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# SYNTHESIS OF HYDROXYAPATITE POWDERS BY SOL-GEL TECHNIQUES

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## 1. ABSTRACT

The formation of hydroxyapatite from aqueous salt solutions has been investigated. Special emphasis was put on the influence of synthesis parameters and on the properties of the precipitates. It was found that the development of crystalline phases during sintering strongly depends on synthesis conditions and can be controlled by sintering temperature and time. Thus, pure hydroxyapatite as well as a mixture of hydroxyapatite and tri-calciumphosphate can be synthesized. Finally, the microstructure of the sintered compacts has been investigated.

## 2. INTRODUCTION

Hydroxyapatite (HAP) is a bioactive ceramic material and used as implants for bones in low mechanical stress applications and for prosthetic purposes in dentistry [1]. Bioactivity requires a certain microstructure which is currently achieved by a hydrothermal exchange process of coral skeletons [2] or by sintering HAP mixed with organic compounds or peroxides [3,4]. The most important properties of this microstructure are sufficient solubility and porosity. The solubility is needed for the resorption of the implant that is the concomitant formation of new calcified tissue with dissolution of the implant material. The porosity has to provide for a homogeneous distribution of calcifying cells or body fluids so that dissolution and resorption can start. For a successful synthesis of these materials the intermediate stages and their corresponding mechanisms must be known. Sintering of crystals prepared by hydrothermal synthesis or solid state reactions will cause simultaneously densification and grain growth which is difficult to control. Our approach for the production of bioactive microstructures is the synthesis of nanometer sized powders by precipitation of calciumphosphates. The small particle size of these precipitates should provide the possibilty for tailoring the required microstructures if the following parameters are known: pH, the stability and hydrolysis of phosphate ions in solution, the chemistry and morphology of the precipitates and the composition and microstructure which will develop upon sintering of these precipitates.

## 3. EXPERIMENTAL

A solution of 0.246 mole/l $(NH_4)_2HPO_4$ was added to a solution of 0.082 mole/l $Ca(NO_3)_2 \cdot 4H_2O$ in bidest water. The pH of both was adjusted with ammonia to pH10. These solutions were stirred for 21 hours at 22°C, 65°C and 75°C and the pH simultaneously monitored. The dried powders were characterized by their Ca- and P- content (molar Ca/P ratio), the morphology of precipitates (TEM), phase composition (XRD) and crystallite size (XRD). The Ca-content was determined by atomic adsorption spectroscopy and the phosphate content spectrophotometrically with the method of Murphey and Riley [5]. The phase composition of the dry-pressed (150MPa) and sintered powders (600°C-1200°C, normal atmosphere) was observed by x-ray diffraction and a relative phase concentration was calculated by comparing the main diffraction peaks of the different phases [6]. The microstructure which developed upon sintering was observed by SEM. The solubility of the sintered

samples was proved by etching in 1M acetic acid for 30 seconds and made visible by SEM.

## 4. RESULTS AND DISCUSSION

The use of $(NH_4)_2HPO_4$ implies the presence of $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$-ions which will affect the development of precursors for hydroxyapatite (HAP) formation [4,7,8]. If their conversion to HAP is incomplete additional phases will develop on sintering, thus, influencing the final microstructure. Therefore it is necessary to determine the concentrations of the three types of ions as a function of the reaction conditions. In figure 1, the development of the pH value at three different temperatures is shown after the phosphate addition to the $Ca(NO_3)_2$ solution.

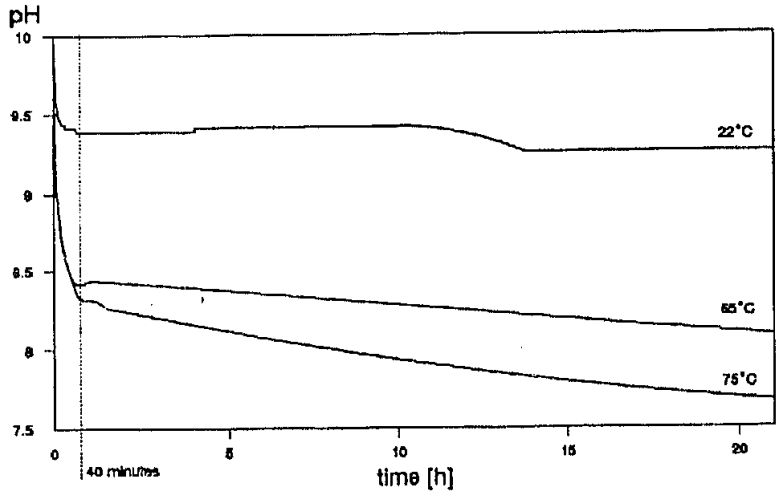


Figure 1: Change of pH during the reaction time of 21 hours. Initial pH was set to 10. End of phosphat addition after 40 minutes.

