



A study of plasma sprayed HAp coatings using the EDX and Raman methods

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Abstract. In this paper the EDX and Raman studies of plasma-sprayed HAp coatings are presented. Parameters of characteristic vibrational bands of phosphate and hydroxyl functional group have been compared for powder feedstock and final coatings. Based on the EDX and Raman studies degenerative effects of the deposition process for the presence hydroxyl function group and symmetry of phosphate groups has been discussed.

Keywords: hydroxyapatite, plasma spraying, coatings, EDX, Raman spectroscopy.

1. Introduction

Hydroxyapatite (HAp) is a nonorganic material of the bones of the vertebrate responsible for their mechanical durability. In human bones it occupies 60-80 % of the volume depending on a number of factors. Synthetic HAp is valued in bone endoprosthesis to its high biocompatibility. It is widely used to fill cavities of bone and as the coating of bone implants to increase their biocompatibility and adhesion to bone surface [1-4].

HAp occurring in bones is continuously absorbed by osteoclasts cells and excreted by osteoblasts. This process is called resorption. Synthetic HAp can also be resorbed if certain conditions are satisfied. This means the HAp is not biocompatible only but also bioactive material.

This paper presents basic information about HAp and its crystallographic and molecular structure. The sample of plasma sprayed HAp on Ti6Al4V was also prepared and analyzed by EDX and Raman methods.

2. HAp - general information

The general formula of HAp is usually written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ [4], rarely $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{OH})_2$ or $\text{Ca}_5(\text{PO}_4)_3 \cdot \text{OH}$ [5-6]. Hydroxyapatite has a hexagonal crystal structure with the space group $P6_3/m$, and a unit cell of 44 atoms. The main dimensions of the cell are $a = 9.41 \text{ \AA}$ and $c = 6.88 \text{ \AA}$; [3]. The tetrahedral phosphate anion (PO_4^{3-}) has a strong covalent character and acts as a robust group in the interaction with the surroundings. Ca^{2+} cations occupy two distinct crystal sites, Ca(I) and Ca(II): thus the formula unit can be rewritten as $\text{Ca}(\text{I})_4\text{Ca}(\text{II})_6(\text{PO}_4)_6(\text{OH})_2$. Ca(I) is 9-fold coordinated to oxygen ions from six neighboring phosphate groups, while Ca(II) is 7-fold coordinated with oxygen ions, six from phosphate groups and one from an OH. Ca(I) lies along the columns parallel to the crystal c-axis, with two Ca(I) ions in each column. Ca(II) cations are distributed in two triangular bases, twisted 60° relative to each other with hydroxyl O in the center, forming a hexagonal channel with the OH array located in the center and parallel to the channel (also the lattice c-axis).

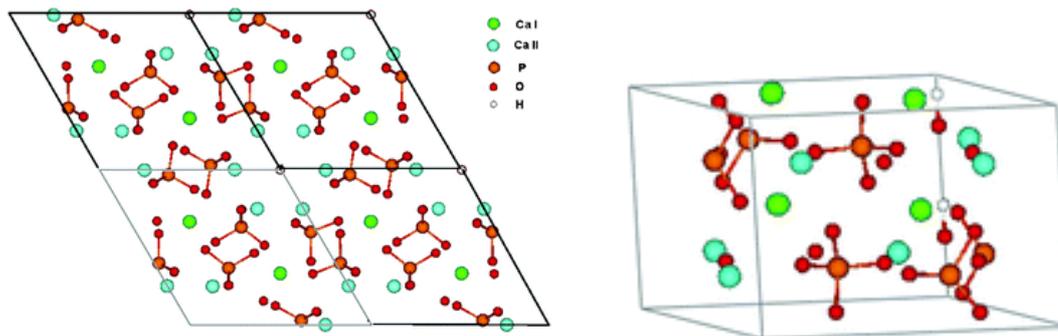


Fig. 1. Structure of hydroxyapatite seen in top view along the *c*-axis (left) and looking along *a* and *b*-axis (right) [3].

In table 1 the Raman vibrational modes of PO₄ tetrahedra of HAp and the other calcium phosphate salts (OCP and TCP) are presented.

