

# CERAMICI COMPOZITE DENSE DE TIP $Y\text{-ZrO}_2 - \text{Al}_2\text{O}_3$ . OBȚINERE ȘI CARACTERIZARE

## YTTRIA-STABILIZED $\text{ZrO}_2\text{-Al}_2\text{O}_3$ DENSE COMPOSITE CERAMICS. OBTAINING AND CHARACTERIZATION

**ȘTEFANIA STOLERIU\*, ALEXANDRU CONSTANTINESCU, ECATERINA ANDRONESCU**

*Universitatea POLITEHNICA București, Str. G. Polizu nr. 1, sect. 1, cod 011061, București, România*

*ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composites were developed using the co-precipitation method starting from the corresponding chlorides (zirconia was fully stabilized by using 8% Y<sub>2</sub>O<sub>3</sub> weight ratio).*

*In order to obtain ceramic composites with high relative density (over 99%) there were used oxide additives such as ZnO, CuO, MnO<sub>2</sub> and TiO<sub>2</sub> (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.*

*Compozitele de tip ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> studiate au fost sinterizate din nanopulberi obținute prin co-precipitare pornind de la clorurile corespunzătoare (oxid de zirconiu a fost total stabilizat cu 8% Y<sub>2</sub>O<sub>3</sub>).*

*Pentru a obține compozite ceramice cu densitate relativă mare (peste 99%), s-au folosit aditivi oxidici în proporție de 2% grav. de ZnO, CuO, MnO<sub>2</sub> și TiO<sub>2</sub>.*

*Procesul de sinterizare al compozitelor crude (obținute prin presare uniaxială) a fost efectuat la temperaturi cuprinse între 1400° și 1600° C, cu un palier de menținere la temperatura maximă de 3 ore. Pentru tratamentul termic de la 1500° C, palierul a fost variat de la 3 la 6 ore.*

*Compoziția fazală și microstructura compozitelor ceramice dense sinterizate au fost evaluate prin difracție de raze X și microscopie electronică de baleiaj. Rezistența mecanică la compresiune și modulul lui Young al ceramicilor sinterizate au fost, de asemenea, măsurate. Rezultatele indică faptul că natura aditivului oxidic și temperatura de sinterizare sunt factorii de influență ai comportamentului mecanic al compozitelor studiate.*

**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<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> 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].

\* Autor corespondent/Corresponding author,  
Tel.: 00 4021 402 39 97, e-mail: [s\\_stoleriu@yahoo.com](mailto:s_stoleriu@yahoo.com)

## 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% Y<sub>2</sub>O<sub>3</sub>.

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

The oxide compositions of the studied composite ceramics  
*Compoziția oxidică a ceramicilor compozite studiate*

Sample code Cod probă	Phase content (% wt.) Conținut fazal (%grav.)	
	ZrO <sub>2</sub> stabilized*	Al <sub>2</sub> O <sub>3</sub>
A20	80	20
A40	60	40
A60	40	60
A80	20	80

\* 92% ZrO<sub>2</sub> + 8% Y<sub>2</sub>O<sub>3</sub>

For achieving high relative densities, there were used oxide additives as sintering aids. The oxide additives such as ZnO, CuO, MnO<sub>2</sub>, TiO<sub>2</sub> 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 TiO<sub>2</sub> additive. An explanation of this behaviour could be the formation of tialite in the A80-TiO<sub>2</sub> mixture which at cooling initiates decomposition processes that induce a higher porosity to the composite.
- It can be observed that the lowest values for absorption and open porosity are recorded for the samples with ZnO (for the entire composition range) and MnO<sub>2</sub> (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 MnO<sub>2</sub>.

