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BIOCOMPATIBLE MATERIALS REALIZED BY PLASMA THERMAL SPRAYING OF HYDROXYAPATITE ON METALLIC SUPPORTS

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Abstract
In this paper is presented the thermal spraying process of the oxidic ceramic (hydroxyapatite) on metalic supports to obtain biocompatible materials with application in general medicine.
Two main applications are obtained by realizing of titanium base implants, dental and orthopedic.
The samples were examined by optical and electronic microscopy, finally the ceramic layers presented the roughness between 8 and 9 μm and the layer thickness between 90 şi 330 μm. No defects can be reported. The samples obtained by plasma thermal spraying were corrosion tested in simulated body fluid (SBF with pH 7,4 la 37°C).
Key words:
thermal spraying, biocompatible materials, oxidic ceramic, SBF

1. INTRODUCTION

The best materials used to the prosthesis fabrication in dental and orthopedic medicine are those which are similar with the composition of the humane bone, the repairing mechanism of the bone is the natural regenerations.

One approach to provide a strong, long-lasting adhesive interface between a bone replacement implant and the surrounding tissue involves the use of bioactive materials.

Hydroxyapatite (HA) is the most well known bioactive ceramic materials used in medicine. The inorganic constituent of bone is made up of biological apatites, which provide strength to the skeleton and act as a storehouse for calcium, phosphorus, sodium, and magnesium.

2. MATERIALS USED

For biocompatible layers deposition hydroxyapatite powders were used with the dimension of the particles between 10-30 μm and Ti-Mo-Al titanium alloy as substrate. The chemical composition of the titanium alloy is presented in table 1. The chemical composition of the two samples (substrates) is conform ASTM grade 11.

Table 1 The chemical composition of the titanium alloy used as substrate

No. sample	Chemical composition %					
	Ti	Mo	Al	Mn	V	Fe
1	97,70	1,641	0,3245	0,1048	0,0921	< 0,032
2	97,75	1,626	0,2989	0,1060	0,0847	< 0,034

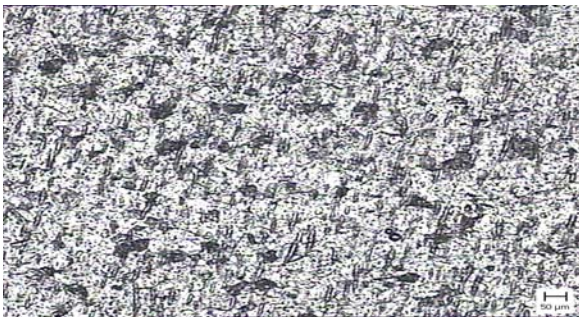

Figure 1. Titanium alloy substrate BM (cupric solution, 50 x)

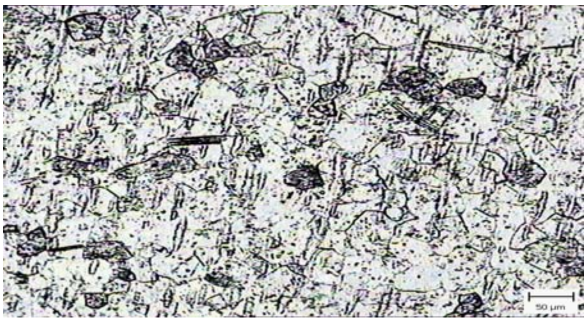

Figure 2. Titanium alloy substrate BM (cupric solution, 100 x)

In figure 1 and 2 the biphasic structure is presented (solid solution α enriched in titanium and intermetallic compounds of Ti-Mo, Ti-Al) of the titanium alloy used as substrate (BM) for the deposition of the hydroxyapatite layers by plasma thermal spraying.
In the base metal (BM) were developed fine macles due to the hot plastic deformation process of the Ti-Mo-Al alloy.

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is a oxidic ceramic which is used to realize the biocompatible layers by plasma thermal spraying or by other methods.

3. SAMPLES PREPARATION

Before thermal spraying, the titanium samples were blasted with electrocorindon with the granulation between 0,8 – 2 mm and the air pressure of 5 bar. The blasting distance was 50±5 mm.

Because the powders presented a high agglomeration tendency the dehydration of the powder (heating to 60 ºC, time 12 h) was necessary.

The deposition of the hydroxyapatite powder on titanium alloy substrate was realized with the plasma thermal spraying installation from ISIM – Timisoara. In figure 3 is presented the thermal spraying gun 3MB of the installation.

