INFLUENȚA CONCENTRAȚIEI DE DOPANT Y_2O_3 ASUPRA CARACTERISTICILOR CERAMICILOR ZIRCONICE SINTERIZATE PRIN PRESARE IZOSTATICĂ LA CALD

INFLUENCE OF Y_2O_3 DOPANT CONCENTRATION ON ZIRCONIA CERAMICS CHARACTERISTICS SINTERED THROUGH HOT ISOSTATIC PRESSING

ALIN GIONEA, ECATERINA ANDRONESCU, VASILE-ADRIAN SURDU, ROXANA TRUŞCĂ, ANDREIA ILIE, ŞTEFANIA STOLERIU*

University Politehnica of Bucharest, G.Polizu Street 1-7, 011061 Bucharest, Romania

The aim of this study is to obtain yttria-stabilized zirconia ceramics with possible applications in dentistry. Firstly, it was obtained zirconia powders doped with different amounts of yttrium oxide (2 mol%, 2.5 mol% and 3 mol%), using the sol-gel method. After synthesis, the powders were dried at 100°C and then heat treated to 500°C for 3 hours. In order to obtain dense ceramics, powders were uniaxial pressed and then the compact green bodies were isostatically hotpressed for 1h and 2h, at temperatures between 1200°C-1300°C, under 150MPa, in argon atmosphere. After the sintering process, the phase composition and microstructure were determined through X-ray diffraction (XRD) and scanning electron microscopy (SEM). Were also studied ceramic properties like apparent density and compressive strength.

Scopul acestei lucrări este de a obține ceramică zirconică cu posibile aplicații în stomatologie. În primul rând, s-au obținut pulberile de zirconă dopată cu oxid de ytriu (2 mol%, 2.5 mol% şi 3 mol%), prin metoda sol-gel. După sinteză, pulberile au fost uscate la 100°C şi apoi calcinate la temperatura de 500°C timp de 3 ore. Pentru a obține ceramicile, pulberile au fost presate uniaxial, apoi epruvetele obținute au fost sinterizate prin presare izostatică la cald, la temperaturi cuprinse între 1200°C şi 1300°C, palier de 1 şi 2 ore, în atmosferă de argon. După procesul de sinterizare, s-au determinat compoziția fazală şi microstructura prin difracție de raze X şi microscopie electronică de baleiaj. Au fost studiate şi alte proprietăți ale ceramicilor ca densitatea aparentă şi rezistența mecanică la compresiune.

Keywords: *zirconia, hot isostatic pressing, ceramic, compressive strength*

1. Introduction

Zirconia, is a very known ceramic, that can be found in nature like zircon ($ZrSiO_4$) and baddeleyite [1]. At atmospheric pressure zirconia has three polymorphic forms: monoclinic at temperatures lower than 1170°C, tetragonal at temperatures between 1170°C and 2370°C, and cubic at temperatures between 2370°C and 2680°C [1-5]. After sintering, and depending on the cooling process, the tetragonal phase becomes monoclinic at about 970°C [5]. This transformation is related with volume expansion, causing cracks during cooling from sintering temperature, which may be fatal for the material [2]. If we add different oxides, such as yttrium oxide (Y_2O_3), calcium oxide (CaO), magnesium oxide (MgO) or cerium oxide (CeO_2) we can stabilize the metastable cubic and tetragonal phases at room temperature. Zirconia fully stabilized is obtained with 16 mol% MgO, 16 mol% of CaO or 8 mol% Y_2O_3. If we use a small amount 3-6 mol% yttria, then the tetragonal phase will form [1, 2, 4-6].

Zirconia is a very studied and used bioceramic material due to his excellent physical properties, chemical resistance, biocompatibility, and excellent esthetic characteristics, reproducing the translucency and color of natural teeth [7-10]. In dentistry zirconia is a common material, especially 3 mol% yttria stabilized ZrO_2, because besides the fact is chemically inert allowing cell adhesion, it presents high strength and fracture toughness [5, 11-13].

