ZrO_2-CaO CERAMICS – A COMPARATIVE STUDY

Alin GIONEA[1], Ecaterina ANDRONESCU[2], Georgeta VOICU[3], Vasile-Adrian SURDU[4], Andreia ILIE[5]

The aim of this paper is the obtaining of final dense ceramics starting from zirconia powders. In the first step, zirconia powders were prepared through sol-gel method, using different amounts of CaO: 6, 7 and 8 mol%. After synthesis, the powders were dried at 100°C and then heat treated at 700°C for 3 hours. In the second step, zirconia ceramics were obtained. The powders were uniaxially pressed, followed by HIP - hot isostatic pressing at temperatures of 1200°C and 1300°C, for 1 hour , under 150 MPa, in an argon atmosphere.

After HIP, the samples were morphologically and structurally characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In this step were also studied ceramic properties like density, compressive strength and Young's modulus.

Keywords: partially stabilized zirconia, sol-gel, ceramics, hot isostatic pressing

1. Introduction

Zirconia can be found in three crystalline forms, depending on temperature: monoclinic (under 1170°C), tetragonal (between 1170 and 2370°C) and cubic (over 2370°C) [1-4]. During cooling zirconia suffers a volume expansion which is critical for the material [2]. In order to prevent this to happen we can stabilize zirconia with different oxides like: CaO, Y_2O_3, MgO, Gd_2O_3, CeO_2, using different methods of synthesis: combustion synthesis, coprecipitation, thermal decomposition of metal alkoxides and hydrothermal routes [1, 2, 5].

Because of its remarkable properties zirconia ceramics have a wide utilization, starting from its use like a biomaterial for femoral heads and ending with its usage for thin-film coatings and catalysts. For example, until 2005 more than 600.000 zirconia femoral heads have been implanted worldwide. Recent

[1] PhD student, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, e-mail: gionea_alin@yahoo.com
[2] PhD Eng., Prof, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, e-mail: ecaterina.andronescu@upb.ro
[3] PhD Eng., Prof, Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, e-mail: getav@yahoo.co.uk
[4] Eng., Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, e-mail: adrian.surdu@live.com
[5] Eng., Faculty of Applied Chemistry and Material Science, University POLITEHNICA of Bucharest, e-mail: andreiailie@yahoo.com

studies show that nanotube structures of zirconia with possible application in micro electromechanical systems in the future have been synthesized [6, 7]. CaO doped zirconia presents high strength and fracture toughness, thus it can be used for metal ware such as kitchen knives and prosthetic teeth [5, 6, 8].

2. Materials and methods

2.1. Preparation of zirconia ceramics

The schematic chart of processing calcia doped zirconia ceramics is presented in Fig. 1. Stoichiometric quantities of the following precursors were used to prepare 6, 7 and 8 mol% CaO stabilized zirconia through sol-gel method: zirconium propoxide (70% in Propanol, Fluka), calcium isopropoxide (99.97%, Fluka) and 2-metoxiethanol (Anhydrous 99.8%, Sigma-Aldrich) [1].

The gel obtained was left for maturation for 24 hours and then was dried at 100°C for 24 hours. The powders were milled with a mortar and pestle and then were calcinated at 700°C for 3h, with a heating rate of 5°C/min.

