Hydroxyapatite Coatings on Titanium Implants

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The coating of titanium and its alloys with hydroxyapatite (HA) by various methods was presented. The vacuum deposition, plasma spraying, sol-gel and coating, electrolytic methods were used.

Keywords: titanium , hydroxyapatite, vacuum deposition, plasma spraying, electrolytic methods

Studies of artificial implant materials involved titanium and its alloy due to their mechanical and biocompatible properties [1-3]. However, these materials experience important problems when implanted in human tissue. Natural tissue does not adhere to implants and they bond poorly to living bones, resulting in displacements when stressed. For this reason, titanium and its alloys were coated with hydroxyapatite (HA) by various methods. An apatite layer on the implant surfaces permits the bonding to bone. The apatites form a vast range of solid solutions. Among the apatites, hydroxyapatite is important because its crystals are the inorganic constituent of osseous and dental tissues.

The bone - like apatite layer has been characterized to be similar to the mineral phase in human bones. The bone tissue has two distinct structural forms: dense cortical bone and cancellous bone. The material of cortical and cancellous bone consists of cells in a mineralized matrix. All skeletal cells are known to differentiate from the mesenchymal stem cells of the embryo. In addition to mesenchymal stem cells, three principal cell types are present in bone: osteoblasts, osteoclasts and osteocytes. Osteoblasts are active bone forming cells and are present at the bone surface [4-7].

The bonding process between implant HA layer and natural bone is similar to the bonding between natural bones. The osteoblasts cells proliferate on the bone - apatite layers and form a biological matrix containing 90 % collagen, bio - apatite and a variety of matrix proteins. Gaps in the collagen fibrils serve as mineral nucleation sites for calcium phosphate which forms the inorganic phase. The result is a composite of collagen phase and a strong ceramic phase giving high strength and toughness to bone [8-11].

A lot of techniques have been developed for preparing HA coatings for titanium implants. These include vacuum deposition, plasma spraying, sol - gel and dip coating and electrolytic methods. These physical techniques produce coatings and films with high density and high bonding strength, but they are expensive, and require sophisticated equipment. Since high temperature is involved, it is difficult to control the coating composition and crystal structure. High temperature often generates cracks in the HA coating resulting from differential expansion between the coating and substrate.

Alternative coating methods rely on biomimetic techniques which are designed to form a crystalline HA layer in a manner similar to the process of natural bone formation. Recent research showed that the biomimetic process is one of the most promising techniques for producing new biomaterials at ambient temperatures. Calcium phosphate coatings [12-15] have been produced in aqueous solutions at physiological temperatures (37 ^{o}C) using simulated body fluid (SBF).

In the present study, a biomimetic technique [14] was used to produce calcium phosphate coatings on titanium substrates in order to use titanium implants in dentistry.

Experimental part

Materials and methods

NaOH pre-treatment of titanium. Titanium alloy (Ti_6Al_4V) was used in coatings with chemical composition shown in table 1. Small rectangular pieces of 10 x 10 x 3 mm in size were cut as samples from a titanium plate. All samples were ultrasonically cleaned in alcohol for 10 min, in acetone for 15 min, and then in deionised water for 5 min. Samples were treated in NaOH solution 0.6 M at 160 ^{o}C in a pressure chamber for 48 h. After the pre-treatment, all the samples were washed in deionised water for 5 min.

SCS preparation and coating process. Hydroxyapatite layer was formed on titanium using a biomimetic method. Supersaturated calcification solution (SCS) was prepared by dissolving the reagent grade chemicals $CaCl_2$, NaH_2PO_4 and $NaHCO_3$ in deionised water successively. Three kinds of SCSs were prepared with different ion concentrations. Masses of salts in 1 L of SCS solution (mg) are shown in table 2. The coating was conducted as follows. Titanium samples were immersed after NaOH - treatment into 200 mL SCS contained in beakers. The beakers were placed in a shaking water bath at 37 ^{o}C for 24 h with a shaking rate

Table 1
CHEMICAL COMPOSITION OF Ti_6Al_4V ALLOY

Elements	Ti	Al	V	Fe	C	O	N	H
%	88.5 – 90.5	5.5 – 6.5	3.5 – 4.5	max. 0.25	max. 0.08	max. 0.13	max. 0.05	max. 0.015

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of 80 rev./min. The samples were taken out after 24 h immersion and thoroughly rinsed with deionised water and then dried in an oven at 60 °C for 2 h.