During the phosphate addition (40 minutes) the pH decreases from 10 to 8.3 (75°C) and 8.4 (65°C) and 9.5 (22°C). The final pH after 21 hours at 75, 65 and 22°C is 7.64, 8.1 and 9.41 respectively. From that measured pH range in fig.1 the respective concentrations for the phosphate ions can be calculated for the three temperatures (tab.1). These results show interesting differences in the ionic concentrations at different reaction conditions, especially the inversion of the tendencies between 22°C on the one and 65°C and 75°C on the other side with respect to $HPO_4^{2-}$ and the similar behaviour of the concentration development of $PO_4^{3-}$.

Table 1: Composition of phosphat solution at different pH and temperatures. The pK values are calculated by some experimental formula [9,10].

| temperature<br>pK | pH | $H_2PO_4^-$<br>[Mol%] | $HPO_4^{2-}$<br>[Mol%] | $PO_4^{3-}$<br>[Mol%] |
|---|---|---|---|---|
| 75°C<br>$pK_3$=11.60 | 10<br>9<br>8 | -<br>-<br>- | 97.6<br>99.7<br>100 | 2.4<br>0.3<br>- |
| 65°C<br>$pK_3$=11.75 | 10<br>9<br>8 | -<br>-<br>- | 98.3<br>99.8<br>100 | 1.7<br>0.2<br>- |
| 22°C<br>$pK_3$=12.39<br>$pK_2$=7.209 | 10<br>9<br>8 | -<br>-<br>13.9 | 99.6<br>99.9<br>86.1 | 0.4<br>0.1<br>- |

A precipitation of pure HAP requires $PO_4^{3-}$ ions which are available only at the beginning of the reaction at 22°C (0.4 mole%), 65°C (1.7 mole%) and 75°C (2.4 mole%). Due to the higher concentration of $PO_4^{3-}$ the most HAP nuclei will be produced at 65°C and 75°C. The presence of these nuclei should improve the yield of HAP during the reaction time of 21 hours by a maturation process. According to [8] the predominance of $HPO_4^{2-}$ will cause the precipitation of precursors (e.g.octacalcium phosphate) which are converted into HAP during aging. The conversion will start on the surfaces of the precipitates leaving a calcium deficiency at the inside. This deficiency can be expressed by the molar Ca/P ratio. Pure HAP, $Ca_5(PO_4)_3OH$, requires a Ca/P of 1.67. The precipitates show Ca/P ratios of 1.48, 1.50 and 1.54 at 22°C, 65°C and 75°C respectively. Ca/P increases with temperature indicating also a non-complete maturation of HAP nuclei and conversion of the precipitates into HAP. Independent of the temperature all precipitates show a HAP-like structure which can be proved by x-ray diffraction (fig.2). The line broadening of the (002) diffraction peak reveals crystallite sizes of 23nm (22°C), 36nm (65°C) and 29nm (75°C) which prove the ability of precipitation for providing nanometer sized particles. The different crystallite sizes suggest differences in the precipitates morphology wich has been monitored by TEM in fig. 3.

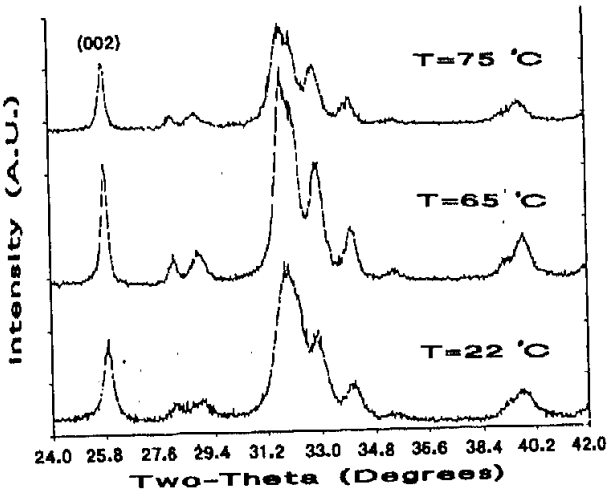


Figure 2: X-ray diffraction pattern of the dried powders precipitated at 22°C, 65°C and 75°C