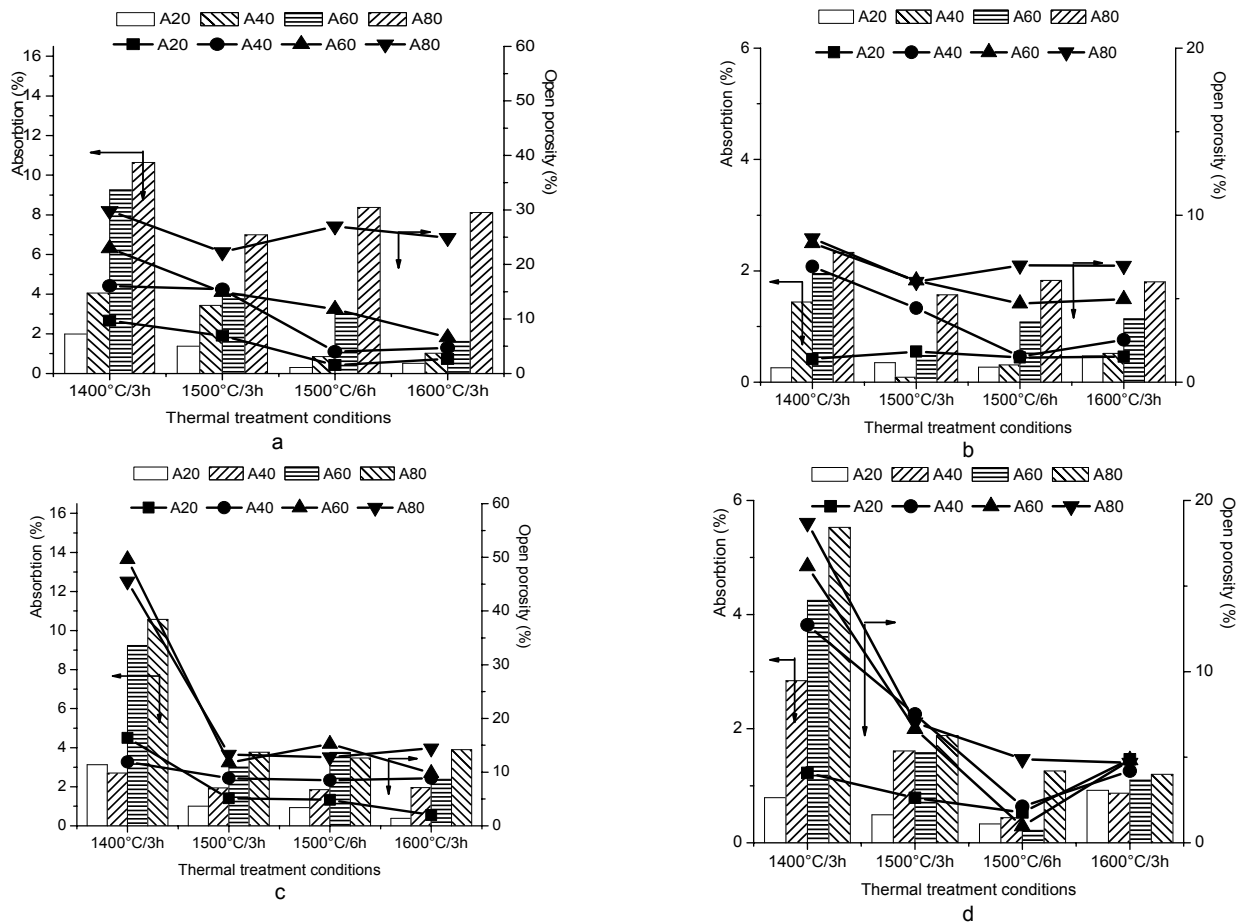


Fig. 1 - Evolution of absorption and open porosity with temperature for studied ceramic composites / Evoluția absorbției și porozității deschise funcție de temperatură, pentru compozitele ceramice: a) without additives / fără aditivi; b) with / cu ZnO; c) with / cu CuO; d) with / cu MnO<sub>2</sub>; e) with / cu TiO<sub>2</sub>

