EFECTUL TANDEMULUI Ca²⁺ şi Mg²⁺ ASUPRA TRANSFORMĂRILOR FAZALE, SINTERIZĂRII ŞI STABILITĂŢII CHIMICE ÎN SALIVĂ ARTIFICIALĂ A BIOCERAMICII ALUMINO - ZIRCONICE
EFFECT OF Ca²⁺ AND Mg²⁺ TANDEM ON PHASE TRANSFORMATION, SINTERING AND CHEMICAL STABILITY IN ARTIFICIAL SALIVA OF ALUMINA – ZIRCONIA BIOCERAMIC

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Alumina and zirconia-based ceramics present reduced wear rates and excellent long-term biocompatibility, which can increase the longevity of the implants.

In this study, the effects of simultaneous admixture of CaO and MgO on the crystalline phases, crystallite sizes and sintering properties of coprecipitated Al_2O_3-ZrO_2 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 Al_2O_3-ZrO_2 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 and cubic phase of zirconia stabilized with Ca²⁺ and Mg²⁺ was effective at 1350 °C and 1500 °C respectively. 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 alumina – zirconia 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.

Ceramica pe bază de alumină și zirconiu prezintă grade reduse de uzură și o biocompatibilitate excelentă pe termen lung, ceea ce poate crește longevitatea lucrărilor protetice. 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 Al_2O_3-ZrO_2 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 alumino-zirconică coprecipitată după sinterizare 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 și cubice de zirconiu în prezența simultană a ionilor Ca²⁺ și Mg²⁺ a fost efectivă la 1350 °C, respectiv 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. În acest context a fost de asemenea investigată, stabilitatea chimică în salivă artificială modificată de tip Fusayama-Meyer a ceramicii alumino - zirconice 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 1500ºC.

Keywords: Zirconia Thoughned Alumina, bioceramic, chemical stability, artificial saliva

1. Introduction

Alumina and zirconia-based ceramics are recommended for load-bearing applications, including hip and knee bearings and dental devices [1-2]. These ceramics present reduced wear rates and excellent long-term biocompatibility, which can increase the longevity of the prosthetic joints.

The alumina oxide used for biomedical applications is typically alfa-alumina, also known as corundum. The molecule of aluminum oxide is characterized by high bond energy with a covalent weight within ionic bonding that makes it one of the most stable oxides. This property makes it inert to galvanic reactions and thus is very stable chemically, even in very acidic or basic conditions at high temperatures. Alumina works very well in compression, but it is brittle under tension. Like most ceramics, alumina does not show (at ambient temperature) plastic deformation before fracture (e.g., no yield strength before fracture in the stress-strain curve), and once started fractures progress very rapidly (low toughness). In general terms, the resistance to traction of alumina improves with higher density and smaller particle size. Alumina producers and researchers, carefully selected raw

materials and the production process is strictly controlled to optimize the mechanical properties [3-5]. Even the presence of NaOH impurities in the powders obtained by the Bayer process, makes them unsuitable for the hi-tech biomedical application.

Biomedical grade zirconia exhibits the best mechanical properties among oxide ceramics, superior of those of alumina [5-7]. In fact, the zirconia fracture toughness is almost double of that of alumina and the strength can reach values around 2 GPa for a fine-grained material. Zirconia ceramics have several advantages over other ceramic materials due to the transformation toughening mechanisms operating in their microstructure [8-11] able to increase the crack propagation resistance in zirconia. By adding suitable a single stabilizers (e.g. Y_2O_3, CeO_2, CaO, MgO, etc) the *tetragonal (t)* phase can be retained at room temperature in a metastable phase, being able to re-transform into the stable *monoclinic (m)* phase under an applied stress. This martensitic transformation (*t* to *m* phase) involves a volume expansion of ~3%–5% and large shear strains (~7%) able to induce compressive stresses at the crack tip and thus to avoid the crack propagation, leading to the well-known toughening effect. Continuous efforts to improve the properties of alumina-zirconia bioceramics have been made, e.g. by introduction of high purity raw materials, hot isostatic pressing, spark plasma sintering, microwaves field sintering [12 - 20].

The low temperature degradation of Zirconia Toughed Alumina in distilled water was investigated in many papers [16 -19]. 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 few information available in the literature about the low temperature degradation of ZTA ceramic in artificial saliva.

