Approved by

A.F. Ilyuschenko

Director

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"Powder-Based Synthesis of Nanocrystalline Material Components for Structural Application"

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Chief of the
Protective Coatings Department

V.S. Ivashko

"24" "09" 1998

Executed by:

A.F. Ilyuschenko

V.S. Ivashko

V.A. Okovity

A.I. Shevtsov

M.A. Andreev

I.V. Fomikhina

A.I. Koulak

L.A. Lesnikovich

T.R. Doubelir

A.A. Kazakova

S.V. Lavrov

Minsk 1998

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Abstract

IMPLANT, COATING, HYDROXIAPATITE (HA), BASE MATERIAL (SUBSTRATE), PLASMA SPRAYING, ION-BEAM SPRAYING, MODE, STRUCTURE, NANOCRYSTALLINE STRUCTURE, SCANNING ELECTRON MICROSCOPY (SEM), TRANSMISSION ELECTRON MICROSCOPY (TEM), X-RAY PHASE ANALYSIS.

Hydroxiapatite spray coatings and substrates for implant production as well as multilayered metal ceramic coatings from nanocrystalline materials are a subject of the investigation.

The work aims at the improvement of quality of said objects.

In the process of work, investigated are processes of hydroxiapatite powder production. Analysed are sizes, shapes and relief of initial HA powder surface using SEM and TEM. Optimized are modes of HA plasma spraying on a substrate from titanium and associated compositions of traditional and nanocrystalline structure. Studied is the quality of the sprayed samples using X-ray phase analysis and metallographic analysis. Theoretically generalized are the results of investigations of bioceramic coating spraying on titanium, taking into account obtained experimental data.

Presented are the results of investigations of ion-beam technology for spraying multilayered coatings consisting of alternating metal-ceramic layers of nanocrystalline structure.

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Introduction

The implants are widely used in clinical conditions. Last years they are produced in the USA, Japan, Germany, Sweden, Russia by spraying bioceramics on the surface of metal substrates. Said products are characterized by combination of increased mechanical strength of base material with biological compatibility of coatings. The required operation properties are formed due to improving coating and substrate materials when optimizing bioceramics spray modes. These directions of work determine the general methodological approach of investigating bioceramic coatings as well as substrates. The development aims at quality improvement of the implants.

Processes of manufacturing HA powder as a material for coating spraying have been investigated in order to hit the target. Sizes, shapes and relief of HA powder initial surface have been analysed using SEM and TEM. Modes for HA plasma spraying on substrates from titanium and associated compositions have been optimized.

Titanium and Ti-TiO₂ compositions of nanocrystalline structure have been developed at the Ufa Technical University for Aircraft. The developers consider this material to be a promising one as a substrate material when manufacturing implants. In this connection there have been optimized HA plasma spray modes for spraying coatings on titanium of traditional and nanocrystalline structure using samples of the Ufa University. The optimization has been conducted using a Plasma-Technik AG unit, Switzerland, as a VPS unit.

One of the chapters of the report was devoted to a technology of ion-beam spraying which is the most controlled, low-temperature and regenerable method of all ion spraying methods. The results of investigations of ion-beam technology for spraying multilayered coatings consisting of alternating metal-ceramic layers of nanocrystalline structure have been presented.

1. Investigation of the processes to manufacture bioceramic powder materials designed for bone implant production

1.1. Investigation of Synthesis Process Parameters for Hydroxiapatite Powder with High Content of Bioactive Phase

Hydroxiapatite (HA) is a structural analogue of the main non-organic component of bone and dental tissues of the organism. In comparison with the latter, it has the same chemical composition, similar physical and mechanical properties, high biocompatibility. HA is considered to be a bioactive ceramics which are able to be dissolved in physiological liquids and to form biological and chemical bond with the vive tissues [1]. Said ceramics does not contain toxic products and may be used to make artificial bones.

$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ hydroxiapatite is reffered to the apatite group and has a hexagonal cristalline structure consisting of a Ca^{2+} ion surrounded by 6 O atoms and connected with PO_4^{3-} and OH^- groups. Phosphorus atoms are thetraedrically surrounded by 4 oxygen atoms forming a structure similar to a regular one.

Hydroxiapatite production is realized by the precipitation from solutions in accordance with the following reaction:

For above reaction, 78,7 g of $\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$ (0,3333 mole) were dissolved in 300 ml of water in a 2 l flask. The pH of the solution was led up to 12 via concentrated ammonia solution and then the initial solution was diluted up to 600 ml (0,5558 mole/l). When intensive agitating, the solution obtained from this one of 26,4 g (0,2000 mole) of $(\text{NH}_4)_2\text{HPO}_4$ / 500 ml of water, with pH led to 12 via ammonia and then dissolved up to 800 ml (0,25 moles/l), was slowly added.

The present investigation offers the results of investigations of optimal synthese modes, forming of cristalline structure and properties of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ hydroxiapatite designed to be used as bioactive ceramics and highly effective

adsorbent. In accordance with literature sources, the hydroxiapatite is precipitated within the relationship $\text{Ca:P}=1,3-1,9$ and $\text{pH}=10-12$. The made attempts to reproduce aforementioned methods for inclusions-free hydroxiapatite production have showed that the hydroxiapatite synthesis has some nuances depending on the precise adherence to stoichiometrical relationship Ca:P , ageing processes under the mother liquor and secondary transformations of tribasiccalciophosphate into hydroxiapatite occurring in the precipitate, as well as on some difficulties corresponding to the precipitation to produce solid product with required physical and mechanical properties.

To determine optimal synthesis modes, chemical interactions in the system $\text{Ca}(\text{NO}_3)_2-(\text{NH}_4)_2\text{HPO}_4-\text{H}_2\text{O}$ or $\text{CaCl}_2-(\text{NH}_4)_2\text{HPO}_4-\text{H}_2\text{O}$ were investigated. To produce high quality syntheses products, the synthesis was conducted in the narrow Ca:P ($n=1,67$) relationship limits. Ammonia solution, cleaned previously from carbon dioxide via distillation, was used for alkali medium creation. The use of non-cleaned solution results in the forming of grey hydroxiapatite.

Tribasic calcium phosphate is precipitated in wide relationship limits in the system soluble calcium salt - two-substituted ammonium phosphate - water. Said tribasic calcium phosphate is able to contaminate the final product as well as to make worse the properties of the latter. That is why it is necessary to investigate the effect of initial reagent relationship on hydroxiapatite forming nearby the formula relationship $n=1,67$.

A sample was originally produced at $n=1,63$. To prepare said sample, two solutions were used, i.e. the solution of calcium nitrate tetrahydrate (19,9975 g of salt in 75 ml of water, concentration being 0,5649 mole/l) and the solution of two-substituted ammonium phosphate (6,8655 g of salt in 125 ml of water, concentration being 0,26 mole/l). The pH values for both solutions were led up to 12, then the solutions were diluted up to the volumes 150 and 200 ml, respectively, and added by drops to the solution of calcium nitrate; the solution of two-substituted ammonium phosphate was added in aforementioned solution at continuous mixing by magnet mixer as well.

This process resulted in the white gel-type difficult to filtrate precipitate which was stood under the mother liquor for 14 days and then washed by distilled water via decantation and on the filters in succession. This resulted in production of a plastic mass which was stood at room temperature up to the state characterized by the constant weight. Air-dry sample can not be separated on particles and presents itself a solid glass-type semi-transparent badly crystallized mass. The latter was pounded in an agate mortar and used for investigations of hydroxiapatite high temperature crystallization and inclusive solid phases.

Fig. 1 shows the X-rayograms for samples obtained at 750 and 1100°C. These X-rayograms indicate that hydroxiapatite crystallinity degree is significantly increased when increasing the temperature (the semi-width of diffraction reflection is decreased, the intensity is increased). However, after the calcining at 1100°C, there are observed on X-rayogram diffraction reflections characteristic for tribasic calcium phosphate formed as a result of the crystallization from roentgeniamorphous state, and not as a result of thermal decomposition of hydroxiapatite which is a thermally stable substance, decomposed at the temperature being higher than 1400°C [2]. The obtained results indicate that hydroxiapatite is precipitated together with tribasic calcium phosphate at the relationships being lower than stoichiometrical ones which is undesirable for the use of hydroxiapatite as bioceramics.

The increase of reagent relationship up to $n=1,75$ does not lead to expected results. However, in this case in comparison with previous one, calcium oxide (no tribasic calcium phosphate) is formed as an inclusion phase in the products of high temperature processing. This formation may be explain thanks to the literature sources [3], where there is indicated that the hydroxiapatite can catch an additional calcium quantity (evidently, as hydroxide) at the stoichiometrical relationships, which provoke CaO forming at high temperatures. The mentioned CaO forming is also shown in Fig. 1. As regards the hydroxiapatite, the crystallinity degree of the latter is sharply increased when temperature increasing just as in previous case.

Fig. 1 - X-rayograms of hydroxiapatite samples produced at Ca:P ratios equal to 1,63 (1,2) and 1,75 (3,4) and thermally theated at 750°C (1,3) and 1100°C (2,4)

The obtained results show that this is necessary to change the methods to synthesize pure easy-to-filtrate hydroxiapatite. This concerns, firstly, the precipitation of hydroxiapatite at stoichiometrical reagent relationship $n=1,67$ used to avoid inclusion precipitation in all following syntheses, and, secondly, the precipitates boiled together with matrix liquor and washed by hot water to improve the filtering process.

The samples were produced in accordance with the following method. There was prepared the solution of calcium nitrate: 7,87 g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 30 ml of distilled water, pH value of said solution was led up to 12 and then the solution was diluted up to 60 ml (the concentration being 0,5558 mole/l). As well, the solution of two-substituted ammonium phosphate was prepared: 2,64 g of $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in 50 ml of water, pH value of said solution was led up to 12 and then the solution was diluted up to 80 ml (the concentration being 0,25 mole/l). The solution of two-substituted ammonium ortophosphate was added by drops to the solution of calcium nitrate when continuous mixing. After reaction mixture standing for 14 days, said mixture was warmed up at 70°C for 1 hour, boiled for 10 minutes, filtrated, washed by hot water on a filter and dried at 150 and 240°C in consequence for 4 hours. Pure hydroxiapatite without $\text{Ca}_3(\text{PO}_4)_2$ and CaO impurities was cristallized from the obtained product (Fig. 2).

This is important for hydroxiapatite synthesis not only initial reagents relationship but also the time of standing of the precipitate under the mother liquor. An independent synthesis was conducted to clear out this problem. The sample was produced in accordance with aforementioned method for $n=1,67$, but it was standed under the mother liquor for 2 days. In this case, in comparison with this one where the sample was standed under thw mother liquor for 14 days, it is characteristic that the air-dry sample represented itself a powder, but the investigations of thermally treated samples (Fig. 3) have showed that this sample contains more additives of tribasic calcium phosphate in comparison with the samples obtained at syntheses

Fig.2 - X-rayograms of hydroxiapatite samples ($\text{Ca:P} = 1,67$, time of standing under the mother liquor - 14 days) thermally theated at 800°C (1) and 1100°C (2)

Fig. 3 - X-rayograms of hydroxiapatite samples ($\text{Ca:P} = 1,67$, time of standing under the mother liquor - 2 days) thermally treated at 240°C (1), 800°C (2) and 1100°C (3)

with $n=1,63$. This is confirmed by $\text{Ca}_3(\text{PO}_4)_2$ diffraction reflections appearing at lower temperatures as well as higher intensity of said reflections at 1100°C .

The obtained results are important not only for the adjustment of optimal synthesis modes. These results provide the possibility to suggest that tribasic calcium phosphate is initially formed in all relationship limits of such systems as $\text{Ca}(\text{NO}_3)_2\text{-(NH}_4)_2\text{HPO}_4\text{-H}_2\text{O}$. The latter transforms into $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ with the velocity which is the higher the nearer it is to $n=1,67$.

The conducted investigations have provided the possibility to determine optimal hydroxiapatite synthesis modes. However, hydroxiapatite samples obtained in accordance with optimal modes at room temperature represent a wet plastic mass of adhered particles. Being dried, said mass becomes hard and difficult-to-pound, moreover, thermal treatment does not effect significantly on the hardness of this mass. Only one powder-type sample was produced from water solutions (at $n=1,67$, 2 days of standing), but this sample was very contaminated by tribasic calcium phosphate. However, the hydroxiapatite should be as a small dispersed powder to be used as a bioceramics.

