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Bioactive coating on NiTi matrix

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Abstract

One of the ways of controlled synthesis of biocomposites is application of functional coatings with required medical and biological properties on the metal substrate with high strength properties. The authors propose a method for vacuum impregnation of highly porous NiTi, which excludes heat treatment and maintains the phase composition and high biological activity of HAP. The developed method of biocomposite preparation makes it possible to produce coatings containing from 1 to 45 wt-% HAP with controllable formation of the structure and biomedical properties of the sample.

Keywords

Biocomposites, Titanium Nickelide (NiTi), Hydroxyapatite (HAP), Functional Coatings

1. Introduction

A topical problem of modern medicine in the field of traumatic surgery, orthopedic surgery and stomatology is synthesis of materials suitable for introduction into the organism with the aim of treatment, restoration or replacement of bone tissues. The materials used in orthopedics should possess a complex of properties: chemical inertness, bioactivity or bioinertness, certain mechanical characteristics (strength, fracture resistance, wear resistance etc.), as well as manufacturability for the production of implants of required shape and size. Such diverse characteristics can be achieved by controlled synthesis of composite materials, in which each component is responsible for certain properties of the whole material. Stainless steel is widely used as a robust metal substrate. However, medical tools made thereof often cause allergic reactions in the organism of patients on the chemical elements entering into the composition of stainless steel [1]. In order to solve this problem, the ISSC UB RAS together with the pilot plant of the Russian Science Center for Traumatology and Orthopaedics named after Acad. G. A. Ilizarov worked out the process regulations for application of titanium nitride layer on 12X18H9 steel pins intended for Ilizarov transosseous osteosynthesis. The developed biologically inert coatings allowed us to obtain positive biomedical and clinical certification of the samples [2]. Simple preparation, high strength characteristics of pins and the optimal quality-to-price ratio set our development apart from its counterparts. More expensive materials for the implant substrate are cobalt-based alloys, as well as titanium and its alloys [3]. Although the latter materials, owing to their high corrosion stability, good biocompatibility and hypoallergenicity, are the leaders among metallic materials, negative reactions of the organism, even to the point of implant rejection, are still observed in some cases [4].

At present, highly porous honeycomb materials (HPHM), in which voids occupy 95% of volume, are finding ever-widening application in the fabrication of bone implants. These materials have low density (0.4–1 g cm^{-3}), developed specific surface, high intercommunicating porosity and high specific strength, as well as low hydraulic resistance [5]. The pore space can be filled with a bioactive substance. Composite materials with such structure have a developed system of open interconnected pores providing free flow of biological fluids in the whole implant volume, which favors osteointegration. Of much interest in terms of implantology are the bioactive materials that actively participate in

biochemical reaction of organism intensifying mutual integration of living bone tissue and the implant. One of the promising bioactive compounds is hydroxyapatite (HAP), $Ca_{10}(PO_4)_6(OH)_2$. The ability of HAP to heal and regenerate bone tissue is well known; however sintered HAP ceramics has a significant drawback – low strength characteristics. The existing methods for ceramics strengthening do not provide any radical solution of this problem [3]. Our work is aimed to contribute to the elimination of this disadvantage.

The useful biomedical properties of HAP can be realized in the preparation of bone implants from composite materials, in which HAP is used for coating of the metal substrate.

To date, different methods for application of HAP coatings have been developed: thermal, electron-beam, laser ablation, magnetron, zol-gel, chemical vapor deposition, electrophoretic precipitation etc. The main method that found commercial application is plasma spraying; and in this case, high-temperature behavior is an important characteristic of materials [3, 4].

It is known that the thermal stability of HAP depends on the method and conditions of synthesis: HAP produced by solid-phase synthesis is stable up to 1100–1200 °C, whereas deposited HAP – a more promising material used as a biodegradable bone tissue substituent most similar to bone HAP – decomposes already at 700–800°C (Figs. 1, 2), which impedes its application in the production of implants for orthopedic surgery with the use of high-temperature methods of coating formation [3]. Besides, the thermal regimes of HAP treatment decrease its biological activity owing to the processes occurring during sintering: compaction of material, reduction of specific surface area. Thus, choosing the method of HAP application on the metal component of implant, one should take into account the possibility of variation of its phase composition and bioactive properties under severe process conditions.