Hot isostatic pressing is a processing technique for obtaining high-density ceramics that simultaneously uses temperature and isostatic pressure. An advantage of this technique is that pressure is applied uniformly in all directions [14,15].

2. Experimental

Zirconia powders were obtained through sol-gel method using as starting materials: zirconium propoxide (70% in Propanol, by Fluka), yttrium butoxide (0,5M Solution in Toluene, 99,9%,

* Autor corespondent/*Corresponding author,*
E-mail: stefania.stoleriu@upb.ro

Sigma-Aldrich) and 2-metoxiethanol (Sigma-Aldrich). Stoichiometric quantities of these reagents were mixed in order to obtain 2 mol%, 2.5 mol% and 3 mol% yttria stabilized zirconia. First zirconium propoxide and yttrium butoxide were dissolved in 2-metoxyethanol. Then these two solutions were mixed together in a Berzelius beaker under vigorous stirring on a magnetic stirrer. A solution of water with 2-metoxiethanol was added, and then the gel began to form. The obtained gel was left to maturate for 3 hours and then was oven-dried at 110°C for 30 hours. The dry gel powders were calcined at 500°C for 3h, with a heating rate of 5°C/min. The calcined powders were characterized by XRD, DTA-TG and SEM [16].

The powders were uniaxially pressed on a hydraulic press (Carver, model 4350.L) to obtain the compact green bodies. The samples were sintered using hot isostatic pressing (HIP) for 1h and 2h, at temperatures between 1200°C-1300°C under 150MPa, with a heating and cooling rate of 5°C/min.[15].

In this study we will use the following nomenclature for the final ceramic dense bodies: 2ZY, 2.5ZY and 3ZY, where 2, 2.5 and 3 represents the molar ratio of yttrium oxide.

The processing flowchart is presented in Figure 1.

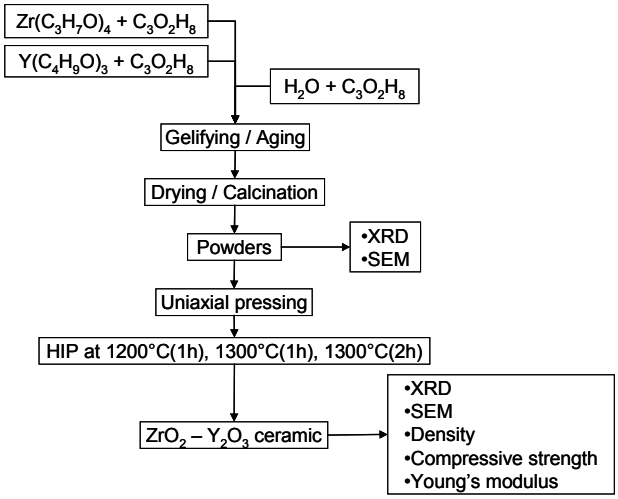


Fig. 1- Processing flowchart / *Fluxul tehnologic utilizat.*

The thermal differential analysis and thermogravimetric diagrams were obtained using a DTA-50 SHIMADZU equipment, in normal conditions of temperature and pressure. The powder was heated up to 1000°C, with a temperature growing rate of 10°C/minute.

X-ray diffraction analysis of powders and sintered samples was performed on a Panalytical Empyrean diffractometer (step size 0.02°, 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.

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.

For apparent density measurements was used a helium pycnometer (Pycnomatic model) and a INSTRON testing machine (model 5982, with an Blue Hill 3 soft) was used to determine the compressive stress and Young's modulus.

3. Results and discussion

The thermogravimetric analysis (Figure 2) indicates a total mass loss of 28.467% until the temperature of 500°C is reached. The exothermic effect from aprox. 87°C and the weight loss of approximately 2.5% between 30°C and 120°C can be explained by the removal of physically attach water and alcohol molecules. The exothermal effects from ~224°C and ~317°C can be attributed to the burning of organic residues. The exothermic peak from ~453°C, with small weight loss, may be attributed to two processes: (i) crystallization of zirconia in tetragonal phase [16, 17] and (ii) residual carbon combustion and its removal from the system. Between 500°C and 1000°C the mass loss percent is only of 1.865 [18, 19].