Figure 3 The thermal spraying gun 3MB of the plasma thermal spraying installation

The plasma spraying process was made in horizontal position the spraying gun position was perpendicularly on the titanium alloy support. In figure 4 is presented image from the plasma thermal spraying process.

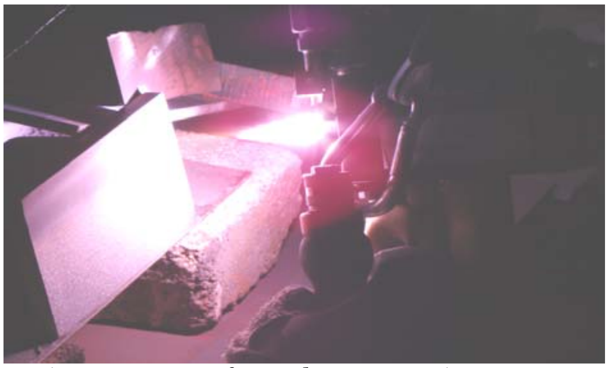
Figure 4. Image form plasma spraying process

In plasma spraying process of the hydroxyapatite the distance between the titanium surface and spraying gun was 100 mm .

The plasma spraying parameters used for the hydroxyapatite deposition are presented in table 2.

With the parameters from table 2 were made two samples:
- A sample (M1) with one hydroxyapatite layer, using Ti-Mo-Al alloy
- A sample (M2) with three hydroxyapatite layers, using Ti-Mo-Al alloy

Table 2. The plasma spraying parameters

I_p A	U_a V	Q_p l/min	Q_{tr} l/min	m_p g/min	d_p mm	N_n	Cooling
500	60	40	6	15	100	3	air
500	60	40	6	15	100	1+1+1	air

4. EXPERIMENTAL RESULT AND INTERPRETATION

The macroscopic examinations show the deposited layers aspect of different thickness (table 3). The determination of the hydroxyapatite layer thickness was made with Leptoskop Pocket device from ISIM – Timisoara. On the examined surfaces no defects were observed.

Table 3. Layer thickness plasma sprayed

No. Sample	No. Layers	Layer thickness [μm]	
		Individual values, g	Average value, $\bar{g}$
M1	1	90, 100, 111, 160, 120, 132, 122, 92, 101, 120	127,8
M2	3	310, 310, 320, 330, 315, 318, 321, 310, 315, 318	316,7

Analyzing the thickness values of the sprayed layers is observed that the values of the sample M1 vary between 90 şi 160 μm and presents a high dispersion on the values with the average 127,8 μm, the sample M2 present values between 310 şi 330 μm with the average 316,7 μm, which attest a high compacting of the layers deposited by thermal spraying. The average roughness of the deposited layers measured with SJ-201P device is maximum 8,50 μm.

Microscopic examinations made according EN1321 show the microstructure of the deposited layers by plasma thermal spraying process, which consist from globular and acicular particles of apatite with the hardness 5 on Mohr hardness scale (figure 5, 6). On the examined sections by optical microscopy no defects were observed (pores, microcracks).

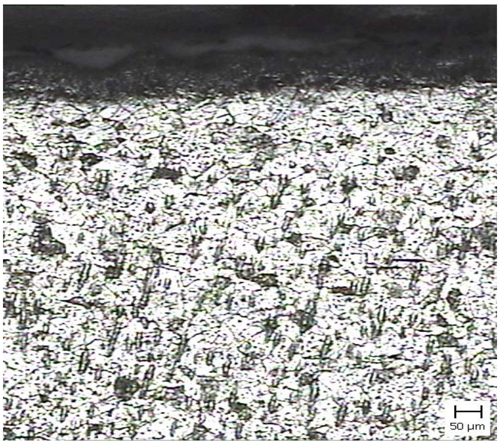

Figure 5 The microstructure of the hydroxyapatite ayer deposited by plasma thermal spraying (ferric chloride , 50 x)