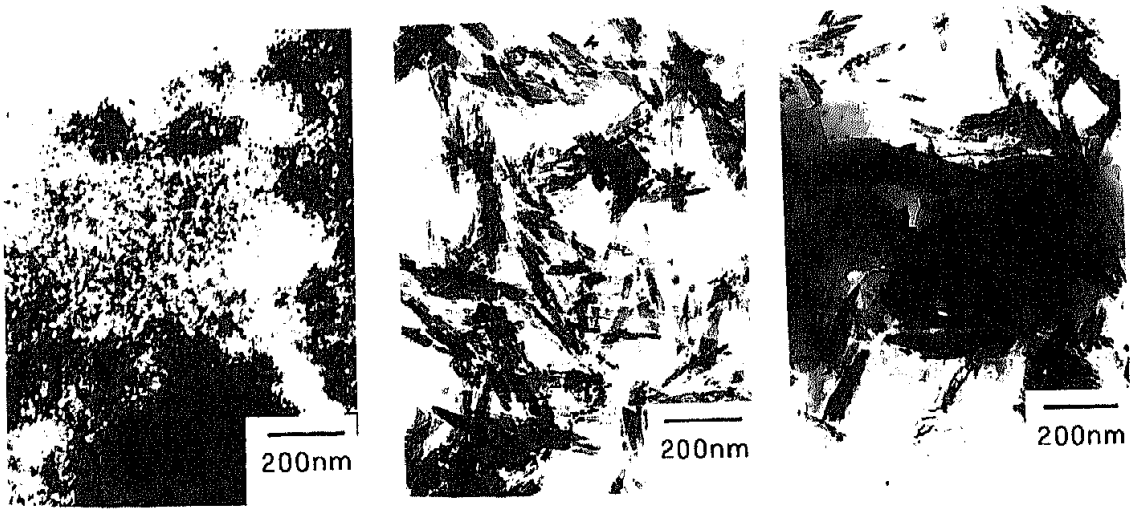


Figure 3: TEM micrographs of dried precipitates. (a) precipitation at 22°C, (b) 65°C and (c) 75°C.

The high temperature precipitates (3b) and (3c) show the needle like structure of HAP. Their length ranges from 60nm to 200nm. The 22°C precipitates consist of spherical particles with a diameter of about 20nm corresponding to x-ray data. Sintering of the 22°C precipitates at temperatures from 600°C-1200°C leads to the development of ß- and $\alpha$-tricalciumphosphate (ßTCP and $\alpha$TCP) (fig.4a). The high temperature precipitates develop only $\alpha$TCP upon sintering at the same temperatures (fig.4b,c). At 1200°C the 22°C precipitates provide HAP to be the dominant phase compared to 65°C and 75°C precipitates where $\alpha$TCP prevails. Although only tendencies can be interpreted from figure 4 due to the measurement procedure [6] these results show that the final phase compositon can be controlled by sintering temperature and time.

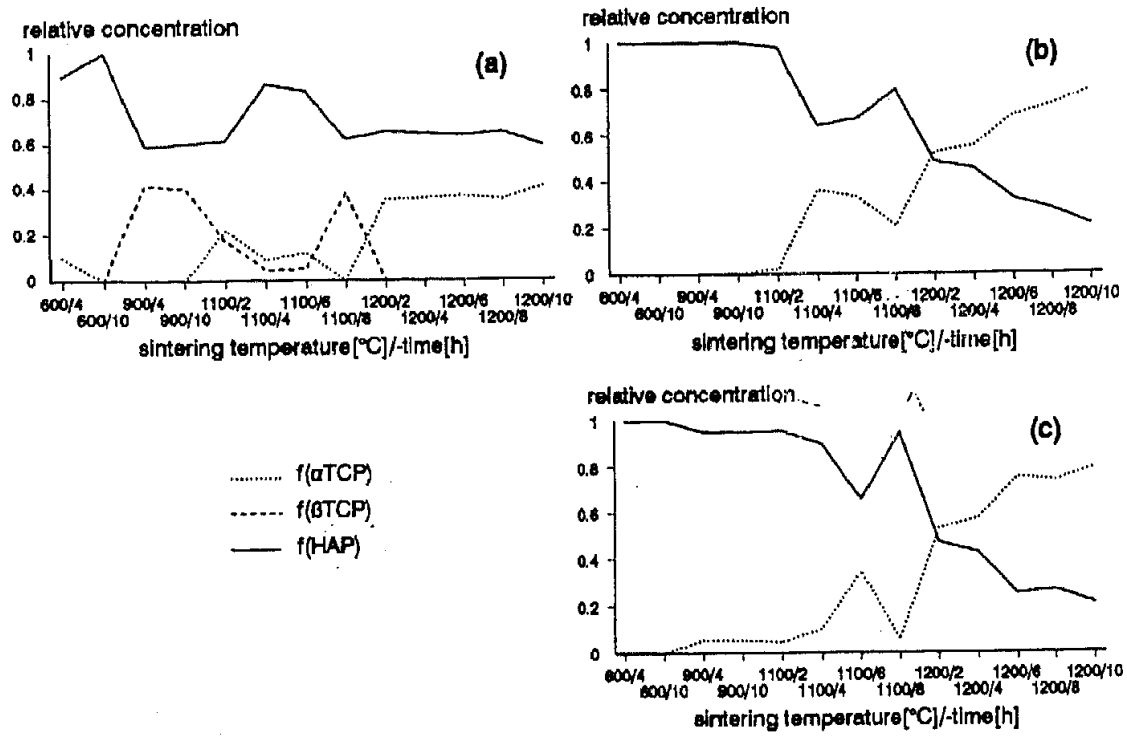


Figure 4: The relative phase concentrations [6] as a function of sintering temperature and time. (a) precipitation at 22°C, (b) 65°C and (c) 75°C.

