

PREPARATION OF BIOACTIVE Ca-P COATING ON Ti ALLOY AND MEASUREMENT OF ITS ADHESION BY SCRATCH TEST

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PRÍPRAVA BIOAKTÍVNEHO Ca-P POVLAKU NA Ti ZLIATINE A MERANIE JEHO ADHÉZIE VRYPOVOU SKÚŠKOU

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Abstrakt

Veľa výskumných prác je v oblasti biomateriálov zameraných na tvorbu bioaktívnych povlakov na kovových a nekovových substrátoch, ktoré sa implantujú do ľudského organizmu. Snahou je využiť mechanické vlastnosti substrátu a bioaktivitu povlaku. Implantáty s bioaktívnym povlakom rýchlejšie interagujú so živým organizmom a dochádza k pevnému spojeniu s tkanivom. Je veľmi dôležité aby mali povlaky dobrú adhéziu k substrátu. K lepšiemu ukotveniu implantátu s kostným tkanivom dochádza ak sú povrchy substrátu pred povlakovaním mechanicky a chemicky upravené.

Táto práca je zameraná na prípravu vápenato-fosforečnanového povlaku (Ca-P) na brúsenej a tryskanej titánovej zliatine Ti6Al4V v kalcifikačných roztokoch a meranie adhézie týchto povlakov k substrátom.

Substráty boli predupravené koncetrovanou HCl a následne roztokom 10 mol.dm⁻³ NaOH. Na povrchu substrátu dochádza k tvorbe gélovitej vrstvy TiO₂ s obsahom Na⁺ iónov. Po expozícii v kalcifikačnom roztoku (SCS) po dobu 2 hodín a 3 dní sa na povrchu vytvára súvislý Ca-P povlak tvorený husto zoskupenými kryštálmi okta fosforečnanu vápenatého (OCP). Adhézia takto získaných Ca-P povlakov na brúsenej a tryskanej titánovej zliatine bola meraná vrypovou skúškou pomocou scratch testeru. Povlaky boli vizuálne sledované rastrovacím elektrónovým mikroskopom (SEM/EDS) a optickým mikroskopom (OM).

Povlaky vytvorené počas dvoch hodín v SCS mali pri nízkych zaťaženiach dobrú odolnosť voči poškodeniu, pri stredných zaťaženiach dochádzalo k poškodeniu povlakov a pri vysokých zaťaženiach došlo k poškodeniu samotného substrátu. Ca-P povlaky vytvorené počas troch dní v SCS mali slabšiu adhéziu substrátu, ktorá bola negatívne ovplyvnená veľkosťou a lámavosťou OCP kryštálov, a väčšou hrúbkou povlaku.

Abstract

Many research works in field of biomaterials are focused on forming of the bioactive coatings on metallic and non-metallic substrates which are implanted into human body. The purpose of the effort of this combination is the utilizing the mechanical properties of substrate and the bioactivity of the coatings. Implants with bioactive coating interact faster with living body and make a strong bond with the tissue. For the coating it is very important to have a very good adhesion to the substrate. Better bonding of implants to tissue can be achieved by mechanical and chemical treatment of the implant surface before the deposition.

This work is focused on preparation of calcium-phosphate (Ca-P) coating on ground and sandblasted titanium alloy Ti6Al4V in calcification solutions and on the measurement of adhesion of these coatings to substrates.

Substrates were pretreated by concentrated HCl and then by solution of 10 mol.dm⁻³ NaOH. The sodium titanate hydrogel is formed on the surface of substrate. The uniform Ca-P coating of densely clustered octacalcium phosphate (OCP) crystals is formed after 2 hours of exposition in calcification solution (SCS). The adhesion of this Ca-P coating on grinded and sandblasted titanium alloy was measured by scratch method using a scratch tester. The coatings were visually observed by scanning electron microscope (SEM/EDS) and optical microscope (OM).

Coatings formed in two hours in SCS had a good adhesion at low load and they peeled at medium load. The substrates damaged at high load. Ca-P coatings formed in three days in SCS solution had a poorer adhesion to substrate, which had been negatively influenced by size of OCP crystals and cracking of thick film of Ca-P compounds.