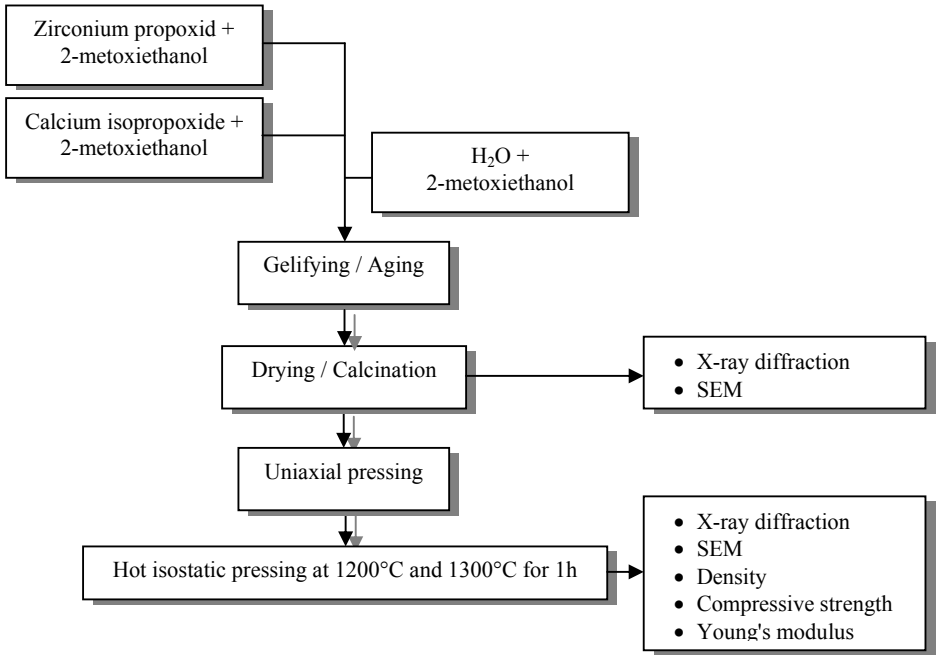


Fig. 1. Schematic chart of processing - calcia doped zirconia ceramics

After uniaxial pressing with a hydraulic press (Carver, model 4350L) the compact green bodies were obtained. The powders were pressed in a steel die as cylindrical pellets (Φ = 13 mm, h = 3 mm), using 1.25 grams for each sample. The

sintering process was conducted through hot isostatic pressing, at the temperature range 1200°C-1300°C with a holding time of 1 hour, with a heating and cooling rate of 5°C/min. Further it will be used the following nomenclature for ceramics: 6ZC, 7ZC and 8ZC, where 6, 7 and 8 represent the molar ratio of calcium oxide.

2.2. X-ray diffraction

X-ray diffraction analysis of powders and sintered samples was performed on a Panalytical Empyrean diffractometer (step size 0.020, time per step 1 sec) at room temperature. In all the cases, Cu Kα radiation with λ=1.541874Å was used. The samples were scanned in the Bragg angle 2θ range of 10-80 degree.

2.3. Scanning Electron Microscopy

For the microstructure analysis of powders and sintered samples was used an INSPECT F50 scanning electron microscope, with field emission gun (FEG, resolution – 1.2 nm) and X-ray spectrometer (EDS, resolution at MnK of 133 eV), on samples covered with a thin gold layer.

2.4. Ceramic properties

Ceramic properties were investigated: for density determination was used a helium pycnometer (Pycnomatic model) and a INSTRON testing machine (model 5982, with an Blue Hill 3 soft) was used to determine of the compressive stress and Young's modulus.

3. Results and discussion

The phase evolution of calcined powder and sintered sample was studied by XRD and the data are shown in Figs. 2 and 3.

As it can be seen in Fig. 2, cubic zirconia is the only phase identified for calcined powder and for all molar ratio 6, 7 and 8 mol%, according to JCPDS 75-0359.

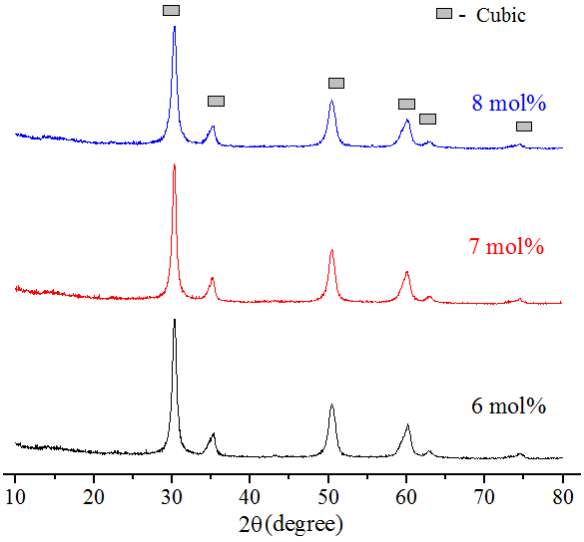


Fig. 2. XRD pattern of calcinated powder at 700°C

The XRD analysis patterns of sintered samples at 1200°C and 1300°C are shown in Figs. 3 a and b. The sharp well defined peaks show the high crystalline nature of hot isostatic pressed samples. For both temperatures of 1200°C and 1300°C, tetragonal and monoclinic phases of zirconia are present, according to JCPDS 05-4207 (T) and JCPDS 07-0343 (M). As the temperature increases from 1200°C to 1300°C the monoclinic phase is the major phase. Also, as the molar ratio reaches 8 mol% the tetragonal phase is the dominating phase, considering the increase of the intensity of diffraction peak from 2θ=30° with molar ratio.

