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CHEMICAL CHARACTERIZATION OF FLUORHYDROXYAPATITE PLASMA-SPRAYING POWDERS AND PLASMA-SPRAYED COATINGS

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ABSTRACT

Fluorapatite and fluorhydroxyapatite with 5 ppm F content (plasma-spraying powder) were prepared by precipitation at 100°C. Chemical characterization of fluorapatite and fluorhydroxyapatite was made by such methods whose accuracy and reproducibility were assessed previously.

By sintering the fluorapatite precipitate at different temperatures, for 60 minutes, its thermal stability was obtained. Characterization of the plasma-sprayed coatings was performed by chemical analyses and XRD.

INTRODUCTION

Plasma-spraying of hydroxyapatite (HAP) coatings onto titanium alloy implants is now a standard procedure widely utilized in medical technology. It was found that plasma-sprayed coatings of HAP ceramic degraded in vivo, possibly because the ceramic material has lost almost 50% of its crystallinity during the plasma-spraying procedure. Fluorapatite (FAP) coatings did not lose their crystallinity during plasma-spraying and had the additional advantage of thermal stability due to the fluoride ion [1].

The thermal stability of HAP, which decomposes into $\text{Ca}_4(\text{PO}_4)_2\text{O} + \text{Ca}_3(\text{PO}_4)_2$ above 1250°C in N_2 , increases markedly with dissolving F even in small amounts, e.g., 10 mol% substitution of F for OH decreased the degree of HAP from 85% to 2% at 1300°C [2].

By wet reaction a series of fluoridated HAP (fluorhydroxyapatites) can be prepared. Fluorapatite prepared by precipitation is usually contaminated by small amounts of OH replacing F. The influence of sintering temperature in chemical and phase composition of samples sintered at different temperatures was evaluated by chemical analyses and X-ray diffractograms.

It was an important problem to find out which was the most adequate quantity of F for substitution part of the OH groups in the HAP structure. In other words, which composition of fluorhydroxyapatites acts as a good biomaterial and is at the same time more stable at plasma-spraying than HAP? According to some authors [3] fluorhydroxyapatite (FHAP) with 5 ppm F content is a good biomaterial. Sumner et al. [4] found that bone ingrowth was enhanced when a combination of HAP and tricalcium-phosphate (TCP) was used as implant coating. In consequence, the plasma-spraying powder used for the experiments had a phase composition of 80% (wt) FHAP (5 ppm F) and 20% (wt) TCP.

EXPERIMENTAL

Preparation

Fluorapatite and fluorhydroxyapatite with 5 ppm F content were prepared using a procedure similar to that previously reported [5] for the preparation of HAP. The reaction vessel was a 1000 cm³ glass flask. Analytical grade $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$ and KF reagents were used to make stock solutions. 200 cm³ of the $\text{Ca}(\text{NO}_3)_2$ stock solution (0.22 M) was transferred into the flask. The flask was brought

to 100°C and finally a mixture of 200 cm³ (NH₄)₂HPO₄ 0.12 M solution and 200 cm³ or 26·10⁻³ cm³ 0.1 M KF solution was added dropwise. The precipitation was adjusted to 9-9.5 pH with concentrated NH₄OH solution. The flask was placed in a thermostated shaker which allowed intensive mixing of the solution and the precipitate. After the desired stirring time the precipitate was filtered, thoroughly washed and dried at 105°C for 10 h. The resulting compact material was ground in an agate mill, then fired at the required temperatures for 1h.

The mineralogical composition of the samples was determined with a Philips PW 1825 type X-ray diffractometer.

For identification of samples the following designations were made: FAP, T (°C), t (min), where FAP is fluorapatite

Chemical analyses

Determination of Ca content

The calcium content of samples was determined by EDTA-titration in the presence of Fluorexon indicator [6]. Stock solutions were prepared as follows: the samples (approx. 0.1 g) were dissolved in 10 cm³ 1:1 HNO₃ solution and then they were filled up to 500 cm³ in a volumetric flask.