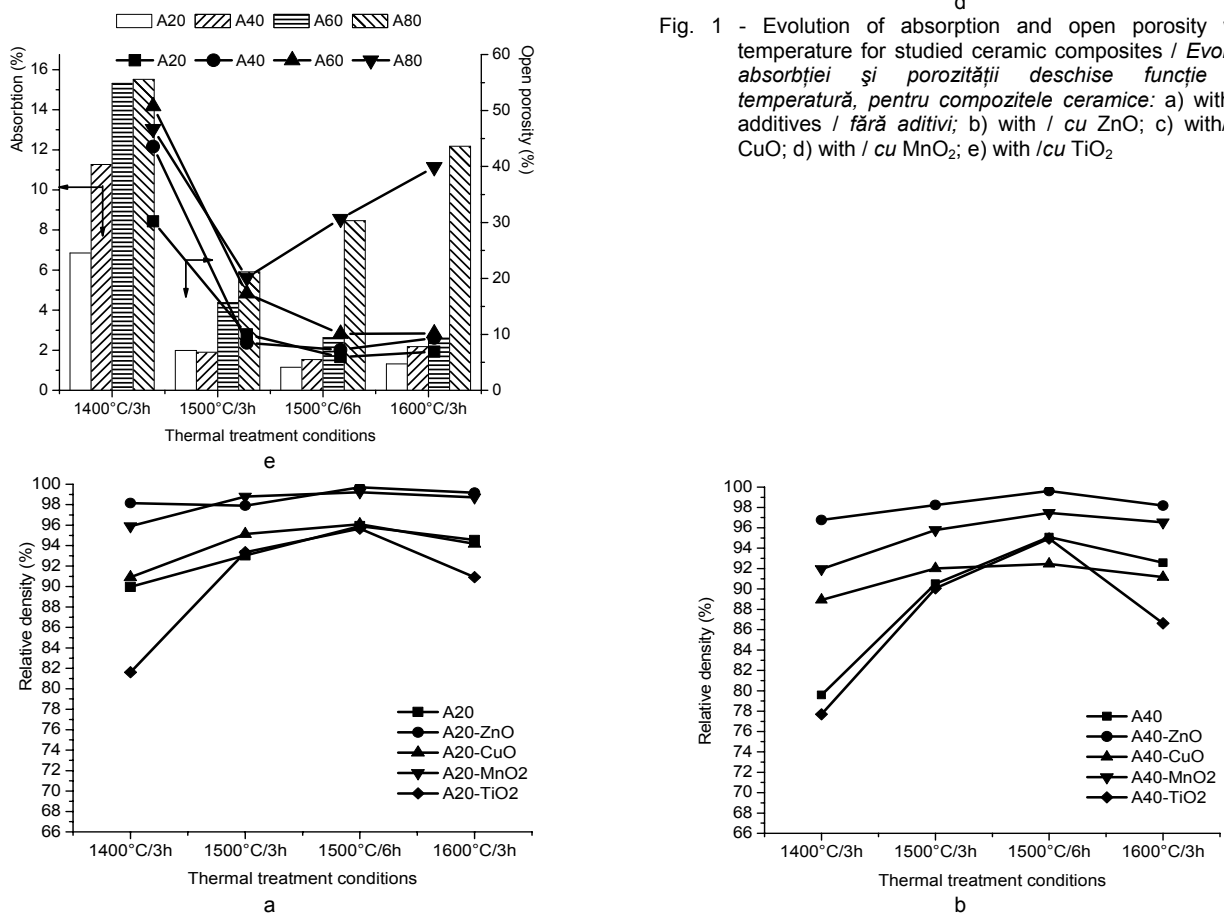


Fig. 2 - Evolution of relative density with treatment temperature for studied ceramic composites / Evoluția densității relative funcție de temperatură, pentru compozitele ceramice: a) with / cu 20% Al<sub>2</sub>O<sub>3</sub>; b) with / cu 40% Al<sub>2</sub>O<sub>3</sub>.

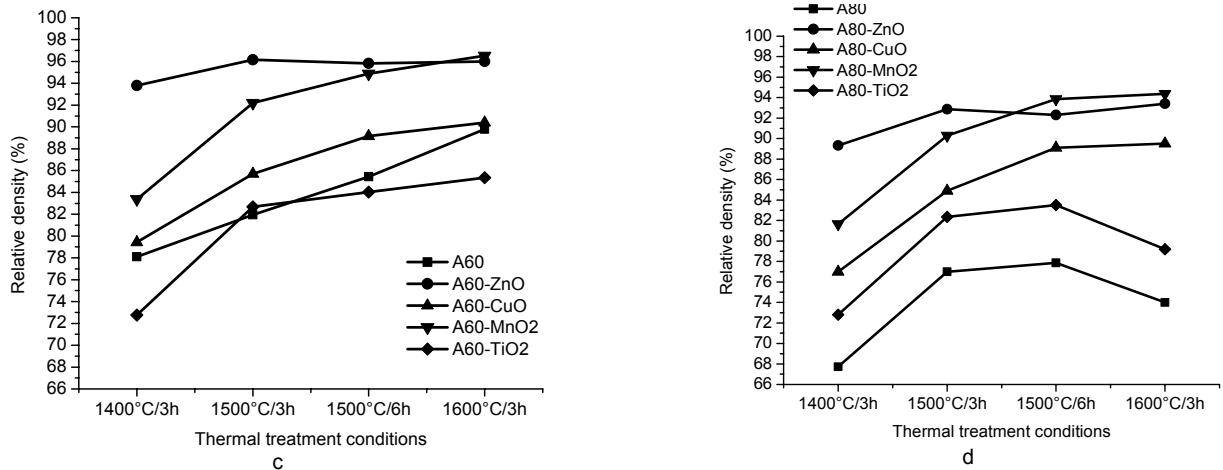


Fig. 2 - Evolution of relative density with treatment temperature for studied ceramic composites / *Evoluția densității relative funcție de temperatură, pentru compozitele ceramice* : c) with /cu 60%Al<sub>2</sub>O<sub>3</sub>; d) with /cu 80%Al<sub>2</sub>O<sub>3</sub>.