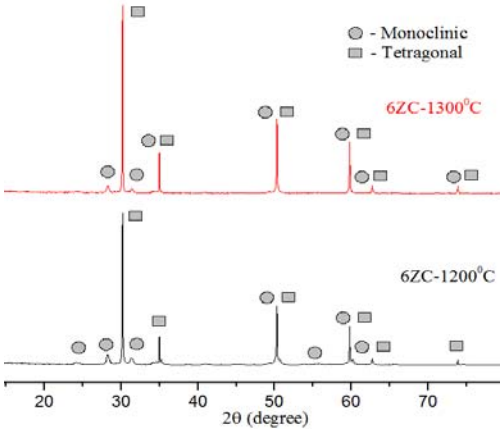
Based on Scherrer's relation the mean crystallite sizes, determined as an average of the size of the most important peaks are presented in Table 1.

Table 1

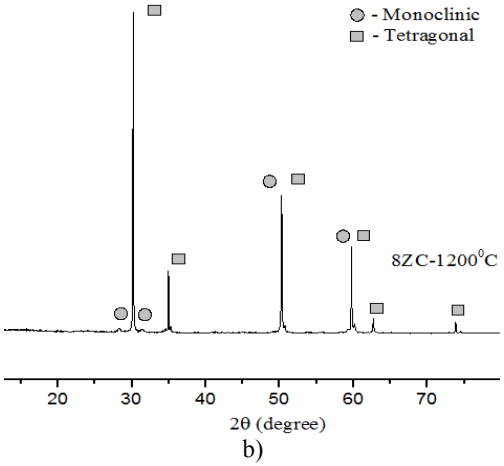
Crystallite size using Scherrer relation

Sample	CaO content	2theta	d, Å	D, nm	D (medium), nm
ZrO_2 calcinated at 700°C	6 mol%	30.29	2.95	9.77	7.56
		35.1	2.55	7.74	
		50.44	1.81	7.00	
		60	1.54	6.03	
		62.95	1.48	8.73	
		74.4	1.27	6.10	
	7 mol%	30.26	2.95	10.46	7.96
		35.08	2.56	8.56	
		50.41	1.81	7.50	

		59.95	1.54	6.19	
		62.91	1.48	9.38	
		74.25	1.28	5.67	
	8 mol%	30.26	2.95	8.41	6.87
		35.05	2.56	7.39	
		50.41	1.81	6.44	
		59.93	1.54	5.42	
		62.9	1.48	7.90	
		74.25	1.28	5.64	



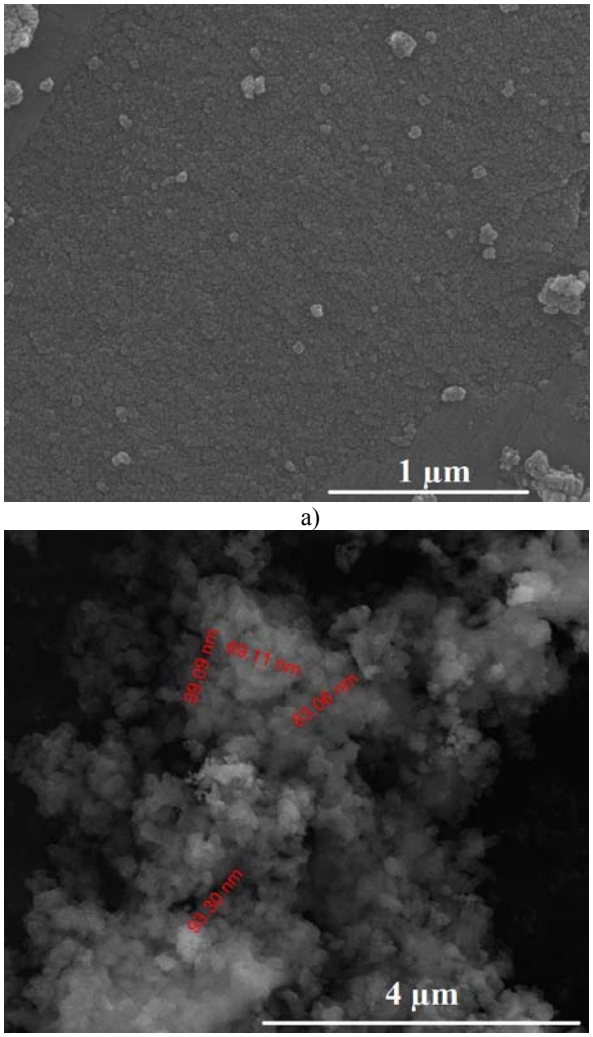
a)