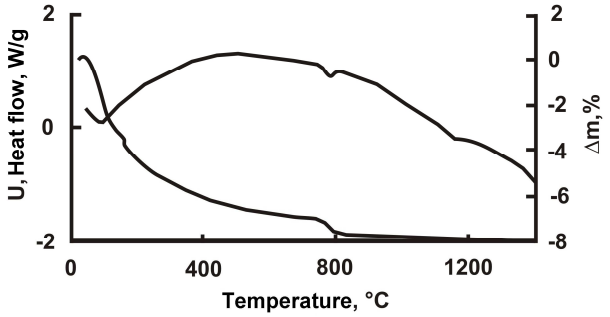

Fig. 1. *The results of thermal analysis of HAP produced at ISSC UB RAS by deposition from solutions.*

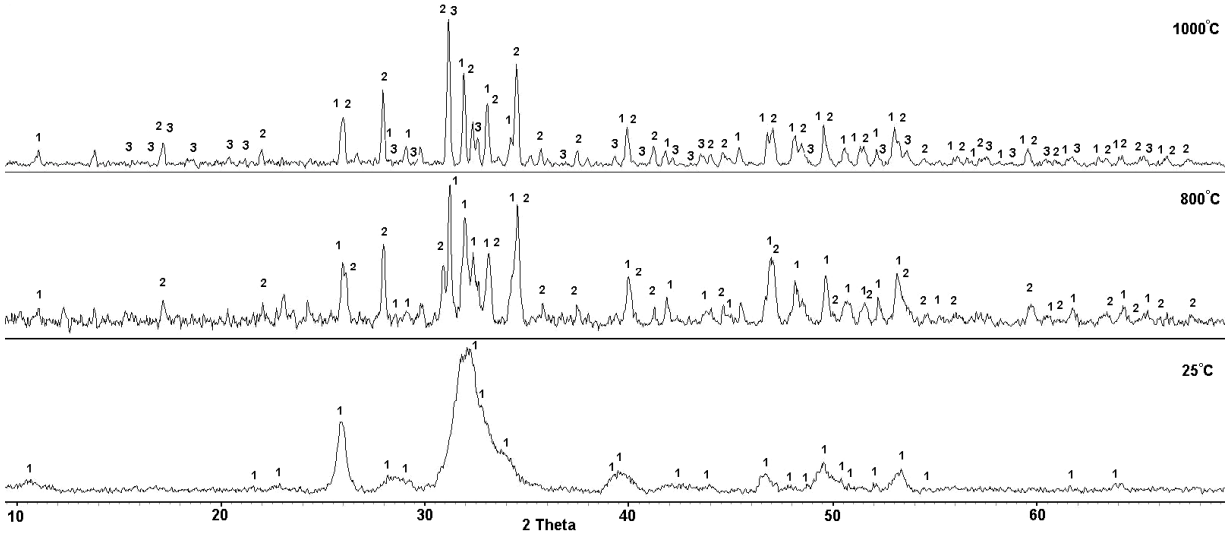

Fig. 2. *The X-ray diffraction patterns of HAP produced at ISSC UB RAS at different annealing temperatures: 1 - $Ca_{10}(PO_4)_6(OH)_2$; 2 - β – $Ca_3(PO_4)_2$; 3 - α – $Ca_3(PO_4)_2$..*

In this work we present the results of our studies devoted to the preparation of composites for bone implants based on titanium nickelide HPHM used as the metallic substrate with a HAP coating.

2. Experimental Methods

Highly porous titanium nickelide was synthesized on the basis of highly porous honeycomb nickel having the following characteristics: general porosity 90±1%, open porosity 65±1%, closed porosity 24±1%, average pore size 400 μm (Fig. 3).