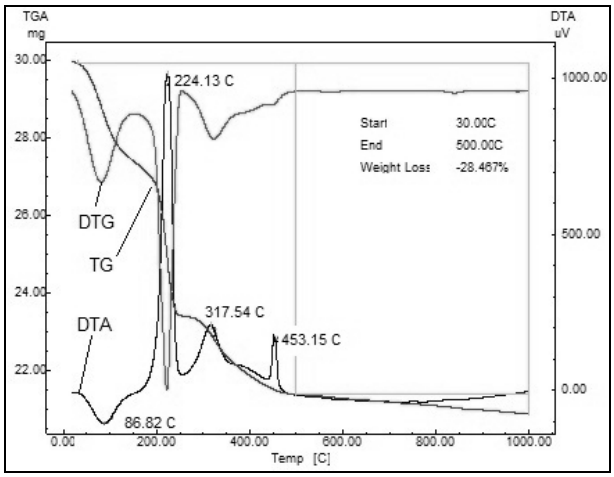


Fig. 2 - Thermal analysis diagram / *Diagrama de analiză termică.*

Determination of zirconia powders phase content was performed using XRD. Figure 3 shows that the calcination at 500°C for 3 hours led to the formation of ZrO_2 tetragonal for all molar ratio, according to JCPDS 13-6621.

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. Crystallite sizes are primarily dependent on Y_2O_3 molar ratio. It is observed that over 2.5 mol% Y_2O_3 the change in crystallite sizes remained insignificant.

Table 1

Crystallite size calculated using Scherrer ecuation / *Dimensiunea de cristalit calculată folosind ecuația lui Scherrer*

Sample	Y_2O_3 content	2theta	d, Å	D, nm	D (average), nm
ZrO_2 calcinated at 500°C	2 mol%	30.16	2.96	11.21	9.36
		34.61	2.59	8.45	
		43.00	2.10	9.37	
		50.14	1.82	8.28	
		59.48	1.55	5.81	
		62.86	1.48	9.99	
		74.49	1.27	12.43	
	2.5 mol%	30.11	2.97	7.14	5.93
		34.91	2.57	6.80	
		43.04	2.10	3.62	
		50.28	1.81	6.04	
		59.80	1.55	5.23	
		62.80	1.48	6.78	
		74.09	1.28	5.89	
	3 mol%	30.11	2.97	7.32	5.91
		34.91	2.57	7.17	
		44	2.08	2.47	
		50.28	1.81	6.11	
		59.80	1.55	5.27	
		62.82	1.48	7.12	
		74.04	1.28	5.90	

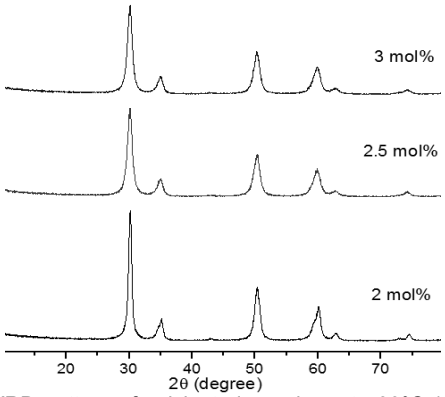
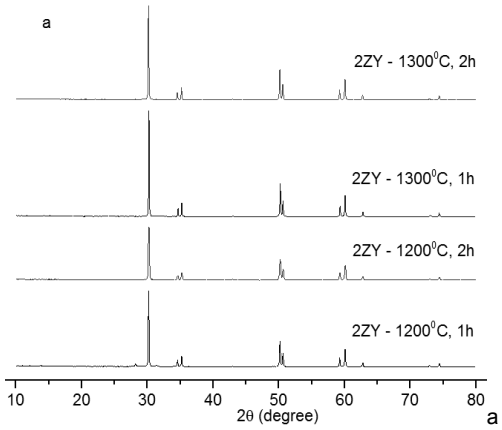
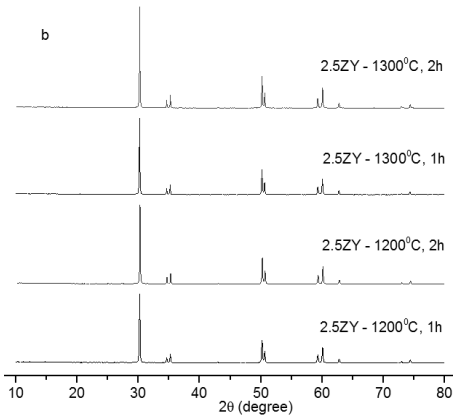