Determination of P content

Spectrophotometric method [7] was used for the determinations.

The reagents used for spectrophotometric determinations were as follows:

- 1) 0.25% NH₄VO₃ pur. spec. solution
- 2) 5% (NH₄)₆Mo₇O₂·4H₂O pur. spec. solution
- 3) 1:1 HNO₃ a.r. solution
- 4) 1mg/cm³ KH₂PO₄ pur. spec. stock solution

The stock solutions were prepared as follows: the samples (approx. 0.07 g) were dissolved in 10 cm³ 1:1 HNO₃ solution and the volume of solutions were adjusted to 200 cm³ in a volumetric flask. Measurements were done at 400 nm with a LAMBDA 20 UV/VIS, Perkin Elmer type spectrophotometer.

Determination of F content

F content of samples were determined with fluoride selective electrode [8]. The samples (approx. 0.1 g) were dissolved in 10 cm³ 1:1 HNO₃ solution. The solutions were adjusted to pH= 5-6 using 1:1 NaOH solution, then 100 cm³ of TISAB reagent was added and the sample was diluted to 500 cm³. According to some authors [9] the use of TISAB reagent as buffer in fluoride determinations leads to an apparently lower result than by other methods. The use of citrate-hydrochloric acid buffer appears to avoid the fluoride loss that occurs with TISAB. The measurements were carried out using citrate-hydrochloric acid buffer too, but no differences were observed in the results. pF values were obtained with the help of an OP- F- 07 fluoride- selective electrode connected to a pH/ion Analyser OP- 271 Radelkis. The reference electrode was a double- junction silver/silver chloride OP- 0820P electrode (Radelkis).

Plasma-spraying

The plasma torch was produced with 500 A current intensity and 50 V voltage, the gas stream was set to 1.1 m³/h Ar and 0.4 m³/h N₂. The surface of titanium alloy sheets was roughened by aluminium-oxide blasting (Al₂O₃ particle size: 300-500 μm). The roughness of the blasted surface was 100 to 150 μm by size. The thickness of the plasma-sprayed coatings were: 140 μm.

RESULTS AND DISCUSSION

The theoretical chemical composition of FAP is: $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$. The influence of the sintering temperature experienced on the chemical composition of the fluorapatite prepared by precipitation was investigated by chemical analyses of samples sintered at different temperatures. The sample sintered at 1000°C for 60 minutes had a composition which best approaches the stoichiometric composition of fluorapatite.

An increase of sintering temperature yields of the decrease of F content in the composition of samples (Table 1.).

Table 1: Ca, P and F content (% wt) of the fluorapatites sintered at different temperatures

Sample	Ca % (wt)	P % (wt)	F % (wt)	Ca:P:F
FAP,1000,60*	36.2±0.7	17.6±0.9	3.0±0.1	9.5:6.0:1.7
FAP,1100,60*	37.1±1.3	18.2±1.2	3.0±0.1	9.5:6.0:1.6
FAP,1200,60	36.8±1.4	17.9±1.9	2.9±0.1	9.6:6.0:1.6
FAP,1300,60	36.9±1.3	17.8±2.0	2.9±0.1	9.6:6.0:1.5
FAP,1370,60	36.1±1.7	17.8±2.0	2.8±0.1	9.4:6.0:1.5

The results were calculated based on 3-5 parallel measurements. The confidence intervals were determined considering a 95% confidence level. Samples FAP,1000,60 and FAP,1100,60 are constituted of a single phase (fluorapatite) for which the authors propose the following formula: $\text{Ca}_{9.5} \otimes_{0.5} (\text{PO}_4)_6 \text{F}_{1.70.3}$ and $\text{Ca}_{9.5} \otimes_{0.5} (\text{PO}_4)_6 \text{F}_{1.60.4}$, where \otimes stands for $(\text{HPO}_4)^{2-}$, but for verification of this further measurements are needed.