Titanium nickelide was synthesized by ion-plasma electronic arc spraying on an NNV 6.6 I1 facility. The low-energy argon ion flow treatment in vacuum provided not only effective cleaning of nickel samples, but also activation of their surface facilitating the formation of titanium nickelide.

The deposition of titanium ions on the porous nickel samples was carried out for 120–140 min during heating up to 700–800°C, the potential on the planetary train being 300–350 V. The process of spraying was interrupted by titanium cathode arc quenching. The produced samples were cooled in the working chamber at a pressure of $(5–7)\times10^{-5}$ mm Hg for 2 h.

The phase composition of the obtained product was determined by comparing the results of X-ray phase analysis (XPA) (DRON 2.0, $Cu_{k\alpha}$ radiation, angle interval $10 \leq 2\Theta \leq 70°$, survey step 0.03°, time at point 2 s) with the data of the Powder Diffraction File JCPDSD-ICDD PDF2 (Release 23.08.2012). The identification of the X-ray diffraction patterns was carried out using the Crystal Match 2 software. The porosity was determined by the known method [6].

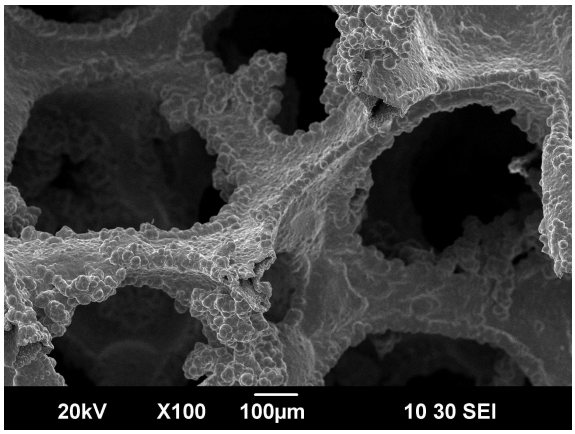

Fig. 3. *The micrograph of highly porous honeycomb nickel.*

A sedimentation-resistant HAP suspension with the concentration of the basic substance of 1–10 mass % produced by the standard solution deposition method [7] was used as a coating material. The interaction was due to mixing of 0.02 M aqueous solution of calcium hydroxide and 0.07 M solution of phosphoric acid taken in the volumetric ratio (3.75÷5) : 1. The initial mixture was mixed at room temperature for 15 min. The resulting dispersed system was filtered, and the deposit was aged in air at room temperature. While drying, the dispersed system transforms into a HAP suspension, which during further ageing forms crystalline HAP of the composition $Ca_{10}(PO_4)_6(OH)_2$.

Choosing the optimal method for HAP application on the metal substrate, which would maintain the phase composition and high biological activity of the coating, we proposed and studied the following techniques: dosed stepwise saturation of HPHM with biomaterial by vacuum impregnation followed by drying in air (method 1); dosed stepwise saturation by vacuum impregnation followed by centrifugation and thermal treatment (method 2); dosed stepwise saturation by ultrasonic treatment of HPHM with HAP suspension with subsequent drying in air (method 3).

In method 1, a dosed amount of HAP suspension was passed through a sample under vacuum (10^{-10}–8×10^{-1} mm Hg) conditions. After impregnation of HPHM with biomaterial, the samples were dried in air.

In method 2, after vacuum impregnation, the sample was placed into HAP suspension and centrifuged for 1 min at a rate of 3500 rev min^{-1}. The resulting composite was then heat treated in a muffle furnace at 100 °C for 1 h.

In method 3, HAP coating was produced by ultrasonic treatment of highly porous titanium nickelide sample in aqueous HAP suspension on an automatic plant (ID–11 ultrasonic disintegrator) with subsequent drying in air.

In all these methods, the amount of sorbed HAP was determined from the difference in the sample weight before and after the application of biomaterial.

The morphological peculiarities of the surface of samples upon application of HAP were studied with the use of the scanning electron microscopy method (SEM).