b)

Fig. 3. XRD pattern of 6ZC (a) and 8ZC (b) HIP'ed at 1200°C and 1300°C

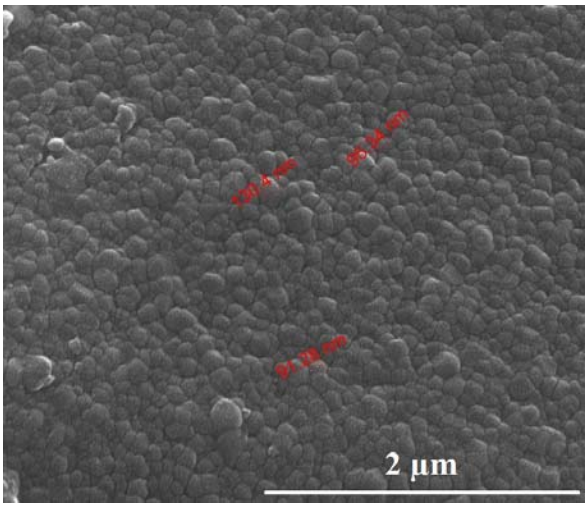
The powders morphology of the sample calcined at 700°C for 3 hours, with 6 mol% content of calcium oxide is shown in Figs. 4 a and b. The micrographs indicate the formation of nanosized powders with average particles dimension of 100 nm. Figs. 5 a and b show the SEM of 6ZC and 7ZC samples sintered in argon atmosphere at 1200°C, respectively 1300°C. It can observe irregular grains with polyhedral shape. The average grain size is about 50 to 150 nm. It also can be observed that dense ceramics with no pores were obtained.



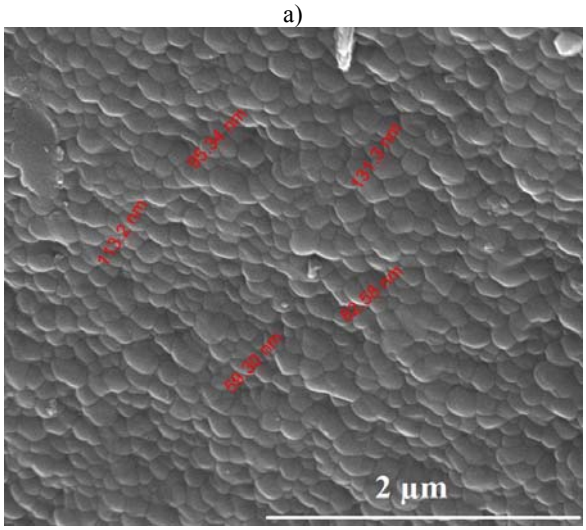
a)

b)

Fig. 4. SEM images of 6 mol% calcinated powder at 700°C



a)



b)

Fig. 5. SEM images of 6ZC- HIP'ed at 1200°C (a) and 7ZC-HIP'ed at 1300°C (b)

Density of 6ZC, 7ZC and 8ZC samples sintered in argon atmosphere at 1200°C and 1300°C was determined using helium displacement technique and the data are shown in Fig. 6. It is observed that density decreases with increasing temperature; this is due to the increase of micro cracks present in the samples.

