt.% CeO$_2$ and 1 wt.% SrO, fired at 1550°C and 1750°C in oxidizing atmosphere, were investigated by diffraction analysis. An advanced stabilization takes place when the quantity of the stabilizing oxide increases. We can observe that the picks for the cubic and tetragonal ZrO$_2$ forms are outlined and the monoclinic form diminishes (Fig. 3.3 a, b). Compositions containing the same percents of stabilizing oxides, thermally treated at 1610°C in vacuum, were investigated by diffraction analysis. A different situation can be observed for these compositions (Fig. 3.3 c): increasing the quantity of the stabilizing oxide would not determine the stabilization of tetragonal and cubic forms of zirconia anymore.

Microstructural studies were performed on the 96Z-3Ce-Sr composition (C’3 in Fig. 3.4) and 79Z-20Ce-Sr (C’20 in Fig. 3.5) after thermal treatment at 1750°C in oxidizing atmosphere and respectively after thermal treatment at 1610°C in vacuum. The investigations were performed on fracture surfaces or smooth surfaces (perpendicular to the pressing direction).
Fig. 3.4. – SEM images of the fracture surfaces for the composite 96Z-3Ce-Sr (C′3) after thermal treatment at 1750°C in oxidizing atmosphere (a), (b) and at 1610°C in vacuum (c), (d) respectively.

Fig. 3.5. – SEM images of the fracture surfaces for the composite 79Z-20Ce-Sr (C′20) after thermal treatment at 1750°C in oxidizing atmosphere (a), (b) and at 1610°C in vacuum (c), (d) respectively.

Studies of samples morphology were performed on ceramics-ceramics composites belonging to the system ZrO₂-CeO₂-SrO, for the compositions
89Z-10Ce-Sr (ZCS C10) and 84Z-15Ce-Sr (ZCS C15), using Atomic Force Microscopy (AFM) – Figs. 3.6–3.9.

The measurements did not evidenced significant differences regarding the surface microstructure between the analyzed samples. The obtained results greatly depend on the investigated zone for each surface.

The obtained information is strongly influenced by the particularities of the preparation method, rather than the intrinsic characteristics of the samples. That leads us to the conclusion that it is absolutely necessary to improve the preparation method of the samples surfaces in order to achieve better results from the AFM investigations.

4. APPLICATIONS OF ZIRCONIA BASED COMPOSITES IN BIOMEDICINE

Partially stabilized zirconia is a bioinert ceramic, which maintains its physical and mechanical properties when implanted in the body and has high
resistance to corrosion and wear in the physiological environment. Zirconia based materials are typically used as structural-support implants, like bone plates, bone screws or femoral heads.

The materials used for implants which have to provide improved motion of the joint or to replace damaged bone structures, are required to transmit and withstand the stress applied to the structure, within the body environment, while interacting with the existing bone such that the function of the bone and prosthetic is maintained over a long period [8].

4.1. APPLICATIONS IN ORTHOPAEDICS

Zirconia materials have been used in orthopaedics since 1985, in order to replace the metals, particularly due to their great resistance during friction [9]. In the period 1985–2001, over 400,000 zirconia femoral heads implants were reported. Due to the improved resistance and high toughness, the heap prostheses may be manufactured at small dimensions, allowing a high degree of articulation. The possibility of polishing to a high surface area leads to the realization of joints with a low friction coefficient.

The resistance of zirconia heads is twice higher than alumina’s, therefore the diameter of the femoral head may be reduced up to 26 mm or less.

The quality of zirconia heads depends on its purity, density, porosity, particle size, crystalline structure (content of tetragonal and monoclinic phases) and bending strength. The zirconia powders for biomedical applications must be very pure, the most common impurities being alumina (its proportion should not exceed 0.5 wt. %). The density of the zirconia should be as close as possible to
Biocompatible ZrO$_2$ composite materials

Theoretical density, which is 6.1. The closer it is to this value, the fewer the spaces between the particles and the greater the mechanical strength and the less the surface roughness. The ceramic particles should be smaller than 0.6 mm [9].