Fig. 3- XRD pattern of calcinated powders at 500°C / *Spectrul de difracție de raze X a pulberilor calcinate la 500°C.*





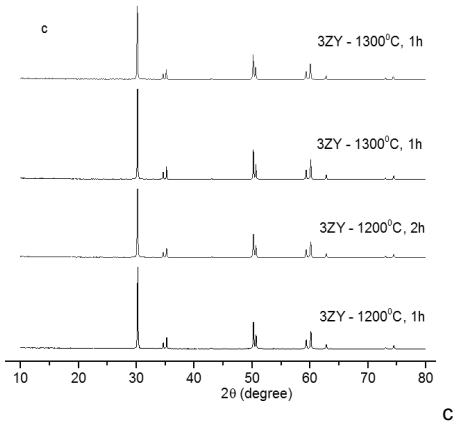
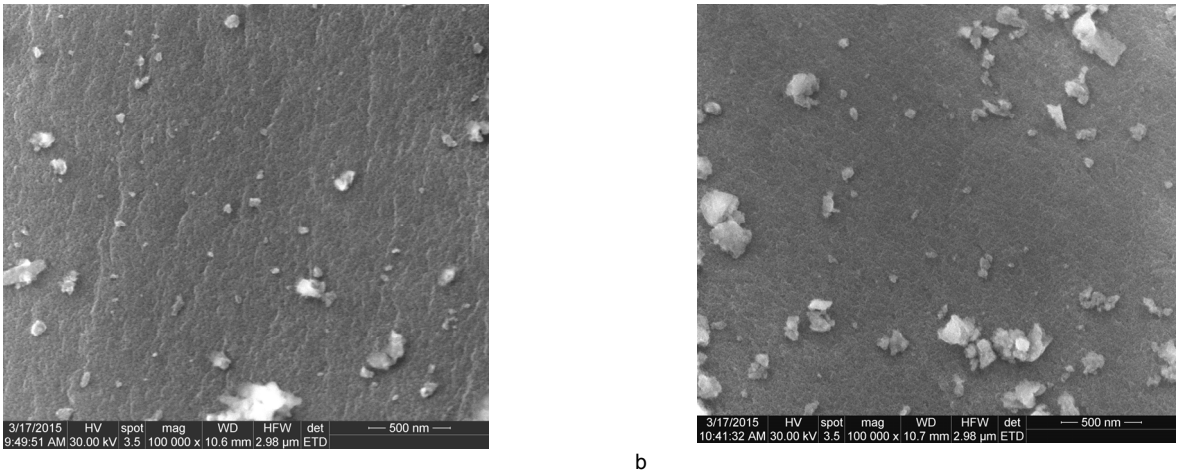


Fig. 4 - XRD of sintered samples: a) 2ZY, b) 2.5ZY, c) 3ZY / *Difracția de raze X a epruvetelor sinterizate: a) 2ZY, b) 2.5ZY, c) 3ZY.*

Figure 4 shows the XRD patterns of sintered green bodies at different temperatures (1200°C and 1300°C), which indicates the tetragonal form being the single crystalline phase for all zirconia ceramics, according to JCPDS 05-4207.