### 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 MnO<sub>2</sub> as additives.

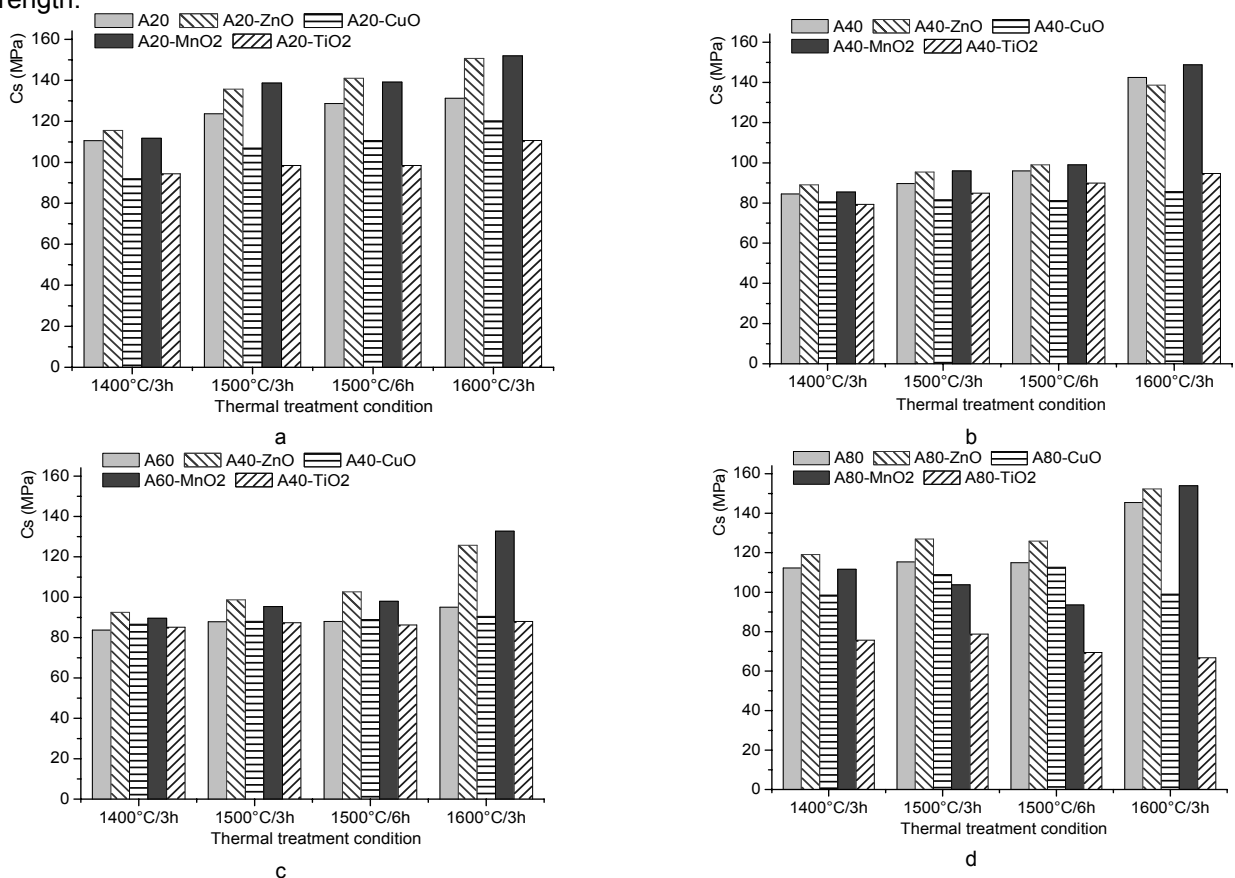


Fig. 3 - Evolution of compressive strength with treatment temperature for the studied ceramic composites / *Evoluția rezistenței mecanice la compresiune funcție de temperatură, pentru compozitele ceramice*: a) with /cu 20%Al<sub>2</sub>O<sub>3</sub>; b) with /cu 40%Al<sub>2</sub>O<sub>3</sub>; c) with /cu 60%Al<sub>2</sub>O<sub>3</sub>; d) with /cu 80%Al<sub>2</sub>O<sub>3</sub>.