Some available patent data [4] state the fact that this is possible to avoid particle adhesion via complex multi-stage thermal treatment which is combined in different stages with organic solvent treatment and ultrasonic one.

The treatment in water and organic medium was also used to produce powder-type products. To do it, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, precipitated from water solutions and washed by water, was separated in three parts, two of which were treated as follows:

Wet product was mixed with organic solvent, volume ratio being 1:2, stood during one day, filtrated and dried at 60°C , moreover the product was easily gone to pieces. Ethanol was used as the organic solvent. Product filtration was significantly faster after said treatment.

The X-rayograms of the products of samples thermal treatment at 60 and 800°C are compared in Fig. 4. The data of X-ray phase analysis show that the cristallinity degree is increased when temperature increasing, however powder samples are

Fig. 4 - X-rayograms of hydroxiapatite extracted from water suspances (1, 2), water and alcohol suspances (3, 4) and water and acetone ones, thermally treated at 60°C (1, 3, 5) and 800°C (2, 4, 6)

cristallized faster which is confirmed by more intensive diffraction reflections and smaller semi-width for the products obtained at 800°C in comparison with the correspondent product previously washed by water and presenting itself a solid mass of adhered particles.

Fig. 5 shows ultrared spectra (UR-20, KB-disk method) of products resulted from the thermal treatment of the sample extracted from alcohol suspension. The lines in the limits within 400 - 800 cm^{-1} result from mainly deformational PO_4 vibrations on which valencial vibrations of Ca-O bonds may be put over; the lines in the limits within 900 - 1200 cm^{-1} result from valencial vibrations of P-O bonds. Deformational vibrations of hydration water molecules are represented by the single line (1640 cm^{-1}) confirming the cristalline equivalence. Valencial vibrations of OH-groups are provided by a wide structure-free line within 2800 - 3700 cm^{-1} , confirming the presence of H bonds. A narrow line at 3575 cm^{-1} , characteristic for H-bond-free OH-groups, coordinated by cation, appears against the background of the wide structure-free line of OH-groups valencial vibrations. However, two OH-groups of hydroxiapatite participate apparently in the forming of H-bonds with hydration water, as the intensity of said line is increased when H-bonds decomposing as a result of hydration water formation at calcination temperature increase. The degree of resolving power and intensity of absorption lines is significantly increased when thermal treatment temperature increasing, especially in the limits of PO_4 deformational vibrations. This confirms the increase of cristallinity degree.

1.2. Method to Produce Hydroxiapatite from Biological Bone

It is known that $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ hydroxiapatite (HA) is the main non-organic component of the biological bone. This fact provides the possibility to produce it from biological bone and allows to avoid expenses to purchase chemical reagents, distilled water, special equipment, etc.

The obtained X-ray phase analysis data concerning a comparison of HA, chemically synthesized from CaCl_2 and $(\text{NH}_4)_2\text{HPO}_4$ water solutions in alkali medium at $\text{pH}=10$

Fig. 5 - Infrared spectra of hydroxiapatite extracted from water and alcohol suspensions and thermally treated at 60°C (1), 240°C (2) and 800°C (3)

and biological bone in initial state at room temperature, as well as these ones thermally treated at 800°C during 4 hours showed (Fig. 6) that their phase composition is identic. Theremore, biological bone contains at the room temperature an organic component, collagen including, and after a calcination this organic part is completly removed; the bone becomes white, fragile, easily rubbed to powder with required particle size. X-raogramme of the obtained powder completly corresponds to the data on hydroxiapatite according to ASTM tables (see Table 1). Thermal treatment provides the possibility to eliminate genetic features of the biological bone, embryonic one including, and to avoid reactions of immuni tearing-away of the coating produced from said hydroxiapatite. We use a sample, the X-raogramme of which is shown in Fig. 6 (curve 5), for plasma spraying.

Table 1 - Diffraction angles (2θ), interplane distances (d , Å) and intensities (I/I_1)

№	Synthetic HA			Biological bone		HA ASTM, 9,,p.432	
	2θ	d , Å	I/I_1	d , Å	I/I_1	d , Å	I/I_1
1	10°46'	8,20	7	8,411	13	8,17	12
2	16°48'	5,27	4	5,342	6	5,26	6
3	18°48'	4,71	2	4,763	4	4,72	4
4	21°45'	4,08	7	4,08	8	4,07	10
5	22°50'	3,89	7	3,89	7	3,88	10
6	25°20'	3,51	3	3,51	3	3,51	3
7	25°50'	3,44	35	3,44	27	3,44	40
8	28°08'	3,17	9	3,317	9	3,17	12
9	28°58'	3,08	15	3,08	18	3,08	18
10	31°45'	2,81	100	2,81	100	2,81	100
11	32°10'	2,78	51	2,89	44	2,78	60
12	32°55'	2,72	63	2,72	68	2,72	60

13	43°04'	2,63	21	2,63	20	2,63	25
14	35°30'	2,52	4	2,53	6	2,53	6
15	39°12'	2,29	7	2,30	7	2,30	8
16	39°50'	2,26	21	2,26	24	2,26	20
17	40°30'	2,224	3	2,224	3	2,228	2
18	42°00'	2,148	9	2,148	7	2,148	10
19	43°52'	2,061	8	2,061	6	2,065	8
20	44°20'	2,040	2	2,040	2	2,040	2
21	45°20'	1,997	5	2,0240	5	2,000	6
22	46°45'	1,941	30	1,941	25	1,943	30
23	48°06'	1,889	14	1,9047	12	1,890	16
24	48°40'	1,868	5	1,88	4	1,871	6
25	49°30'	1,838	34	1,838	25	1,841	40
26	50°30'	1,804	15	1,8201	15	1,806	20
27	51°18'	1,778	13	1,778	11	1,780	12
28	52°06'	1,753	12	1,753	11	1,754	16
29	53°12'	1,719	12	1,719	10	1,722	20
30	54°25'	1,684	3	1,684	2	1,684	4
31	55°55'	1,642	7	1,642	7	1,644	10
32	57°10'	1,609	5	1,609	4	1,611	8
33	58°10'	1,583	2	1,583	2	1,587	4
34	60°00'	1,539	5	1,539	3	1,542	6
35	60°30'	1,528	4	1,534	3	1,530	6
36	61°10'	1,504	7	1,513	6	1,503	10
37	62°40'	1,476	9	1,480	7	1,474	12
38	63°20'	1,469	5	1,466	3	1,465	4

Fig. 6 - X-raogrammes of synthetic hydroxiapatite (1, 4), pig bone (2, 5) and hen bone (3, 6) in initial state (1, 2, 3) and after thermal treatment at 800°C during 4 hours (4, 5, 6).

1.3. Determination of the optimal chemical and phase compositions of hydroxapatite powder

We investigated the possibility to produce HA and Al_2O_3 -based composite materials. Said work results from the requirements of adhesion improvement between HA and titanium implant at plasma spraying. Our aim is to produce materials of maximal dispersion and uniformity, because a coating from said materials has to be uniform, homogeneous as well as to have good adhesion with titanium implant surface. Al_2O_3 is selected because of biological inertness, non-toxicity, availability and cheapness.

Compositions from HA and Al_2O_3 are prepared by three ways:

1. Mechanical mixing of dry HA and Al_2O_3 powders as 80:20 (A^{20} composite) and 30:70 (A^{70} composite) with following twofold screening through a screen having cells of 0,09 mm.

2. Wet mixing in acetone. HA powder acetone suspension is mixed with α - Al_2O_3 powder acetone suspension. This mixture is pounded with a pestle until the acetone has been evaporated. Then the mixture is dried in a drying oven at 70°C until the rest of acetone has been completely evaporated. HA and α - Al_2O_3 powders are taken as 80:20 (B^{20} composite) and 30:70 (B^{70} composite). Note: aforementioned relationships are given in mass. %.

3. Joint deposition of nanocrystalline HA suspension and $\text{Al}(\text{OH})_3$ suspension.

In the case of A and B composites, industrial Al_2O_3 with big particles is used. To produce closer mixture, we have tried to produce $\text{Al}(\text{OH})_3$ suspension, mix the latter with washed HA suspension, extract a sediment and calcinate the latter at 800°C until $\text{Al}(\text{OH})_3$ has been transformed into Al_2O_3 and amorphous HA - into crystalline one.

Aluminium hydroxide is deposited according to the following reaction:

To produce B²⁰ composite, containing 2,5 g of HA and 0,62 g of Al₂O₃ as 80:20, 1,63 g of AlCl₃ is dissolved in 16 ml of distilled water. The produced 10 % solution of AlCl₃ is added to 7,4 ml of 25 % solution of NH₄OH to obtain a suspension having pH=11-12. This suspension is added by drops to 180 ml of washed HA suspension containing 2,5 g of HA when mixing. The mixture is washed by NH₄OH solution and filtrated. The sediment is dried and calcinated at 800°C during 3,5 hours. B⁷⁰ mixture is prepared by the same way, but the proportion of HA and Al₂O₃ is 30:70. G²⁰ and G⁷⁰ composites are made according to the same method, but solution volumes are increased 2 times for producing suspension being less thick.

A method to produce D²⁰ and D⁷⁰ composites corresponds to the method of G²⁰ and G⁷⁰ production excepting the following:

- 1) Order of merging is changed: washed HA suspension is added by drops to Al(OH)₃ suspension;
- 2) Composite sediments washing is made by distilled water, pH of the latter is observed as alkaline one (pH=8-9);
- 3) sediment washing and separation is made at once after the deposition, because the sediment is divided in two phases should said condition be not observed.

E²⁰ and E⁷⁰ composites are prepared as B-D ones, but the order of component merging is changed, i.e. NH₄OH solution is added to the washed HA suspension and then AlCl₃ solution is added. It means that the Al(OH)₃ is deposited directly onto HA suspension particles.

All produced compositions (A-E) are investigated by the method of X-ray phase analysis using a ДРОН-2 diffractometer with Cu and α -radiation; electron microscopy and electron diffractometry are used as well.

X-rayogrammes of A and B compositions are given in Fig. 7. Calculation of said X-rayogrammes confirms the presence of HA and α -Al₂O₃ crystalline phases in powders. The same is confirmed by electron diffractometry. Electron microscopy shows that A and B compositions consist of grain-crystallites of 5-100 nm, moreover, Al₂O₃ particles of 5-20 nm are located around HA particles as disorderly rash. A and B

Fig. 7 - X-rayograms of composite materials:

a - A^{20}

c - A^{70}

b - B^{20}

d - B^{70}

composites spraying reveals that the coating are produced as non-uniform ones, Al_2O_3 particles are distributed as agglomerates. Moreover, disorder of Al_2O_3 particle location is increased when increasing Al_2O_3 content. In this connection, we have tried to chemically deposit $\text{Al}(\text{OH})_3$ and mix the suspension of the latter with HA suspension to produce maximally close mixture in B^{20} and B^{70} compositions. However, it is ascertained in the process of investigations that it is required to accept more deluted initial components because $\text{Al}(\text{OH})_3$ suspension is produced as too thick (gel-type) one, which causes non-uniformity in mixing with HA suspension. G^{20} and G^{70} have been prepared taking into account this fact. In such a case there is observed that sediments become non-uniform at the washing during 2 days, white blobs are clearly seen. We consider this fact to be related to $\text{Al}(\text{OH})_3$ aging because the same is never observed in HA sediment. As a result, the composition becomes unhomogeneous.

D^{20} and D^{70} compositions are washed during a short period of time, which results in blob avoiding as well as solid phase homogeneity. E^{20} and E^{70} compositions are prepared by aluminium hydroxide deposition onto HA suspensions.