Mode	Symmetry	Observed bands [cm ⁻¹]		
		HAp	OCP	TCP
v ₁	A ₁	961 (vs)	958 (vs)	970 (vs)
v ₂	E	447 (m), 433 (w)	449 (m), 429 (m)	460 (w), 439 (m)
v ₃	T ₂	1076 (w), 1054 (w) 1046 (m), 1030 (w)	1080 (w), 1049 (vw)	1074 (w), 1046 (m)
v ₄	T ₂	610 (w), 594 (m), 582 (w)	610 (m), 593 (m), 582 (m)	624 (w), 612 (m), 599 (w), 578 (w)

vs: very strong, m: medium, w: weak, vw: very weak

Table 1. Raman shifts observed and assigned to HAp and the other calcium phosphate salts [4].

3. Experimental

The coatings were deposited on flat Ti6Al4V (6% Al, 4% V) samples with dimensions of 15 mm x 15mm x 1 mm. Before plasma spraying all of the samples were degreased and grit blasted with electrocorundum EB-12 at a pressure of 0.5 MPa.

Sulzer Metco XPT-D-703 hydroxyapatite powder feedstock was applied in this study. Plasma spraying was performed by means of a Plancer PN-120 plasma spraying system with a Thermal Miller 1264 powder feeder. The plasma spraying parameters were set as following: current - 600 A, voltage - 60 V, plasma gas pressure - 0.7 MPa, spraying distance - 100 mm, powder feeding rate - 60 g/min were applied to deposit coatings [10]. After the deposition thickness of the coatings was around 0.3 mm.

The HAp powder (I) and the HAp coating (II) deposited on the Ti alloy substrate by plasma spraying [5] were studied using the EDX (Energy-dispersive X-ray spectroscopy - Jaol SEM microscope) and Raman spectroscopy methods. The Raman studies was performed using an automated micro-Raman Nicolet Almega XR spectrometer (Thermo Scientific) with the 532nm excitation. The spectra were obtained in the micro mode in the low (200 - 4000cm⁻¹ range, 6 cm⁻¹ resolution) and the high (range 200 - 1200cm⁻¹, 2cm⁻¹ resolution) resolution modes. The obtained spectra were processed using Nicolet Omnic 8 software to remove the luminescent background.

4. Results and Discussion

4.1. SEM and EDX study

Figure 2 presents an EDX spectrum and SEM images of the deposited HAp coating (II). The identification of chemical compounds and stoichiometric ratio were done based on energy dispersive X-ray microanalysis – Table 2.

