STABILITATEA CHIMICĂ ÎN SALIVĂ ARTIFICIALĂ A BIOCERAMICII ZIRCONICE
CHEMICAL STABILITY IN ARTIFICIAL SALIVA OF ZIRCONIA BIOCERAMICS

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In this study, the effects of simultaneous admixture of CaO and MgO on the crystalline phases, crystallite sizes and sintering properties of coprecipitated zirconia-alumina powder are investigated using complex thermal analysis (TG, DTA, DTG), X-ray diffractometry (XRD), scanning electron microscopy (SEM) coupled with EDS. Correlations among composition - microstructure and properties of the coprecipitated $85ZrO_2$. $15Al_2O_3$ powder after sintering at 1050 °C, 1350 °C, and 1500 °C with 2 hours soaking time at each temperature were performed. The results showed that development of tetragonal phase of zirconia stabilized with Ca^{2+} and Mg^{2+} was effective at 1500 °C. In dental applications, dental materials are soaked in saliva, which contains a large number of ions which in turn may accelerate the corrosion of materials. In such context, the chemical stability in modified Fusayama-Meyer type artificial saliva of sintered zirconia- alumina ceramics was also investigated. The ceramic samples sintered at 1500 °C show a better chemical stability, as the pH variation is lower when using a starting immersion solution with pH = 7.4. However, the variation of pH after immersion in artificial saliva is obvious after 216-288 hours due to the ionic transport between ceramic and the solution, even after sintering at 1500 °C.

În acest studiu se investighează efectele adiției simultane de CaO și MgO asupra fazelor cristaline, a dimensiunilor cristalitelor și a proprietăților de sinterizare a pulberii coprecipitate de ZrO_2 - Al_2O_3 utilizând analize termice complexe (TG, DTA, DTG), difractometria cu raze X, analize electronomicroscopice de baleiaj (SEM) cuplate cu sistem dispersiv de energie (EDS). S-au efectuat corelații compoziție – microstructură - proprietăți pentru pulberea zirconio-aluminoasă coprecipitată după sinterizarea la 1050 °C, 1350 °C și 1500 °C cu menținerea unui palier de 2 ore la fiecare temperatură. Rezultatele au arătat că dezvoltarea fazei tetragonale a zirconei în prezența simultană a ionilor Ca^{2+} și Mg^{2+} a fost efectivă la 1500 °C. În aplicațiile dentare, materialele dentare sunt în contact cu saliva, care conține un număr mare de ioni care la rândul lor pot accelera coroziunea materialelor. In acest context a fost de asemenea investigată, stabilitatea chimică în salivă artificială modificată de tip Fusayama-Meyer a ceramicii zirconio-aluminoase sinterizate. Probele ceramice sinterizate la 1500 °C prezintă o stabilitate chimică mai bună, iar variația pH-ului soluției de imersie este mai scăzută atunci când se utilizează o soluție de pornire cu pH = 7,4. Cu toate acestea, variația pH-ului după imersie în saliva artificială este evidentă după 216-288 ore datorită transportului ionic între ceramică și soluție, chiar după sinterizarea la 1500°C.

Keywords: *Zirconia, Alumina, bioceramic, chemical stability, artificial saliva, corrosion*

1. Introduction

Zirconium oxide solid solutions containing oxide of divalent or trivalent metal cations are important technological materials. In fact the incorporation of lower-valent cations in ZrO_2 causes the formation of anionic vacancies and the solid acquires interesting properties such as electrical (ionic conductivity) [1, 2] and structural features (stabilization of crystalline modifications) [3]. Biomedical-grade tetragonal zirconia polycrystals doped with 3mol% Y_2O_3 (3Y-TZP) may be one of the most controversial materials used in dentistry. However, biomedical-grade zirconia exhibits the best mechanical properties of oxide ceramics [4,5]. Also, zirconia is prone to aging in the presence of water [6], which is called low-temperature degradation in which in the initial stages and in the presence of water, a tetragonal-to-monoclinic (*t-m*) phase transformation takes place at fairly low temperatures (65-300 °C), with the degradation process occurring gradually from the surface into the bulk of the ceramic. Subsequently, microcracks and macrocracks develop after the expansion in volume associated with the phase transformation [7,8]. This ultimately affects the 3Y-TZP's mechanical properties detrimentally [9,10]. This leads to the failure of a large number of femoral heads in a very short time [4]. The field of dentistry is also faced with the possibility that such incidents will happen. Strength, abrasion resistance, chemical stability of alumina (Al_2O_3) ceramic have made it to be used for bone and dental implants.

Bioceramics are attractive as biological implants for their biocompatibility. The analysis of the results of animal experiments and the evaluation of clinical follow up studies show that alumina ceramic with high mechanical strength show minimal or no tissue reaction, nontoxic to tissues and blood compatibility tests were also

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satisfactory [11]. Zirconia ceramic revealed its bioinertness and noncytotoxicity [11]. Since both materials are biocompatible, this could prove to be a new approach to dental prosthetic restoration [8]. A composite material processed with 80% tetragonal zirconia polycrystals (ZrO_2-TZP) and 20% alumina (Al_2O_3) is reported to have outstanding mechanical and tribological properties. Using composite materials can improve the reliability and lifetime of zirconia by providing higher fracture toughness and mechanical strength [12-19].

Many papers discussed the degradation at low temperature of zirconia-alumina composites in distilled water [9-15]. However, in dental applications, dental materials are soaked in saliva, which contains a large number of ions which in turn may accelerate the corrosion of materials. There is little information available in the literature about the zirconia-alumina composites in artificial saliva.

The present study aimed to determine the longterm aging behavior of sintered zirconia - alumina ceramic in Fusayama Meyer artificial saliva. Moreover, in this study, the effects of simultaneous admixture of CaO and MgO on the crystalline phases, crystallite sizes and sintering properties of coprecipitated ZrO_2- Al_2O_3 powders were investigated.