X-rayogrammes of B-E mixtures before and after thermal treatment at 800°C during 3,5 hours are given in Fig. 8, 9. Lines corresponding to HA are clearly seen after sample thermal treatment in compositions with decreased Al_2O_3 content ($\text{B}^{20}\text{-E}^{20}$) at HA: $\text{Al}_2\text{O}_3 = 80:20$ (Fig. 8 a, c, e, g). At the same time, a new phase having diffraction lines not characteristic for HA, Al_2O_3 , Al and Ca phosphates are observed on the X-rayogrammes of composites having high content of Al_2O_3 ($\text{B}^{70}\text{-E}^{70}$) at HA: $\text{Al}_2\text{O}_3=30:70$. Evidently, complex interactions related to middle and main Ca and Al phosphate forming, occur in the process of equilibrium setting at a system where Ca^{2+} , Al^{3+} , PO_4^{3-} , NH_4^+ , OH^- ions present simultaneously and relationships of said ions are changing for a time both in solid phase and in liquid one. The compositions produced in this case have been not investigated in detail, but the results obtained provide the possibility to state that the production of a composite material from HA and Al_2O_3 by chemical deposition is not possible. Bulk and real densities of the

Fig. 8 - X-rayograms of composite materials, HA ratios being as follows:

$\text{Al}_2\text{O}_3 = 80:20$: a - B^{20} , b, c - G^{20} , d, e - D^{20} , f, g - E^{20} ;

a, c, e, g - thermally treated samples; b, d, f - initial samples.

Fig. 9 - X-rayograms of composite materials, HA rations being as follows:

$\text{Al}_2\text{O}_3 = 30:70$: a - B^{70} , b, c - G^{70} , d, e - D^{70} , f, g - E^{70} ;

a, c, e, g - thermally treated samples; b, d, f - initial samples.

powders are measured for producing A and B compositions. The measuring results are presented in Table 2. One can see, both bulk density and real one of pure HA are increased at thermal treatment and transformation from amorphous phase into crystalline one. This is caused by dehydration, porosity reduction as well as HA powder particle sintering. As a result, particle size is increased. That is confirmed by the results of electron microscopy. The fact, that the values of real density for compositions produced by wet mixing of B²⁰ and B⁷⁰ are more in comparison with compositions produced by dry mixing (A²⁰, A⁷⁰), indicates that the mixing used for B²⁰ and B⁷⁰ is more efficient.

So, investigated is a possibility to produce HA- and Al₂O₃-based composite materials. It is stated that the most acceptable way is to mechanically mix powders of said substances. During the mixing of HA and Al(OH)₃ suspensions, chemical interaction occurs in the system containing Ca²⁺, Al³⁺, PO₄³⁻, NH₄⁺, OH⁻ ions thus resulting in HA phase transformation into other phosphates.

Table 2 - Results of measurements of bulk and real density of HA powders and associated compositions

Material	Bulk density, D, g/cm ³	Real density, d, g/cm ³
amorphous HA	0,39	2,62
crystalline HA	0,53	2,87
industrial Al ₂ O ₃	1,01	3,38
A ²⁰ composite	0,66	3,04
B ²⁰ composite	0,58	3,11
A ⁷⁰ composite	0,96	3,21
B ⁷⁰ composite	0,81	3,29

2. Investigation of bioceramic powder materials

2.1. Size, shape and relief evaluation of powder surface provided by scanning electron microscopy

The preparation of powders to be investigated in scanning electron microscope is conducted by two ways:

- free pouring on object glass;
- dispersing in ultrasound with following powder pouring on object glass.

The dispersing provides the possibility to break up the grains and to separate powder particles.

The simplest dispersing method is the method of ultrasonic effect on the powder in liquid to obtain uniform suspension.

The liquid for dispersing should correspond to the following requirements:

- to evaporate completely and quickly without any traces;
- do not dissolve the substrate to avoid distortions;
- to have as far as possible low surface tension coefficient thus avoiding the formation of large conglomerates by separate particles.

The liquids for dispersing are acetone, ethyl and methyl alcohol, etc. Hydroxiapatite powder dispersing is conducted in acetone.

The material having even, defect-free surface and not showing own structure, should be used as a substrate on which the suspension is sprayed. The best material in this case is considered to be an object glass.

The object glass is stucked on the object table by silver glue and wiped by ethanol.

The dispersed powder is placed by preparation spatula in a clean chemical glass of 50 ml in volume. Then 10 ml of ethanol is poured out. The obtained powder is mixed by glass stick. The beaker with prepared solution is placed on the basis of ultrasonic УЗДН-2Т dispersor. In the beaker placed is the ultrasonic vibrator so that the melt is

not splashed out when device switching on. The melt is treated by ultrasound for 2-3 min. at the frequency 22 kHz and current 40-50 mA.

With vibration amplitude increase a suspension cloud is formed around the dispersor disk. In the cloud area placed is an object table provided with glass on which separate particles of the investigated powder are deposited.

When investigating in SEM dielectric materials, i.e. metal oxides and nitrides, present themselves the most difficult problem. When electron probe touches the dielectric, the absorbed electrons are accumulated on the probe surface because of the absence of charge running off on the earth. Electron accumulation provokes charged area forming on the sample surface. When following scanning said area may unregularly diverge initial probe beam thus significantly distorting the image. Moreover, surface charge presence significantly changes the second electron emission which is especially not desirable when conducting semi-quantitative and quantitative micro X-ray and spectral analysis.

To escape this effect provided is the possibility to apply on the sample surface a current conducting coating.

Thin current conductive coat or metal (Al, Au, Au-Pt) film is applied on sample surface by thermal evaporation or cathode spraying in vacuum.

The conductive layer is made as far as thinner, but the layer should be solid to provide well charge running off.

In connection with the fact that the pure gold is the cheapest and accessible material from all aforementioned ones, the gold is frequently used for high quality image receipt [5]. In "Sputter Coater" vacuum section the current conducting layer is formed by cathode gold spraying.

The object table with applied powder is placed in the chamber of "Sputter Coater" vacuum section. Initial vacuum in the chamber is $(6-8) \times 10^{-1}$ mbar. Voltage, current and time are 10 kV, 30 mA and 1,5-2 min., respectively. At said conditions made is a

solid current conductive gold coating of 100 angstrom in thickness providing high quality image.

The object table with prepared powder is placed in SEM chamber. SEM investigations of hydroxiapatite in initial state (№ 1) show that powder grain size is within 2-35 μm for free poured on the object glass powder and 200 angstrom-2 μm for dispersed in vacuum powder.

Fig. 10, 11 show the photos of free poured hydroxiapatite powder in initial state (Fig. 10) and after ultrasonic dispersing (Fig. 11). Majority of large particles has the shape approximating the spherical one as well as smooth surface relief. There exists also some particles having fragmental shape. Hydroxiapatite powder grain size after thermal treatment at 800°C (№ 2) for free poured and ultrasonic dispersed powder is within 2-60 μm and 0,5-2 μm , respectively. The particles have arbitrary geometrical shape and developed surface relief. Fig. 12, 13 present the photos of free poured hydroxiapatite powder after thermal treatment (Fig. 12) and ultrasonic dispersed powder (Fig. 13). The particles being up to 1 μm max. are investigated by transmission electron microscope, while SEM resolving power does not provide the possibility to evaluate morphological characteristics of hydroxiapatite powder in initial state and after thermal treatment.

The aforementioned investigations result in the conclusion that the size determination and size distribution histogram forming for the materials of the kind should be conducted in two stages:

- SEM evaluation of large particles (1 μm min.);
- TEM evaluation of small particles (1 μm max.).

When using one method only, it is lost the information either on large particles or on small ones.

To calculate powders on Mini-Magiscan it is necessary to join the results obtained by both methods.

Fig. 10 - Photos of free poured hydroxiapatite powder in initial state from the scanning electron microscope

Fig.11 - Photos of free poured hydroxiapatite powder after ultrasonic dispersing from the scanning electron microscope

Fig.12 - Photos of free poured hydroxiapatite powder after thermal treatment from the scanning electron microscope

Fig.13 - Photos of free poured hydroxiapatite powder after thermal treatment after ultrasonic dispersing from the scanning electron microscope

2.2. Evaluation of hydroxiapatite powder size and shape by transmission electron microscopy

Coal films are the most applicable to be the replica fixing powder particles because while said films are chemically inert, amorphous; do not show own structure.

To dissolve the substrate (NaCl salt crystals) used is the distilled water which dissolves well the salt and does not interact with powder particles and coal film.

The plates of 3 mm in thickness are breaked off by scalpel from NaCl salt monocrystal. One of the crystal plane should be absolutely even, i.e. do not have ckraks, roughnesses, small crystals, protuberances. Said deffect-free crystal may be used as a substrate to be applied by the dispersed powder suspense.

In the bottle with acetone poured is dispersed powder (on the scalpel end) which is dispersed in Y3DM-2T ultrasonic dispersor using ultrasonic vibrator at the frequency 22 kHz and current 40-50 mA for 1-2 min.

After suspense preparing the ultrasonic vibrator is lifted so that it touches suspense surface. Surface flat salt crystal is brought on the distance of 2-3 cm from vibrator end; the suspense is sprayed on the crystal surface.

Dried salt crystals with applied powder are put into a vacuum chamber of VUP-5 section on special support at an angle of 90o to the direction of coal spraying.

Coal spraying is realized in vacuum in the place of point contact between two coal bars at $I=60-70$ A for the period when the replica becomes brown (dark brown and dark blue are not acceptable, while the replica will be thick and not permeable for electrons).

Replica with fixed powder particles is separated from salt crystals in the distilled water. To provide it, the coal film is carefully cutted by needle point or scalpel on 3-mm squares and separate when salt crystal immersing into Petry cup with distilled water at an angle of 20-30°, deissolving thereby salt crystal. Coal film squares containing the introduced particles are caught from water surface with the help of

platinum wire ring and transferred to the object gauze of 3 mm in diameter when said squares become dry; the latter are investigated by TEM.

Preliminary investigations on hydroxiapatite powder particle size and shape using SEM show that it is impossible to investigate powders with particle size 0,5 mm max. because of resolving power limits (100 angstrom min.). That's why TEM method (resolving power is within 3-10 Å) is used to investigate dispersed and ultradispersed powders.

Powder shape study and size determination are carried out using EM-125 transmission electron microscope with accelerating voltage 100 kV. Phase composition determination is realized in accordance with microdiffraction images.

Diffraction electron microscopy (DEM) presents itself a complex of specific experimental and theoretical methods to obtain, measure, jointly calculate and interpret electron microphotos and microdiffraction images, providing the possibility to determine material phase composition.

The electrography is the radiography electron analogue. Wave electron properties provide the possibility to obtain the diffraction image from crystal lattice similar to radiological image. The main difference consists of radiation wave length: for radiography - about 1 Å, for electrography - 0,05-0,07 Å. Small wave length of electron beams results directly in the increase of resolving power for small dissipation area, which provides the possibility to conduct phase analysis of structural components with size 1 Mm max. At analysis of the phases being 1000 Å max., X-ray lines start to broaden (wash away), and at size about 200 Å become practically indiscernible. The electrography offers the reflexes for said crystalline size. Thus, small particle electron diffraction give more reliable data for phase analysis in comparison with X-ray beam diffraction. Fig. 14a shows the photos of initial hydroxiapatite powder. The main powder mass presents the particles consisting of the separate crystallite grains with size 10-60 nm. Phase composition identification in accordance with electron diffraction pattern (Fig. 14b) shows the

x 60000

x 60000

x 100000

b

Fig.14 - Transmission electron microscope photos of initial hydroxiapatite powder(a)
electron diffraction pattern (b)

presence of hydroxiapatite $\text{Ca}_{10}(\text{P}_0_4)_6(\text{OH})_2$ in the powder. On the microdiffraction images of crystallite grains with size 10-30 nm observed is gala dispersions typical for amorphous state.

Fig. 15a shows the photos of hydroxiapatite powder after heattreatment (800°C). Crystallite grain size is within 20-100 nm. Phase composition identification in accordance with electron diffraction pattern (Fig. 15b) shows the presence of hydroxiapatite $\text{Ca}_{10}(\text{P}_0_4)_6(\text{OH})_2$; there is observed no amorphous state.

Priliminary TEM evaluation of sizes and shapes of dispersed and ultradispersed powders is carried out without the use of automatic methods for statistical result processing. To determine granulometrical composition it is necessary to join the results provided by SEM and TEM with following processing on special image analysis device such as Mini-Magiscan.

2.3. X-ray phase analysis

X-ray phase analysis is carried out on ДРОН-3.0 X-ray diffractometer (U=40 kV, I=20 mA) in Cu k_α monochromatic radiation at continious meter movem,ent within the angle interval 20-120° per 0,1°. To improve line geometry used is the system consisting of two Sm1-Sm0.25 Coller slots. Phase composition interpretation is realized in accordance with "X-RAY" program of X-ray analysis.