In this study, the effects of simultaneous admixture of CaO and MgO on the crystalline phases, crystallite sizes and sintering properties of coprecipitated Al_2O_3- ZrO_2 powders are investigated. The chemical stability in Fusayama Meyer type artificial saliva of sintered alumina – zirconia ceramics was also investigated.

2.Materials and methods

2.1 Preparation of zirconia reinforced alumina ceramic

$ZrOCl_2$ x $8H_2O$ (Merck) and $Al_2(SO_4)_3$ x $18H_2O$ (Chimopar, Romania) were disolved in distilled water to preparare the initial solutions in order to achive for the Al_2O_3-ZrO_2 powder composition a ratio of 85 mole% Al_2O_3 and 15 mole% ZrO_2.

$MgCl_2$ x $6H_2O$ (Chimopar) and $CaCl_2$ x $6H_2O$ (Chimopar) were dissolved in distilled water

and calculated to bring 6% mole MgO and 4% mole CaO to stabilize zirconia. The four starting solutions were mixed and precipitated by adding NH_4OH solution (Chimopar) to achive 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 2 hours range at each maximum curing temperature. The heating and cooling rate was 50 ^{o}C / min, in Nabertherm type owen. 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 analyzes 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 [21] 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
$CO(NH_2)_2$ (ureea)	1.000 g/l.

Fig.1 -TG/DTA / DTG diagrams for the synthesized Al_2O_3- ZrO_2 powder / *Diagrame TG / DTA/ DTG pentru pulberea alumino-zirconică sintetizată.*

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 °C.

3. Results and discussion

3.1. Complex thermal analysis of coprecipitated Al_2O_3- ZrO_2 powder

The TG / DTA /DTG diagrams for the synthesized Al_2O_3- ZrO_2 powder are shown in Figure 1.

The complex thermal analysis of the ceramic powder indicates for the entire heating range a mass loss of 77.74%.   The endothermic peak at 105°C corresponds to the loss of physically bonded water, whereas, the exothermic peak at 290°C is attributed to the crystallization of t-ZrO_2 [22]. The endothermic peak at 309°C corresponds to the transformation of $Al(OH)_3$ and γ-AlOOH into $γ – Al_2O_3$.

The endothermic   decomposition which undergoes at 332-346 °C is attributable to the magnesium hydroxide, according to the equation:

$$Mg(OH)_2 → MgO + H_2O$$

The thermal decomposition of calcium hydroxide produces calcium oxide and water. This reaction takes place at a temperature of 520-580°C, with a maximum rate at 534 °C.

$$Ca(OH)_2 → CaO + H_2O$$

The very weak endothermic effect at 711°C and 786 °C could be assigned to decomposition of zirconium hydroxide [23].

The formation of α-Al_2O_3 occurs at 1200 °C with a small exothermic peak [24]. The phase transformation from γ -AlOOH to α -Al_2O_3 takes place according to the following the reactions: [25]

$$γ –AlOOH \xrightarrow{400°C} γ\text{-}Al_2O_3 \xrightarrow{800°C} δ\text{-}Al_2O_3 \xrightarrow{1000°C}$$

$$\xrightarrow{} θ\text{-}Al_2O_3 \xrightarrow{1200°C} α\text{-}Al_2O_3$$

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 [26].

Beside alpha(α) -Al_2O_3, there are other forms of metastable Al_2O_3 structures, such as: gama (γ), delta(δ), theta (θ), eta (η), chi (χ) and