Table 2
MASSES OF SALTS IN 1 L OF SCS SOLUTION (mg)

Solution \ Salt	$CaCl_2$	NaH_2PO_4	$NaHCO_3$
SCS-1	555	600	126
SCS-2	555	300	126
SCS-3	1110	300	126

Characterization. The pH value of the solutions was measured during the coating process with a calibrated pH meter (CONSORT 381). The substrates and coatings were investigated by X-ray diffraction (XRD) with a DRON - 2.0 diffractometer with a CuKα target. To observe the morphology of the coatings by optic microscopy, freshly coated surfaces were exposed.

Results and discussion

The initial pH value was measured to be 5.88, 6.26 and 6.14 for SCS-1, SCS-2 and SCS-3, respectively. The pH value of the solutions increased to a maximum within the first 2 h in SCS-1 and SCS-3, and within 3 h in SCS-2. This led to the supersaturation of the solutions with Ca^{2+} ions, and subsequently precipitation was induced on the titanium substrates. During the deposition process, the *p*H values decreased steadily to an observation time of 24 h.

Biomimetic treatment in supersaturated calcium solutions (SCS) was carried out in 2 steps:

- 1. *Titanium alloy oxidizing*: in NAOH solution 0.6 M, at 160 °C, for 48 h, in a pressure chamber (an autoclave). Complex sodium titanate is synthesized.

$$Ti + 2\,NaOH \xrightarrow{160^oC} Na_2Ti_5O_{11}$$

- 2. *Deposition of ceramic layer* (apatite and calcium phosphates) in SCS solutions.

The chemical reactions can be envisaged as follows [14]:

1) $H_2PO_4 \leftrightarrow HPO_4^{2-} + H^+$

2) $HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+$

3) $H^+ + HCO_3^- \leftrightarrow H_2O + CO_2$

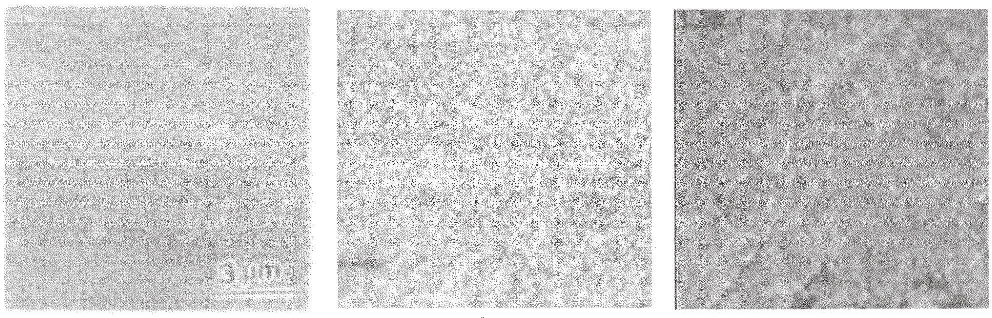
4) $10\,Ca^{2+} + 6PO_4^{3-} + 2OH^- \xrightarrow{37^oC} Ca_{10}(PO_4)_6 \cdot (OH)_2 \downarrow$
hydroxyapatite

5) $Ca^{2+} + HPO_4^{2-} + 2H_2O \xrightarrow{37^oC} CaHPO_4 \cdot 2H_2O \downarrow$
brushite

Figure 1 displays optical morphological features for successive conversion of the metallic surface to the ceramic surface: surface of Ti piece (fig. 1a), Ti oxide layer (figure 1b) and hydroxyapatite ceramic layer (fig. 1c).

Figure 2 shows optical morphological features of the coatings in low magnification. A uniform calcium phosphate coating was formed on the substrates of samples in SCS-1 and in SCS-3 after 24 h immersion, while some dispersed crystals were formed on the substrate of samples in SCS-2.

The surfaces of the coated titanium substrates were investigated by XRD method. X-ray diffraction patterns of all samples (SCS-1, SCS-2 and SCS-3), recorded in air at room temperature, contain the diffraction lines characteristic to the hydroxyapatite and their intensity is a measure of crystallinity (fig. 3).



a b c

Fig. 1. Optical microscopy data for successive conversion of the metallic surface to the ceramic surface: a) surface of Ti piece; b) Ti oxide layer; c) hydroxyapatite ceramic layer

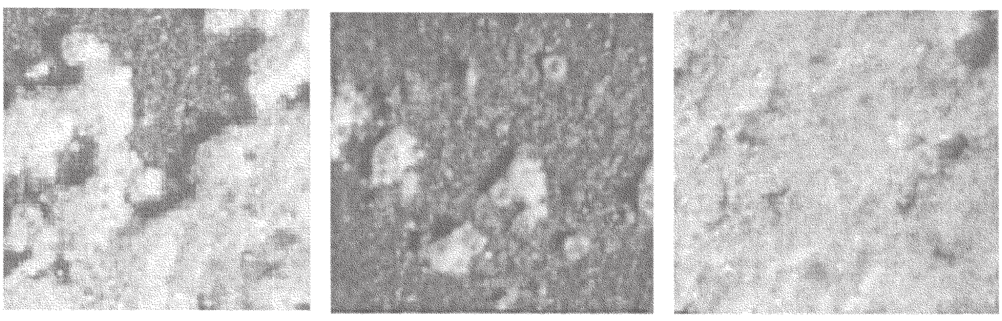

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Fig. 2. Optical microscopy - Ceramic layers deposited by biomimetic method in: a) SCS-1 solution, b) SCS-2 solution, c) SCS-3 solution (x 300 magnitude).