The phase composition of the sintered samples as a function of sintering temperature was investigated based on the X-ray diffractograms. The diffractograms of the samples sintered at different temperatures showed that decomposition of fluorapatite, prepared by wet reaction, started at 1200°C. The diffractogram of the sample sintered at 1000°C, however, showed a single phase: fluorapatite (Fig.1.).

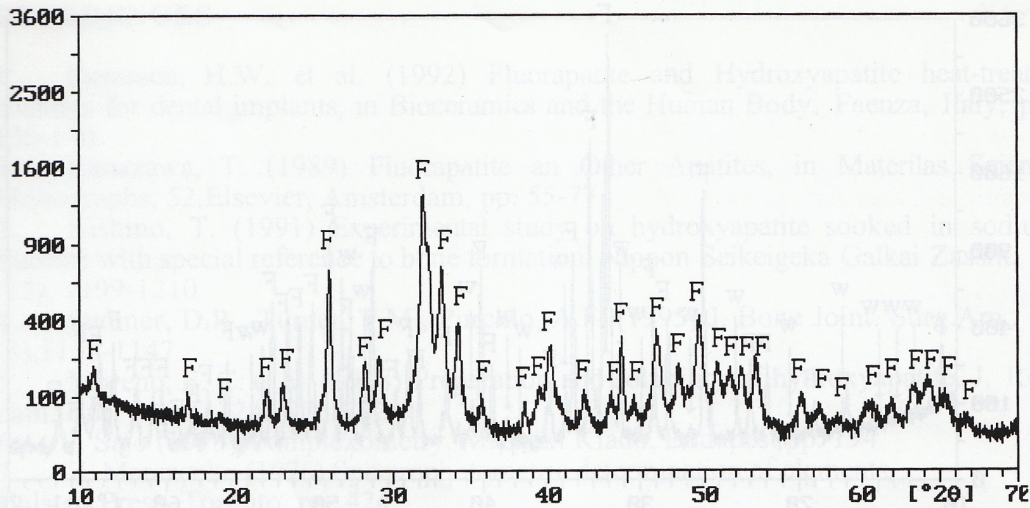


Figure 1: X-ray diffractogram of FAP prepared by precipitation and sintered at 1000°C for 60 minutes

On the diffractogram of the FAP,1200,60 near the reflexions of fluorapatite it appeared two low intensity XRD reflexions characteristic for α -whitlockite (Fig.2.).

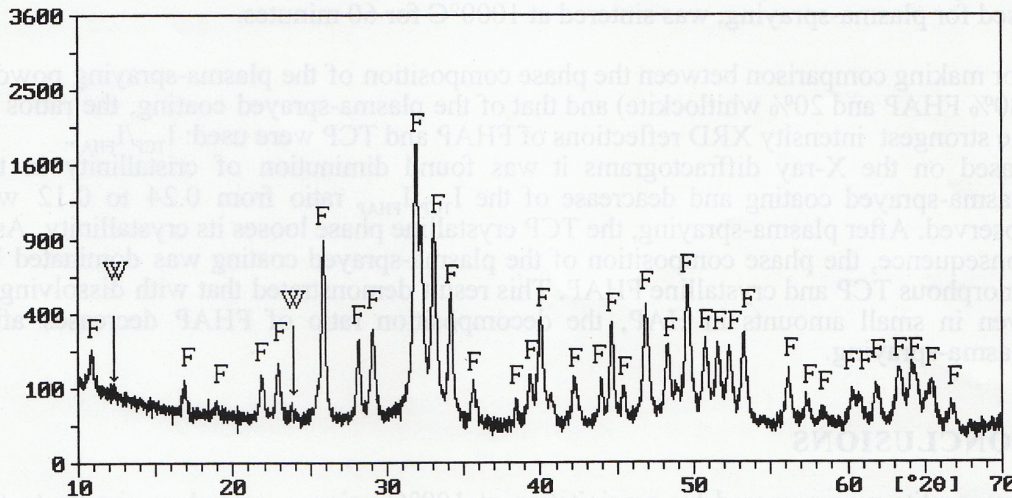


Figure 2:. X-ray diffractogram of FAP prepared by precipitation and sintered at 1200°C for 60 minutes

The diffractogram of the FAP,1370,60 showed that the increase of the sintering temperature enhanced the degree of decomposition (Fig 3.).