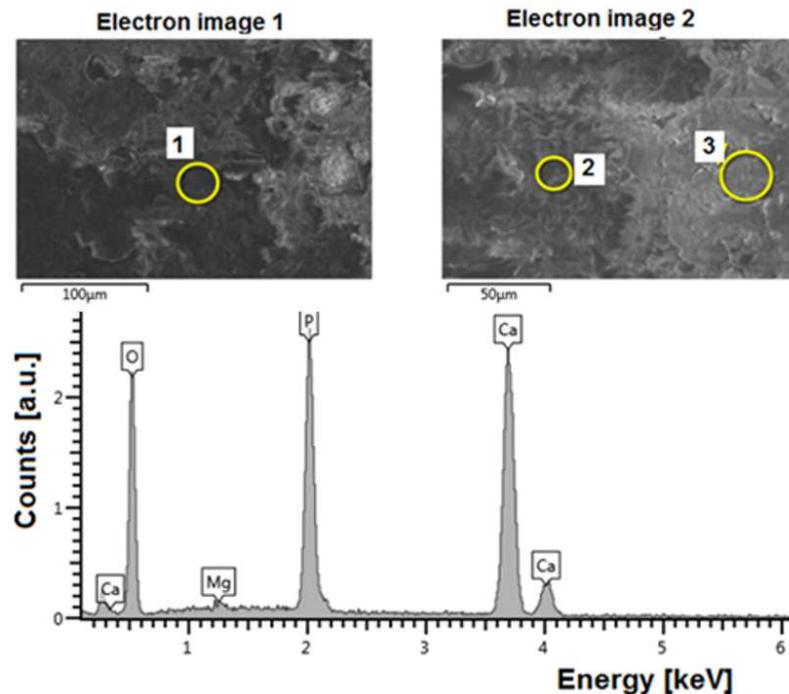


Fig.2. EDX spectrum (1) of HAp coating (II) deposited on Ti6A4V substrate

Spectrum Label	Atomic percentage			Ca/P ratio
	Mg	P	Ca	
Spectrum 1	0.33	11.06	17.06	1.542
Spectrum 2	0.26	9.24	16.66	1.803
Spectrum 3	0.19	9.67	16.68	1.725
Average	-	-	-	1.690
Theoretical	0	-	-	1.667

Table 2. Atomic percentage in investigated HAp coating (II).

The X-ray microanalysis shows that the molar Ca/P ratio is clearly not uniform (fluctuations of approx. 1.54-1.8), but the average value is close to the theoretical value for HAp. The presence of calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ (tricalcium phosphate - TCP) [2] cannot be excluded. It is not possible to determinate without additional research if structure of HAp is stoichiometric. However results indicate that the structure is close to non-stoichiometric due to big fluctuation Ca/P ratio which is characteristic of ns-HAp (1.5-2.0) [9].

Small fractions (1-2%) of Mg suggest the presence of magnesium phosphate [7]. The Mg admixture probably leads to a decrease in the grain size, which on the other hand causes a reduction of the anisotropic properties. While spraying Ca^{2+} ions can be substituted by Mg^{2+} [9].

4.2. Raman study

In figure 3 the Raman spectra of HAp powder (I) and plasma-spraying deposited HAp coating (II) were presented. The four characteristic modes for PO_4 tetrahedron [4] are clearly observed.

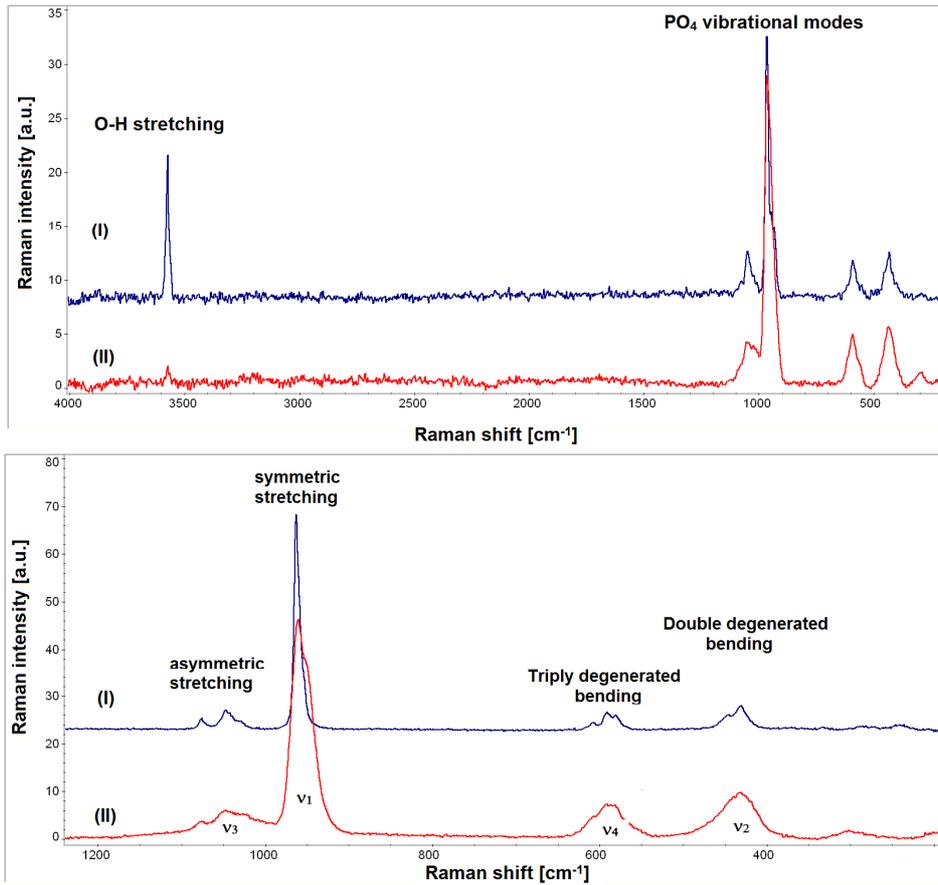


Fig 3. Raman spectra of HAp powder (I) and plasma-spraying deposited layer (II) in low (top) and high (bottom) resolution modes