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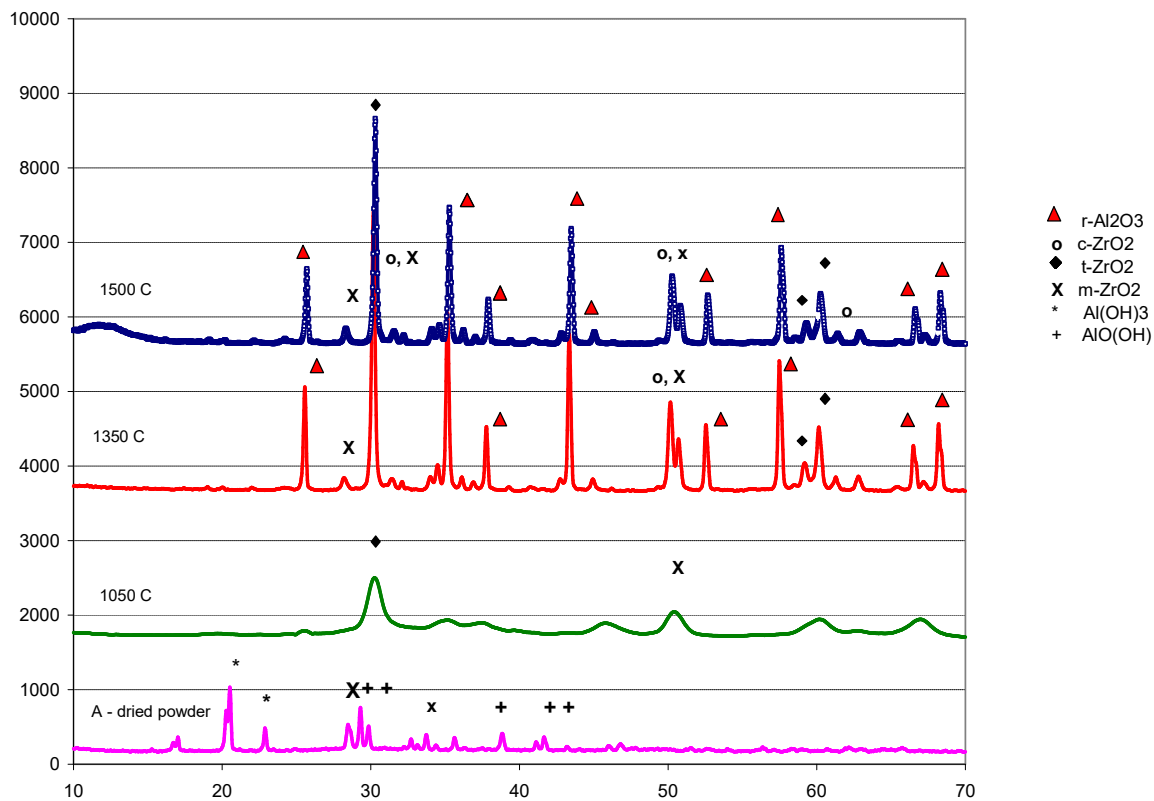and chemical stability in artificial saliva of alumina – zirconia bioceramic
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Fig. 2 - XRD diffraction pattern of starting dried powder A, respectively of sintered powder at 1050°C, 1350°C and 1500°C/
Difractograma de raze X a pulberii iniţiale uscate A, respectiv a pulberii sinterizate la 1050 °C, 1350 °C şi 1500 °C

kappa (k) -Al_2O_3. Those kinds of transition Al_2O_3 can be produced from heat treatment of aluminium hydroxides or aluminium salts [3]. It is observed the reduction of specific volume in the phase transformation of boehmite (0.332 cm^3/g) to α - Al_2O_3 (0.251 cm^3/g), which assists the structure of meso-porous particles [3].

It is expected that finer particles will reduce the transformation temperature due to a very high specific surface area.

3.2. *Mineralogical and morphological characteristics*

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

The dried starting alumina zirconia powder (A) consist of AlO(OH) and Al(OH)₃ and amorphous ZrO_2.

At 1050°C the boemite and Al(OH)₃ has not been transformed into roemboedral α-Al_2O_3, the alumina being still mainly amorphous. The amorphous ZrO_2 formed during gel formation which is transformed into t-ZrO_2 and m-ZrO_2.

At 1350°C and 1500°C, 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)

However, after sintering at 1350°C and 1500°C, some minor amount of cubic ZrO_2 (c-ZrO_2) (d = 2.96 Å, 2.82 Å, 2.54 Å, 1.80 Å, 1.53 Å) occurs due to the simultaneous presence of Ca²⁺ and Mg²⁺ as stabilizator oxides for zirconia and the mass transport was improved during solid state sintering, and ceramics reached better densification at lower temperatures.

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

At 1050°C it can be observed the precipitation of smaller size particles of c-ZrO_2 and t-ZrO_2 (35-50 nm) within the α-Al_2O_3 matrix and large pores (up to 350-400 nm) .

The average grain size of alumina varies from 0.5 μm to 1.5 μm and fairly homogeneous in the entire matrix.

At 1350°C large pores (0.1- 0.5 μm), fine white particles of c-ZrO_2 and t-ZrO_2 embedded within the coarse α-Al_2O_3 grains are present due to the development of a coarse, vermicular pore structure (dark) during transformation to α- Al_2O_3 revealed as grey grains.

