1. Introduction

During the last years many researches have been devoted to develop and improve the properties of hydroxiapatite (HAP) like bioeconomic materials. HAP based implants present important advantages such as: high biocompatibility, bioactivity and less influence on biodegradation [1-5]. However, the utilisation of hydroxiapatite is limited by the brittleness and the fracture toughness \( K_{IC} \) is 1.0 MPa-m\(^{1/2}\) (comparatively with the human bones: 2 - 12 MPa m\(^{1/2}\)). Additionally the Weibull modulus \( n \) is low in wet environment \( n = 5 - 12 \), which leads to a weak structure of the HAP implants [2].

No HAP ceramics could be used as high load resistant implants, such as: tooth and artificial bones. Their applications are limited to small implants, powders for layers deposition and porous implant with low strength.

Recently, Pramatarova et al. [12] have shown that Ca and P ion-beam patterning carried on various substrates yielded by simple soaking in simulated body fluid, the growth of a sponge-like Co3 containing HA layer on the non-ion implanted areas, and a flat dense layer with white CaP particles on the implanted areas.

In order to improve the mechanical strengths of HAP ceramics were used various reinforcing materials (ceramics, metals or polymers). The aim of this work is to investigates the influence of zirconia addition to a HAP matrix on mechanical strengths and the interaction mechanism between zirconia and its polymorphs with calcium phosphates after sintering at 1250 °C.

2. Experimental method

Stabilised zirconia powder (95% ZrO\(_2\)+HfO\(_2\), 4%CaO, \( d_m = 0.9 \) μm) and hydroxiapatite (99.9% Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\), Fluka) mixtures batches were prepared according to Table 1, was homogenised, wetted with isopropil alcohol and pressed uniaxially at 15 MPa.

After drying the powder mixtures (were passed through a 0.09 mm sieve. The batches were pressed as cylinders (\( \phi = h = 18 \) mm). The specimens were cured at 1250 °C in air in electric kiln, during 4 hours at maximum temperature.

A TUR-4 diffractometer with Cu \( K_\alpha \) radiation was used to analyse the developed mineralogical phases. The particles size distribution of the powders was determined by using a laser granulometer (Fritsch). The sintering bulk density was measured by the hydrostatic method. A Hitachi S 2600N scanning electron microscope (SEM) incorporating a microanalysis detector for energy dispersive X-rays (EDAX) was used to observe the surface microstructure of samples.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>ZrO(_2) (% by weight)</th>
<th>HAP (% by weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Z2</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>Z3</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Z4</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Z5</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>

3. Results and discussions

3.1. Ceramic properties

The ceramic properties of zirconia-HAP composites (Z1 – Z5) after sintering at 1250 °C are given in Table 2. It could be noticed a non-monotone evolution (with a minimum value) for the composition Z2 with 30% ZrO\(_2\), both in the case of water absorption and of open porosity. The same composition has the best densification. This increasing of porosity (excepting the composition with 40% ZrO\(_2\)) is due probably to the HAP\(\rightarrow\) β- TCP transformation and to the martensitic transformation of zirconia \( t \leftrightarrow m \) ZrO\(_2\). Concerning the mechanical
behaviour, the best value are developed by the composite with 40% ZrO₂, indicating a better compactness of the structure.

Table 2. Ceramic properties of zirconia-HAP composites after sintering at 1250 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk density (g/cm³)</th>
<th>Water absorption (%)</th>
<th>Open porosity (%)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>2.51</td>
<td>7.5</td>
<td>18.33</td>
<td>115.4</td>
</tr>
<tr>
<td>Z2</td>
<td>2.39</td>
<td>10.9</td>
<td>26.33</td>
<td>51.5</td>
</tr>
<tr>
<td>Z3</td>
<td>2.80</td>
<td>3.56</td>
<td>10.00</td>
<td>200</td>
</tr>
<tr>
<td>Z4</td>
<td>2.27</td>
<td>13.3</td>
<td>29.60</td>
<td>58.2</td>
</tr>
<tr>
<td>Z5</td>
<td>2.24</td>
<td>15.4</td>
<td>34.33</td>
<td>62.9</td>
</tr>
</tbody>
</table>

3.2. Structural evaluations

3.2.1. Crystalline structure

X-ray diffraction analysis was performed to determine the unit cell parameters for HAP considering the peaks of (212), (312), (213), (410), (004) and (502) and for tricalcium phosphate β-TCP using (006), (300), (202), (104) (214) interference.