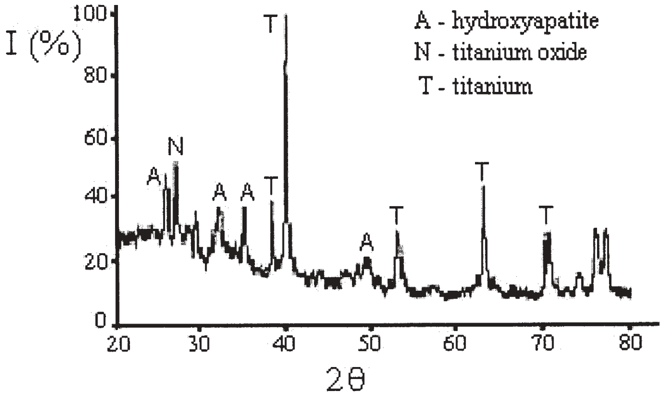

Fig. 3. XRD pattern (CoK$_a$ radiation) of the biomimetic apatite layer deposited in SCS-3

Conclusions

Hydroxyapatite coatings show attractive properties such as lack of toxicity, the possibility of forming a direct bond with bone and the possibility to stimulate bone growth.

The used biomimetic method confirm the approach and results of previous works [13,14] and shows a simple and low energy way to grow calcium phosphate coatings on titanium substrates at body temperature.

This method can be considered a promising technique to prepare hydroxyapatite coatings for dentistry implants.

References

1. POPA, M.V., DROB, P., RÃDUCANU, D., CASTRO, J.R., MÂRZA-ROªCA, J.C., Rev. Chim. (Bucureºti), **58**, nr. 2, 2007, p. 179
2. POPA, M.V., VASILESCU, E., DROB, P., IONITA, D., VASILESCU, C., Rev.Chim. (Bucuresti), **57**, nr. 2, 2006, p.158
3. RADUCANU, D., VASILESCU, E., DROB, P., CINCA, I., VASILESCU, C., Rev.Chim. (Bucuresti), **57**, nr.12, 2006, p. 1221
4. MEULEN, M., PRENDERGAST, P., Phil. Trans. Royal Soc. Lond. A, **358**, 2000, p. 565
5. MARTIN, R.B., BURR, D.B., Structure, function and adaptation of compact bone, Raven Press, New York, 2001, p.226
6. YAMADA, S., HEYMANN, D., BOULER, J.M., DACULSI, G., Biomater., **18**, 1997, p. 1037
7. CAMERON, H.U., MACNAB, I., PILLIAR, R.M., J. Biomed. Mater. Res., **11**, 1977, p. 179
8. HARADA, Y., WANG, J.T., DOPPALAPUDI, V.A., WILLIS, A.A., JASTY, M., HARRIS, W.H., NAGASE, M., GOLDRING, S.R., J. Biomed. Mater. Res., **31**, 1996, p. 19
9. HEYMANN, D., PRADAL, G., BENAHMED, M., Histol. Histopathol., **14**, 1999, p. 871
10. HAIBO, W., LEE, J.K., MOURSI, A., LANNUTTI, J.J., J. Biomed. Mater. Res., **68A**, 2004, p. 61
11. HAIBO, W., LEE, J.K., MOURSI, A., ANDERSON, D., WINNARD, P., POWELL, H., LANNUTTI, J.J., J. Biomed. Mater. Res., **67A**, 2003, p. 599.
12. BARRERE, F., LAYROLLE, P., BLITTERSWIJK, C.A., GROOT, K., Bone, **25**, nr. 2**,** 1999, p. 107
13. FENG, Q.L., WANG, H., CUI, F.Z., KIM, T.N., J. Cryst. Growth., **200**, 1999, p. 550
14. LI, F., FENG, Q.L., CUI, F.Z., LI, H.D., SCHUBERT, H., Surface and Coatings Technology, **154**, 2002, p. 88
15. TRETINNIKOV, O.N., KATO, K., IKADA, Y., J. Biomed. Mater. Res., **28**, 1994, p. 1365

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