For the sample sintered at 1500°C the crystallite growth of α-Al_2O_3 was suppressed due to the pinning effect of intergranular cubic and tetragonal ZrO_2 after the θ→α-Al_2O_3 phase
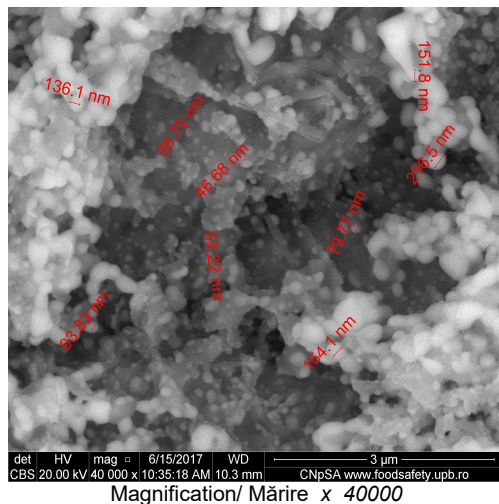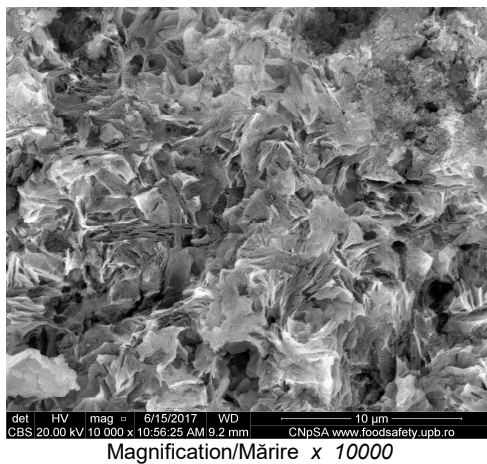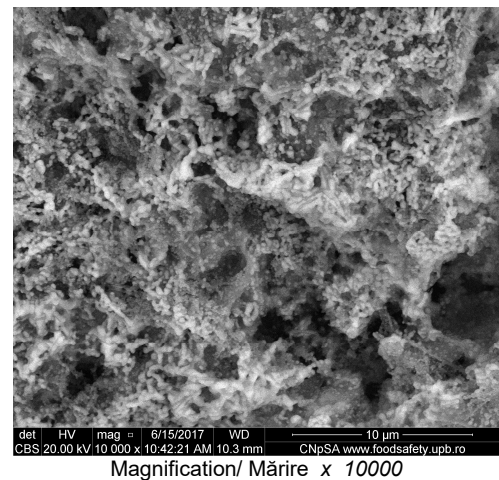
Magnification/ Mărire *x 5000*

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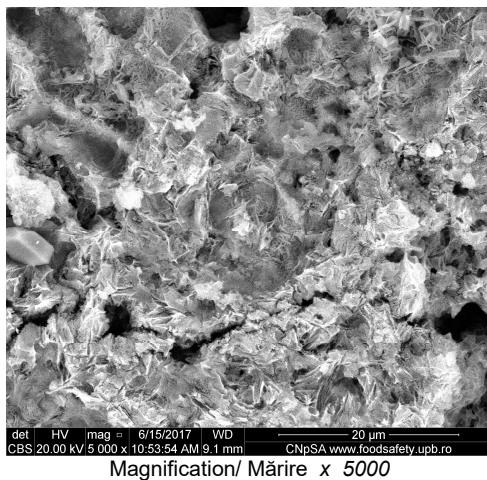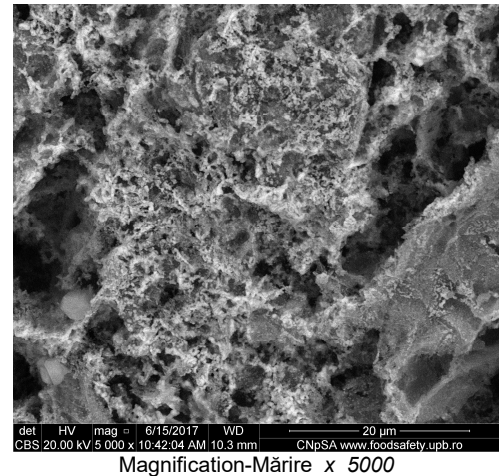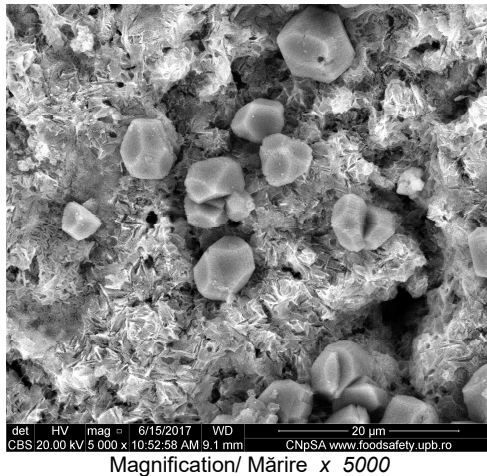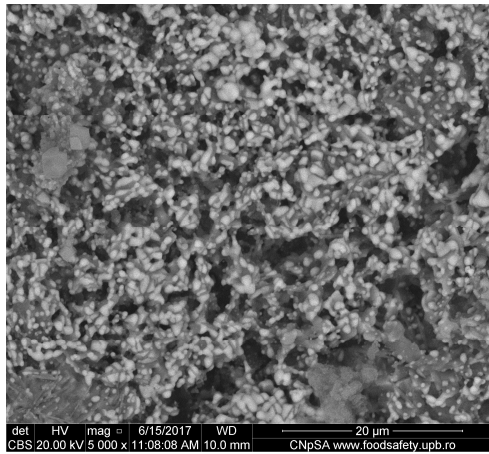