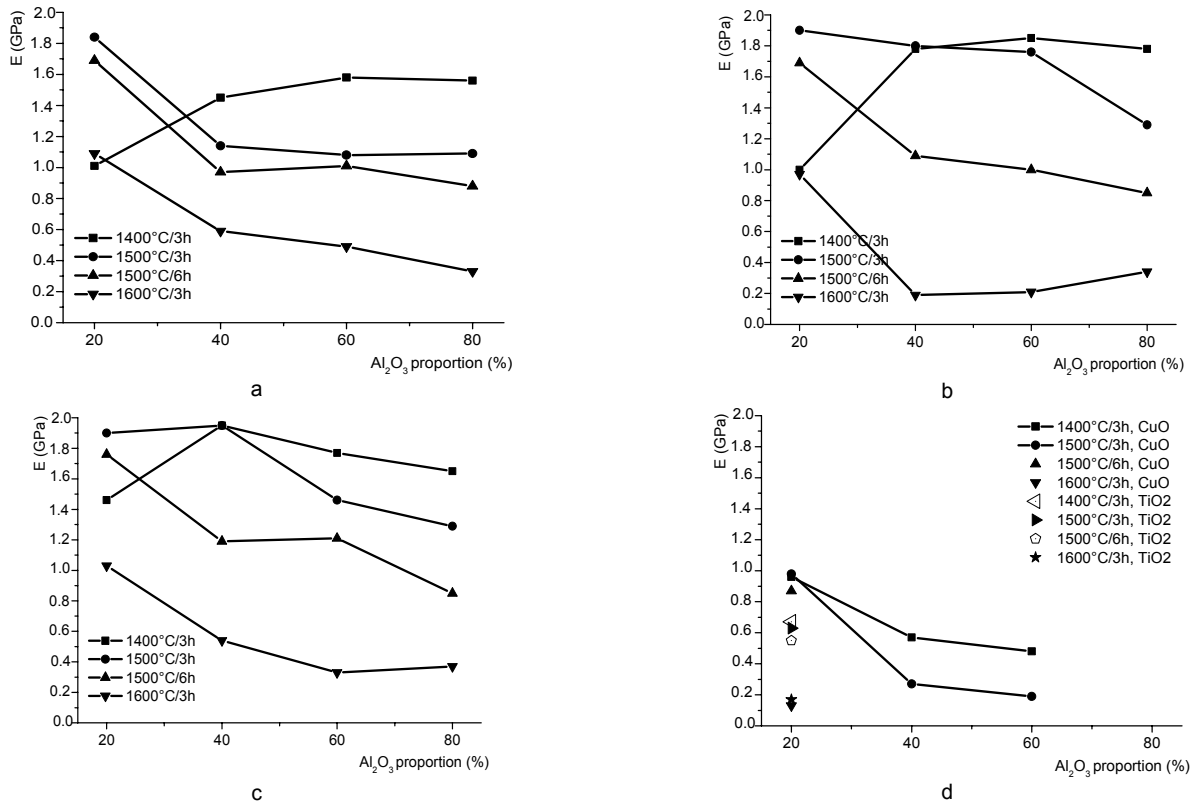


Fig. 4 - Evolution of the elasticity modulus with Al<sub>2</sub>O<sub>3</sub> ratio, for the studied ceramic composites / Evoluția modului de elasticitate funcție de proporția de Al<sub>2</sub>O<sub>3</sub>, pentru compozitele ceramice: a) without additives / fără aditivi; b) with /cu ZnO; c) with /cu MnO<sub>2</sub>; d) with /cu CuO and / și TiO<sub>2</sub>.

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

MnO<sub>2</sub> as additives. The samples with TiO<sub>2</sub> additives exhibit elastic behavior only for the sample set A20. The samples with CuO<sub>2</sub> 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:

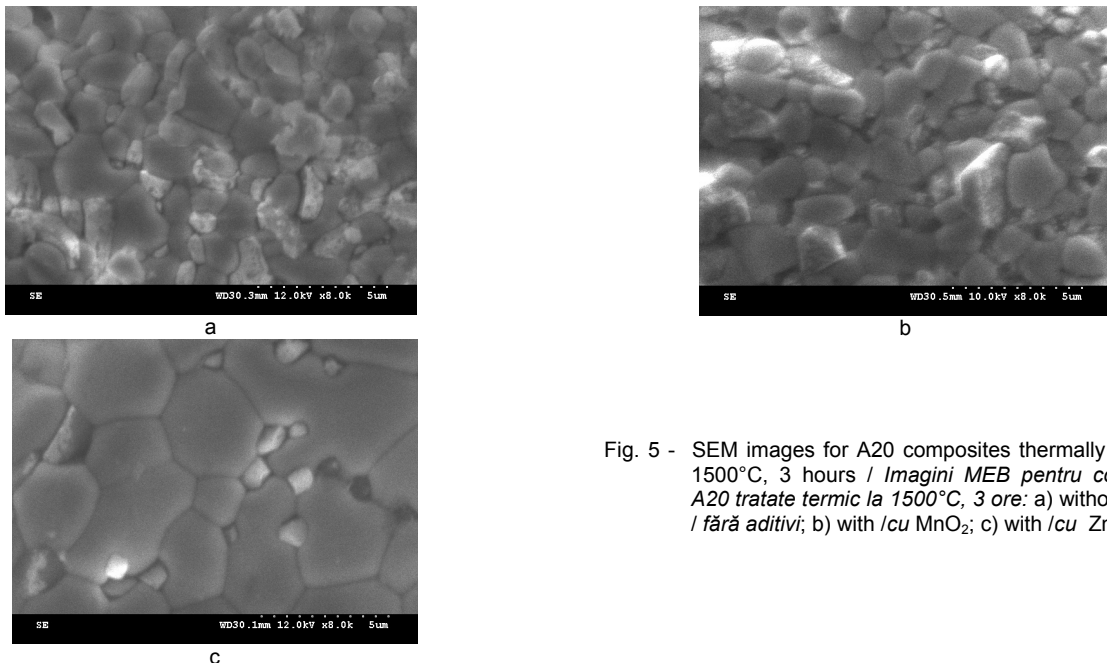


Fig. 5 - SEM images for A20 composites thermally treated at 1500°C, 3 hours / Imagini MEB pentru compozitele A20 tratate termic la 1500°C, 3 ore: a) without additive / fără aditivi; b) with /cu MnO<sub>2</sub>; c) with /cu ZnO.