3. Results and Discussion

The choice of titanium nickelide as a porous implant substrate was due to its biological inertness, good strength and anticorrosion properties [8]. Ion-plasma spraying provides close adhesion of titanium coating to the nickel surface (Fig. 4).

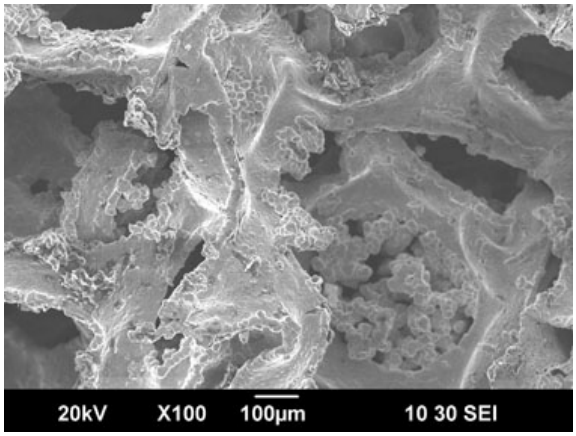

Fig. 4. *The micrograph of the surface of highly porous honeycomb nickel upon application of titanium coating.*

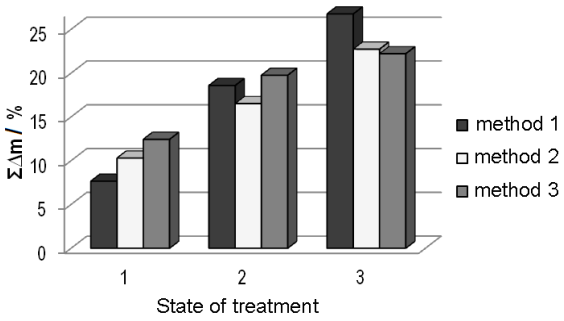

Fig. 5. *The variation in the biocomposite mass as a result of dosed stepwise saturation of highly porous titanium nickelide with HAP with the use of different methods.*

The suspensoid-type colloidal HAP solution necessary for impregnation of HPHM was prepared by interaction of calcium hydroxide and phosphoric acid in the ratio (3.75÷5) : 1. Highly dispersed colloidal HAP can be obtained exactly under these conditions. If this parameter is decreased, calcium hydrophosphates and tribasic calcium phosphate are formed, whereas an increase in the parameter gives rise to calcium carbonate because the reaction is incomplete [9, 10]. In both cases, the end product is contaminated. The obtained suspensoid-type HAP is not only convenient for application on the implant surface, but, as distinct from crystalline HAP,

it can stimulate the osteorestorative processes more effectively [11, 12].

The results of investigation into dosed filling of the pore space of titanium nickelide with HAP are listed in Tables 1–3.

Analysis of the obtained data reveals that the most efficient technique is method 1 – vacuum impregnation of sample with subsequent drying in air, which provides an increase in the sample mass of 44.87 wt.-% at the eighth stage of treatment (Table 1). The use of centrifugation and thermal treatment in method 2 do not increase this parameter (Table 2). Note that the application of ultrasound for the application of HAP on the porous substrate of the sample leads to a rapid increase in its mass at the first stage of treatment, but at further treatment no considerable growth of the mass is observed (Fig. 5). Probably, the increase in the dispersity of HAP suspension under the action of ultrasound promotes the filling of small substrate pores, and subsequently the increase in mass is due only to the surface sorption of HAP. Figure 6 displays the SEM photographs of titanium nickelide samples with HAP coating, which are indicative of uniform and continuous sorption of the bioactive material with the use of method 1, whereas in method 2 even insignificant heating results in coating cracking, and method 3 does not allow a uniform coating to be produced throughout the volume.

