CERAMICI COMPOZITE DENSE DE TIP Y-ZrO$_2$ – Al$_2$O$_3$.
OBŢINERE ŞI CARACTERIZARE
YTTRIA-STABILIZED ZrO$_2$-Al$_2$O$_3$ DENSE COMPOSITE CERAMICS. 
OBTAINING AND CHARACTERIZATION

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ZrO$_2$–Al$_2$O$_3$ composites were developed using the co-precipitation method starting from the corresponding chlorides (zirconia was fully stabilized by using 8% Y$_2$O$_3$ weight ratio).

In order to obtain ceramic composites with high relative density (over 99%) there were used oxide additives such as ZnO, CuO, MnO$_2$ and TiO$_2$ (2% weight ratio).

The sintering process of the compacted green bodies (obtained by uniaxial pressing) was carried out at temperatures between 1400° and 1600°C, with a maintaining time at highest temperature of 3 hours at the maximum temperature. For the heat treatment at 1500°C the soaking time was varied from 3 to 6 hours.

The microstructure and phase composition of the dense sintered ceramic composites were determined through the scanning electron microscopy (SEM) and X-ray diffraction (XRD). The compressive strength and Young’s modulus of sintered composites were measured, too. The results have indicated that the nature of the additive oxide and the sintering temperature are the key factors in controlling the mechanical behavior of studied ceramics composites.

Keywords: dense ceramic composite, high relative density, sintering additive.

1. Introduction

Ceramic materials with thermo-mechanical properties represent a priority in research and development programs for new materials. The properties they exhibit, both at room temperature and more important at elevated temperatures, propel these materials for more and more applications as replacements for metallic materials. The research done over composite ceramic materials, starting from very fine grains has proven their high performance characteristics, confirming in this way their high versatility [1-4].

One of the main problems in ceramic composite manufacturing is the elaboration of such materials (the powder dispersion, the sintering process and so on). For example, the properties of these materials are highly dependent on their microtexture and microstructure – the shape of the crystals and pores, their distribution, the nature of the present phases and the interaction between grains [5-7].

Zirconia-toughened alumina (ZTA) ceramics have been studied because it presents high hardness, mechanical strength, toughness and chemical stability. These Al$_2$O$_3$/ZrO$_2$ ceramics are useful as insulator, refractory, cutting tools, high temperature filters, biomedical application, etc. [2,4,6]. The enhanced strength and toughness have made the ZTAs more widely applicable and more productive than plain ceramics and cermets in machining steels and cast irons. In addition, their mechanical properties are known to depend strongly on their microstructure. With the development of nanoscience and nanotechnology, the interest in the preparation of ultra-structured ceramics is growing, since they have improved mechanical properties and might find promising application in engineering [2].

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2. Experimental

Present paper is aimed, as main objective, to the obtaining and investigation of alumina-zirconia ceramics with respect to the structural-textural determinations of their mechanical behavior, in a general compositional frame. As the stabilizing oxide for zirconia yttrium oxide was used. In this experiment the zirconia dioxide was totally stabilized with 8% Y₂O₃.

The amount of alumina oxide varied, so that it was either a reinforcing phase (dispersoids) of the zirconia matrix as well as a continuous phase – the matrix (having the zirconia oxide as reinforcing material). Four different oxide composition were synthesized as shown in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Phase content (% wt.)</th>
<th>Continut fazal (%grav.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZrO₂ stabilized*</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>A20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>A40</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>A60</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>A80</td>
<td>20</td>
<td>80</td>
</tr>
</tbody>
</table>

* 92% ZrO₂ + 8% Y₂O₃

For achieving high relative densities, there were used oxide additives as sintering aids. The oxide additives such as ZnO, CuO, MnO₂, TiO₂ were used in a 2% weight ratio which by their action allowed the obtaining of the highest relative densities and the lowest open porosity.

The starting alumina and zirconia powders were obtained via co-precipitation, from corresponding chloride, as described in a previous work [8].

The powders were shaped in cylinders by uniaxial pressing at 150MPa, and then subjected to thermal treatments at temperatures between 1400°C and 1600°C. The heating rate was of 10°C/min, and the soaking time was 3 hours. The cooling of the samples was done at a rapid rate. For the thermal treatment at 1500°C, the maintaining time at highest temperature was varied from 3 to 6 hours, to see if increasing of the soaking time may compensate a temperature increase.

After the sintering process the samples were subjected to the following tests:

- Determination of ceramic properties – absorption, open porosity and relative density , respectively.
- Determination of compression mechanical strength – using a mechanical testing machine LFM 50kN, no. 596.
- Electron scanning microscopy analysis - SEM to observe the morphology and composition of the sintered samples (SEM images were obtained with an electronic microscope HITACHI S2600N).
- Diffractometric analysis to establish the mineral composition of the samples (performed with a XRD 6000 Shimadzu diffractometer).

3. Results and discussions

3.1. Ceramic characterization of the sintered ceramic composites

For the four composite compositions, associated with oxide additives, thermally treated at temperatures between 1400°C–1600°C, the values of ceramic properties are represented in Figures 1 and 2.