2.Materials and methods

2.1 Preparation of zirconia-alumina ceramic

Solid salt of $Al_2(SO_4)_3$ x $18H_2O$ (Chimopar, Romania) and respectively, $ZrOCl_2$ x $8H_2O$ (Merck) were dissolved in distilled water to prepare the initial solutions in order to achieve zirconia-alumina powder having a ratio of 85 mole% ZrO_2 and 15 Al_2O_3 mole%. $MgCl_2$ x $6H_2O$ (Chimopar) and $CaCl_2$ x $6H_2O$ (Chimopar) were dissolved in distilled water and calculated to bring 2% mole MgO and 6% mole CaO to stabilize zirconia. The four starting solutions were mixed and precipitated by adding NH_4OH solution (Chimopar) to achieve pH=9 under stirring. The precipitates were aged for 24 hours. After aging the precipitate was washed with distilled water and filtered for four times and then washed with ethanol and dried at 105 ^{o}C for 12 hours. The resulted agglomerated powder was passed through a 006 mm mesh sieve and then, shaped by uniaxially pressing at 6.9 MPa, as ceramic discs with a diameter of 13 mm and a height of 10 mm. The green ceramic bodies were calcinate at several temperatures (1050°C, 1350°C and 1500°C) with a 2h range at each maximum curing temperature.

The heating and cooling rate was 50 ^{o}C / min, in Nabertherm type oven. Finally, the sintered specimens were gradually cooled to ambient temperature in the furnace. The effectiveness of the sintering process was evaluated as a function of the sintering time and specimen composition.

2.2. Physical analysis

General physical characterization of cumulative average samples was focused to establish the limits of variation for the basic parameters, as: moisture content (according to SR ISO 331:1994, Total moisture content), bulk density (STAS 5630-73, Determination of bulk density).

2.3. Mineralogical analysis

Mineralogical phase analyses were performed by X-ray diffraction method with parallel beam - scanning axis 2θ / θ, on bulk samples. A Shimadzu XRD 6000 diffractometer with the radiation generator tube power of 1200 W, with Cu-Kα characteristic radiation (λ = 1,541874 Å) was employed. Scanning range (2θ) of goniometry was located between 5° and 70°, with 5°/minute angular speed and 0.02^o step.

2.4. Complex thermal analysis

TG/ATD/DTG curves were recorded on a Mettler Toledo 851 equipment in the temperature range of 25 – 1200°C, under normal atmosphere (air) and a heating rate of 10°C/min. For determination the dried alumina-zirconia coprecipitate was placed in crucibles of high purity aluminium oxide.

2.5. Chemical stability analysis of ceramic bodies

The hydrolytic stability of ceramic samples was tested in modified Fusayama-Meyer type artificial saliva solution [19-20] prepared from distilled water and the following reagent salts:

KCl	0.400 g/l
NaCl	0.400 g/l
$CaCl_2$.$2H_2O$	0.906 g/l
NaH_2PO_4.$2H_2O$	0.690 g/l
Na_2S.$9H_2O$	0.005 g/l
$CO(NH_2)_2$ (urea)	1.000 g/l.

After preparation the starting solution of artificial saliva has pH = 7.4. Another solution was adjusted to pH = 6.4 by adding lactic acid to the starting solution.

Samples were kept in artificial saliva solution at pH 7.4 and 6.4, respectively, for 9, 10 and 12 days and measured their chemical stability, under similar temperature conditions ~ 25 ^{o}C.

3. Results and discussion

3.1. Complex thermal analysis of coprecipitated ZrO_2 - Al_2O_3 - powder

The TG / DTA /DTG diagrams for the synthesized ZrO_2 - Al_2O_3 powder (assigned with Z) are shown in Figure 1.