Table 1. *The variation in the biocomposite mass as a result of saturation of highly porous titanium nickelide with HAP using vacuum impregnation and subsequent drying in air under normal conditions – method 1*

Stage of treatment	Initial mass/g	Final mass/g	Δm/g	Δm/wt-%	ΣΔm/g	ΣΔm/wt- %
1	0.72550	0.78100	0.05550	7.65	0.05550	7.65
2	0.78100	0.86030	0.07930	10.15	0.13480	18.58
3	0.86030	0.91955	0.05925	6.89	0.19405	26.75
4	0.91955	0.96200	0.04245	4.62	0.23650	32.60
5	0.96200	0.99600	0.03400	3.53	0.27050	37.29
6	0.99600	1.02100	0.02500	2.51	0.29550	40.73
7	1.02100	1.04645	0.02545	2.49	0.32095	44.24
8	1.04645	1.05100	0.00455	0.44	0.32550	44.87
9	1.05100	1.05965	0.00865	0.82	0.33415	46.06

Table 2. *The variation in the biocomposite mass as a result of saturation of HPHM with HAP using vacuum impregnation with subsequent centrifugation (1 min, 3500 rev min^{-1}) and thermal treatment (T = 100 °C, 1 h) – method 2*

Stage of treatment	Initial mass/g	Final mass/g	Δm/g	Δm/wt-%	ΣΔm/g	ΣΔm/wt- %
1	0.57850	0.63800	0.05950	10.29	0.05950	10.29
2	0.63800	0.67400	0.03600	5.64	0.09550	16.51
3	0.67400	0.7100	0.03600	5.34	0.13150	22.73
4	0.7100	0.73875	0.02875	4.05	0.16025	27.70
5	0.73875	0.75800	0.01925	2.61	0.17950	31.03
6	0.75800	0.79200	0.03400	4.49	0.21350	36.91
7	0.79200	0.80700	0.01500	1.89	0.22850	39.50
8	0.80700	0.82730	0.02030	2.52	0.24880	43.01

Table 3. *The variation in the biocomposite mass as a result of saturation of HPHM with HAP using ultrasonic treatment of highly porous titanium nickelide in aqueous HAP suspension with subsequent drying in air under normal conditions – method 3*

Stage of treatment	Initial mass/g	Final mass/g	Δm/g	Δm/wt-%	ΣΔm/g	ΣΔm/wt- %
1	0.89600	1.00735	0.11135	12.43	0.11135	12.43
2	1.00735	1.07300	0.06565	6.52	0.17700	19.75
3	1.07300	1.09500	0.02200	2.05	0.19900	22.21

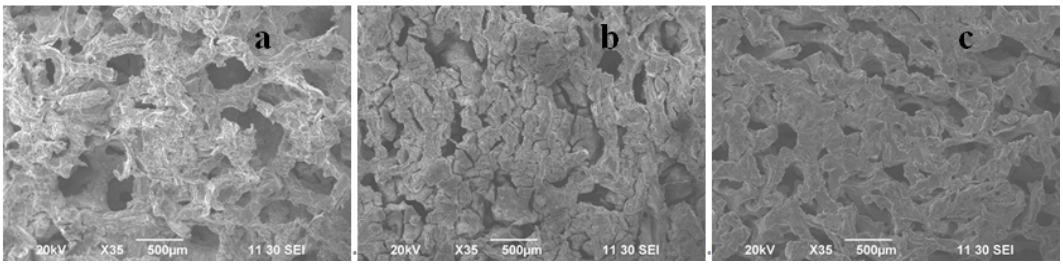

Fig. 6. *The micrographs of the biocomposite prepared by different methods: method 1 (a), method 2 (b), method 3 (c).*

4. Conclusions

The research performed allowed us to choose and prepare the biocomposite components – highly porous honeycomb titanium nickelide [13] and a sedimentation-resistant HAP suspension [7] suitable for application on the metal substrate of bone implant. Different methods of coating application have been examined. It was established that the method of dosed stepwise saturation of highly porous titanium nickelide with HAP by vacuum impregnation with intermediate drying in air under normal conditions is more advantageous since it

allows one to vary in a wide range (1–45 wt-%) the mass of introduced HAP and the pore size of the biocomposite, thus providing controlled formation of the structure and biomedical properties of the biomaterial. The results are of particular interest bone surgery, prosthetics and orthopedics in practical terms as well as for the technology of coating in general.

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