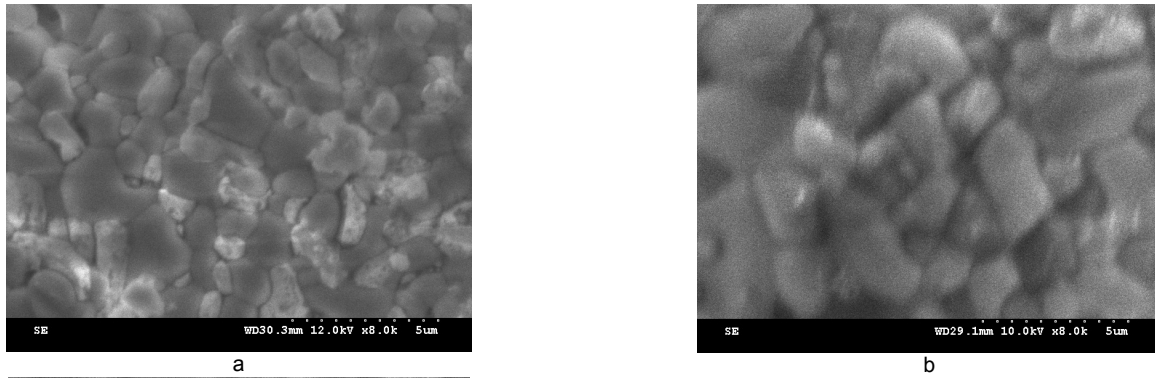


Fig. 6 - SEM images for A40 composites thermally treated at 1500°C, 3 hours / Imagini MEB pentru compozitele A40 tratate termic la 1500°C, 3 ore: a) without additive / fără aditivi; b) with / cu MnO<sub>2</sub>; c) with / cu ZnO.

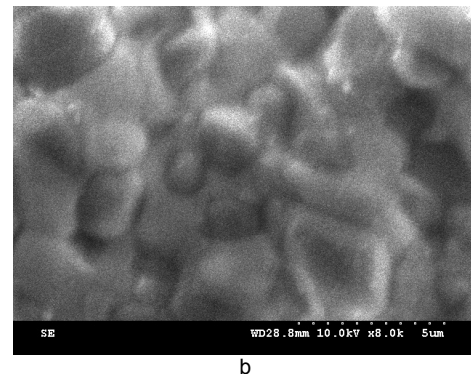
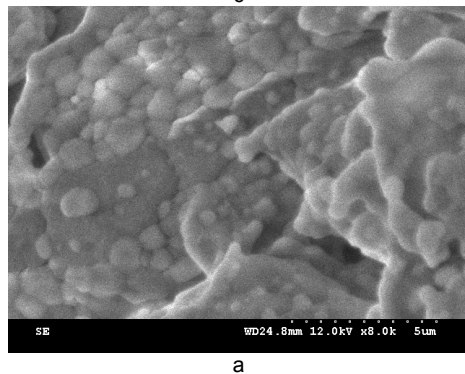
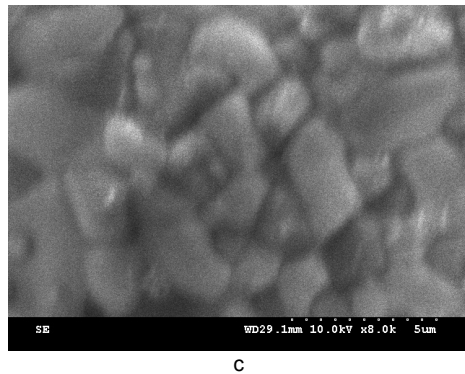
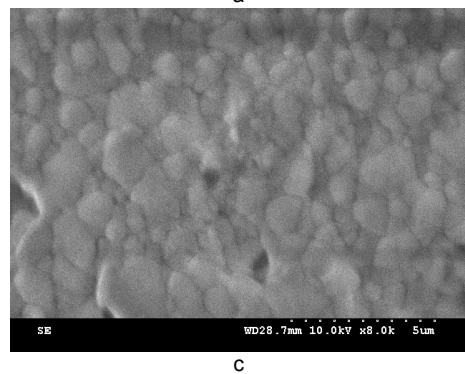


Fig. 7 - SEM images for A60 composites thermally treated at 1500°C, 3 hours / Imagini MEB pentru compozitele A60 tratate termic la 1500°C, 3 ore: a) without additive / fără aditivi; b) with / cu MnO<sub>2</sub>; c) with / cu ZnO.