In initial state observed is line washing away, which marks amorphous and crystalline material state. X-ray pattern calculation reveals the presence of $\text{Ca}_{10}(\text{P}_0_4)_6(\text{OH})_2$ hydroxiapatite phase in powder as well as the absence of any other phases.

x 60000

x 60000

a x 60000

38

Fig.15 - Transmission electron microscope photos of hydroxiapatite powder after thermal treatment (a) and electron diffraction pattern (b)

2.4. Determination of granulometrical composition of hydroxiapatite powders using mini-magiscan image analyser

Quantitative evaluation of powder geometrical parameters provides the possibility to use effective mathematic technique and computer technique to obtain reliable dependences of properties and particle sizes, particle size, composition and powder production method. Determination of reliable value of any geometrical parameter by qualitative and description method as well as semi-quantitative one is a long-term and labour-intensive process while it is necessary to measure and calculate hundred or sometimes thousand particles. Modern multifunctional automatic Mini-Magiscan image analyser significantly accelerate the process, besides that it offers highest result accuracy.

Quantitative stereological powder analysis on Mini-Magiscan is carried out in accordance with Genias-26 program. However, simple calculation of the particles from photos provided by SEM or TEM will give in this case distorted image. That's why the method to determine hydroxiapatite powder granulometrical composition comprises the following stages:

1. Powder particle calculation based on the photos provided by SEM in accordance with "Genias-26" program.
2. Powder particle calculation based on the negative films provided by TEM in accordance with "Genias-26" program.
3. Combination of the data obtained at the first and second stages in one data file.
4. Presentation of the results of powder particle quantitative analysis in accordance with "Results" program.

"Genias-26" program is universal one; it provides the possibility to carry out quantitative and stereological analysis of practically any structure, particle, inclusion or phase.

To solve each concrete problem choosed is the appointed list and realization order of necessary functions. Analysis of given powder geometrical parameters comprises the following stages:

1. image adjustment;
2. image fixing;
3. segmentation;
4. choice of necessary measurements

Image adjustment is conducted to set a scale. In "Genias-26" program the adjustment is realized by "Calibration" function choice. At the work with the photos provided by SEM, m-prime is used as scale section (prime length is known). It is possible to receive scale coefficient for the given image (scale-factor) marking the starting and final length and introduced m-prime value.

At the work with the photos provided by SEM scale-factor is equal to $2,11 \times 10^{-1}$ mkm/pixel.

The term "fixing" means the image transformation into electrical signal suitable for digital processing and memorizing. The image in the system based on Mini-Magiscan is formed by Hitachi KP-143 TV camera with analog-to-digital converter. At the work with the photos it is necessary to reach uniform artificial shadow-free field lighting with the help of upper board lighting. Image memorizing in "Genias-26" program is realized by "Capture" function.

The segmentation "separe" the investigated elements from the background which results in dubble image forming, each element of which may be in one state only (investigation state or background state).

In "Genias-26" program the segmentation is realized by "Threshold" operation. For supplimentary image correction in manual mode used is "Editor" operation.

From ten possible parameters for this stage choiced are the following characteristics as main geometrical ones:

- maximum particle diameter (OA);
- particle square (OA);
- shape factor (OC).

During quality stereology analysis according to "Genias-26" program of the powders image provided with the help of transmission electron microscope the main program stages are the same but have certain peculiarities because of the source of the image are X-ray films but not photos. Calculations made directly from the X-ray film decrease the analysis period and additional consumption of photo materials because the photo print is excluded.

To provide the image directly from the X-ray film, the film is evenly lighted not by the upper light means but by the adjustment of the lower light source.

When working with negative films provided by TEM, the scale factor for the given image is changed.

Scale factor = $3,326 \times 10^{-3} \mu\text{m}/\text{pixel}$.

Combination of investigation results for scanning and transmission microscopy into one file was provided with the help of program "Mergedata".

Fig. 16, 17 presents statistical data on maximum powder particles diameter (Fig. 16) and histogram for granulometric composition of hydroxiapatite (Fig. 17) in initial state provided when calculating the photos from scanning electron microscope. Mean value of maximum diameter equals to 2 μm .

Fig. 18, 19 presents statistical data on maximum powder particles diameter (Fig. 18) and histogram for granulometric composition of hydroxiapatite (Fig. 19) in initial state provided when calculating the X-ray films from transmission electron microscope. Mean value of maximum diameter is 40 nm.

Fig. 20, 21 presents statistical data on maximum powder particles diameter (Fig. 20) and histogram for granulometric composition of hydroxiapatite after thermal

treatment (Fig. 21) provided by calculation of photos from scanning electron microscope. Mean value of maximum diameter equals to 20 μm .

Fig. 22, 23 presents statistical data on maximum powder particles diameter (Fig. 22) histogram for granulometric composition of hydroxiapatite after thermal treatment (Fig. 23) provided by calculation of the X-ray films from transmission electron microscope. Mean value of maximum diameter is 60 nm.

2.5. Investigation of Hydroxiapatite Chemical Composition

Chemical analysis of the synthesized hydroxiapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ for toxic elements (Pb, As, Cd, Fe, Hg) was conducted by atomic emission spectrometer ARL3410 (USA). All measurements and investigation techniques were approved by Metrology and Standardization Institute (1997). Limits for detection of the investigated elements when conducting analysis by ICP-spectrometer (induction-binded plasma) type ARL 3410, concentration of said elements in the substance under investigation and in comparison null solution (in % and mg/l) are given in the table.

Table 3

Element	Wavelength (nm)	Concentration Detection Limit (mg/l)	Concentration in Null Solution (mg/l)	In the sample under investigation (mg/l)	In the sample under investigation (%)
As	193,77	0,03	< 0,03	< 0,03	< 0,00003
Hg	194,24	0,01	< 0,01	< 0,01	< 0,00001
Cd	214,43	0,0027	< 0,0027	< 0,05	< 0,00005
Pb	220,34	0,03	< 0,03	< 0,03	< 0,00003
Fe	259,93	0,006	0,043	1,42	< 0,001377

Joyce-Loebl

RESULTS

Magiscan

STATISTICS SUMMARY

*** STATISTICS OF OL : {0<1} ***

over 174 objects.

Sample identifier: 1862-45

Minimum = 2.960754E-02
 Maximum = 4.740086E+00
 Mode [3] = 4.572663E-02
 Median = 7.029040E-02
 25% Quartile = 5.366411E-02
 75% Quartile = 1.623929E+00
 Total value = 1.42450767821E+002
 Mean = 8.18682573682E-001
 Geometric mean = 2.08192042860E-001
 Harmonic mean = 8.54941078976E-002
 Sample variance = 1.33953728952E+000
 Sample standard deviation = 1.15738381254E+000
 Population variance = 1.34728027963E+000
 Population standard deviation = 1.16072403250E+000
 Standard deviation of the mean = 8.77410429714E-002
 Relative standard error = 1.07173458666E-001
 Skew = 2.17713533392E+000
 Kurtosis = 7.30774768386E+000

Sample identifier : 1862-45
 Data file author : NO NAME
 Reference number : 0

File name : 1862-45.DAT
 File date : 17-Jan-97

Fig. 16 - Statistical data on maximum hydroxiapatite initial powder particles diameter provided when calculating the photos from the scanning electron microscope.

Joyce-Loebl

RESULTS

0.00% <= 0.00E+00 < 0.00% <= 0.00E+00 < 100.00%

Sample identifier : 1862-45
Reference number : 0

File name : 1862-45.DAT
File date : 17-Jan-97

Data file author : NO NAME

Fig. 17 - Histogram for granulometric composition of hydroxiapatite powder in initial state provided when calculating the photos from SEM.

Joyce-Loebl

RESULTS

Magiscan

STATISTICS SUMMARY

*** STATISTICS OF OL : (0<1) ***

over 110 objects.

Sample identifier: RESULTS

Minimum = 2.960754E-02
 Maximum = 1.508507E-01
 Mode [3] = 4.572663E-02
 Median = 5.693378E-02
 25% Quartile = 5.030055E-02
 75% Quartile = 6.792824E-02
 Total value = 6.67337954603E+000
 Mean = 6.06670867821E-002
 Geometric mean = 5.77588667627E-002
 Harmonic mean = 5.51571947648E-002
 Sample variance = 4.24176244287E-004
 Sample standard deviation = 2.05955394270E-002
 Population variance = 4.28067769464E-004
 Population standard deviation = 2.06897986811E-002
 Standard deviation of the mean = 1.96370761129E-003
 Relative standard error = 3.23685826277E-002
 Skew = 1.57795524142E-005
 Kurtosis = 1.46985876441E-006

Sample identifier : RESULTS

File name : 1862y45.DAT

Data file author : NO NAME

File date : 17-Jan-97

Reference number : 0

Comment :

Fig. 18.- Statistical data on maximum powder particles diameter provided when calculating the X-ray films from transmission electron microscope.

Joyce-Loebl

RESULTS

 $0.00\% \leq 0.00E+00 < 0.00\% \leq 0.00E+00 < 100.00\%$

Sample identifier : 1862-45
Reference number : 0

File name : 1862-45.DAT
File date : 17-Jan-97

Data file author : NO NAME

Fig. 19 - Histogram for granulometric composition of hydroxiapatite powder in initial state provided when calculating the X-ray films from transmission electron microscope.

Joyce-Loebl

RESULTS

Magiscan

STATISTICS SUMMARY

*** STATISTICS OF OL : [0<1] ***

over 304 objects.

Sample identifier: 1862-44

Minimum = 1.985716E-02
 Maximum = 9.843194E+01
 Mode [7] = 1.027940E+00
 Median = 7.334687E-02
 25% Quartile = 5.704657E-02
 75% Quartile = 1.014770E+00
 Total value = 5.62749049917E+002
 Mean = 1.85114819052E+000
 Geometric mean = 2.10413050540E-001
 Harmonic mean = 8.98474127063E-002
 Sample variance = 5.88118764626E+001
 Sample standard deviation = 7.66889017150E+000
 Population variance = 5.90059750647E+001
 Population standard deviation = 7.68153468181E+000
 Standard deviation of the mean = 4.39840999213E-001
 Relative standard error = 2.37604423820E-001
 Skew = 3.90743074563E+003
 Kurtosis = 3.26233507383E+005

Sample identifier : 1862-44
 Data file author : NO NAME
 Reference number : 0

File name : 1862-44.DAT
 File date : 17-Jan-97

Fig. 20 - Statistical data on maximum hydroxiapatite powder particles diameter after thermal treatment provided when calculating the photos from the scanning electron microscope.

Joyce-Loebl

RESULTS

H

 $0.00\% \leq 0.00E+00 < 0.00\% \leq 0.00E+00 < 100.00\%$

Sample identifier : RESULTS
Reference number : 0

File name : 1862x44.DAT
File date : 17-Jan-97

Data file author : NO NAME
Comment :

Fig. 21 - Histogram for granulometric composition of hydroxiapatite after thermal treatment provided by calculation of photos from the scanning electron microscope.

Joyce-Loebl

RESULTS

Magiscan

STATISTICS SUMMARY

*** STATISTICS OF OL : (0<1) ***

over 103 objects.

Sample identifier: RESULTS

Minimum = 3.346503E-02
 Maximum = 1.090186E-01
 Mode [4] = 5.677529E-02
 Median = 5.844558E-02
 25% Quartile = 4.866453E-02
 75% Quartile = 6.789319E-02
 Total value = 6.18294042721E+000
 Mean = 6.00285478370E-002
 Geometric mean = 5.82026724462E-002
 Harmonic mean = 5.64954863459E-002
 Sample variance = 2.35364908252E-004
 Sample standard deviation = 1.53416070948E-002
 Population variance = 2.37672407353E-004
 Population standard deviation = 1.54166276258E-002
 Standard deviation of the mean = 1.51165348176E-003
 Relative standard error = 2.51822430531E-002
 Skew = 3.04510084784E-006
 Kurtosis = 1.97358905708E-007

Sample identifier : RESULTS
 Data file author : NO NAME
 Reference number : 0

File name : 1862a44.DAT
 File date : 17-Jan-97
 Comment :

Fig. 22 - Statistical data on maximum powder particles diameter after thermal treatment provided when calculating the X-ray films from transmission electron microscope.