Keywords: titanium alloy, calcification, octacalcium phosphate, adhesion, scratch test

1. Introduction

Biomaterials are the synthetic materials produced to repair, support or substitution of the injured or missing tissues or organs. Biomaterials can be divided into four groups: metals, ceramics, polymers and composites. These materials have to provide physical, mechanical and chemical behavior conditions in the body and they have to be biocompatible. Nowadays the metal materials have wide application in dental and surgical implantation. Stainless steel, titanium and titanium alloy are used as screws, washers or hip prostheses. They show high resistance to corrosion and good mechanical properties.

The surface of the implant substrates is mechanically and chemically pretreated to achieve the biocompatibility. At present, there exist many methods for coating of metal and non-metal substrates, each of them have advantages and disadvantages. The most famous are plasma and flame spraying, electrophoretic deposition, sol-gel dipping method and biomimetic deposition.

In case of biomimetic deposition the substrates are soaked into calcium phosphate solutions of different ion concentration where the simulated biomineralized process takes place. This process includes a controlled nucleation and growth crystals. During a short period the substrate surfaces are coated by uniform calcium phosphate crystals showing a shape of plates organized like a rosette and arranged into spherulites [1-4].

Common methods for measurement of adhesion are tape test, scratch test, pull off test, knife test et al. The selection of test depends on type and thickness of coating or layer [7].

The aim of this work was the preparation of octacalcium phosphate coatings on ground and sandblasted titanium alloy in supersaturated calcification solution and the

measurement of their adhesion to substrate by scratch test. The coatings before and after adhesive measurement of adhesion were observed by scanning electron (SEM/EDS) and optical microscope (OM).

2. Material and methodics

Titanium alloy samples (Ti6Al4V) of a size of 10 x 10 x 0,8 mm were divided into two groups. The samples from the first group were grinded by SiC paper No. 500, the samples from the second group were sandblasted by electro-corundum, the size of particles was 125 μm , at 0,4 MPa for 3 sec. All samples were subsequently washed by acetone in ultrasonic bath and by demineralized water.

After drying all samples have been leached in concentrated chloride acid (36% HCl) at laboratory temperature for 90 min. and subsequently 5-times washed by demineralized water. After drying at air all samples have been soaked in 10 mol.dm⁻³ NaOH solution at 60°C for 24 hrs. and again washed by demineralized water [2].

The supersaturated calcification solution (SCS, high concentration of Ca²⁺ and PO₄³⁻ ions) was prepared from reagents CaCl₂, NaH₂PO₄ and NaHCO₃ with concentration showed in tab.1, pH value of solution was 6,2 [2].

Table 1 Ion concentration of calcification solution [2]

Ion concentration of SCS (mmol.dm ⁻³)				
Na ⁺	Ca ²⁺	Cl ⁻	H ₂ PO ₄ ⁻	HCO ₃ ⁻
4	5	10	2.5	1.5

The samples have been exposed in SCS at $S/V = 0,1 \text{ cm}^{-1}$ (S-sample surface, V-volume of SCS solution) at 36,5°C for 2 hours and 3 days in biological thermostat under static condition. After exposition all samples were softly washed by demineralized water and dried at air.

The measurement of adhesion was performed by scratch test (EN 1071-3) at DMS in Pilsen. The measurement of samples resistance to damage was performed by scratch indentation test CSEM REVETEST. Normal force constantly increased from 0 N to 80 N. The Rockwell diamond indenter was used for this measurement (fig. 1a). The morphology of damage at coating - substrate system at load 0 - 80 N was monitored. Normal load at which damage can first be observed is called a critical load L_c . Several failure events as cracking or coating peeling can be seen at higher critical load. The beginning of cracking is marked L_{c1} , exfoliation of the coating (typically at the edges) L_{c2} and penetration of coating to the substrate at the center of the track L_{c3} (fig. 1b). The surfaces were observed by optical microscope [5,6].