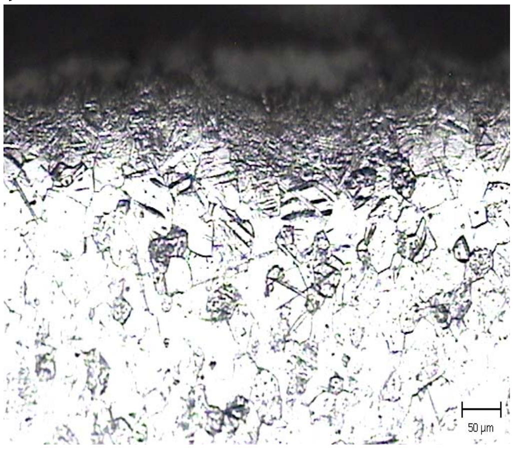

Figure 5 The microstructure of the hydroxyapatite layer deposited by plasma thermal spraying (ferric chloride , 100 x)

In figure 7 and 8 are presented the images of the deposited layer by plasma thermal spraying of the hydroxyapatite powder on titanium alloy substrate using SEM (scanning electronic microscopy).

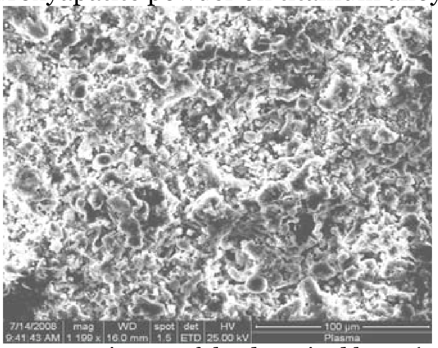

Figure 7. SEM image of the deposited layer (1200 x)

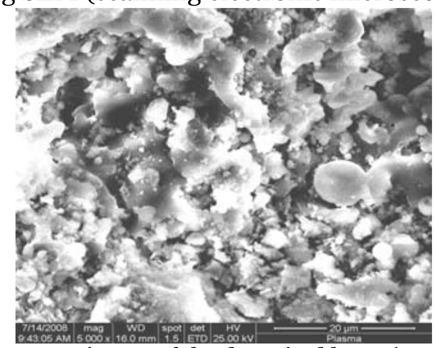

Figure 8. SEM image of the deposited layer (5000 x)

The SEM analysis of the deposited layer by plasma thermal spraying shows a characteristic morphology of the deposited layer by plasma thermal spraying with fine and big particles disposed uniformly on the surface.

5. CORROSION TESTS

The samples for corrosion tests deposited with hydroxyapatite layers have the aspect presented in figures 9 an 10. Before the corrosion test the samples were weighed with an analytic balance and presented the values: M1 = 9,8973 g

M2 = 11,7419 g

The test samples were introduced in simulated body fluid (SBF). In table 3 is presented the chemical composition of the corrosion testing solution.

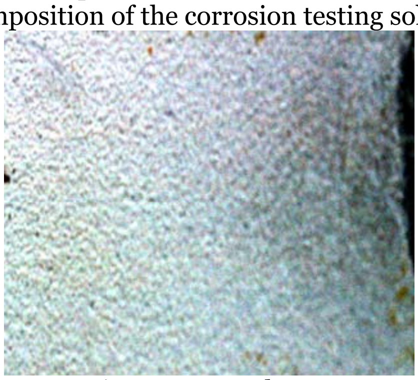

Figure 9. Sample M1

Figure 10. Sample M2

Table 3 Regents for preparing SBF (pH7.4, 1l)

Order	Reagent	Amount
1	NaCl	7.996 g
2	$NaHCO_3$	0.350 g
3	KCl	0.224 g
4	$K_2HPO_4 .3H_2O$	0.228 g
5	$MgCl_2.6H_2O$	0.305 g
6	1M-HCl	40 mL
(About 90 % of total amount of HCl to be added)		
7	$CaCl_2$	0.278 g
8	Na_2SO_4	0.071 g
9	$(CH_2OH)_3CNH_2$	6.057 g

The corrosion test is realized on 28 days, after every 7 days is verified the mass losing of the samples. In the first step was not observed cracks on the surface of the tested samples.

6. CONCLUSIONS

6.1 The best materials used to the prosthesis fabrication in dental and orthopedic medicine are those which are similar the composition of the humane bone, and the repairing mechanism of the bone is the natural regenerations. One approach to providing a strong, long-lasting adhesive interface between a bone replacement implant and the surrounding tissue involves the use of bioactive materials.

6.2 Macro and microscopic examinations of the realized combination show specific structure of the materials used, without plasma spraying defects (pores, cracks, microcraks).

6.3 The generalized corrosion tests are made in simulated body fluid (SBF) by the determination of the mass losing in the tests cycles. The test results confirm the corrosion resistance of the investigated specimens.

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