The endothermic peak at 105°C corresponds to the loss of physically bonded water. In the range 20-270°C a mass loss of
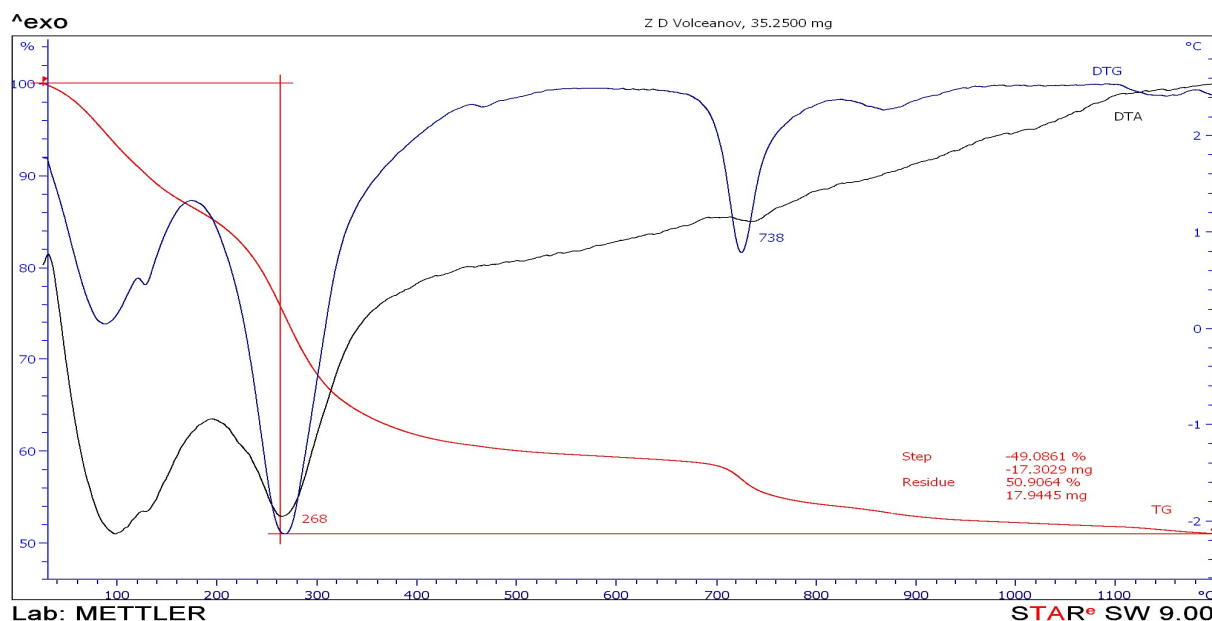
Fig.1 -TG/DTA / DTG diagrams for the synthesized ZrO_2 - Al_2O_3 powder (Z)
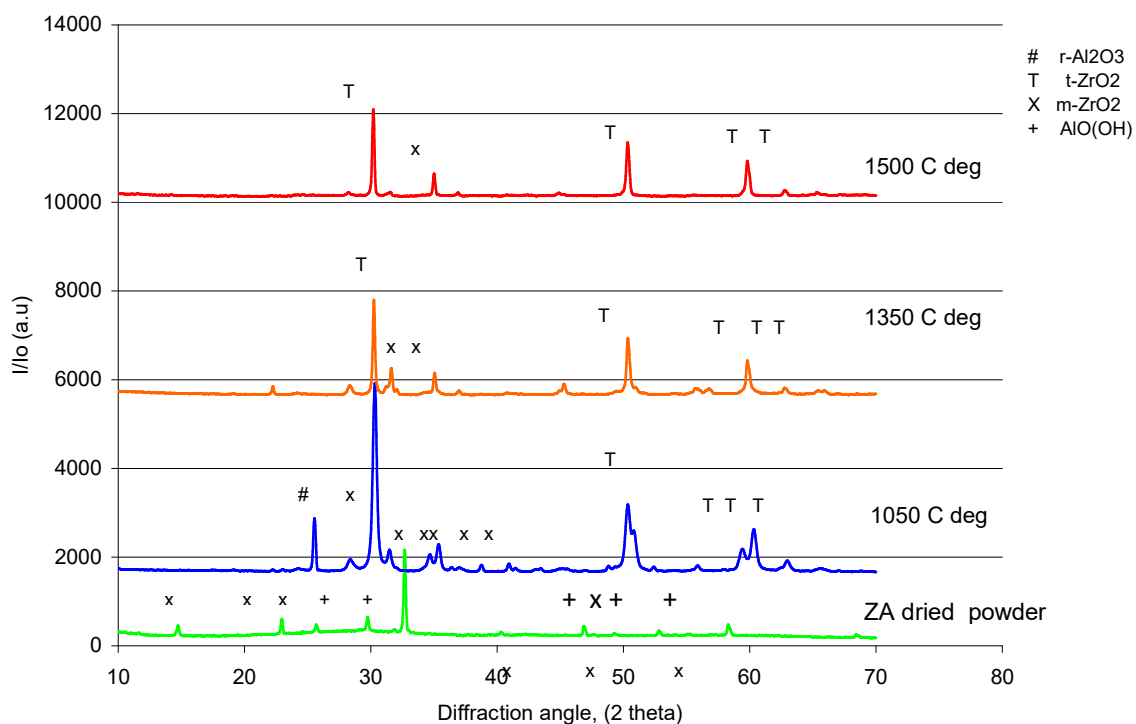   *Diagrame TG / DTA/ DTG pentru pulberea zirconio- aluminoasa ZA sintetizată.*

Fig. 2 -XRD diffraction pattern of starting dried powder Z respectively of sintered powder at 1050°C, 1350°C and 1500°C/
   Difractograma de raze X a pulberii iniţiale uscate Z, respectiv a pulberii sinterizate la 1050 °C, 1350 °C şi 1500 °C.

approximately 49.09% occurs. Between 90º-120ºC water is lost with maximum velocity.

   At 738 ° C, $ZrOCl_2$ decomposes, according to the endothermic effect.

   The endothermic peak at 268ºC corresponds to the transformation of $Al(OH)_3$ and γ-AlOOH into $\gamma - Al_2O_3$ [21].

   The endothermic effect at 738°C could be assigned to decomposition of zirconium hydroxide [22, 23].

   The aluminium hydroxides can exist in four well defined forms: the monohydrate AlOOH, as boehmite (γ-monohydrate) and diaspore (α-monohydrate), and the trihydrate $Al(OH)_3$, as gibbsite (γ-trihydrate) and bayerite (α-trihydrate).

   At high temperatures, all of the heat treatment paths will terminate in α-Al_2O_3 .

3.2. Mineralogical and morphological characteristics

The XRD patterns of the starting powder after drying at 105ºC for 12 hours and sintered at 1050ºC, 1350ºC and 1500ºC respectively are given in Figure 2.

The dried starting zirconia-alumina powder (ZA) consist of monoclinic ZrO_2 and AlO(OH).

At 1050ºC the boehmite has not been transformed into rhombohedral α-Al_2O_3. The amorphous ZrO_2 formed during gel formation is transformed into t-ZrO_2 and m-ZrO_2.

At 1350ºC and 1500ºC, the patterns revealed the presence of α-Al_2O_3 (d = 3.48 Å, 2,55 Å, 2.37 Å, 2.08Å, 1.74 Å, 1.60 Å, 1.40 Å, 1.37 Å,), major amount of t-ZrO_2 (XRD file 90-0784) and small amount of m-ZrO_2 form (d = 3.16 Å, 2,86 Å, 2.65 Å, 2.59 Å, 1.80 Å)

Scanning Electron Microscopy (SEM) images on the surface of sample A after firing at 1050ºC, 1350ºC and 1500ºC are shown in Fig.3-5.

At 1050ºC it can be observed the small size particles of α-Al_2O_3 in 47- 112 nm range within zirconia matrix and large pores (up to 120- 320 nm).