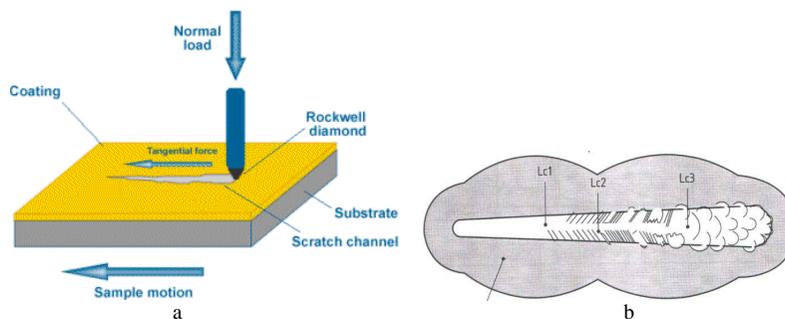


Fig.1 Schematic representation of: a) scratch test, b) critical loads indicating start damage [5,6]

3. Results and discussion

The thicker passivating TiO_2 layer and impurities from surface were removed by grinding and sandblasting. Sandblasting led to more considerable surface roughness than grinding. The stress of surface caused by quick mechanical changes during sandblasting and grinding was eliminated by leaching of substrates in concentrated chloride acid. The changes of surface roughness are documented by results of measurement of microgeometric parameter R_a in tab. 2 and by recorded profiles in fig. 2.

Table 2 Parameter of the surface roughness R_a of ground and sandblasted Ti6Al4V samples after chemical treatments in HCl and NaOH solutions

reagent	R_a [μm]	
	ground	sandblasted
surface after mech. treatment	0.130	0.480
surface after HCl	0.290	0.530
surface after NaOH	0.710	4.100

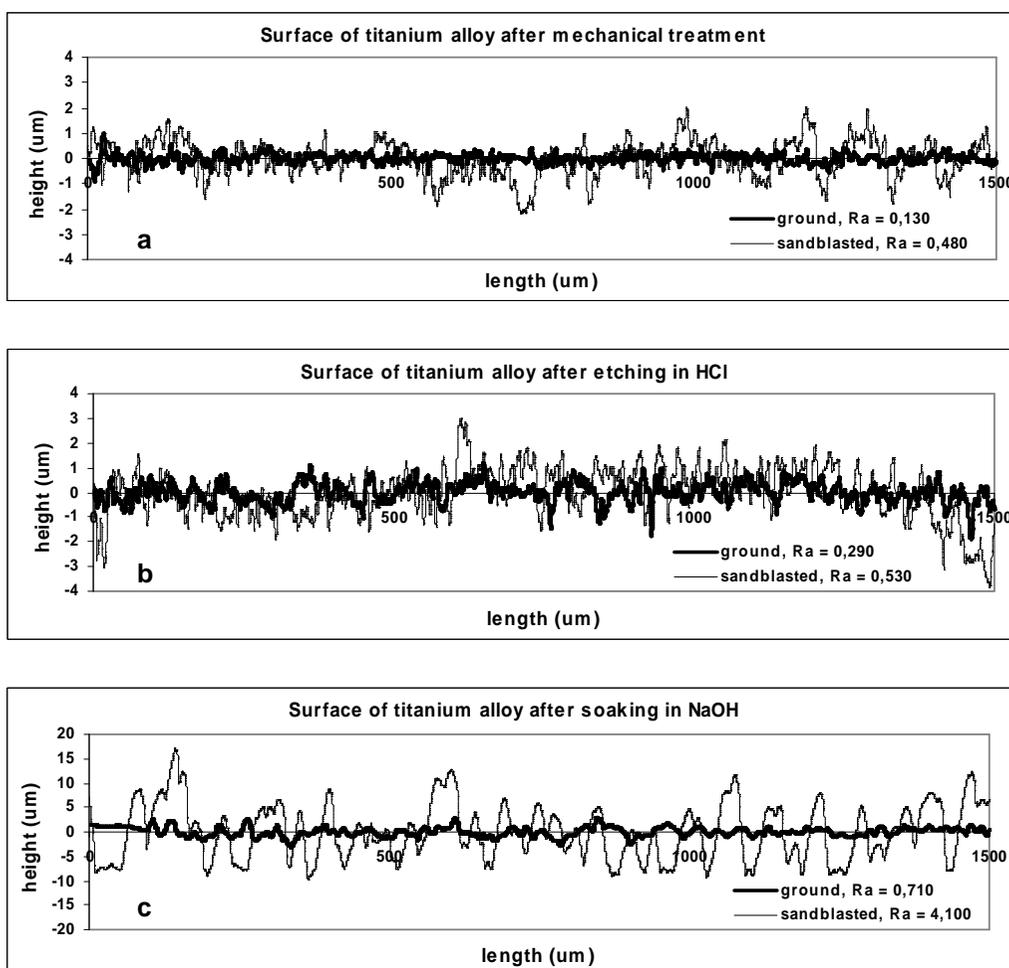


Fig.2 Profile comparison of the ground and sandblasted Ti6Al4V samples: a) surface after mechanical treatment; b) surface after etching in HCl; c) surface after soaking in NaOH