The different powder morphologies and compositions of the sintered bodies result in different microstructures. SEM images of calciumphosphate ceramics sintered at 1200°C for 4 hours (fig.5) show these differences clearly. 75°C and 22°C precipitation provides small grains ($\approx 1\mu$m) compared to 65°C precipitation ($\approx$10-15$\mu$m). This can be explained by oriented growth of the well crystallized 65°C precipitates leading to larger grains during Ostwald ripening. Leaching of the sintered samples in acetic acid leads to porous structures (fig.5, upper row). A sponge-like structure appears at the 22°C precipitation. Thus, a combination of porosity and solubilty is possible within the investigated systems.

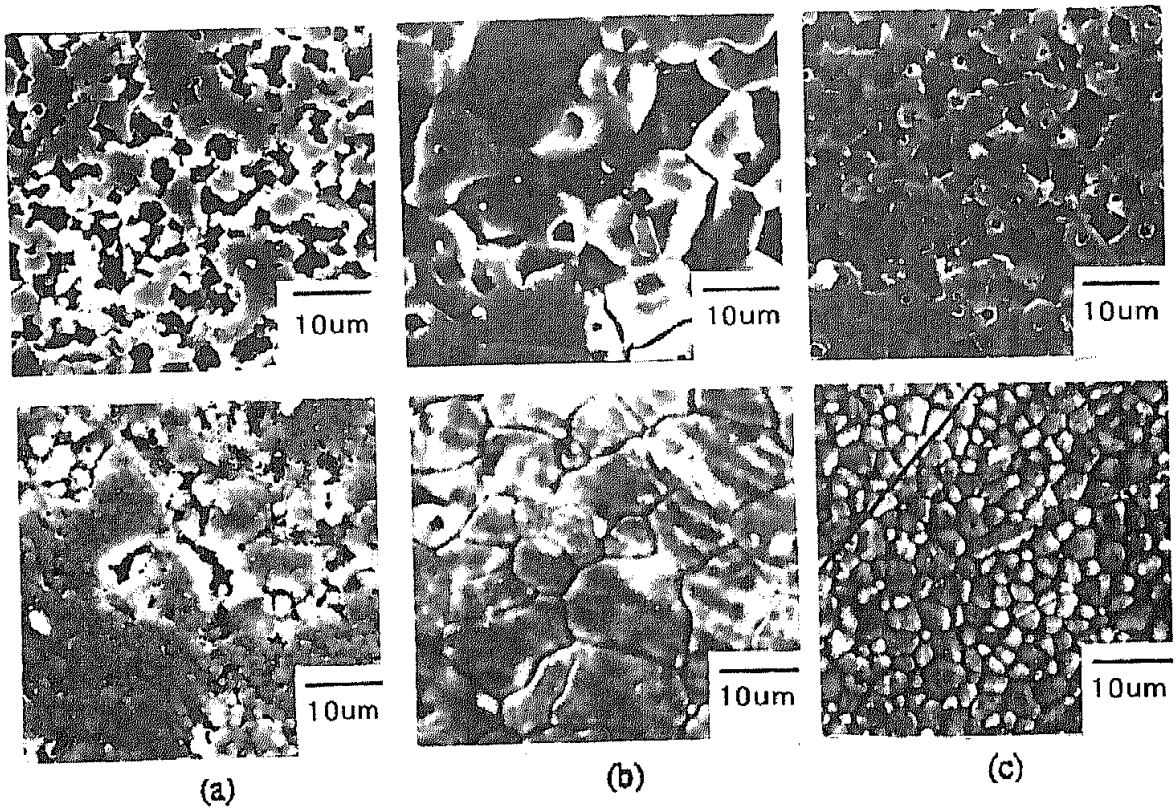


Figure 5: Microstructure of sintered compacts (1200°C, 4h) from precipitates at (a) 22°C, (b) 65°C and (c) 75°C. The upper row shows etched samples.

## 5.CONCLUSIONS

A synthesis of nanometer sized HAP-powders by sol-gel techniques can be used for the production of bioactive calciumphosphates which show both solubility and porosity. As can be expressed by the ratio of pore surface to pore volume [11] the bioactivity of the room temperature precipitated powders with the "sponge-like" structure after etching should be favoured as a bioactive implant in regions where pore sizes of about 1$\mu$m to 10$\mu$m are prevalent.

## 6. REFERENCES

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