At 1350ºC large pores (300 -760 nm) are embedded in a fine white particles of tetragonal ZrO_2 present.

For the sample sintered at 1500ºC the crystallite growth of t-ZrO_2 was suppressed due to the pinning effect of intergranular alumina after the $\theta \rightarrow \alpha$-$Al_2O_3$ phase transformation, which leaded to a better densification than samples sintered at lower temperatures.
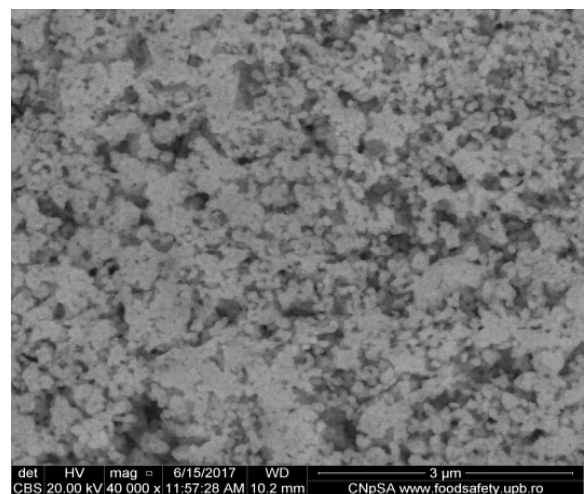
The SEM image reveals that Al_2O_3 particles are present as either intergranular or intragranular in the ZrO_2 matrix, with a larger amount for intergranular particles. These intergranular grains have a major role in the transformation mechanism. In all cases of the samples the Al_2O_3 particles remain mainly at the grain boundaries.
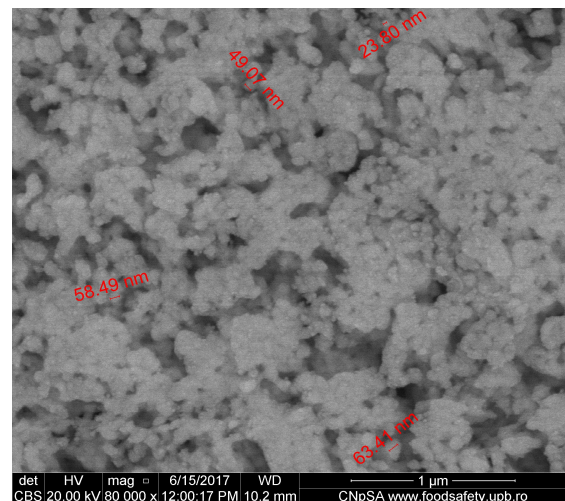

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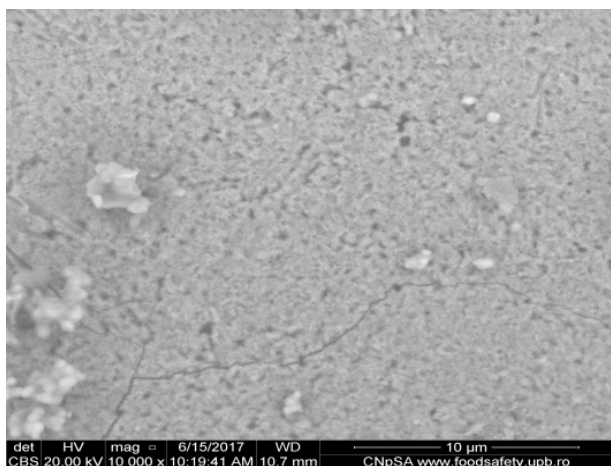

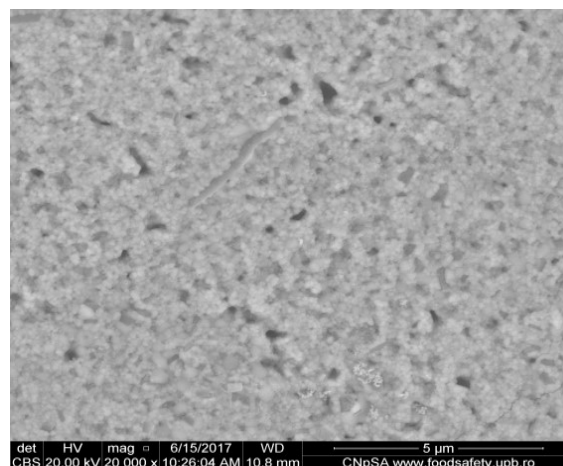Magnification/ Mărire x 40000
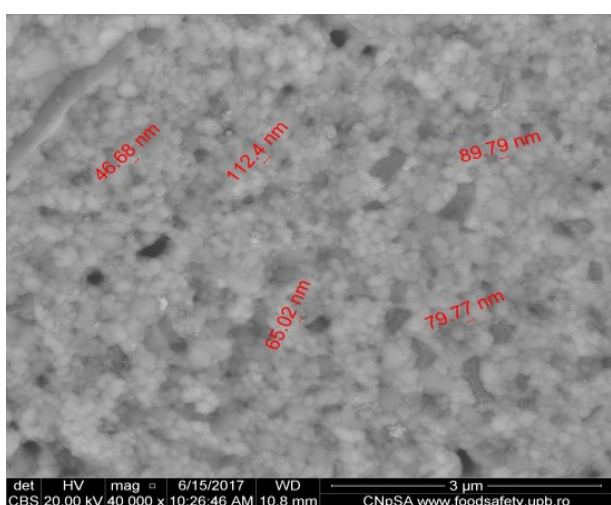