Compressive strength tests were performed for each ceramic sample. Fig. 7 shows the values obtained for 6 mol%, 7 mol% and 8 mol% CaO-ZrO_2 after hot isostatic pressing. The compressive strength increases with temperature increase to 1300°C. It can be observed that the compressive strength of 7ZC sintered at 1300°C has the highest value of all ceramics.

Young's modulus was also determined using the software of testing machine (Fig. 8). The obtained values are between 129 and 218 GPa and they are higher for sintering temperature of 1300°C. Ceramic 7ZC sintered at 1300°C presented the most pronounced elastic behavior.

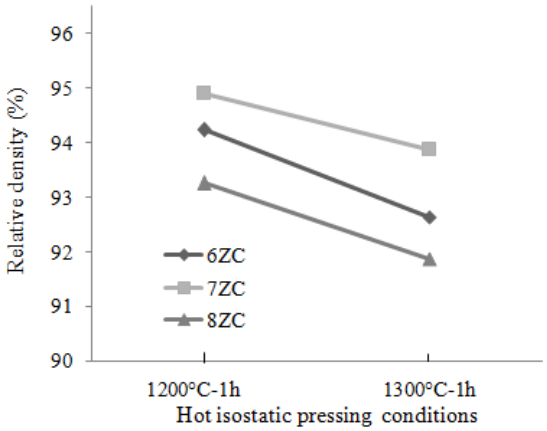


Fig. 6 Relative density of $CaO\text{-}ZrO_2$ samples sintered at 1200°C and 1300°C

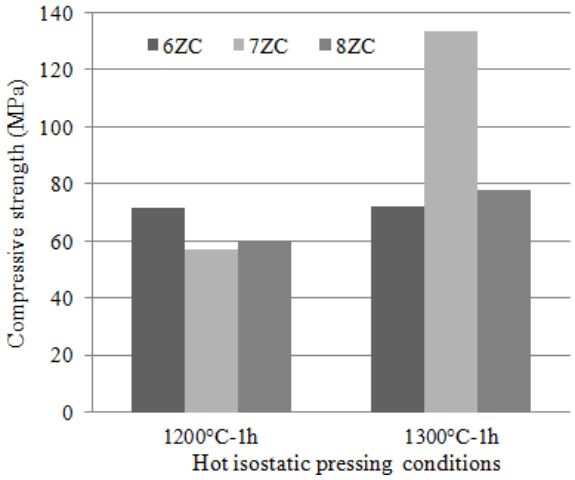


Fig. 7 Compressive strength of $CaO\text{-}ZrO_2$ samples sintered at 1200°C and 1300°C

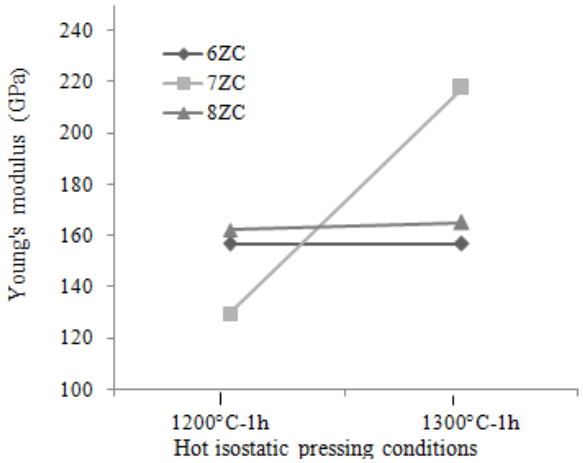


Fig. 8 Young's modulus of CaO-ZrO_2 samples sintered at 1200°C and 1300°C

4. Conclusions

The effect of CaO content on densification and mechanical properties of zirconia ceramics was investigated. Final dense ceramics were obtained after hot isostatic pressing at 1200°C and 1300°C.

Density values were higher for sintering temperature of 1200°C than for 1300°C. This could be explained by the increase of monoclinic phase in the samples at temperature of 1300°C which increases micro cracks.

The compressive strengths of 6ZC, 7ZC and 8ZC increase with sintering temperature increasing. Values were similarly for all molar ratios, between 57-80MPa, excepting sample 7ZC sintered at 1300°C which presented the highest value - 134 MPa.

All samples presented Young's modulus values between 129-218 GPa.

Acknowledgement

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R E F E R E N C E S

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