Joyce-Loebl

RESULTS

Ma

 $0.00\% \leq 0.00E+00 < 0.00\% \leq 0.00E+00 < 100.00\%$

Sample identifier : 1862-44
Reference number : 0

File name : 1862-44.DAT
File date : 17-Jan-97

Data file author : NO NAME

Fig. 23 - Histogram for granulometric composition of hydroxiapatite powder in initial state provided by calculation of the X-ray films from transmission electron microscope.

3. Investigation and adjustment of a technology of hydroxiapatite plasma spraying on a titanium substrate

3.1. *Investigation methods*

The following parameters of the coating quality are investigated depending on spraying modes:

- Sprayed hydroxiapatite powder utilization factor (PUF);
- Sprayed material structure;
- Coating phase composition.

PUF provides the possibility to evaluate the quantity of sprayed particles which do not form a coating because of insufficient plasticity and flight speed. It provides in turn the possibility to evaluate particle warm-up rate, distance as well as other spraying modes. There are formed prerequisites for an impartial evaluation of the optimality of spraying modes which provide increased adhesion and cohesion characteristics of the coating. Maximal PUF value serves as an optimization criterium when changing one or another mode.

Utilization factor of 63-100 μm hydroxiapatite powder, thermally treated at 1573 K, is determined using the samples designed as steel sheets of 200 x 200 x 2 mm in size, having a distinctly marked spraying area of 80 x 890 mm. Said samples are subjected to the blasting and abrasive treatment and then cleaned from the abrasive.

Blasting and abrasive treatment is made by electrocorundum grains of 22000...26000 MPa in hardness. Sample surface roughness after the treatment shall be R_a 12,5 ... 25 μm . A sample for spraying is shown in Fig. 24.

Fig. 24 - A sample for spraying.

The time interval between blasting and abrasive treatment and coating application for all the samples is constant and does not exceed 2 hours. Spraying area boundary according to Fig. 24 shall be marked; area outline shall be distinctly observed after the blasting and abrasive preparation.

Powder utilization factor is calculated as follows:

$$\eta = \frac{m_1 - m_2}{m_3 - m_4} \quad (1)$$

where: m_1 - sprayed sample weight (weighing accuracy is $\pm 0,005$ g);

m_2 - sample weight before spraying;

m_3 - weight of the hydroxiapatite powder placed in the tank of plasma unit powder portiometer before spraying;

m_4 - weight of the hydroxiapatite powder remaining in the tank of plasma unit powder portiometer after spraying during t period, time determination accuracy is ± 1 s.

m_3 value from equation (1) as well as t value are not changed during the PUF determination experiment.

Simultaneously conducted is an experiment serie aiming at the application of 0,4... 0,5 hydroxiapatite layer onto plate samples from BT1-0 titanium alloy which is used for bone implant production. Therewith the phase composition and coating structure when changing plasma spraying modes are investigated. Optimization criteria in this case are the minimal content of hydroxiapatite decomposition products as well as spraying density of the material (porosity being within 15 ... 30 %).

Order of titanium sample analysis is as follows:

- X-ray phase analysis of the coating using DRON-3.0 diffractometer ($U=40$ kV, $I=20$ mA) in monochromatized Cu $\kappa\alpha$ -radiation when continuous meter motion within angle range $20 \dots 120^\circ$ every $0,1^\circ$. A system consisting of two Soller slits Sm1-Sm0,25 is used to improve line geometry. Phase composition interpretation is done in accordance with X-ray structural analysis program "X-RAY";
- Study of coating structure on a brittle fracture of the samples after the cross-section of the latter have been decreased and treated with liquid nitrogen. To decrease the cross-section, several holes have been made on the sample side, opposite to this one provided with a coating. Brittle fracture studies are made via scanning electron microscope "Nanolab-7" manufactured by "Opton", Germany, at magnifications: x 500, x 2500, x 5000;
- Coating porosity measurements on a semi-automatic image analyser MOP-AMO3.

Study of utilization factor of the sprayed hydroxiapatite powder as well as coating phase composition and structure are made depending on plasma spraying modes change intervals of which in VPS chamber of a unit furnished by "PlasmaTechnik AG", Switzerland, are indicated in Table 4.

Table 4

Spraying mode	Values of varied mode			
Plasmatron current, A	450	500	550	600
Arc voltage, V	62	62	62	62
Spraying distance, mm	70	80	90	100
Plasma forming gas (argon) consumption, arbitrary units VPS (SLPM)	45	45	45	45
Plasma forming gas (hydrogen) consumption, SLPM	10	11	12	13
Transportation gas (argon) consumption, SLPM	9	9	9	9

To obtain comparative data, hydroxiapatite coatings with titanium sublayer were also sprayed in accordance with optimized modes. Sublayer application is done using 45-75 μm titanium powder, sublayer thickness being 0,05 mm, general coating thickness is 0,4-0,5 mm.

In accordance with optimal modes an effect of heterogeneous plasma jet on the sample surface is investigated as well. Plasma jet with sprayed powder material heats the surface of titanium alloy sample. With this some undesirable change of alloy properties is possible, in particular, the hardness of products from said alloy may be increased. At present, developed are implants titanium alloys characterized by low hardness due to the nanocrystalline structure. The developer consider that the low hardness of alloys of the kind is preserved up to 573 K. That is why, investigations of the thermal effect of plasma jet on the sprayed substrate surface from implant

material, as well as comparison of said effect with the given temperature limit are urgent.

To investigate thermal effect, titanium samples are sprayed with hydroxiapatite with application of metal sublayer and without it. The samples are previously provided with chromel thermocouples connected to a KCI-4 potentiometer so that the sensitive element of the thermocouple is on the titanium alloy surface to be studied. Surface temperature is registered on a diagramme band of the KCI-4 device.

3.2. Investigation results

When varying spraying modes according to Table 2, hydroxiapatite PUF value is changing from 0,25 to 0,70. Plasmotron arc current increase leads to a monotone PUF increase (Fig. 25). There is observed a practically linear dependence. Maximum powder utilization factor is reached at current value 600 A. However, when increasing current within 550-600 A, hydroxiapatite thermal decomposition intensity occurs. This fact is proved by sample X-ray phase analysis. Touching upon a porosity of coatings to be studied, there is to note that, when current increasing, this one is enough sharply decreased with following stabilization on the level of 10-15 % at the current being > 500 A. Thus, such parameters as high PUF, insignificant hydroxiapatite decomposition, required porosity of the coating are provided at arc current 550 A.

Fig. 25 - Change of the hydroxiapatite PUF depending on plasmatron arc current I and consumption of the plasma forming gas H_2 addition at constant spraying distance.

When varying spraying modes within 70-80 mm there is observed some PUF value decrease (Fig. 26). Further increase in spraying distance produces an increased rate of powder utilization factor decrease. X-ray phase analysis shows that the maximum hydroxiapatite decomposition is characteristic for the distance of 70 mm and is decreased when increasing the distance within variation limits 70-100 mm. In tour, coating porosity is changed from 10 up to 17 %. Taking into account the obtained results it may be state that the required quantity of the coating from hydroxiapatite is reached at the spraying distance being 80 mm.

Fig. 26 - Change of the hydroxiapatite PUF depending on spraying distance L at optimum values I , H_2 .

Powder utilization factor value is increased when adding some hydrogen (10, 11, 12 and 13 arbitrary units of VPS (SLPM) consumption) in a plasma forming gas - argon

(Fig. 25). Growth rate within 12-13 SLPM is slowed down. Relating to arc current and spraying distance, hydrogen addition does not significantly effect PUF within the given additive variation range. When increasing hydrogen quantity other coating quality parameters are changed as follows: hydroxiapatite decomposition is stimulated (in the range within 12-13 SLPM the intensity is the maximum one); coating porosity is increased from 12 up to 21 %. Basing on the obtained data it is to state that the required quantity of hydroxiapatite coating is reached when adding 12 SLPM of hydrogen to the plasma forming gas (argon).

Table 5 indicates the results of hydroxiapatite spraying mode optimization.

Table 5

Spraying mode	Optimal mode value
Plasmotron arc current, A	550
Arc voltage, V	62
Spraying distance, mm	80
Plasma forming gas (argon) consumption, SLPM	45
Plasma forming gas (hydrogen) consumption, SLPM	12
Transportation gas (argon) consumption, SLPM	9

Results of investigations of heterogeneous plasma jet thermal effect on titanium sample surface are given in Fig. 27. Shown is the dependence of middle surface temperature on the duration of hydroxiapatite plasma spraying.

Fig. 27 - Change of the temperature of titanium alloy substrate surface:

- 1 - Coating application on a sublayer, sprayed with titanium powder;
- 2 - coating application without the sublayer.

In accordance with Fig. 27, when spraying hydroxiapatite without the sublayer, the substrate surface is more heated, temperature increase occurs with different intensity in initial and final stages of the coating formation periods (at the beginning the temperature is increased more intensive). When spraying with the sublayer, substrate temperature is increased enough evenly during all hydroxiapatite spraying process.

Temperature of substrate heating by heterogeneous plasma jet when spraying with sublayer and without the latter is within 397-428 K, which does not exceed the maximum value characterized by undesirable hardness increase of an implant from titanium alloy with nanocrystalline structure (the latter is a promising material for implant production).

Fig. 28, 29 show the X-rayograms of hydroxiapatite coatings sprayed at the optimal modes onto titanium alloy samples without preliminary sublayer application but with preliminary titanium powder spraying. In accordance with Fig. 28, 29 the coatings contain the following phases: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ hydroxiapatite, $\text{Ca}_3(\text{PO}_4)_2$ tribasic calcium phosphate, CaO. $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ phase is the main one both in a sample provided with the sublayer and sublayer-free one. The ratio among phase lines

intensities on X-rayograms shows that the samples with sublayer as well as sublayer-free ones have the identical phase composition. Total $\text{Ca}_3(\text{PO}_4)_2$ and CaO phase content is about 20 % from the total phase volume of the sprayed coating.

No	2 Theta	Iint	Imax	FWHM	D	I/Imax	No	2 Theta	Iint	Imax	FWHM	D	I/Imax
1	21.80	58	153	0.38	4.077	7.4	26	46.70	279	636	0.44	1.945	30.7
2	22.90	93	287	0.32	3.883	13.9	27	47.20	14	73	0.20	1.926	3.5
3	25.70	320	629	0.51	3.466	30.4	28	47.60	10	61	0.17	1.910	2.9
4	28.10	87	176	0.50	3.175	8.5	29	48.10	102	227	0.45	1.892	11.0
5	29.00	168	376	0.45	3.079	18.1	30	48.70	30	114	0.27	1.870	5.5
6	29.30	53	236	0.22	3.048	11.4	31	49.40	251	434	0.58	1.845	20.9
7	29.80	94	241	0.39	2.998	11.6	32	50.30	16	89	0.18	1.814	4.2
8	30.30	20	71	0.28	2.950	3.4	33	50.60	115	261	0.44	1.804	12.6
9	30.50	24	95	0.26	2.931	4.6	34	51.40	82	177	0.47	1.778	8.5
10	31.10	165	255	0.65	2.876	12.3	35	51.80	27	114	0.24	1.765	5.5
11	31.80	925	2072	0.45	2.814	100.0	36	52.20	120	257	0.47	1.752	12.4
12	32.10	235	1155	0.20	2.788	55.7	37	52.80	64	201	0.32	1.734	9.7
13	33.00	577	1094	0.53	2.714	52.8	38	53.20	35	147	0.24	1.722	7.1
14	34.00	180	420	0.43	2.637	20.3	39	54.00	55	138	0.40	1.698	6.7
15	35.50	43	117	0.37	2.529	5.6	40	56.00	38	93	0.40	1.642	4.5
16	37.40	48	160	0.30	2.404	7.7	41	57.10	23	76	0.30	1.613	3.7
17	39.20	47	122	0.38	2.298	5.9	42	60.10	25	81	0.30	1.539	3.9
18	39.90	136	333	0.41	2.259	16.1	43	60.60	16	65	0.25	1.528	3.1
19	40.50	13	56	0.22	2.227	2.7	44	61.40	28	68	0.41	1.510	3.3
20	40.70	9	53	0.16	2.217	2.6	45	61.60	39	78	0.50	1.506	3.8
21	42.10	30	118	0.25	2.146	5.7	46	63.00	53	133	0.40	1.475	6.4
22	42.30	16	68	0.23	2.137	3.3	47	63.80	65	121	0.54	1.459	5.8
23	43.70	35	68	0.51	2.071	3.3	48	64.00	77	134	0.58	1.455	6.5
24	45.00	17	56	0.31	2.014	2.7	49	65.20	36	89	0.40	1.431	4.3
25	46.20	31	73	0.43	1.965	3.5							

Fig. 28 - X-rayogram of sublayer-free hydroxiapatite coating.

