INFLUENCE OF PH ON SYNTHESIS OF $\alpha$-TRICALCIUM PHOSPHATE BY SELF-PROPAGATING COMBUSTION SYNTHESIS

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Abstract. The biomaterials most used as bone substitutes are the bioceramics based on calcium phosphates, with the emphasis on hydroxyapatite and tricalcium phosphates (TCP). The objective of this work is to obtain $\alpha$-tricalcium phosphate by the self-propagating combustion synthesis. The self-propagating combustion synthesis can be considered as faster and simpler as other methods. Besides, it allows achieving nanometric, homogeneous and highly crystalline powders, without contamination. In the present paper the influence of the synthesis pH on the phase composition was investigated, by means of the X-ray diffraction technique. The size of particles was assessed by means of laser diffraction transmission electron microscopy. The major presence of the $\alpha$-TCP phase was confirmed by X-ray diffraction. The pH synthesis influences the final product, as the lower the pH the more favorable is the formation $\alpha$-tricalcium phosphate. The highest pH, near to 6.5, favors the formation of hydroxyapatite.

Keywords: calcium phosphate, bioceramics, self-propagating combustion synthesis

1. INTRODUÇÃO

Bioceramics based on calcium phosphate, emphasizing hydroxyapatite and tricalcium phosphates (TCP), are the most used bone substitute biomaterials. The $\alpha$ tricalcium phosphate phase [Ca$_3$(PO$_4$)$_2$], when blended with an aqueous solution to form a paste, which reacts yielding a precipitate containing hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$). Such a paste is known as $\alpha$-TCP bone cement. The chemical and morphological similarity between this biomaterial and the mineral part of the bone tissues allows the osteoconduction. With time, the cement is replaced by a new bone tissue, with the advantage of not deflagrating inflammatory processes or rejection of a foreign body, with the eventual expulsion of the implanted material.

Hydroxyapatite (HA) or $\beta$-TCP powders, to be applied in the area of bioceramics, are generally synthesized as aqueous solutions [1]. It is known that hydroxyapatite is the least soluble and most stable calcium phosphate in aqueous solutions at a pH higher than 4.2 [2]. Hydroxyapatite is synthesized both in neutral and high alkalinity media [3], in order to assure the thermal stability of the phase formed after high temperature (1100-1300°C) sintering. The synthesis of pure HA in a neutral [4] or slightly acid [5] media is a more difficult task, occurring normally the appearing of the $\beta$-TCP phase. Conversely, $\alpha$-TCP is a metastable phase and can only be obtained after the thermal treatment of the $\beta$-TCP. In such treatment, $\beta$-TCP is heated at 1250°C for 15 hours, followed by a thermal shock, yielding a material composed mainly of the $\alpha$-TCP phase [6].

The Self-Propagating Combustion Synthesis (SPCS) is based on a blend of easily oxidizing reactants (such as nitrates, sulfates, carbonates, etc.) and an organic fuel (such as urea, carboxyhydrazide, maleic hydrazide, etc.), which acts as a reducing agent [7]. The solution is heated until boiling and auto-ignition, a rapid and self-sustained reaction. Normally a fine, dry, mostly crystalline and de-agglomerated powder is obtained. Although reduction reactions such as these are exothermal and normally lead to explosion, if they are not controlled, the
combustion of blends of nitrates and urea are normally self-propagating, but not explosive reactions.

Self-Propagating Combustion Synthesis (SPCS) is a technique of proven use for the synthesis of high purity α-alumina \[8\]. The combustion method, as it is rapid and with a low energy consumption, has attracted a great deal of interest and was utilized in the synthesis of several oxides, such as: α-FeO\(_3\) and FeO\(_4\) \[9\], nanocrystalline CrO\(_3\) and amorphous CrO\(_3\) \[10\] and NiO \[11\]. Recently, the use of the combustion method using glycine \[12\] and urea \[13-14\] for the preparation of Ca-doped LaCrO\(_3\), LaAlO\(_3\) and the binary phases of the CaO-AlO\(_3\) system was also reported, respectively. A similar combustion route was demonstrated for the synthesis of YAG:Cr and Y\(_2\)O\(_3\):Eu \[15\] and also of YAG:Nd and YIG:Nd \[16\] powders, using the aforementioned fuels.