The zirconia calcinated powders morphology was determinate using scanning electron microscopy. The micrographs from Figure 5 reveal the formation of nanosized powders with average particles dimension from 5 to 20 nm.

The microstructure of sintered samples at 1200°C and 1300°C (1h, 2h) was also investigated by SEM (Figure 6), on the fractured surfaces. From the SEM micrographs it can be said that final dense ceramics were created after hot isostatic pressing, with polyhedral grains having an average size between 90 and 250 nm. It also can be noticed the absence of porosity.



a b

Fig. 5 - SEM images of calcined powders at 500°C for 3 hours: a) 2 mol% Y_2O_3 and b) 3 mol% Y_2O_3, / *Imaginile SEM a pulberilor calcinate la 500°C pentru 3 ore: a) 2 mol% Y_2O_3 şi b) 3 mol% Y_2O_3*

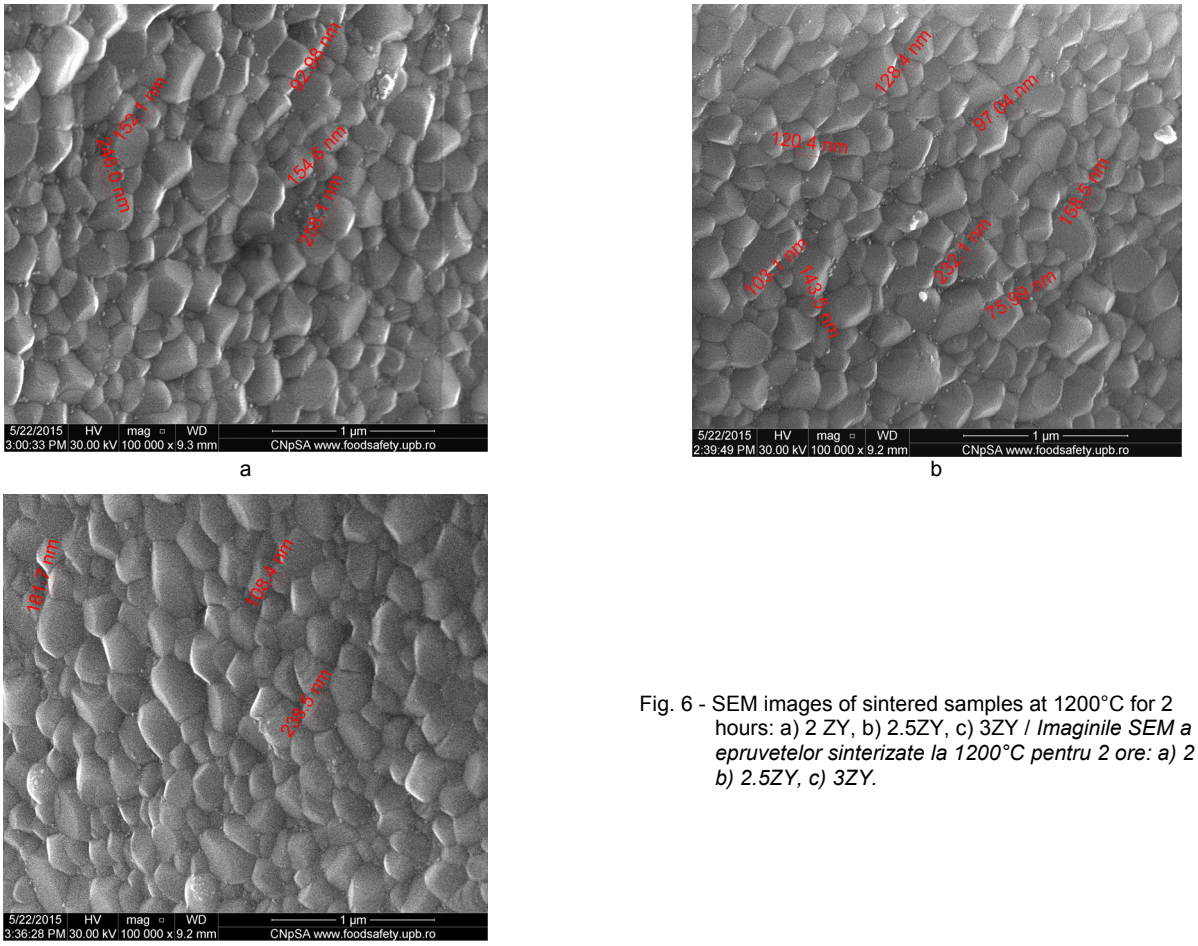


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Fig. 6 - SEM images of sintered samples at 1200°C for 2 hours: a) 2 ZY, b) 2.5ZY, c) 3ZY / *Imaginile SEM a epruvetelor sinterizate la 1200°C pentru 2 ore: a) 2 ZY, b) 2.5ZY, c) 3ZY.*

Table 2

HIP conditions of zirconia ceramics and resulting apparent density / *Condiţiile HIP şi densitatea aparentă rezultată a ceramicilor zirconice*

	HIP conditions	Y_2O_3 content, mol%		
		2	2.5	3
Apparent density (g/cm^3)	1200°C, 1h	6.06147	6.03593	6.06054
	1200°C, 2h	6.00887	6.05997	6.05695
	1300°C, 1h	5.79292	5.85725	5.89687
	1300°C, 2h	5.87702	5.87424	5.94416