The increasing of ZrO₂ content in the samples fired at 1250 °C leads to a different behaviour for the lattice parameters, namely decreasing of a and an increases of c) (Fig. 1). This phenomenon should be determined by the dehydroxylation and the transformation in oxyhydroxyapatite. However, this modification of elementary cell was observed in presence of ZrO₂, and the x-ray diffraction analysis the presence of HAP also, consequently this variation would be attributed to the elimination of CO₂ groups present in hydroxyapatite.

β-TCP presents a stronger contraction of elementary cell, parallel with the increasing of ZrO₂ amount (Fig. 2).

This behaviour could be explained on the basis of the possible reaction of hydroxyapatite and unstabilised ZrO₂:

\[
\text{Ca}_5(\text{PO}_4)(\text{OH})_2 + \text{ZrO}_2 \rightarrow \text{Ca}_3(\text{ZrO}_2)(\text{PO}_4)_2 + \text{H}_2\text{O} \quad (1')
\]

(additional to the standard reaction (1)):

\[
\text{Ca}_5(\text{PO}_4)(\text{OH})_2 \rightarrow 3\text{Ca}_3(\text{PO}_4)_2 + \text{CaO} + \text{H}_2\text{O} \quad (1^a)
\]

![Fig. 1. Variation of unit cell parameters of hexagonal HAP versus ZrO₂ content in hydroxyapatite – zirconia composites after sintering at 1250 °C.](image1)

![Fig. 2. Variation of unit cell parameters of β-TCP in hydroxyapatite – zirconia composites versus ZrO₂ content after sintering at 1250 °C.](image2)

Strongly decrease of HAP amount and the increase of β-TCP amount might be determined by the formation of CaZrO₃ solid solution and of the corresponding amount of de β-TCP, and the H₂O loss could help partially to the developing of porous structure of the material.

Two other reactions should be considered, according to which the formation of CaZrO₃ as secondary product is possible:

\[
\text{Ca}_5(\text{PO}_4)(\text{OH})_2 + \text{ZrO}_2 \rightarrow \beta\text{Ca}_3(\text{PO}_4)_2 + \text{CaZrO}_3 \quad (2)
\]

\[
\beta\text{Ca}_3(\text{PO}_4)_2 \rightarrow \alpha\text{Ca}_3(\text{PO}_4)_2 \quad (3)
\]

These reactions are not arc were not certain, related to the discussed, because the CaZrO₃ is on the X-ray diffraction detection limit and the amount of a – TCP is very small. The formation of TCP (β or α) on HAP and ZrO₂ interface might determine some functional negative aspects, because is dissolving more rapidly in physiological fluids.

In the case of totally stabilised zirconia addition the situation is dramatically changed, and the reaction (1) doesn’t take place practically, due to the presence of stabilised form of zirconia. This fact, explain the presence of HAP in high amount in the initial composites, detected by x-ray diffraction, instead of a heat treatment at 1250 °C during 4 hours. On the samples with totally stabilised ZrO₂ show no maxim peaks characteristic CaZrO₃, consequently the reaction (2) doesn’t have any role in the TCP development. At the same time the amount of α- TCP is very low.