The recorded profiles of sandblasted surfaces show more considerable relief changes due to chemical treatments. The differences of profiles caused by mechanical treatments and the changes caused by chemical agents can be seen in the graphs. The values of Ra with sandblasted samples are higher than with ground samples and they increase by subsequent chemical treatment. Sandblasting induces considerable roughness of surface, makes deeper notches and ledges against the ground surface. The surface profile deepens by etching in HCl but the differences between the ground and the sandblasted surfaces become less apparent (fig. 2b). Soaking in NaOH significantly deepens the relief of the sandblasted surfaces (fig. 2c).

The aim of treatment in alkali solution 10 mol.dm^{-3} NaOH was the formation of TiO_2 amorphous hydrogel layer containing Na^+ ions at the substrate surface (fig. 3b). This layer supports the forming of calcium phosphate (Ca-P) coating during exposition in supersaturated calcification solution (SCS).

The exchange of Na^+ to Ca^{2+} ions and simultaneously interaction of $(\text{PO}_4)^{3-}$ ions from the solution with OH^- groups and Ca^{2+} ions from the surface takes place during their exposition as chemically treated samples in SCS. In a short time the surface of ground and sandblasted substrate is covered by uniform coating composed by densely grouped rosette like crystals arranged into small and big spherulites (fig. 4). EDS analyses of crystals confirm the molar ratio $\text{Ca/P} = 1, 3 - 1, 1$ which indicates a presence of octacalcium phosphate. The thickness of Ca-P coating after 2 hours in SCS is approximately $15 - 20 \mu\text{m}$.

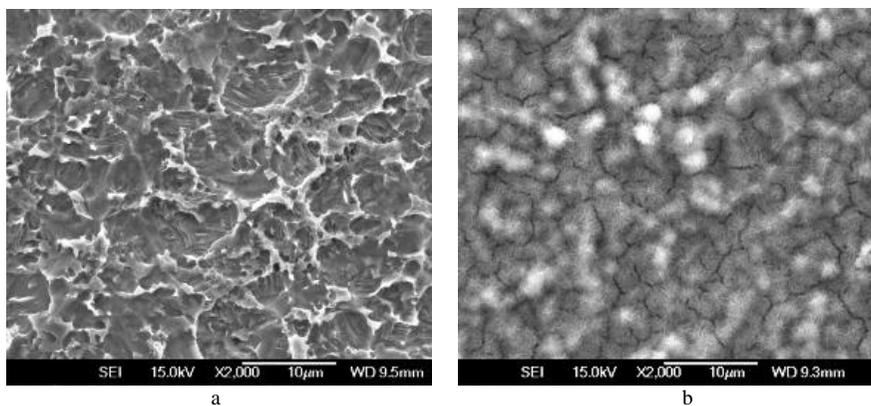


Fig.3 (SEM) Surface of sandblasted Ti6Al4V samples after a) HCl and b) alkali treatment

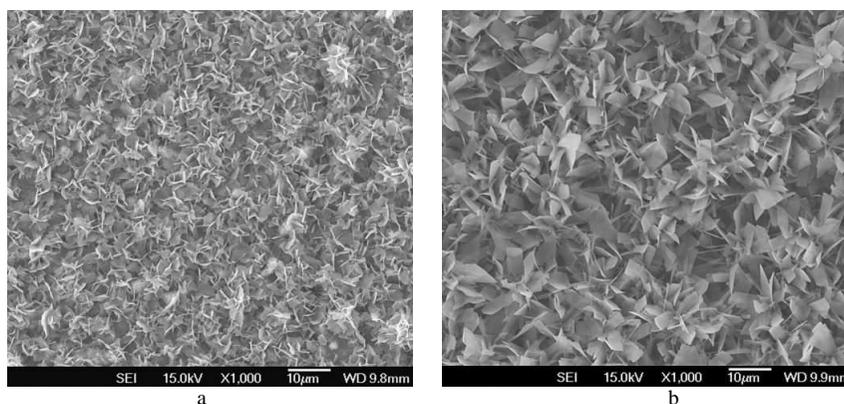


Fig.4 (SEM) Ca-P coating on ground Ti6Al4V samples created during the exposure to SCS for a) 2 hrs, b) 3 days

Adhesion of Ca-P coatings to ground and sandblasted titanium alloy was measured by scratch test. Fig. 5 shows the morphologies of scratch on Ca-P coating formed in SCS for 2 hrs. on Ti-alloy samples. The smallest damage at low load (7N) is on Ca-P coating on ground Ti-alloy. Increasing of load causes quick wear of surface coat (14N). The considerable damage at the beginning of the scratch can be observed on the coating of the sandblasted Ti-alloy (3N).