The apparent density of all ceramic bodies was determined with helium displacement technique, one of the most precise methods because of helium small dimension mono-atomic molecule that can permeate even extremely narrow pores. The pycnometer operates on Archimedes principle of gas displacement to determine the volume. Ceramics apparent density can be determined using the ceramics weight and volume[20]. The relative density was calculated using the value 6,1 g/cm^3 for theoretical density of yttria stabilized zirconia [12]. Results are listed in Table 2.

The relative density of ceramics subjected to HIP increased with increasing amount of yttrium oxide. As it can be seen in Figure 7 the highest values of relative densities were obtained for hot isostatic pressing at 1200°C for 1h (>99% of theoretical density), while increasing temperature at 1300°C resulted in the lowest values for density (95%-97% of theoretical density). This decrease in density can be attributed to the emergence of small pores, which does not affect mechanical properties. The ceramics containing 3 mol% Y_2O_3 (3ZY) exhibited the highest relative density (>96,8% of theoretical density) for all sintering schedules.

Further it was studied the compressive strength and Young's modulus of ceramics, the results being illustrated in Figure 8 and 9.

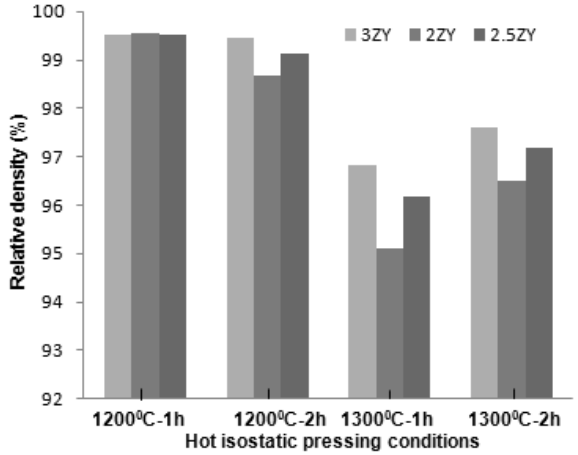

Fig. 7 - Relative density evolution with HIP conditions/ *Evoluţia densităţii faţă cu condiţiile de presare izostatică la cald.*

The highest compressive strength values obtained from this study are for sintering temperature of 1300°C (1h and 2h) for all molar ratios. Also, the highest values obtained for compressive strength, considering the HIP