Magnification/Mărire x 80000

Fig.3 - Scanning electron micrographs of the coprecipitated ZrO_2 - Al_2O_3 powder sintered at 1050⁰C with 2 hours soaking time/ Micrografii SEM ale pulberii coprecipitate zirconio-aluminoase sinterizate la 1050 ºC, palier 2 ore.
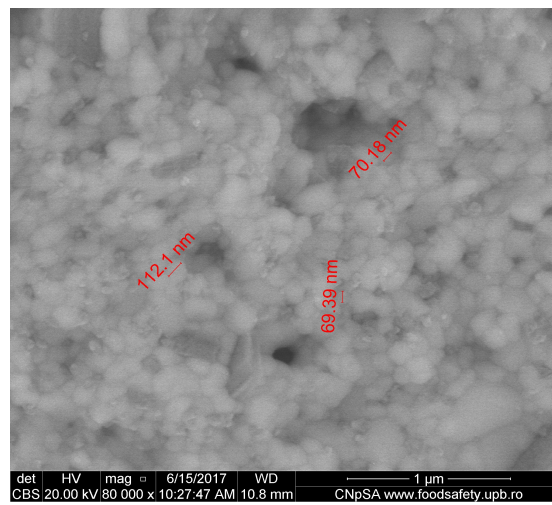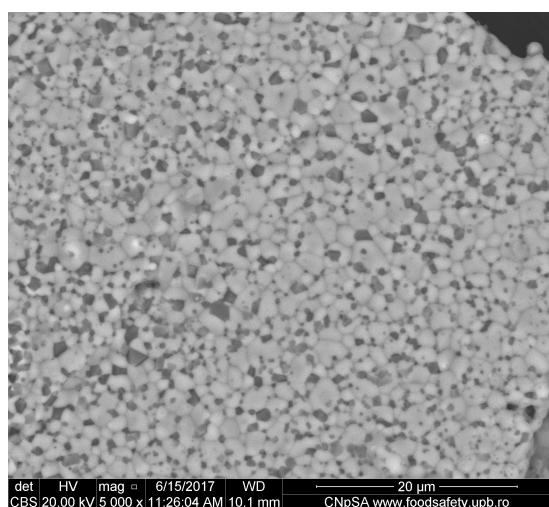

Magnification/ Mărire x 10000

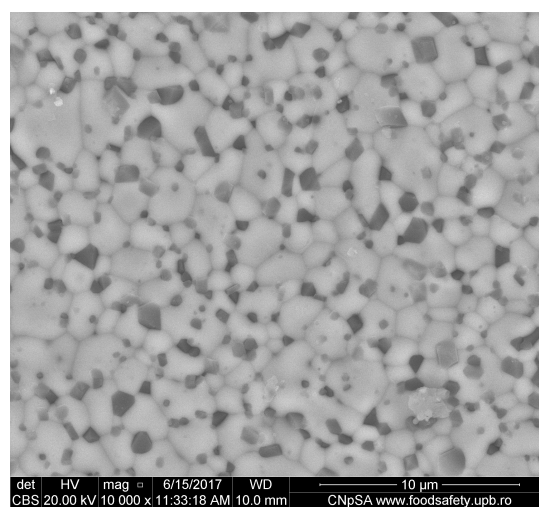Magnification/ Mărire *x 10000*

Magnification/ Mărire *x 20000*

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Magnification/ *Mărire x 80000*

Fig.4 - Scanning electron micrographs of the coprecipitated ZrO_2 -Al_2O_3 powder sintered at 1350^0C with 2 hours soaking time/ *Micrografii SEM ale pulberii coprecipitate alumino-zirconice sinterizate la 1350 °C, palier 2 ore.*

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Magnification/ *Mărire x10000*
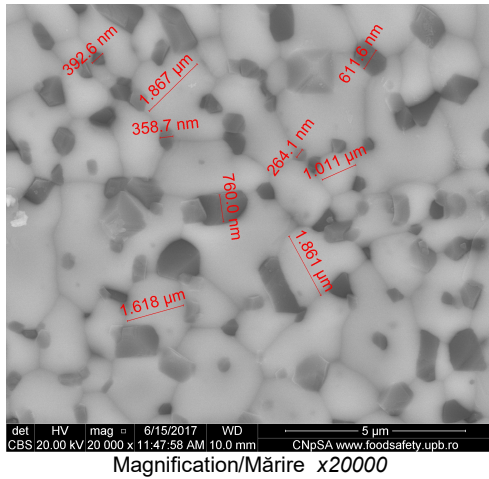
Fig. 5 continues on next page

Magnification/Mărire *x20000*

Fig.5 - Scanning electron micrographs of the coprecipitated ZrO_2- Al_2O_3 powder sintered at 1500^0C with 2 hours soaking time/ *Micrografii SEM ale pulberii coprecipitate zirconio-aluminoase sinterizate la 1500 °C, palier 2 ore*.
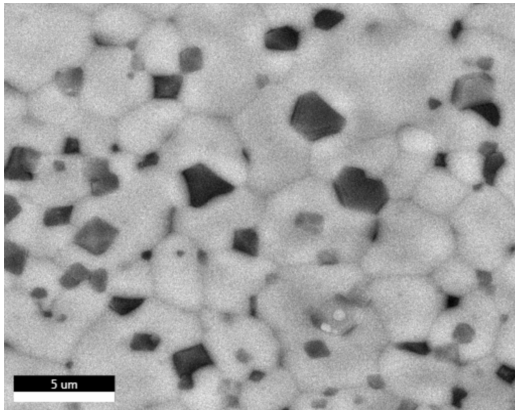

Fig.6 - Global SEM micrograph image of the coprecipitated ZrO_2 -Al_2O_3 powder sintered at 1500^0C /2h. / *Imagine globală SEM a pulberii coprecipitate zirconio-aluminoase sinterizate la 1500 °C, palier 2 ore*
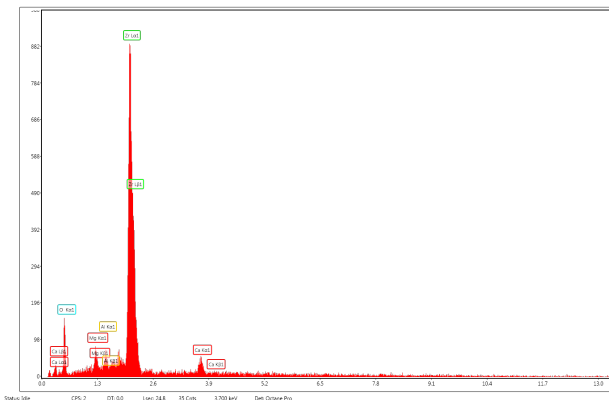

Fig.7 - Global spectrum of component elements: Al, Zr, Ca, Mg, O. A slight impurification with Si could be noticed due to samples manipulation. / *Spectrul global al elementelor componente: Al, Zr, Ca, Mg, O. O uşoară impurificare cu Si poate fi observată după manipularea probelor*.