No	2 Theta	Iint	Iaax	FWHM	D	I/Iaax		No	2 Theta	Iint	Iaax	FWHM	D	I/Iaax	
1	21.80	50	150	0.33	4.077	7.7	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	25	45.30	15	65	0.22	2.002	3.3	
2	22.80	116	269	0.43	3.900	13.8		26	46.70	218	504	0.43	1.945	25.8	
3	24.10	19	52	0.36	3.693	2.7		27	47.60	33	51	0.64	1.910	2.6	
4	25.70	219	530	0.41	3.466	27.1	$\alpha\text{-Ca}_3(\text{PO}_4)_2$	28	48.10	77	197	0.39	1.892	10.1	
5	28.00	110	214	0.51	3.187	10.9		29	48.70	38	97	0.40	1.870	5.0	
6	29.00	212	392	0.54	3.079	20.1		30	49.30	186	381	0.49	1.848	19.5	
7	29.70	72	216	0.33	3.008	11.0	$\alpha\text{-Ca}_3(\text{PO}_4)_2$	31	50.20	17	51	0.33	1.817	2.6	
8	30.20	29	84	0.34	2.959	4.3		32	50.60	102	213	0.48	1.804	10.9	
9	30.60	63	114	0.55	2.921	5.8		33	51.00	21	74	0.28	1.791	3.8	
10	31.10	172	281	0.61	2.876	14.4		34	51.40	89	179	0.50	1.778	9.2	
11	31.80	876	1955	0.45	2.814	100.0	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	35	52.10	76	211	0.36	1.755	10.8	
12	32.10	238	1107	0.22	2.788	56.6	two phases	36	52.80	129	184	0.70	1.734	9.4	
13	32.90	485	1040	0.47	2.722	53.2		37	53.90	92	159	0.58	1.701	8.1	CaO
14	34.00	229	438	0.52	2.637	22.4	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	38	55.90	35	89	0.40	1.645	4.6	
15	35.50	45	128	0.35	2.529	6.5		39	57.10	15	61	0.25	1.613	3.1	
16	37.40	94	218	0.43	2.404	11.2	CaO	40	58.30	12	49	0.25	1.583	2.5	
17	39.10	35	105	0.33	2.304	5.4		41	60.60	9	51	0.17	1.528	2.6	
18	39.50	4	50	0.07	2.281	2.6		42	61.50	39	97	0.40	1.508	5.0	
19	39.90	131	326	0.40	2.259	16.7		43	61.70	27	75	0.36	1.503	3.8	
20	40.60	10	56	0.18	2.222	2.9		44	63.10	32	166	0.30	1.473	5.4	
21	40.80	12	50	0.23	2.212	2.6		45	63.90	64	119	0.54	1.457	6.0	
22	42.10	31	101	0.30	2.146	5.2		46	64.10	75	147	0.51	1.453	7.5	CaO
23	43.90	27	73	0.37	2.062	3.7		47	65.20	32	79	0.41	1.431	4.0	
24	45.10	17	77	0.23	2.010	3.9									

Fig. 29 - X-rayogram of hydroxiapatite coating with sublayer.

Fig. 30, 31, 32, 33 present coating microstructure photos. It is given for the coatings sprayed at the optimal modes. The photos are obtained on brittle fracture of the samples from titanium alloy. According to the figures the coating is formed from deformed hydroxiapatite particles. On the photos there is observed the boundaries among the particles applied layer-by-layer, coating and the main material. The pores of a round shape as well as of a complicated one present. Total and opened porosities of the sprayed hydroxiapatite make up correspondingly: sublayer-free samples - 16,0 % and 1,4 % ; samples provided with sublayer - 19,0 % and 4,6 %.

Comparative analysis of both kinds of samples confirms the fact that said samples have the identical structure character. However, a preliminary titanium powder spraying and adhesive rough sublayer producing provide the possibility for firm hydroxiapatite bending.

Fig. 30 - Microstructure of sublayer-free hydroxiapatite coating.

Fig. 31 - Microstructure of hydroxiapatite coating provided with a sublayer sprayed with titanium powder.

Fig. 32 - Boundary between hydroxiapatite sublayer-free coating and sample base.

Fig. 33 - Boundary between hydroxiapatite coating provided with a sublayer sprayed with titanium powder and sample base.

3.3. The experimental studies of particles velocity in plasma spraying processes

An experimental unit for research of optical characteristics of powder within a plasma jet is represented in Fig. 34 /6/. It includes standard equipment for plasma spraying (plasma gun, power source, console, powder feeder, etc.) and an optical set. The unit VPS of the firm "Plasma-Technik" served as a plasma spraying unit.

Fig. 34 - VPS experimental unit:

1. Vacuum chamber; 2. Robot; 3. Plasma gun; 4. Plasma jet; 5. Powder feeder; 6. Plasma console; 7. Power supply; 8. Freon chillier; 9. Adapter; 10. ISSO-1.

The device consists of lens and a screen mounted on the same optical axis (Fig. 34). Between them there is flat mirror pivoting about axis, the later being parallel to the main plane of the lens and kinetically connected to an electric driver and tachometer. The tachometer is connected, in its turn, to an indicator. Dead surface of "Zenit" camera lens, installed on the meter, serves as a screen. On the screen there are put three lines, one of them being parallel to the rotation axis, the second one being perpendicular to it, and the third being at the angle of which the second line, all of them being calculated by the formula:

$$V_p = \frac{r \cdot n \cdot \operatorname{tg} \alpha}{15M} \quad (2)$$

where:

r -the distance between the surface of the rotating mirror and the screen, m ;

n - the number of rotations of the screen, rmp;

M - the scale.

When looking in the viewfinder of the camera, one adjusts mirror rotation rate so as traces of particles or plasma jets were parallel to the line making angle with the meter's screen ordinate. These calculations are made according to the readings of the point - type indicator.

Application of this equipment with a special attachment allowed investigation of the particles velocities by cross-section of the plasma jet at different points of indication. Thus, an average particles velocity is determined depending on different parameters of plasma spraying process. The particles velocity within the distance projected on the film is assumed to be constant. Table 6 presents the measurement characteristics.

Table 6 - Technical Data

Range of rates to be measured:	
visual	6 - 780 m/s
photographically	10 - 1300 m/s
Accuracy of measuring of one particle velocity by photographic method	5%
Distance between the lens and the object to be measured	255 mm
Scale M	0,573

The operation of the device is based on comparison of rates of investigated and reference objects. That is obtained by developing of time - base of the object image perpendicular to its motion direction with the help of the mirror rotating at a known rate.

The optical scheme of the meter (Fig. 35) consists of the lens (1), a light filter (2), a rotating double, sided mirror (3), a pivoting mirror (4) and camera (5).

Fig. 35 - Optical scheme of measuring device

The light from incandescent particles moving perpendicular to the optical lens axis is projected by the lens and by means of the rotating (3) and pivoting (4) mirrors to the dead surface of the collecting lens of the viewfinder and to the film in the "Zenit" camera. There are two relative - perpendicular lines on the dead surface of the lens (6), thus forming a rectangular coordinate system. Two more lines, datum ones, make up $\alpha=45$ and $\alpha=28\ 32'$ to the horizontal axis. According to it, with scanning speed V_p and angle known, it is possible to get V_u with the equation:

$$V_u = V_p \cdot \text{Ctg} \alpha \quad (3)$$

The scanning speed equals to:

$$V_p = 2\omega R = \frac{2R \cdot 2\pi \cdot NZ}{60Z_m} \quad (4)$$

where:

R = 105.2 mm, the distance between the rotation axis of the mirror and the film in the camera;

N - rotation speed of the electric-motor shaft, rpm;

- Z - number of teeth in the gear mounted on the motor shaft;
 Z_m - number of teeth in the gear mounted on the mirror shaft.

The (3) - (4) taken in account, we get

$$V_u = \frac{\pi \cdot N \cdot R \cdot Z}{15 \operatorname{tg} \alpha \cdot Z_m} \quad (5)$$

The real particle velocity equals to:

$$V = \frac{V_u}{M} = \frac{\pi \cdot N \cdot R \cdot Z}{15 M \cdot \operatorname{tg} \alpha \cdot Z_m} \quad (6)$$

where $M=0,573$ is an across magnification of the lens. The plasma jet image, obtained with described device is shown at Fig. 36.

Fig. 36 - Plasma jet image

It was sprayed $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ powder with fraction 40-63 μm , consumption - 12,7 g/min. Plasma forming gas - argon with consumption 72 l/min, pressure in operation chamber - 560 mBar.

The results of particle velocity, also simulation results are shown on Fig. 37; 38. At the distance 0,07 - 0,1 m, velocity of particles reaches values 110-160 m/s depending

on their diameter. From the comparison of simulation and experimental results, it is possible to conclude on adequacy of developed models to the real process (error of simulation does not exceed 5-8%).

Fig. 37 - Results of experimental measurement and simulation of the particle velocity:

1 - theoretical (simulation) curve (velocity of hydroxiapatite particles with the grain size 50 μm); 2 - experimental curve (velocity of hydroxiapatite particles with the grain size 50 μm); 3-- experimental curve (velocity of hydroxiapatite particles with the grain size 63 μm).

Fig. 38 - Plasma spraying particles tracks.

a)

b)

Fig. 39 - SEM micrographs of Ti (a) and $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (b) powder following the WIPE test.

Mathematical and computer models for the processes of moving of powder particles in a plasma jet under low pressure condition are developed in /7, 8/. Mathematical model is based on the laws of molecular-kinetic gas theory and describes the dynamics of interaction between plasma forming gas molecules and powder particles.

Computer simulation and experimental measurements of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ particles velocity in low pressure plasma jet are conducted.. It was established, that the developed models are adequate to real process (error of 5-8 %) and may be used for

study and improvement of VPS processes at minimum expensive experimental investigations.

Considering the coating forming mechanism as well as this one of forming binders among the sprayed particles and sublayer it may be supposed that an effect of oxygen from the environment affects during particle flight. When interacting among melted particles (Ti) and the environment atmosphere, there are formed surface oxide layers, TiO_2 formation energy is released. Thanks to the relatively high molar heat of oxide forming, particle temperature should increase thus providing thereby adhesion strength among the particles and substrate, as well as sprayed material utilization factor, due to increased heat content. However, above process does not occur because the particles are intensively cooled by gas flow from the atmosphere. The lower pressure is in the spraying chamber, the less are said effects. Particle flight and oxidization durations are very low, which results in forming thin films only. TiO_2 cannot exist in fluid state during the the spraying because of relatively high melting point. TiO_2 presents as a hard enclosure onto a liquid drop (Fig. 39).

4. Investigation and optimization of spray modes for application of hydroxiapatite coatings on titanium and associated compositions of nanocrystalline structure

4.1. *Methods of investigation*

The optimal modes of HA coating plasma spraying on titanium with traditional structure are considered as initial base information. The optimization has been carried out at the preceeding stages of the work. This is not expected significant modification in optimal modes when spraying HA on nanocrystalline titanium and associated compositions, because the technology as well as chemical compositions of the sprayed material and substrate are observed. However, adjustment of HA spraying parameters is probable because of modification in substrate structure. That is why the optimal values of parameters are experimentally checked by studying effect of variations of said parameters (increase and decrease in values). Utilization factor for HA sprayed powder (PUF) is considered to be a figure of aforementioned effect.

PUF provides the possibility to estimate number of sprayed particles which do not form coating because of insufficient plasticity and flight velocity. In tour, it provides the possibility to estimate particle heating rate, distance as well as other spraying modes. That results in objective estimation of spraying mode optimality thus providing thereby improved adhesion- and cohesion characteristics of the coating. The maximal PUF is a criterion of optimization of one or anpther mode.