Magnification/ Mărire *x 10000*

Magnification/Mărire *x 10000*

Fig.3 - Scanning electron micrographs of the coprecipitated Al$_2$O$_3$-ZrO$_2$ powder sintered at 1050^{0}C with 2 hours soaking time/ *Micrografii SEM ale pulberii coprecipitate alumino-zirconice sinterizate la 1050 °C, palier 2 ore.*
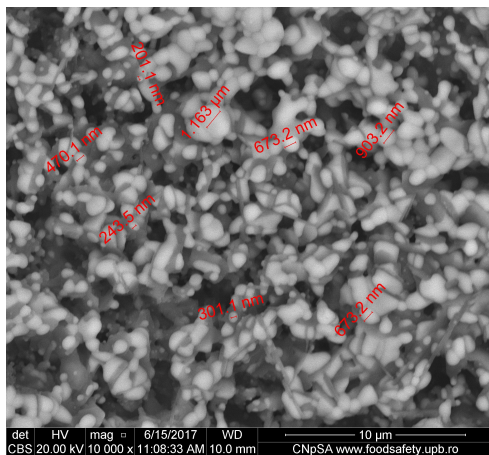

Magnification/ Mărire *x 40000*

Fig.4 - Scanning electron micrographs of the coprecipitated Al$_2$O$_3$-ZrO$_2$ powder sintered at 1350^{0}C with 2 hours soaking time/ *Micrografii SEM ale pulberii coprecipitate alumino-zirconice sinterizate la 1350 °C, palier 2 ore .*

transformation, which leaded to a better densification than samples sintered at lower temperatures.

The SEM image reveals that ZrO$_2$ particles are present as either intergranular or intragranular in the Al$_2$O$_3$ 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 ZrO$_2$ particles remain mainly at the grain boundaries and cannot be observed within the alumina matrix grains.

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Magnification/ Mărire *x5000*

Magnification/ Mărire *x10000*
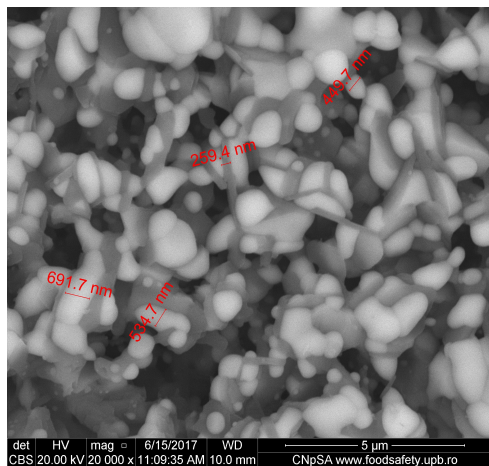
Magnification/Mărire *x20000*

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

Densification

At 1500^oC for 2 hours the relative density increases from 58% at $1350\ ^oC$ for 2 hours to 72%, since pore coalescence in alumina matrix and segregation of zirconia particles takes place.