Densification

At 1500^oC for 2 hours the relative density increases with 19,4 % comparatively with 1350 °C for 2 hours since pore coalescence in zirconia
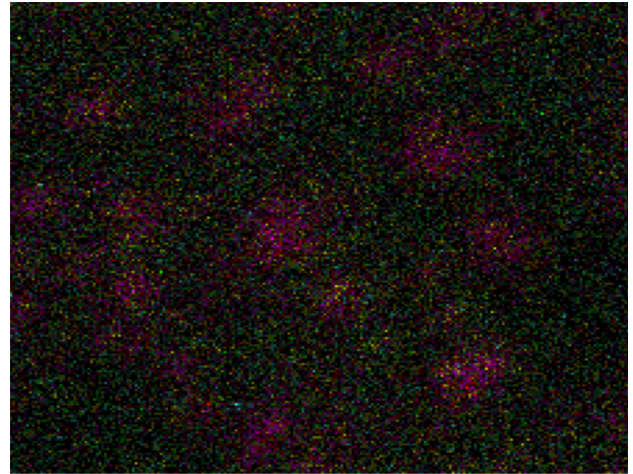

Fig.8 - Assembly image of all component elements distribution / *Imagine de ansamblu a distribuţiei tuturor elementelor componente.*
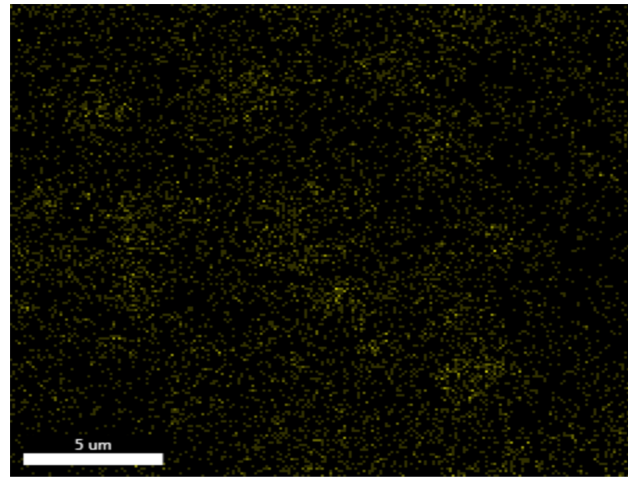

Fig.9 - Distribution of the element OK_α/ *Distribuţia elementului OK_α*
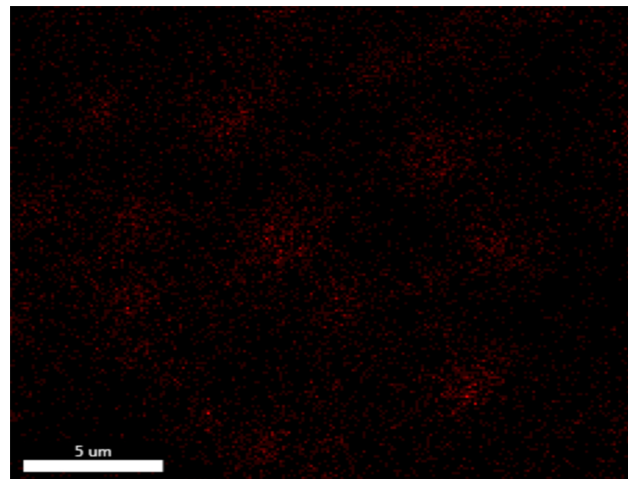

Fig.10 - Distribution of the element $Mg\ K_\alpha$/ *Distribuţia elementului $Mg\ K_\alpha$*

matrix and segregation of alumina particles takes place.

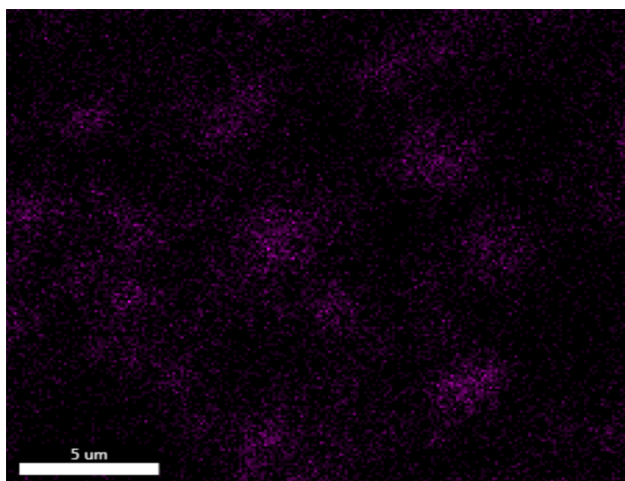*EDS mapping* on ceramic sample surface after sintering at 1500^oC are given in Figures 6-13