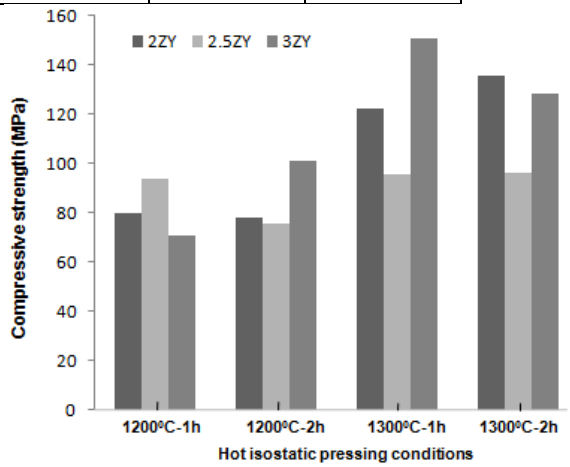

Fig. 8 - Variation of compressive strength with HIP conditions / *Variaţia rezistenţei la compresiune în funcţie de condiţiile de presare izostatică la cald.*

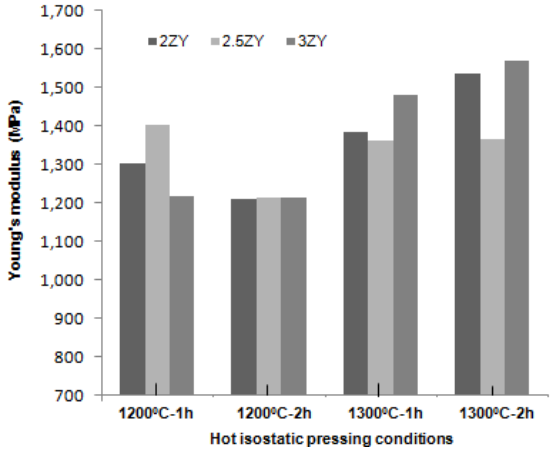

Fig. 9 - Variation of Young's modulus and HIP conditions / *Variaţia modulul lui Young cu condiţiile de HIP.*

conditions and the molar ratio of dopant are for 3ZY ceramics sintered at 1300°C for 1 hour (Figure 8).

Modulus of elasticity (Young's modulus) of the tested ceramics was determined using the software of testing machine. Young's modulus is a measure of the stiffness of the ceramic's resistance to elastic deformation, meaning that for higher values of the module, we will have a stiffer material. Tested zirconia ceramics exhibit elastic modulus values in the range 1,200-1,600 MPa (Figure 9). The elastic behavior it was more pronounced for samples isostatically hotpressed at temperature of 1300°C for 2 hours, while samples sintered at 1200°C for 2 hours presents the lowest elastic behaviour.

4. Conclusions

In this paper fully dense ceramics were obtained from zirconia nanopowders doped with 2, 2.5 and 3 mol% yttrium oxide through hot isostatic pressing. Ceramic properties investigated (density, compressive strength and Young's Modulus) are influenced by the yttria content in the starting powder and hot isostatic pressing conditions.

Samples of 3 mol% Y_2O_3 amount showed better densification compared to those of composition 2 and 2.5 mol%. The additions of higher amounts of yttria produced an increase in relative density values.

The mechanical properties indicated that as the HIP temperature was increased, the compressive strength also increased. The optimum compressive strength for ZrO_2-Y_2O_3 was achieved at a hot pressing temperature of 1300°C and a yttria amount of 3 mol%.

Regarding Young's modulus of tested ceramics, it was dependent on sintering conditions and yttria content, ceramics with better elastic behavior being obtained for 3 mol% Y_2O_3 and 1300°C HIP temperature.

Considering the above mentioned, one can conclude that zirconia ceramics with best characteristics is 3ZY (3 mol% yttria) sintered at temperature of 1300°C for 2 hours.

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