EDS mapping on ceramic sample surface after sintering at 1500^oC are given in Figures 6-13
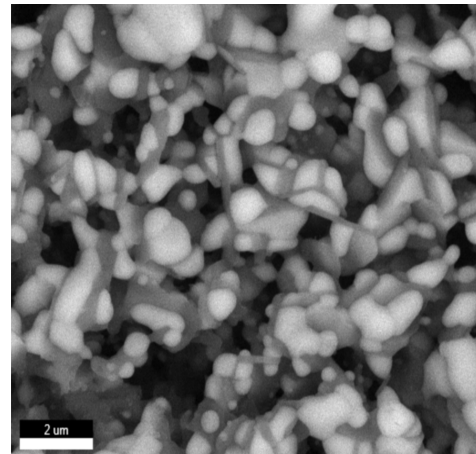
Fig.6 - Global SEM micrograph image of the coprecipitated Al_2O_3-ZrO_2 powder sintered at 1500^0C /2h. / *Imagine globală SEM a pulberii coprecipitate alumino-zirconice sinterizate la 1500 °C, palier 2 ore*
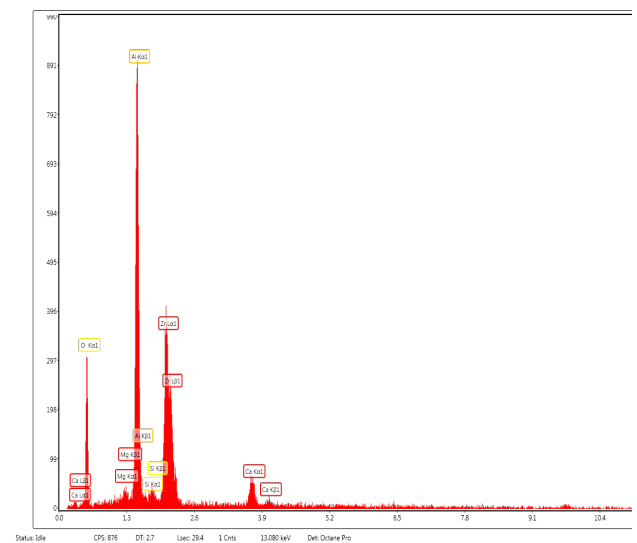
Fig.7 - Global spectrum of component elements: Al, Zr, Ca, Mg, O. A slight impurification with Si could be noticed due to samples manipulation. / *Spectrul global al elementelor componente: Al, Zr, Ca, Mg, O. O uşoară impurificare cu Si poate fi observată după manipularea probelor.*
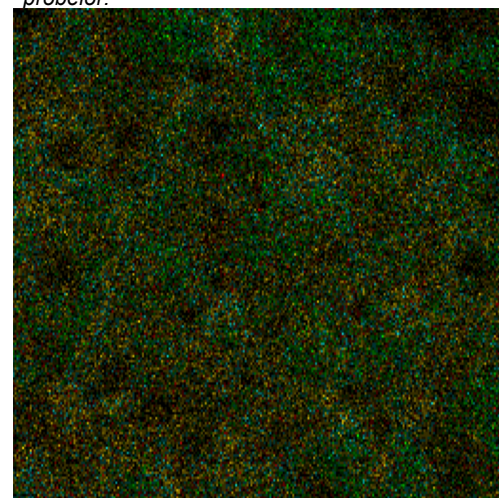

Fig.8 - Assembly image of all component elements distribution / *Imagine de asamblare a distribuţiei tuturor elementelor componente.*
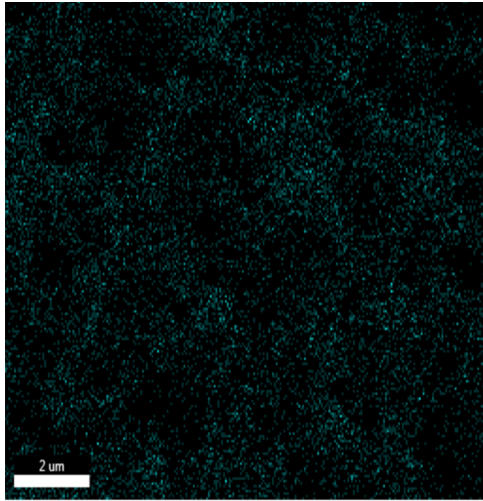
Fig.9 - Distribution of the element OK_α
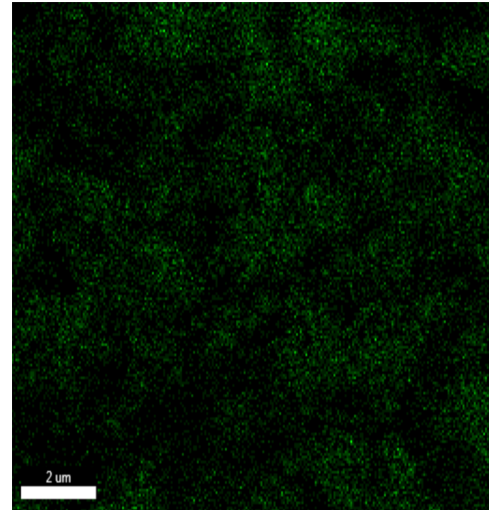*Distribuţia elementului OK_α*