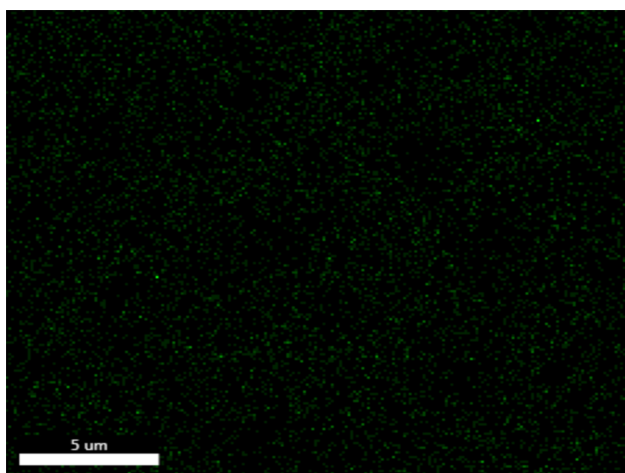Fig.11 - Distribution of the element Al K_α
Distribuţia elementului Al K_α

Fig.12 - Distribution of the element Zr L_α/
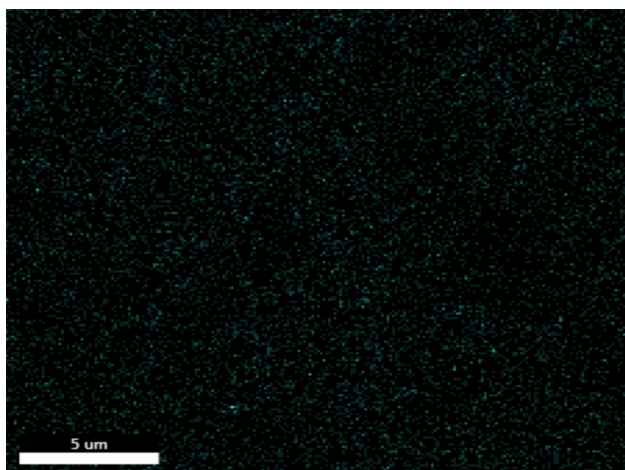*Distribuţia elementului Zr L_α*

Fig. 13 - Distribution of the element Ca K_α/
Distribuţia elementului Ca K_α

with details on distribution of ceramic components: O, Zr, Al, Ca, Mg. These images confirm a very good homogeneity of the composition of the ceramic mass due to the co-precipitation process from salt solutions which allows this by mixing the ionic components of the precursor gels to obtain

the ceramic powder.

3.3. Chemical stability in artificial saliva of coprecipitated alumina – zirconia ceramic

The hydrolytic stability of ceramic samples was tested in Fusayama-Meyer artificial saliva solution. Samples were kept in artificial saliva solution at room temperature for 9, 10 and 12 days under similar temperature conditions.

With a portable HACH (US production) Sension 156 type was measured:
- the pH of the solution
- the electrolytic conductivity (µS / cm)
- the current reading (in mV absolute) in the range - 2000 to 2000 mV.

Conductivity of solutions containing salts or other ions is measured using a special constructive probe specifically created by Hach, equipped with a double conductivity measurement cell allowing it to be measured over the entire measuring range with values between 0.1 µS / cm and 1000 mS / cm. Conductivity is the ability of a material to drive electricity. Positive and negative ions present in a solution will move to opposite sign electrodes when applying an electrical current to it. The displacement of ions in the solution is influenced by both the electrical current and the solvent properties (concentration, viscosity) and their properties (ion size, concentration, load). As the temperature rises, the speed of the ions in the solution increases, thus increasing the conductivity at the same time. Theoretically, a cell with two 1 cm^2 electrodes spaced 1 cm apart is used to measure conductivity. Note with K the constant of the cell that is calculated by the formula:

K = L / A relationship; where:

L= the length of the cell
A = cross-section area

For a standard cell of the type described above, K = 1.0 cm^{-1}. For cells with other dimensions, the value of the constant K is different depending on its size. The Hach conductivity measurement system keeps taking into account the bicellular form of the probe used, no need for a probe specific to the geometry of the cell to be measured. The device also compensates for the temperature variation during the measurement.

The pH of human body fluids is usually within the range of 7.0 - 7.35, while human saliva is slightly acid (pH ~ 5.8). In the oral cavity, extremely low pH values (2.0 - 3.0) can occur in the case of its pathological diseases [24-27].

The evolution of pH artificial saliva solution (initial pH=6.4) versus immersion time of ceramic samples fired at 1350 °C and 1500 °C, respectively is given in Figure 14.

After 216 -288 hours immersion, a variation of artificial saliva solution pH was registered as increasing from 6.4 up to 7.2 - 7.3.
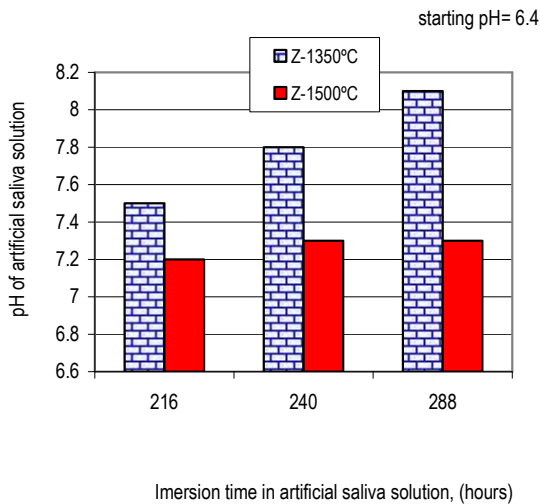
Fig. 14 - Evolution of pH artificial saliva solution (initial pH=6.4) versus immersion time of ceramic samples Z sintered at 1350 ºC and 1500 ºC respectively / *Evoluţia pH-ului soluţiei de salivă artificială (pH iniţial = 6.4) în funcţie de timpul de imersie al probelor ceramice Z sinterizate la 1350 ºC şi respectiv la 1500 ºC.*
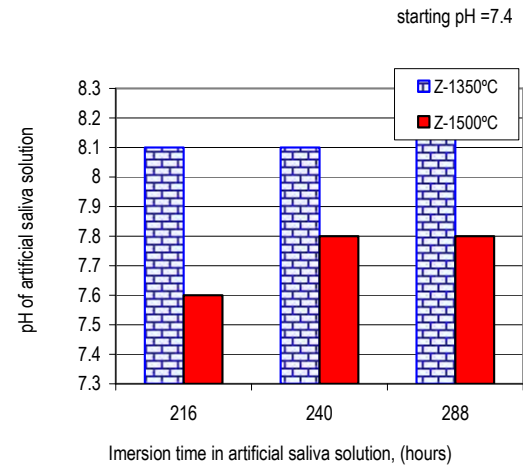