Based on these figures, the following statements can be pointed out:

- The increase of alumina content in these composite materials leads to an increase in the absorption and the open porosity, respectively for all sets of samples studied, due to the low sinterability behavior.
- The increase of the thermal treatment temperature allows a decrease of absorption and open porosity, with the exception of A80 sample with TiO₂ additive. An explanation of this behaviour could be the formation of tialite in the A80-TiO₂ mixture which at cooling initiates decomposition processes that induce a higher porosity to the composite.
- It can observed that the lowest values for absorption and open porosity are recorded for the samples with ZnO (for the entire composition range) and MnO₂ (with the exception of A20, even if these values are lower than in the case of the compounds without additives).
- Regarding the values for relative density ($\rho_{rel}$) it can be observed the same influence as in the case of absorption and open porosity (the increase of temperature of the thermal treatment increases the relative density and the increase of alumina content decreases the relative density). For certain sets of samples thermally treated at 1600°C for 3 hours it can be noticed a decrease of relative densities caused by the creep behavior of the sample (which implies a deformation under the sample’s own weight which became possible due to the liquid phase formed in the sintering process).
- Also, in the case of relative densities we have noticed the superiority of the samples with ZnO and MnO₂.
Obtaining and characterization

Fig. 1 - Evolution of absorption and open porosity with temperature for studied ceramic composites / Evoluția absorbției și porozității deschise funcție de temperatură, pentru compozitele ceramice: a) without additives / fără aditivi; b) with / cu ZnO; c) with / cu CuO; d) with / cu MnO₂; e) with / cu TiO₂.

Fig. 2 - Evolution of relative density with treatment temperature for studied ceramic composites / Evoluția densității relative funcție de temperatură, pentru compozitele ceramice: a) with / cu 20%Al₂O₃; b) with / cu 40%Al₂O₃.
3.2. Mechanical properties

The software of the equipment for mechanical testing also allows the calculation of elasticity modulus. The mechanical results were plotted in Figures 3 and 4 – the compressive strength and the elasticity modulus.

From these figures one can be stated the following conclusions:

- The increase of the heat treatment temperature to 1600°C and its maintaining for 3 hours has lead to the best overall results for the compressive strength.
- The A20 and A80 sample sets have the highest values for compressive strength. The explanation is that the continuous phase – the matrix, and the discontinuous phase – the reinforcing phase is clearly divided, each serving for their role.
- The best values for the compressive strength for all compositions and thermal treatment range, compared to the samples without additives, were obtained for the samples with ZnO and MnO₂ as additives.
Regarding the elastic behavior of the studied samples, the following assessments are to be recorded:

- Increasing the alumina ratio as well as the temperature of thermal treatment causes the decreasing of elasticity modulus for all studied samples.
- The elasticity modulus was determined for the entire compositional range and not only for the sample sets without additives and with ZnO and MnO₂ as additives. The samples with TiO₂ additives exhibit elastic behavior only for the sample set A20. The samples with CuO₂ additives show very poor elastic behavior for the sample sets A20, A40 and A60 until the temperature of 1500°C, for three hours thermal treatment.

3.3. Scanning electronic microscopy analysis

The resulting images are shown below:
For all shown SEM micrographs one can say the following:

- One can notice the absence of porosity.
- The ZnO additive determines a ZrO$_2$ grain growth in the sample set A20 which is not present for the other sample sets.
- The MnO$_2$ additive determines a larger grains growth only in the A80 sample set, and not showing similar influence in other sample sets.

- The micrographs were done on the surfaces created from the compressive strength tests and therefore it can stated that the fracture takes place in intergranular mode (the chemical bonds in the grains are stronger than the chemical bonds between the grains).
3.4. Phase composition by X-ray diffraction

The obtained X-ray patterns of the samples sintered at different temperatures are shown in Figure 9.

From the above diffraction patterns, it can be observed that all samples are well crystallized with well defined peaks and thus one can state the following:

- All samples contain cubic zirconia solid solutions alongside alumina solid solution.
- Adding a small amount of alumina (20%) causes the shift of the phase composition of the ceramic zirconia matrix, the compound having very small peaks corresponding to the alumina crystals.
- The additives, which have shown to be most suitable (ZnO and MnO$_2$), have no negative influence on the studied compounds from the phase composition point of view.

4. Conclusions

From the present study it can be conclude the following:

- There were obtained dense alumina-zirconia composites for mechanical applications.
- Regardless the composition of the matrix phase, the ceramic composite behaved better than the reference compound concerning the ceramic properties.
- The SEM study has shown a well sintered and crystallized morphological structure for all composites obtained, with a homogenous microstructure.
- The best results were obtained for the sample sets having ZnO and MnO$_2$ additives. The sample sets with TiO$_2$ behaved well under our expectations proving that it is not suitable for our particular ceramic material considering the weight ratios used.
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REFERENCES

MANIFESTĂRI ȘTIINȚIFICE / SCIENTIFIC EVENTS

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