Fig.12 - Distribution of the element $Zr\ L_\alpha$
Distribuţia elementului $Zr\ L_\alpha$
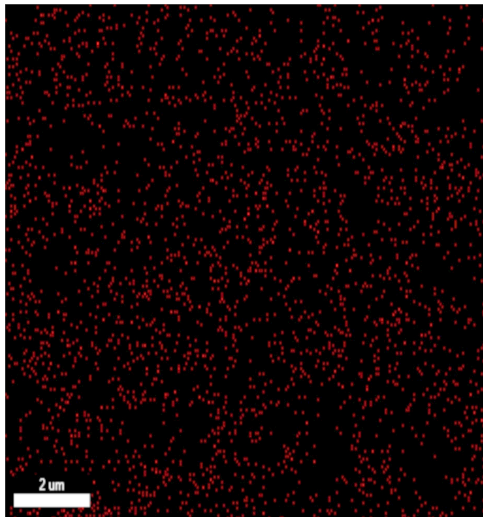
Fig.10 **-** Distribution of the element $Mg\ K_\alpha$
Distribuţia elementului $Mg\ K_\alpha$
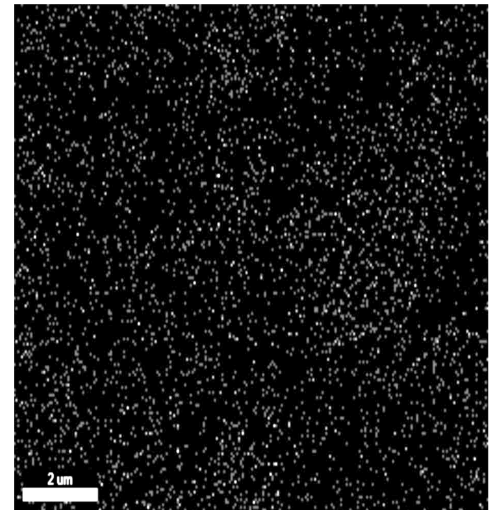
Fig. 13 - Distribution of the element $Ca\ K_\alpha$
Distribuţia elementului $Ca\ K_\alpha$

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.

Fig.11 - Distribution of the element $Al\ K_\alpha$
Distribuţia elementului $Al\ K_\alpha$

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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 cm² 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 [27-29].

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 7.8-7.9.

For the second kind of artificial saliva solution (initial pH=7.4), the evolution versus immersion time of ceramic samples fired at 1350 °C and 1500 °C 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 7.9-8.0.

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 °C and 1500 °C, respectively is showed in Figure 16, while in Figure 17 is given the
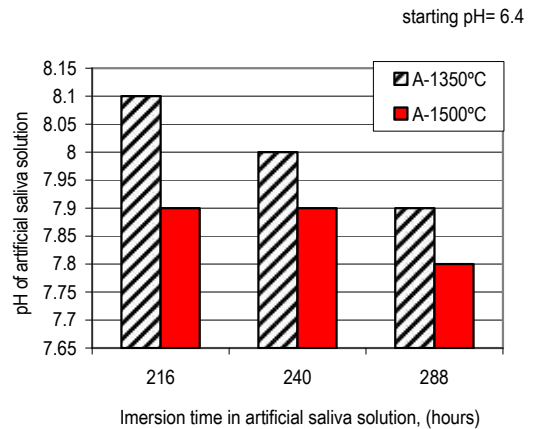