For all shown SEM micrographs one can say the following:

- One can notice the absence of porosity.
- The ZnO additive determines a ZrO<sub>2</sub> grain growth in the sample set A<sub>20</sub> which is not present for the other sample sets.
- The MnO<sub>2</sub> 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 be stated that the fracture takes place in intergranular mode (the chemical bonds in the grains are stronger than the chemical bonds between the grains).

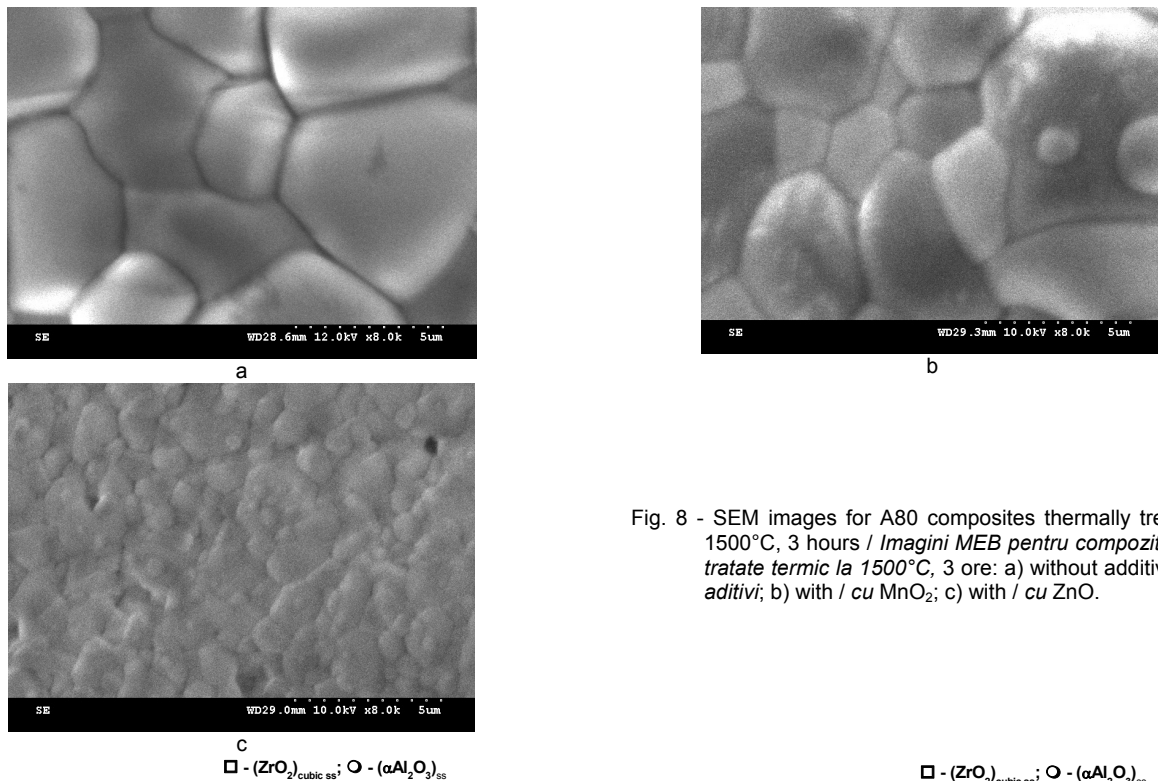


Fig. 8 - SEM images for A80 composites thermally treated at 1500°C, 3 hours / Imagini MEB pentru compozitele A80 tratate termic la 1500°C, 3 ore: a) without additive / fără aditivi; b) with / cu  $MnO_2$ ; c) with / cu  $ZnO$ .