Utilization factor for thermally treated at 1573 K HA powder of 63...100 μm is determined using combined samples designed as a steel sheet of 200 x 200 x 3 mm with a locating hole where a titanium disk of 3 mm in thickness is placed with a small clearance, provided that the surfaces of the steel sheet and titanium disk face are coincided.

When preparing the combined sample, the disks are cut by a diamond wheel from a bar manufactured from technically pure nanocrystalline titanium (structural grain

size being about 300 nm). Both sides of the disks are grinded by a diamond wheel using a grinding machine.

The combined samples provided with a zone to be sprayed (80 x 80 mm), clearly indicated in center, are blasted and cleaned from abrasive consisting of grains of electrocorundum of 22000...26000 MPa in hardness. The roughness of sample surface after the preparation should be within Ra 12,5...25 μm . A sample for PUF determination is shown in Fig. 40.

Figure 40 - Combined sample for PUF determination

The titanium disks are repeatedly used at various spraying modes in the process of investigations provided that the disks are reginded to remove HA layer and re-blasted.

Break time between blasting and coating application is constant and does not exceed two hours for all samples. Spraying zone limits (Fig. 40) should be marked and clearly seen after the blasting.

Powder utilization factor is determined in accordance with equation (1).

4.2. Results of investigation

Table 7 shows the results of mode adjustment to spray substrate from titanium with traditional structure. Said adjustment aims at the production of qualitative coatings on nanocrystalline titanium and associated compositions. The Table reveals initial basic modes, variation of the latter as well as the adjusted optimal value characterized by the maximal PUF. Variation of spraying distance is done at the optimal values of plasmatron arc current and consumption of supplementary plasma-forming gas (hydrogen).

Table 7 - Results of mode adjustment to spray HA coatings

Spraying mode	Values of a mode to be varied		
	PUF values		
1	2	3	4
Plasmatron current, A	<u>500</u> 0,43	<u>*550**</u> 0,58	<u>600</u> 0,62
Arc voltage, V	62	62	62
Spraying distance, mm	<u>*80</u> 0,58	<u>**85</u> 0,54	<u>90</u> 0,44
Consumption of argon as plasma-forming gas, standard units VPS (SLPM)	45	45	45
Consumption of hydrogen as plasma-forming gas, SLPM	<u>11</u> 0,51	<u>*12**</u> 0,58	<u>13</u> 0,56
Consumption of argon as transportation gas, SLPM	9	9	9

* Initial basic modes

** Optimal modes after adjustment

As indicated in Table 7, increase in plasmatron arc current leads to monotonic increase in PUF. However, preceeding investigations have showed that when increasing current within 550...600 A the intensity of HA thermal decomposition is increasing. As to coating porosity, it is to be noted that when increasing current, the porosity is enough sharply decreasing with further stabilization within 10...15 % at current being more than 500 A. Thus, combination of high PUF, insignificant HA decomposition and required porosity is provided at arc current 550 A.

A slight decrease in PUF is observed when varying spraying distance within 80...85 mm. Further distance elongation provokes intensity of PUF decrease. At the same time, it is revealed that the maximal thermal decomposition of the sprayed HA is characteristic for distance of 70 mm; but the decomposition value is reducing at the increase in distance, porosity being within 10...17 %.

Thus, taking into account Table 1 and preceeding results, the required quality of HA coating on nanocrystalline titanium and associated compositions is provided at spraying distance of 85 mm.

When adding 11, 12 and 13 VPS (SLPM) consumption standard units to plasma-forming gas (hydrogen), the PUF value is insignificantly changed in comparison with other modes (arc current, spraying distance). The optimal hydrogen content makes up 12 SLPM according to Table 7. Besides, it is known that further increase in hydrogen consumption intensifies HA decomposition and porosity (up to 21 %).

Having generalized results of plasma spraying mode adjustment it is to be stated that technological parameters of HA application on titanium with traditional structure are available for nanocrystalline titanium and associated compositions.

The modes differ in spraying distance values (the latter for nanocrystalline titanium is increased). This difference may be explained by finer structure and increase in number of active centers located along structure grains boundaries. Said centers become available on substrate surface and are characterized by higher energy. Increase in number of said centers provides adhesion of the sprayed particles with the substrate. That is why a qualitative HA coatings may be produced at the optimal PUF

only at elongated spraying distance. At the same time, there were similarly tested and adjusted modes for plasma spraying of titanium powders of 45...75 μm . Above powder is applied on nanocrystalline substrate as a sublayer and followed with HA coating spraying (Table 8).

Table 8 - Results of mode adjustment for spraying sublayer

Spraying mode	Mode optimal value
Plasmatron arc current, A	360
Arc voltage, V	62
Spraying distance, mm	110
Consumption of plasma-forming gas (argon), SLPM	35
Consumption of plasma-forming gas (hydrogen), SLPM	10
Consumption of transportation gas (argon), SLPM	9
Titanium powder consumption, RPM	20

The optimal mode for spraying sublayer insignificantly differ from one for substrate with traditional structure in spraying distance which is by 10 mm longer. The modes, adjusted in the process of preceeding stages, are used for further spraying HA on the sublayer.

Samples from titanium and associated compositions, sprayed according to the optimal technology with HA, provided with sublayer as well as without the latter, are analysed with high accuracy. Thicknesses of sublayer and coating make up 0,05 and 0,3...0,4 mm, respectively; HA coating thickness is 0,3...0,4 mm.

4.3. Analysis of the quality of hydroxiapatite coatings sprayed at optimized modes

It is stated that X-rayograms and structure of HA sprayed on titanium and associated compositions with sublayer and without the latter are practically identic. However, previous titanium powder spraying and production of a rough adhesive sublayer provide adhesion between HA and base material.

Fig. 41, 42, 43 show X-rayograms of HA coatings sprayed at the optimal modes on nanocrystalline material (technically pure titanium and associated compositions) provided with a sublayer. According to the Figures, the coatings contain phases of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ hydroxiapatite, $\text{Ca}_3(\text{PO}_4)_2$ tribasic calcium phosphate, CaO calcium oxide. HA phase is the main one on all specimens. It is confirmed by phase line intensity. Total amount of HA decomposition products ($\text{Ca}_3(\text{PO}_4)_2$ and CaO compounds) is within 14...20% of all phases of the sprayed coating.

Figures 44, 45, 46 show photos of microstructure of a coating sprayed with sublayer at the optimal modes. The photos are studied subject to brittle fracture of samples from nanocrystalline material.

As shown in the Figures, the coatings are formed from deformed HA particles. One can see boundaries among coating, substrate and particles sprayed layer-by-layer. There are presented pores of round and complicated shape. Total and open porosity of the sprayed HA on the samples from technically pure nanocrystalline titanium make up 17,5 and 4,1 %, respectively; these values for samples from a composite nanocrystalline material (Ti + 5 % TiO_2) are as follows: 19,3 and 5,9%, respectively; the same for (Ti + 10 % TiO_2) – 20,4 and 6,3, respectively.

4.4. Investigation of the state of a coated nanocrystalline substrate

The developer of the material considers that significant change in operation properties of nanocrystalline titanium and associated compositions occurs at ≈ 573 K min. The real temperature of the surface of titanium samples with traditional structure, sprayed with HA coatings at the optimal modes, is controlled with the help of thermal couplings and is within 397...428 K. The latter is significantly lower in comparison with critical values. Comparison of the optimal modes to spray HA or sublayer on nanocrystalline titanium or traditional one shows that technological parameters are practically similar, excepting spraying distance. The latter is by 5...10 mm longer for nanocrystalline substrate. Besides, substrate surface heating is decreased. It guarantees stable operation properties of base material and implant. Thus, supplementary

No	2 Theta	hkl	lmax	FWHM	D	I/I _{max}		No	2 Theta	hkl	lmax	FWHM	D	I/I _{max}	
1	10.70	22	55	0.41	8.268	11.3		51	52.10	23	56	0.41	1.755	11.5	a
2	12.20	61	120	0.50	7.254	24.7	c	52	53.10	39	70	0.56	1.725	14.4	
3	13.30	6	27	0.21	6.657	5.6		53	53.90	20	39	0.50	1.701	8.0	
4	17.00	0	3	0.15	5.215	0.6		54	55.00	7	21	0.35	1.670	4.3	
5	18.30	8	20	0.42	4.848	4.1		55	55.70	6	20	0.32	1.650	4.1	
6	19.50	2	13	0.14	4.552	2.7		56	58.80	5	26	0.21	1.570	5.4	
7	20.40	4	19	0.21	4.353	3.9		57	60.50	11	34	0.31	1.530	7.0	
8	21.60	17	42	0.41	4.114	8.7		58	61.10	10	19	0.54	1.517	3.9	
9	22.30	1	4	0.13	3.986	0.8		59	61.70	7	19	0.36	1.503	3.9	
10	22.80	30	73	0.41	3.900	15.1	c	60	63.00	21	48	0.44	1.475	9.9	
11	23.60	8	25	0.31	3.770	5.2		61	64.10	83	67	1.24	1.453	13.6	
12	24.10	12	31	0.37	3.693	6.4	c	62	64.60	70	63	1.11	1.443	13.0	
13	24.80	42	99	0.43	3.590	20.4		63	65.00	60	65	0.93	1.435	13.4	
14	25.20	13	34	0.38	3.534	7.0		64	66.10	7	21	0.32	1.414	4.3	
15	25.70	47	128	0.37	3.466	26.4		65	66.50	10	25	0.39	1.406	5.2	
16	26.20	26	28	0.93	3.401	5.8		66	68.60	5	24	0.21	1.368	4.9	
17	26.50	23	23	0.99	3.363	4.7		67	70.70	9	23	0.38	1.332	4.7	
18	27.60	14	34	0.40	3.232	7.0		68	71.10	16	30	0.53	1.326	6.2	
19	28.00	45	62	0.73	3.187	12.8	a	69	71.40	8	22	0.37	1.321	4.5	
20	28.30	26	51	0.51	3.153	10.5		70	71.80	9	16	0.53	1.315	3.3	
21	28.90	83	124	0.67	3.089	25.6	a	71	73.50	3	15	0.21	1.288	3.1	
22	29.70	82	86	0.96	3.008	17.7		72	74.00	7	22	0.33	1.281	4.5	
23	30.70	161	106	1.51	2.912	21.9		73	74.30	7	20	0.35	1.277	4.1	
24	31.10	158	152	1.04	2.876	31.3		74	74.90	13	29	0.46	1.268	6.0	
25	31.70	187	485	0.39	2.823	100.0	a	75	75.60	7	24	0.28	1.258	4.9	
26	32.00	51	287	0.18	2.797	59.2	a c	76	76.00	24	29	0.83	1.252	6.0	
27	32.90	129	265	0.49	2.722	54.6		77	77.10	74	72	1.03	1.237	14.8	
28	33.90	65	148	0.44	2.644	30.5	a	78	78.00	45	49	0.92	1.225	10.1	
29	34.40	6	21	0.30	2.607	4.3		79	78.40	39	46	0.85	1.220	9.5	
30	35.40	6	19	0.32	2.536	3.9		80	81.40	9	26	0.35	1.182	5.4	
31	36.10	14	27	0.51	2.488	5.6		81	81.80	10	36	0.29	1.177	7.4	
32	38.10	306	380	0.81	2.362	78.4		82	82.40	6	20	0.32	1.170	4.1	
33	39.00	73	88	0.83	2.309	18.1		83	84.60	3	15	0.21	1.145	3.1	
34	39.80	49	112	0.44	2.265	23.1	a	84	89.30	6	18	0.32	1.097	3.7	
35	40.50	23	30	0.75	2.227	6.2		85	96.50	10	18	0.53	1.033	3.7	
36	40.80	9	20	0.44	2.212	4.1		86	96.90	6	15	0.41	1.030	3.1	
37	41.00	6	19	0.34	2.201	3.9		87	97.10	7	18	0.39	1.028	3.7	
38	42.00	13	30	0.43	2.151	6.2		88	98.70	4	16	0.25	1.016	3.3	
39	42.20	6	21	0.29	2.141	4.3		89	99.90	5	16	0.32	1.007	3.3	
40	43.20	32	39	0.81	2.094	8.0		90	110.60	6	21	0.27	0.938	4.3	
41	44.30	110	116	0.95	2.045	23.9		91	110.90	6	24	0.27	0.936	4.9	
42	44.90	47	60	0.79	2.019	12.4		92	111.30	5	16	0.30	0.934	3.3	
43	45.80	13	29	0.45	1.981	6.0		93	113.10	6	15	0.41	0.924	3.1	
44	46.60	89	147	0.61	1.949	30.3	a	94	113.90	7	19	0.38	0.920	3.9	
45	47.40	10	33	0.31	1.918	6.8		95	114.30	6	17	0.36	0.918	3.5	
46	48.00	30	61	0.50	1.895	12.6		96	114.60	9	18	0.51	0.916	3.7	
47	48.50	15	30	0.50	1.877	6.2		97	114.90	15	19	0.81	0.915	3.9	
48	49.40	73	117	0.67	1.845	24.1	a	98	115.70	9	22	0.47	0.911	4.5	

Fig. 41- X-rayogram of a HA coating sprayed on a sample from technically pure nanocrystalline titanium: a - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; c - $\alpha\text{-Ca}_3(\text{PO}_4)_2$.