Fig. 14 - Evolution of pH artificial saliva solution (initial pH=6.4) versus immersion time of ceramic samples sintered at 1350 °C and 1500 °C respectively / *Evoluţia pH-ului soluţiei de salivă artificială (pH iniţial = 6,4) în funcţie de timpul de imersie al probelor ceramice sinterizate la 1350 °C şi respectiv la 1500 °C.*
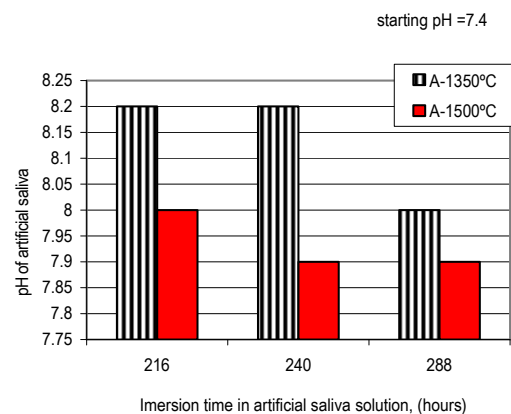

Fig.15 - Evolution of pH artificial saliva solution (initial pH=7.4) versus immersion time of ceramic samples fired at 1350 °C and 1500 °C respectively / *Evoluţia pH-ului soluţiei de salivă artificială (pH iniţial = 7,4) în funcţie de timpul de imersie al probelor ceramice sinterizate la 1350 °C şi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

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 23,3 mV and after 216, 240 and 288 hours immersion was: -72.1 mV, -75.3 mV and -76.4 mV for the samples sintered at lower temperature, while the sample sintered at 1500 °C has lower values - 60.1mV, -60.4 mV and -60.6 mV as shown in Figure 16.

The measured current in the solution with pH of 6.4 initially was 23,9 mV and after 216, 240 and 288 hours immersion was: -75.3 mV, -75.5 mV and -76.4 mV for the samples sintered at lower temperature, while for the sample sintered at 1500 °C
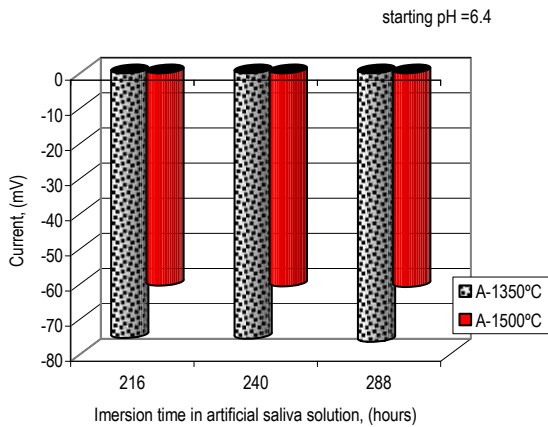
starting pH =6.4

Fig. 16 - Evolution of current measured in artificial saliva solution (initial pH=6.4) versus immersion time of ceramic samples 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 sinterizate la 1350 °C şi respectiv la 1500 °C.*
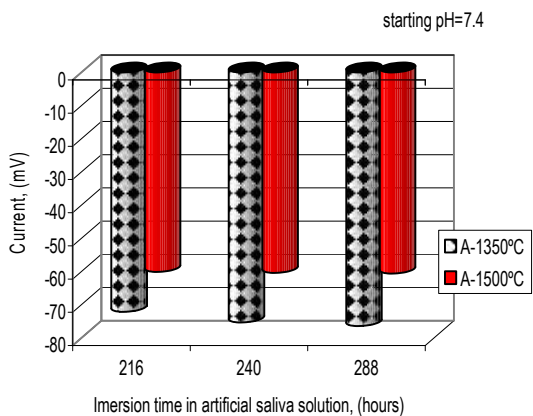
starting pH=7.4

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 °C şi respectiv la 1500 °C.*

has lower values - 60.4mV, -60.6 mV and -60.8 mV as shown in Figure 17.

The ceramic samples sintered at 1500 ºC 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 1500ºC.

4. Conclusion

The co-precipitation method ensures the homogeneity and magnitude of the nanometric initial granules of the sample and good compatibility after sintering at 1500ºC.

MgO and CaO used in tandem have a double role: stabilize zirconium oxide and are biocompatible with bone mineralogy. Hence the biological activity of bioceramics has to be understood through various in vitro and in vivo studies and the knowledge on mechanical feature would join its hand to play a key role for the choice of the bioceramic in accord to the site of implantation and their broad implication as implants.

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