This work has the purposes of obtaining α-tricalcium phosphate powders by means of the combustion synthesis method as well studying the influence of the synthesis pH on the phase composition of the powders. The precursors used in the combustion reaction were calcium nitrate (Ca(NO\(_3\))\(_2\)), ammonium phosphate dibasic ((NH\(_4\))\(_2\)HPO\(_4\)) and urea (NH\(_2\)CONH\(_2\)).

2. MATERIALS AND METHODS

The solutions used in the combustion reactions were prepared as demonstrated in Table 1, in six groups of experiments. The salts Ca(NO3)\(_2\)-4H2O and (NH4)\(_2\)HPO\(_4\) were added in the amounts described in Table 1. The pH was controlled by the proper addition of 0.5 M nitric acid, to achieve a more acid pH, or 0.5 M potassium hydroxide, in order to increase the pH. After blending all the reagents at room temperature, the vitreous silica crucible, containing the reacting solution, was placed on hot plate heated at 300±20°C for 15 minutes and then it was taken to a SANCHIS N-1110 oven pre-heated to 550±5°C, in which it remained for 15 minutes. The product of combustion, in the form of a brittle foam was easily de-agglomerated into a fine powder, using a mortar and pestle. The resulting powder was submitted to calcinations in an α-alumina crucible in a static air atmosphere, at a temperature of 1250°C, for 15 hours, next the powder received a quenching in order to stabilize the α-TCP phase.

<table>
<thead>
<tr>
<th>pH</th>
<th>Ca(NO(_3))(_2)-4H(_2)O (g)</th>
<th>(NH(_4))(_2)HPO(_4) (g)</th>
<th>Urea (g)</th>
<th>HNO(_3) (mL)</th>
<th>KOH (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>5.83</td>
<td>2.17</td>
<td>24.0</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>4.0</td>
<td>5.83</td>
<td>2.17</td>
<td>24.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2.8</td>
<td>5.83</td>
<td>2.17</td>
<td>24.0</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>1.9</td>
<td>5.83</td>
<td>2.17</td>
<td>24.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>1.7</td>
<td>5.83</td>
<td>2.17</td>
<td>24.0</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>1.5</td>
<td>5.83</td>
<td>2.17</td>
<td>24.0</td>
<td>4.0</td>
<td>-</td>
</tr>
</tbody>
</table>

The powders were characterized by X-ray diffraction aiming at verifying the phases obtained and also by laser diffraction and transmission electron microscopy to assess the particle sizes. X-ray diffraction was utilized for the characterization of the samples, both before and after the heat treatment. A X’Pert MPD Phillips Diffractometer, featuring a copper tube (K\(_\alpha\) radiation of 1.5418 Å) and a θ – θ geometry was used, employing a voltage and a current of 40 kV and 40 mA, respectively. The scanning range was from 10° to 75°, with a goniometer scanning speed of 0.05°/s. In order to verify the particle sizes before and after the heat treatment transmission electron microscopy were utilized. A JEM 2010 Jeol transmission electron microscope was utilized.
3. RESULTS AND DISCUSSION

Nitrate solutions usually decompose at temperatures lower than 700ºC liberating gases such as NO₂, NO and N₂O₅ \[17\]. It is known that urea decomposes into biuret \[14, 17\], cyanuric acid and ammonia, when heated up to about 200ºC. Biuret then decomposes when heated at temperatures over 300ºC. Thus, in an aqueous solution of a metal nitrate and urea, it is expected that the gas decomposition products consist of nitrogen oxides, NH₃ and HCNO. This gas blend will undertake instantaneous ignition when the temperature reaches 500ºC \[14\]. It is believed that ignition increases the temperature locally in the foam to about 1300ºC \[17\], what is similar to a case of instantaneous pyrolysis.

The calcium phosphate solution placed at a vitreous silica crucible within an oven at 500ºC boils and de-hydrates followed by decomposition, with swelling and foam formation, yielding a fine and porous powders with a “foamy” aspect. The whole process takes less than 15 minutes. In Figure 1, the presence of amorphous calcium phosphate can be seen in the as-synthesized powder, prior to the heat treatment. Due to amorphous character, it could not be identified by X-ray diffraction, but is possible to suppose that the obtained material is a amorphous calcium phosphate compound. Information provided by figure 1 is that as lower is the pH, as higher is the intensity of the peaks present in the diffraction pattern.