The small shift of the specific peaks of HAP suggests a potential formation of some solid solutions between zirconia and HAP based on a substitution mechanism. This mechanism implies the substitution of two calcium ions from the lattice of HAP phase with a zirconium ion from the ZrO₂ phase (2Ca²⁺ ↔ Zr⁴⁺) during the sintering process. The substitution reaction 2Ca²⁺ ↔ Zr⁴⁺ can be expressed as:

\[
\text{Ca}_5(\text{PO}_4)(\text{OH})_2 + n\text{ZrO}_2 \rightarrow \text{Zr}_n\text{Ca}_{5-n}(\text{PO}_4)(\text{OH})_2 + 2n\text{Ca}^{2+} \quad (\text{solid solution})
\]
The possible embedding of Zr$^{4+}$ ion within the HAP lattice as a result of the substitution Zr$\rightarrow$Ca, might be a consequence of its smaller ionic radius (0.080 nm) as compared with that of Ca$^{2+}$ (0.099 nm) that favours the partial substitution of Ca$^{2+}$ with Zr$^{4+}$. In this way is also reduced the crystallinity degree of HAP and thus a higher potential reactivity.

### 3.2.2. Microstructure

The microstructure of HAP-ZrO$_2$ composites after sintering versus ZrO$_2$ content was investigated by scanning electron microscopy (SEM). In addition, the intensities of Ca, P and Zr were compared by EDAX. The analysis has been performed both on sintered HAP and on composites with ZrO$_2$. In Fig. 3(a) (HAP free of ZrO$_2$) can be observed the presence of a basic matrix with traces of melting that still retains the shape of boundary limits (dark zone). In the HAP clusters one can distinguish several contact zones as bridges between two or more special HAP grains, showing a remarkable increase of the (1.2 – 2.5 µm). A significant part of tubular pores collapsed in isolated pores. The coincidence of grain growth transition with tubular pores collapsing into isolated pores is in agreement with the idea of limited grain growth by pores mobility. The EDAX spectrum - Fig. 3(b) records the typical maximum for Ca and P of HAP, being complementary with x-ray diffraction data.

The composite with lowest ZrO$_2$ content exhibits a unique rounded grain growth (3-5 µm) - Fig. 3(c). The basic zone is formed from elongated grains with several areas with connecting bridges and elliptical pores. Dimensional variation of particles or pores from the inner zone can determine the growth of larger particles on the expenses of the lower size particles. EDAX spectrum - Fig. 3(d) records the maxim for Ca, P and Zr. For the composite with 30% ZrO$_2$ only minor differences is recorded.

![Fig. 3. SEM micrographs and EDAX signals of HAP (a,b) and on HAP-ZrO$_2$ composites: Z1(c,d), Z3 (e,f) and Z5 (g,h) sintered at 1250°C.](image-url)
An amount of ZrO$_2$ (40\%) in composite Z3 leads to a longitudinal parallel structure and alignment that crosses the visual field. Several morphologies of HAP and β-TCP can be observed in the initial HAP grains - Fig. 3(e). EDAX spectrum – Fig. 3(f) of composite Z3 shows its enrichment in Ca, P and Zr.

Micrographs of composites Z4 reveals two separate phases of rounded HAP aggregates (bright zone) with traces of grain boundaries (Fig. 3(g)) and typically precipitated grains (0.1 µm) probably belonging to tetragonal ZrO$_2$ stabilised with Ca. It seems that a higher proportion of ZrO$_2$ blocks the growth of HAP grains. Thus two types of phases are present: one non-crystalline produces during sintering with a smooth surface and a phase with plate shape crystals.

The EDAX spectrum of the agglomerated zone on composite Z4 is characterised by enhanced intensity for the maximum of Zr and lower intensity for the peaks of P and Ca - Fig. 3(b). This fact is in agreement with those recorded for the composites with low ZrO$_2$ content and suggests that crystalline phases that are growing are made of a combination of different crystalline components.

### 4. Conclusions

The results highlighted the possibility of mechanical properties improvement for hydroxiapatite matrix composites cured in air at 1250°C.

An interaction mechanism between zirconia and its polymorphs with calcium phosphates that exists or is formed after sintering is discussed.

The nature and amount of reinforcing zirconia seem to have a great influence and determine major changes of ceramic properties of hydroxiapatite matrix composites.

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**References**


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