Fig.15 - Evolution of pH artificial saliva solution (initial pH=7.4) versus immersion time of Z ceramic samples fired at 1350 ºC and 1500 ºC respectively / *Evoluţia pH-ului soluţiei de salivă artificială (pH iniţial = 7,4) în funcţie de timpul de imersie al probelor ceramice Z sinterizate la 1350 ºC şi respectiv la 1500 ºC*
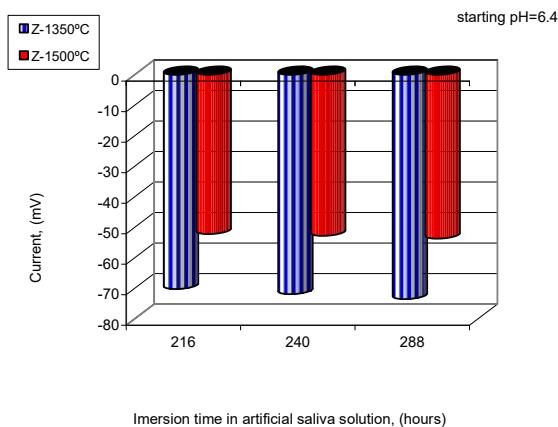

Fig. 16 - Evolution of current measured in artificial saliva solution (initial pH=6.4) versus immersion time of ceramic samples Z sintered at 1350 ºC and 1500 ºC respectively / *Evoluţia curentului măsurat în soluţiade salivă artificială (pH iniţial = 6,4) în funcţie de timpul de imersie al probelor ceramice Z sinterizate la 1350 ºC şi respectiv la 1500 ºC.*
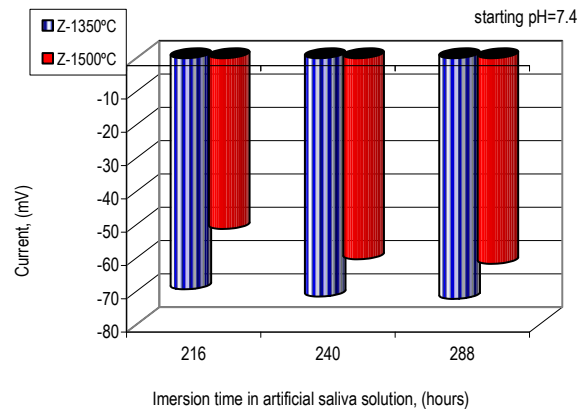

Fig.17 - Evolution of current measured in artificial saliva solution (initial pH=7.4) versus immersion time of ceramic samples fired at 1350 ºC and 1500 ºC respectively / *Evoluţia curentului măsurat în soluţiade salivă artificială (pH iniţial = 7,4) în funcţie de timpul de imersie al probelor ceramice sinterizate la 1350 ºC şi respectiv la 1500 ºC.*

For the second kind of artificial saliva solution (initial pH=7.4), the evolution versus immersion time of ceramic samples fired at 1350 ºC and 1500 ºC respectively is presented in Figure 15.

After the same immersion time in artificial saliva solution, the same behavior of pH was registered a slightly increasing from 7.4 up to 7.6-7.8.

The evolution of current measured (in mV absolute) in artificial saliva solution with initial pH=6.4 versus immersion time of ceramic samples fired at 1350 ºC and 1500 ºC, respectively is showed in Figure 16, while in Figure 17 is given the evolution of current measured in artificial saliva

solution (initial pH=7.4) versus immersion time of the same ceramic samples, respectively.

The measured current in the solution with pH of 7.4 initially was 28.9 mV and after 216, 240 and 288 hours immersion was: -71.9 mV, -75.3 mV and -76.4 mV for the samples sintered at lower temperature, while the sample sintered at 1500 ºC has lower values – 53.8 mV, - 54.6.4 mV and -54.9 mV as shown in Figure 16.

The measured current in the solution with pH of 6.4 initially was 24,5 mV and after 216, 240 and 288 hours immersion was: -72.1 mV, -72.7 mV and -73.1 mV for the samples sintered at lower temperature, while for the sample sintered at 1500 ºC

has lower values – 62.6 mV, -63.1mV and -63.5 mV as shown in Figure 17.

The ceramic samples sintered at 1500 °C show a better chemical stability, as the pH variation is lower when using a starting solution with pH = 7.4 (close to neutral). However, the variation of pH after immersion in artificial saliva is obvious after 216-288 hours due to the ionic transport between ceramic and solution, even sintered at 1500°C.

4. Conclusion

Bioceramics are attractive as biological implants for their biocompatibility. The analysis of the results of corrosion in artificial saliva of zirconia-alumina ceramic composite revealed its superiority due to similarity with bone minerals. In dental applications, dental materials are soaked in saliva, which contains a large number of ions which in turn may accelerate the corrosion of materials. The present study aimed to determine the longterm aging behavior of sintered zirconia -alumina ceramic in Fusayama Meyer artificial saliva. Moreover, the effects of simultaneous admixture of CaO and MgO on the crystalline phases, crystallite sizes and sintering properties of coprecipitated ZrO_2-Al_2O_3 powders after sintering at 1500°C exhibiting a relative chemical stability and are able to be shaped into definite size. However, the variation of pH after immersion in artificial saliva is obvious after 216-288 hours due to the ionic transport between ceramic and the solution, even after sintering at 1500 °C.

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