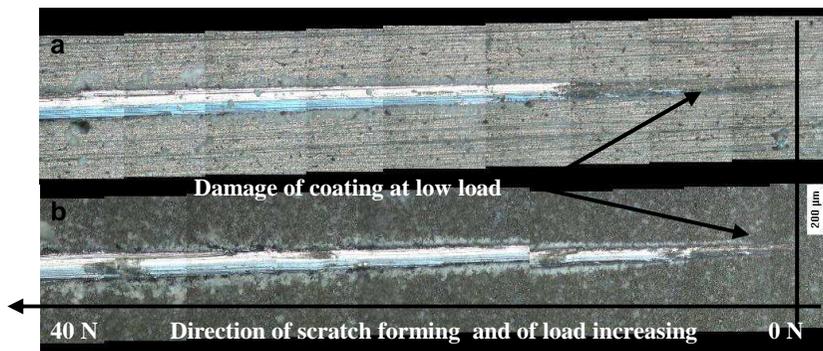


Fig.5 OM Morphologies of scratch on Ca-P coating formed during 2-hours exposition in calcification solution on Ti-alloy: a) ground, b) sandblasted

In Fig. 6 are shown the surface morphologies after indentation of the substrates treated in NaOH solution with subsequent exposition in calcification solution for three days. Ca-P coating on ground Ti-alloy has a poorer adhesion (6-9N). Coating on sandblasted Ti-alloy compared with coating on ground Ti-alloy shows higher resistance (5-11N), but the cohesive damage at scratch edge appears with increasing of normal load.

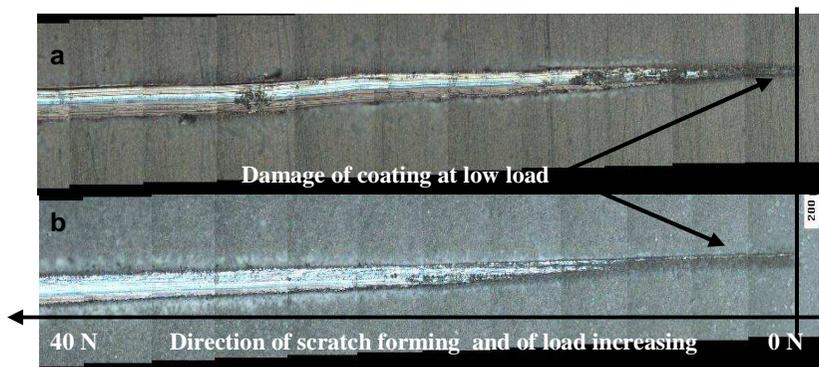


Fig.6 OM Morphologies of scratch on Ca-P coating formed during 3-days exposition in calcification solution on Ti-alloy: a) ground, b) sandblasted

4. Conclusion

Pre-calcification by supersaturated calcification solution accelerates the precipitation of calcium phosphate coating with octa calcium phosphate crystals on ground and sandblasted titanium alloy. The substrates were pretreated by concentrated chloride acid and subsequently by sodium hydroxide. Thanks to this pretreatment Ca-P coating is formed in calcification solution in a short time. Ca-P coating exposed in simulated body fluid (*in vitro* test) is able to accelerate

the interaction with solution result in forming of hydroxyapatite in the body fluids. According to the results of adhesion measurement only Ca-P coatings formed on metal substrate in calcification solution during short time (2 hrs.) showed a good adhesion.

These tests are only an informative evaluation of adhesion because accuracy and correctness of measurement depend on several factors. It is necessary take into consideration the conditions under which the measurement of adhesion was realized: size of samples, type of substrate, type of coating and method of scratching. However for testing of quality of Ca-P coatings the mentioned adhesion test satisfyingly indicates that the prepared bioactive coating on Ti substrates is applicable for next testing.

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