![Figure 1. X-ray diffraction patterns of the as-synthesized samples, before the heat treatments.](image)

Since the amorphous character of the diffraction pattern, which have peaks with low intensity, to determine the particle size was necessary the usage of laser diffraction and transmission electron microscopy (TEM) techniques.
Analyzing Figure 2, it can be noticed that after quenching, the major phase, for all samples was $\alpha$-TCP. The initial solution pH was shown to be very important for the determination of final product, after the combustion reaction, calcinations and quenching. For pH 4.0, the major presence of the $\alpha$-TCP phase was noted, but intense peaks $\beta$-TCP and $\alpha$-calcium pyrophosphate phases were also displayed. However, the formation of hydroxyapatite did not occur, as it is only stable in aqueous solutions at a pH higher than 4.2\textsuperscript{[19]}.

On the other hand, to the pH 6.4, the major phase present was $\alpha$-TCP. Nevertheless, peaks of $\beta$-TCP and $\alpha$-calcium pyrophosphate were detected at a lower amount. Besides this, the hydroxyapatite phase was also formed.

In the samples from pH 2.8 to pH 1.5 it can be noticed the decreasing of $\beta$-TCP and $\alpha$-calcium pyrophosphate phases formation. The lowest pH (1.5), achieved the highest content of $\alpha$-TCP and the lowest contents of $\beta$-TCP and $\alpha$-calcium pyrophosphate.

The analysis of the laser diffraction data allowed to assess the particle size of powders obtained after the combustion reaction. The particle size of the different samples are displayed in Table 2.

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>Smaller than pH 6.4</th>
<th>pH 4.0</th>
<th>pH 2.8</th>
<th>pH 1.9</th>
<th>pH 1.7</th>
<th>pH 1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% vol</td>
<td>1.35</td>
<td>1.45</td>
<td>1.50</td>
<td>1.12</td>
<td>1.35</td>
<td>1.11</td>
</tr>
<tr>
<td>50% vol</td>
<td>11.68</td>
<td>11.62</td>
<td>14.22</td>
<td>9.65</td>
<td>11.68</td>
<td>10.03</td>
</tr>
<tr>
<td>90% vol</td>
<td>35.51</td>
<td>33.59</td>
<td>35.49</td>
<td>25.20</td>
<td>35.51</td>
<td>27.91</td>
</tr>
<tr>
<td>MPS</td>
<td>15.35</td>
<td>14.92</td>
<td>16.61</td>
<td>11.66</td>
<td>15.35</td>
<td>12.54</td>
</tr>
</tbody>
</table>
A small variation took place in the mean particle size. The laser diffraction analysis showed a particle size in the order of µm as with such technique the size of agglomerates is measured. It happens due to the small volume of the particles with a high surface area, so the formation of agglomerates is more stable.

![Figure 3. TEM micrograph of the pH1.5 sample.](image)

Transmission electron microscopy was utilized to verify the morphology and the particles sizes. The mean particle size was calculated from the micrographs of sample pH1.5, employing the software *image tool*. Strong bonded aggregates were observed in the micrograph (Figure 3) and the diameter of 50 particles was measured from several agglomerates. A meaningful difference between the mean particle sizes of different agglomerates was observed. The TEM micrograph displayed in Figure 3 shows that the obtained material presents a nanometric particle size, with a mean particle size varying between 10 and 100 nm. Those particles presented a hexagonal shape. A better homogenization of the reactants before the combustion synthesis could be an option to achieve a more homogeneous particle size distribution.
4. CONCLUSIONS

α-tricalcium phosphate powders were successfully synthesized by means of the Self-Propagating Combustion Synthesis. Such combustion synthesis method was shown efficient and rapid for obtaining calcium phosphates. The pH synthesis influences the final product, as the lower the pH the more favorable is the formation α-tricalcium phosphate. The highest pH, near to 6.5, favors the formation of hydroxyapatite. Laser diffraction measures the mean size of the agglomerates. TEM micrographs prove that the powders obtained are nanometric and crystalline. A better homogenization of the reactants before the combustion synthesis could be an option to achieve a more homogeneous particle size distribution. There is the necessity to verify the possibility to use this α-tricalcium phosphate powders as calcium phosphates cements.

5. ACKNOWLEDGMENTS

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6. REFERENCES