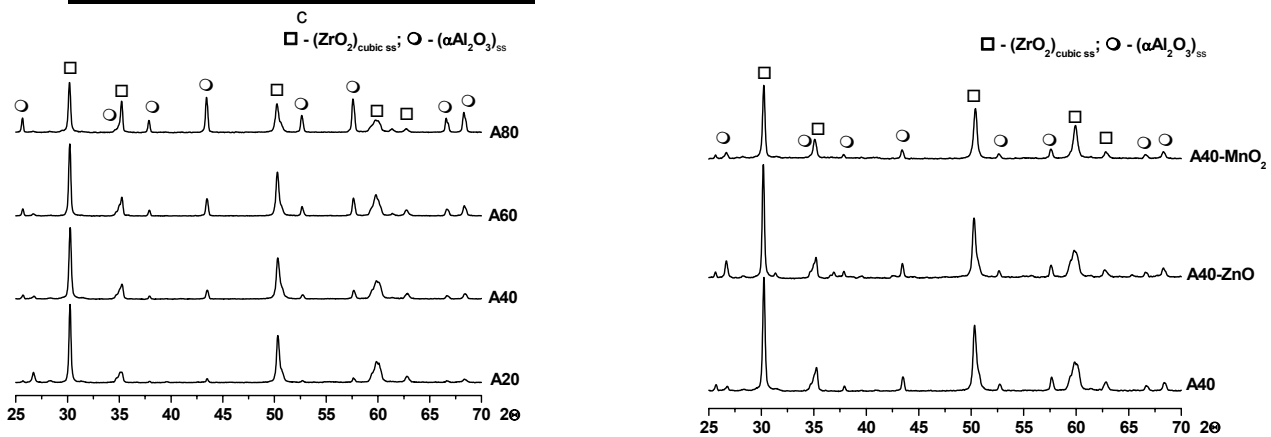


Fig. 9 - X-rays diffraction pattern for: a) for samples without additives thermally treated at 1500°C; b) for sample set A40 without additives and with  $ZnO$  and  $MnO_2$  thermally treated at 1500°C, 3 hours / Spectrele de difracție a razelor X pentru: a) compozitele fără aditivi, tratate termic la 1500°C; b) compozitele A40 cu și fără aditivi ( $ZnO$  și  $MnO_2$ ) tratate termic la 1500°C, 3 ore.

### 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.

**ACKNOWLEDGEMENTS**

Authors recognize financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: "Postdoctoral Program for Advanced Research in the field of nanomaterials".

**REFERENCES**

1. G. Fantozzi, and G. Orange, Thermomechanical properties of zirconia toughened alumina materials. In: Moya JS, De Aza S, editors. Processing of advanced ceramics. Soc Esp Ceram Vidr Arganda de Rey Madrid, Spain, 1986, 187.
2. A. Hirvonen, R. Nowaka, Y. Yamamoto, T. Sekino, and K. Niihara, Fabrication, structure, mechanical and thermal properties of zirconia-based ceramic nanocomposites, Journal of the European Ceramic Society, 2006 **26**, 1497, ISSN 0955-2219.
3. K. Niihara, New design concept of structural ceramics-ceramic nanocomposites, Journal of Ceramic Society of Japan, 1991, **99**, 974, ISSN 0914-5400.
4. S. Schmidt, S. Beyer, H. Immich, H. Knabe, R. Meistring, and A. Gessler, Ceramic Matrix Composites: A Challenge in Space - Propulsion Technology Applications. International Journal of Applied Ceramic Technology 2005, **2**(2), 85, ISSN 1546-542X.
5. F.A.T. Guimaraes, K.L. Silva, V. Trombini, J.J. Pierri, J.A. Rodrigues, R. Tomasi, and E.M.J.A. Pallone, Correlation between microstructure and mechanical properties of Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> nanocomposites Ceramics International, 2009, **35**, 741, ISSN 0272-8842.
6. D. Sarkar, S. Adak, and N.K. Mitra, Preparation and characterization of an Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> nanocomposite, Part I: Powder synthesis and transformation behavior during fracture. Composites: Part A, 2007, **38**, 124, ISSN 1359-835X (A).
7. D.D. Jayaseelan, D.A. Rani, T. Nishikawa, H. Awaji, and F.D. Gnanam, Powder Characteristics, Sintering Behaviour and Microstructure of Sol-Gel Derived ZTA Composites, Journal of European Ceramic Society, 2000, **20**, 2000, 267, ISSN 0955-2219.
8. Ș. Stoleriu, E. Andronescu, A. Carabăț, and B.S. Vasile, Influence of preparation conditions on nanometric characteristics of zirconia and alumina powders, Romanian Journal of Materials, 2011, **41** (3), 255, ISSN: 1583-3186.

\*\*\*\*\*

**MANIFESTĂRI ȘTIINȚIFICE / SCIENTIFIC EVENTS**



The ECerS XIII Conference is organised by the **French Ceramic Group** and is hosted by the **Ceramic European Center**, a research and teaching institution under the tutelage of the **French National Research Council (CNRS)**, the **University of Limoges** and the **National Engineering College for Industrial Ceramics (ENSCI)**.

Organised every two years, the **ECerS Conference is the place to be** for scientists, students and industrialists willing to have a direct access to one of the **largest community of international experts of ceramic science and technology**.

The presentations will cover a **broad range of topics from basic to applied science in relationship with major issues such as energy, environment, information and communication technologies, biotechnologies...** The conference will also be a unique occasion for students to introduce their work, some of them having the possibility to take part to the student speech contest, and for exhibitors to meet their customers.

**Contact:** [www.ecers2013.fr](http://www.ecers2013.fr)

\*\*\*\*\*