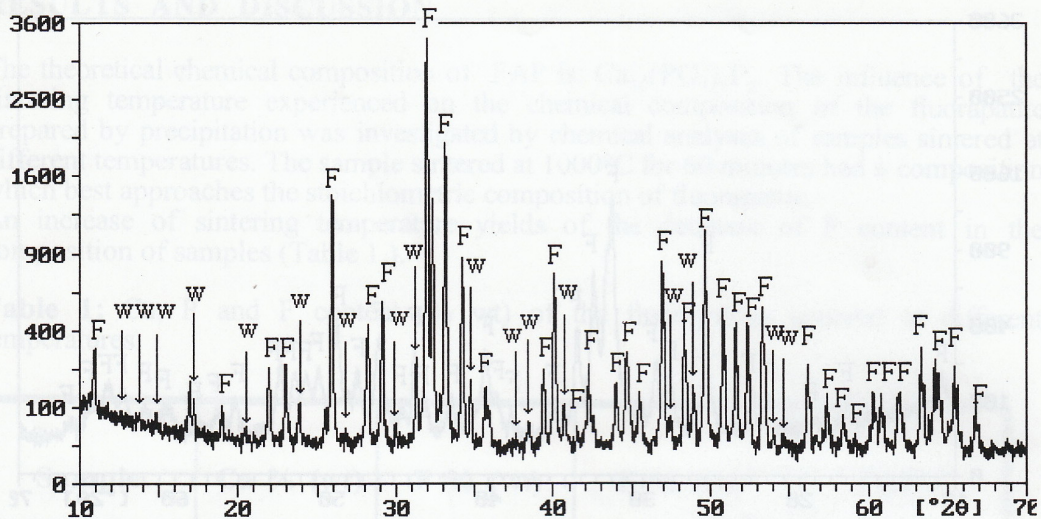


Figure 3: X-ray diffractogram of FAP prepared by precipitation and sintered at 1370°C for 60 minutes

Relying upon these findings, the sample sintered at 1000°C for 60 minutes had a chemical and phase composition which best approaches the theoretical composition of fluorapatite. In consequence, the fluorhydroxyapatite precipitate with 5 ppm F content, used for plasma-spraying, was sintered at 1000°C for 60 minutes.

For making comparison between the phase composition of the plasma-spraying powder (80% FHAP and 20% whitlockite) and that of the plasma-sprayed coating, the ratios of the strongest intensity XRD reflections of FHAP and TCP were used: I_{TCP}/I_{FHAP} . Based on the X-ray diffractograms it was found diminution of crystallinity in the plasma-sprayed coating and decrease of the I_{TCP}/I_{FHAP} ratio from 0.24 to 0.12 was observed. After plasma-spraying, the TCP crystalline phase loses its crystallinity. As a consequence, the phase composition of the plasma-sprayed coating was dominated by amorphous TCP and crystalline FHAP. This result demonstrated that with dissolving F even in small amounts in HAP, the decomposition ratio of FHAP decreases after plasma-spraying.

CONCLUSIONS

Fluorapatite was prepared by precipitation at 100°C using a procedure similar to the preparation of HAP. The precipitate sintered at 1000°C for 60 minutes had a chemical and phase composition which best approaches the theoretical composition of fluorapatite.

An increase of sintering temperature results in a decrease of F content in the composition of fluorapatites sintered at different temperatures and enhances the degree of decomposition of these. The plasma-spraying powder having a phase composition of 80% (wt) FHAP (5 ppm F) and 20% (wt) TCP was prepared using a precipitate with 5 ppm F content, which was sintered at 1000°C for 60 minutes.

Based on the X-ray diffractograms it was found diminution of crystallinity in the plasma-sprayed coating and decrease of the TCP crystalline phase quantity was observed.

The phase composition of the plasma-sprayed coating was dominated by amorphous TCP and crystalline FHAP.

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