The apatite-forming ability on a nano-composite of a ceria-stabilized tetragonal zirconia polycrystals (Ce-TZP) and Al$_2$O$_3$ polycrystals via chemical treatment with aqueous solutions of H$_3$PO$_4$, H$_2$SO$_4$, HCl or NaOH has been investigated [10]. Hydroxyapatite is the most bioactive calcium phosphate that links very fast to the living tissues and can assure the adherence of other implant materials, like metals or bioinert ceramics to the living tissues. The chemical treatments produced Zr-OH surface functional groups. The composite, after chemical treatment, was shown to form a bonelike apatite layer when immersed in a simulated body fluid, which implies that it may form apatite in the living body and bond to living bone through the apatite layer. This type of bioactive Ce-TZP/Al$_2$O$_3$ composite is therefore expected to be useful as a bone substitute, even under load-bearing conditions. The phase stability of Ce-TZP/Al$_2$O$_3$ nanocomposite and Y-TZP after aging and its influence on wear resistance were also investigated. Y-TZP showed marked phase transformation (80%) after aging in an autoclave (121°C) for 190 h, whereas the composite remained almost resistant to degradation [11].

4.2. APPLICATIONS IN DENTISTRY

Materials for tooth replacement require biocompatibility, acceptable strength and hardness for the mechanical action of the teeth and the ability to be formed into the exact shape required and also to match the natural tissues in color and translucency [8].

Composite materials are used in dentistry for the restoration of natural teeth and manufacturing of artificial dentures, implant abutments, bridges and crowns.

Fig. 4.2. – Zirconia bridges for dentistry.

Ceramic materials have been successfully used for dental restorations for very long time, especially due to their aesthetic aspect and mechanical strength.
Surgical grade yttria stabilized tetragonal zirconia (Y-TZP), is characterized by high fracture strength (< 1500 MPa), high fracture toughness and an outstanding slow crack growth behavior. This material has been proved to lead to the lowest plaque accumulation, compared to other metallic and ceramic dental materials. Current surgical grade Y-TZP zirconia has a light ivory color which is not appropriate for dental restoration and specific colored zirconia grades have to be developed with a color closed to that of teeth. Three main coloring additives proved to give brown to yellow colors, their toxicity was very low or negligible and the amount of coloring additive was very small: Fe$_2$O$_3$, CeO$_2$ and Bi$_2$O$_3$ [12].

The colored zirconias do not exhibit a marked translucency, as required for some tooth restorations, so they need to be combined with veneers. The coating with veneer does not significantly change the flexural strength of the zirconia ceramic, due to the strong adherence of the veneer on the zirconia ceramic surface.

5. CONCLUSIONS

The investigations performed on zirconia samples stabilized with 3–20 wt.% CeO$_2$ and 1 wt.% SrO and samples with the same content of CeO$_2$ but without doping oxide show that the stabilization of zirconia powder depends to a great extent on the stabilizing oxide and compositional domain.

Studies for determining the ceramic and structural characteristics and also the microstructure and surface morphology of the samples lead to the conclusion that for samples thermally treated at 1550°C and 1750°C in oxidizing atmosphere a better densification and advanced stabilization takes place when the quantity of the stabilizing oxide increases. For the samples treated in vacuum at 1610°C, an opposite situation is observed.

The properties exhibited by zirconia ceramics depend upon the degree and type of stabilisation and on the processing used. By varying the type and distribution of reinforcing phase in the composite material, it is possible to obtain a wide range of mechanical and biological properties and hence to optimize the structure of the implant and its interaction of the surrounding tissue.

The density of zirconia powders must be very close to the theoretical density (6.1 g/cm$^3$). In the case of the investigated zirconia samples burned in oxidizing atmosphere, the better density was obtained for using 20 wt.% CeO$_2$ + 1 wt.% SrO (5.25 g/cm$^3$).

The samples investigations using Atomic Force Microscopy did not evidenced significant differences regarding the surface microstructure between the analyzed samples. The obtained results greatly depend on the investigated zone for each surface.
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