In Raman spectra of HAp powder (I) the four basic vibrational modes of PO_4 group (denoted as ν_{1-4}) were observed in region of $400 - 1100\text{cm}^{-1}$ and also strong O-H vibrational mode exists at 3573cm^{-1} . In deposited coating (II) O-H mode are distinctly attenuated and ν_{1-4} modes are broadened. It is connected, probably, in disordering of crystalline structure of HAp during deposition process to non-stoichiometric.

mod	Band no	Powder (I)			Deposited coating (II)		
		Pos [cm^{-1}]	Int	FWHM	Pos [cm^{-1}]	Int	FWHM
ν_1	Band 1	958.7	18.27	11.20	949.5	29.72	23.32
	Band 2	963.2	33.62	5.60	963.1	30.93	15.45
ν_3	Band 3	1030.2	1.44	9.50	1021.7	3.12	27.23
	Band 4	1041.6	2.06	9.41	1039.2	1.90	14.31
	Band 5	1049.0	3.26	10.48	1052.0	3.49	19.07
	Band 6	1076.0	2.09	9.01	1076.7	1.88	13.80
ν_2	Band 7	430.3	4.58	17.31	429.0	9.01	43.10
	Band 8	448.2	2.18	17.87	454.3	2.26	42.81
ν_4	Band 9	580.2	2.81	12.61	565.5	1.69	27.04
	Band 10	591.4	3.00	9.57	587.3	5.93	26.33
	Band 11	607.8	1.41	11.49	609.9	3.40	29.86

Table 3. Comparison of Raman band parameters of HAp powder (I) and deposited coating (II).

In the deconvolution process of the spectra the 2 component functions to approximate a non-degenerated ν_1 mode were used as a result of the presence of band shoulder and 4 functions to approximate ν_3 module. In results, total of 11 bands were isolated for both powder HAp (I) and

HAp coating (II). This demonstrates the breaking of ideal T_d symmetry of phosphate groups both in powder and deposited HAp.

In table 3 values of Raman band parameters of HAp powder (I) and deposited coating (II) are presented. There was a distinct widening (2-3 times) of bandwidths in HAp coating (II) as compared with the powder (I) - it may indicate an increase of structure disordering (amorphization). The ν_1 mode was approximated by two basis functions. As a result, the position of the band no 2, was located at position approx. 963cm^{-1} (both the powder and the layer), so it was approx. 2 cm^{-1} higher than in the literature [4]. However, the average position of maximum of the mode were exactly at 961cm^{-1} , which is characteristic for HAp, no other form of calcium phosphate.

In the case of HAp powder, band 1 can be treated as shoulder (differing positions less than 5 cm^{-1}). However, in the case of HAp layer positions of the 1 and 2 bands differ at approx. 14 cm^{-1} . Band 1 will may be characteristic of calcium phosphate (TCP).

5. Conclusion

The averaged Ca/P ratio and positions of vibration modes of $(\text{PO}_4)^{3-}$ phosphate group in the Raman indicate the hydroxyapatite (HAp) as material deposited on the substrate during a plasma-spraying process. Nevertheless, some parameters (FWHM and intensities) of characteristic bands in Raman spectra of powder and deposited HAp have been clear different. It can be concluded, deposition process influents on crystal disordering and homogeneity of HAp.

Spatial heterogeneity of Ca/P ratio and the attenuation (absence) of OH bending mode in Raman spectra may indicate formation of other molecules, e.g. calcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$). We can suppose that structure is non-stoichiometric or partially anisotropic.

We found that hydroxyapatite was modified by magnesium. It is justified by dust destination.

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