No	2 Theta	hkl	Imax	FWHM	D	I/Imax	No	2 Theta	hkl	Imax	FWHM	D	I/Imax
1	10.70	27	67	0.41	9.266	9.2	51	49.40	104	212	0.49	1.845	29.2
2	12.20	1	11	0.11	7.254	1.5	52	49.90	15	48	0.32	1.828	6.6
3	13.00	6	22	0.26	6.810	3.0	53	50.50	56	118	0.47	1.807	16.3
4	13.40	10	32	0.31	6.607	4.4	54	51.30	37	75	0.49	1.781	19.3
5	16.70	7	24	0.29	5.308	3.3	55	52.10	42	89	0.47	1.755	12.3
6	21.70	15	50	0.31	4.495	6.9	56	53.10	42	76	0.56	1.725	19.5
7	22.30	2	11	0.22	3.986	1.5	57	54.00	1	4	0.13	1.698	9.6
8	22.80	30	73	0.41	3.900	10.1	58	54.60	2	7	0.28	1.681	1.0
9	24.10	5	17	0.27	3.693	2.3	59	54.90	1	5	0.17	1.672	0.7
10	24.50	3	10	0.30	3.633	1.4	60	55.90	9	30	0.31	1.645	4.1
11	25.30	22	36	0.60	3.520	5.0	61	57.20	4	18	0.21	1.610	2.5
12	25.80	92	195	0.47	3.453	26.9	62	58.20	1	9	0.11	1.585	1.2
13	27.10	29	37	0.77	3.290	5.1	63	60.00	9	42	0.20	1.542	5.8
14	27.60	21	34	0.62	3.232	4.7	64	60.30	10	39	0.25	1.535	5.4
15	28.10	57	93	0.61	3.175	12.8	65	61.70	34	53	0.65	1.503	7.3
16	28.50	24	70	0.34	3.132	9.7	66	62.10	26	44	0.50	1.495	6.1
17	28.90	115	195	0.59	3.089	26.9	67	62.60	18	38	0.48	1.484	5.2
18	29.30	32	86	0.37	3.049	11.9	68	63.10	30	58	0.51	1.473	8.0
19	29.50	112	82	1.37	3.028	11.3	69	64.10	80	92	0.87	1.453	12.7
20	30.20	141	75	1.88	2.959	10.3	70	64.50	54	57	0.95	1.445	7.9
21	31.10	202	127	1.59	2.876	17.5	71	65.00	62	74	0.84	1.435	10.2
22	31.70	343	725	0.47	2.823	100.0	72	66.50	8	19	0.42	1.406	2.6
23	32.10	115	403	0.28	2.788	55.6	73	67.70	17	25	0.67	1.349	3.4
24	32.90	189	428	0.44	2.722	59.0	74	71.70	9	23	0.41	1.316	3.2
25	34.00	93	171	0.54	2.637	23.6	75	72.30	8	19	0.42	1.307	2.6
26	35.00	10	14	0.70	2.564	1.9	76	74.20	30	32	0.94	1.278	4.4
27	35.50	12	26	0.46	2.529	3.6	77	75.00	14	36	0.38	1.266	5.0
28	35.70	7	20	0.36	2.515	2.8	78	75.60	12	33	0.37	1.258	4.6
29	36.20	8	23	0.33	2.481	3.2	79	76.20	24	31	0.78	1.249	4.3
30	36.80	31	54	0.57	2.442	7.4	80	76.50	28	38	0.72	1.245	5.2
31	37.00	33	51	0.64	2.429	7.0	81	76.80	42	56	0.75	1.241	7.7
32	38.20	208	229	0.91	2.356	31.6	82	77.20	50	67	0.74	1.236	9.2
33	39.10	59	106	0.56	2.304	14.6	83	77.80	56	41	1.37	1.228	5.7
34	39.80	80	200	0.40	2.265	27.6	84	78.40	22	54	0.41	1.220	7.4
35	40.30	39	55	0.54	2.238	7.6	85	78.80	10	29	0.35	1.215	4.0
36	41.00	17	28	0.60	2.201	3.9	86	81.50	18	21	0.84	1.181	2.9
37	41.50	14	28	0.51	2.176	3.9	87	81.70	9	20	0.44	1.175	2.8
38	42.00	27	64	0.42	2.151	8.8	88	82.00	9	21	0.42	1.175	2.9
39	42.60	37	57	0.66	2.122	7.9	89	84.30	10	25	0.39	1.149	3.4
40	42.90	50	58	0.87	2.108	8.0	90	88.60	10	23	0.42	1.104	3.2
41	43.30	43	57	0.76	2.089	7.9	91	91.20	4	11	0.33	1.079	1.5
42	43.80	57	87	0.65	2.067	12.0	92	92.50	3	8	0.32	1.067	1.1
43	44.30	110	79	1.39	2.045	10.9	93	95.79	3	13	0.22	1.040	1.8
44	44.70	61	77	0.80	2.027	10.6	94	96.60	8	19	0.41	1.032	2.6
45	45.20	42	67	0.62	2.006	9.2	95	104.90	9	21	0.42	0.972	2.9
46	45.80	17	38	0.45	1.981	5.2	96	109.90	6	23	0.26	0.942	3.2
47	46.70	123	228	0.54	1.945	31.4	97	110.40	11	31	0.36	0.939	4.3
48	47.60	12	28	0.43	1.910	3.9	98	110.70	9	21	0.42	0.937	2.9

Fig. 42- X-rayogram of a HA coating sprayed on a sample from nanocrystalline composite material (Ti + 5 % TiO₂): a - Ca₁₀(PO₄)₆(OH)₂; d - α-Ca₃(PO₄)₂.

No	2 Theta	I _{int}	I _{max}	FWHM	D	I/I _{max}	No	2 Theta	I _{int}	I _{max}	FWHM	D	I/I _{max}
1	10.50	3	20	0.16	8.425	3.1	51	44.60	30	46	0.66	2.032	7.1
2	10.80	11	35	0.30	8.192	5.4	52	45.20	33	50	0.67	2.006	7.7
3	12.20	2	15	0.11	7.254	2.3	53	45.70	13	20	0.67	1.985	3.1
4	12.70	3	14	0.22	6.970	2.1	54	46.00	16	22	0.73	1.973	3.4
5	14.00	1	5	0.13	6.326	0.8	55	46.70	125	226	0.55	1.945	34.7
6	14.70	1	9	0.11	6.026	1.4	56	47.40	9	21	0.42	1.918	3.2
7	15.50	2	11	0.18	5.717	1.7	57	48.10	39	103	0.36	1.892	15.9
8	15.80	5	16	0.30	5.609	2.5	58	48.70	25	46	0.55	1.870	7.1
9	16.80	6	18	0.32	5.277	2.8	59	49.40	89	186	0.48	1.845	28.5
10	17.60	2	11	0.22	5.039	1.7	60	50.50	47	105	0.45	1.807	16.1
11	18.80	4	20	0.21	4.720	3.1	61	51.30	37	79	0.46	1.781	12.1
12	19.60	2	14	0.11	4.529	2.1	62	52.10	28	87	0.32	1.755	13.3
13	21.70	10	34	0.28	4.095	5.2	63	53.10	45	75	0.60	1.725	11.5
14	22.10	1	11	0.08	4.022	1.7	64	54.30	2	11	0.22	1.689	1.7
15	22.80	31	77	0.41	3.900	11.8	65	54.90	2	8	0.23	1.672	1.2
16	23.80	3	12	0.22	3.738	1.8	66	55.40	1	6	0.17	1.658	0.9
17	24.00	1	9	0.16	3.708	1.4	67	55.80	10	27	0.37	1.647	4.1
18	25.20	8	21	0.39	3.534	3.2	68	57.20	3	14	0.22	1.610	2.1
19	25.80	75	175	0.43	3.453	26.8	69	60.10	17	33	0.52	1.539	5.1
20	26.30	6	17	0.34	3.389	2.6	70	60.40	15	27	0.54	1.533	4.1
21	27.00	18	27	0.68	3.302	4.1	71	61.70	22	44	0.49	1.503	6.7
22	27.50	15	27	0.54	3.243	4.1	72	62.10	26	32	0.80	1.495	4.9
23	28.10	45	92	0.49	3.175	14.1	73	63.10	38	48	0.80	1.473	7.4
24	28.40	26	57	0.46	3.143	8.7	74	64.00	65	91	0.71	1.455	14.0
25	28.90	98	166	0.59	3.089	25.5	75	65.20	43	69	0.62	1.431	10.6
26	29.50	101	71	1.42	3.028	10.9	76	66.40	7	23	0.31	1.408	3.5
27	29.80	146	74	1.97	2.998	11.3	77	67.30	1	5	0.25	1.391	0.8
28	30.10	154	68	2.27	2.969	10.4	78	69.70	5	17	0.32	1.349	2.6
29	30.50	96	82	1.17	2.931	12.6	79	71.80	6	22	0.28	1.315	3.4
30	30.80	97	96	1.01	2.903	14.7	80	72.30	10	22	0.44	1.307	3.4
31	31.20	132	112	1.18	2.867	17.2	81	74.10	13	22	0.59	1.279	3.4
32	31.80	304	652	0.47	2.814	100.0	82	74.30	12	22	0.55	1.277	3.4
33	32.10	133	382	0.35	2.788	58.6	83	75.40	24	36	0.65	1.261	5.5
34	32.90	179	415	0.43	2.722	63.7	84	75.80	10	22	0.44	1.255	3.4
35	34.00	104	188	0.55	2.637	28.8	85	76.10	10	20	0.50	1.251	3.1
36	34.50	8	18	0.45	2.600	2.8	86	77.00	64	61	1.05	1.238	9.4
37	35.50	11	35	0.31	2.529	5.4	87	78.20	28	47	0.59	1.222	7.2
38	37.00	15	29	0.52	2.429	4.4	88	79.40	3	8	0.32	1.207	1.2
39	38.10	147	161	0.91	2.362	24.7	89	81.80	12	28	0.43	1.177	4.3
40	39.10	49	69	0.71	2.304	10.6	90	83.40	9	22	0.39	1.159	3.4
41	39.90	78	159	0.49	2.259	24.4	91	84.40	8	23	0.33	1.148	3.5
42	40.50	12	27	0.45	2.227	4.1	92	87.30	11	26	0.42	1.117	4.0
43	41.00	14	26	0.52	2.201	4.0	93	88.50	8	17	0.49	1.105	2.6
44	41.60	12	27	0.45	2.171	4.1	94	88.80	5	17	0.32	1.102	2.6
45	42.00	31	50	0.63	2.151	7.7	95	91.20	8	22	0.35	1.079	3.4
46	42.60	43	36	1.20	2.122	5.5	96	96.60	11	26	0.43	1.032	4.0
47	42.90	44	38	1.17	2.108	5.8	97	97.10	15	21	0.70	1.028	3.2
48	43.50	24	41	0.59	2.080	6.3	98	100.40	7	17	0.39	1.003	2.6

Fig. 43 - X-rayogram of a HA coating sprayed on a sample from nanocrystalline composite material (Ti + 10 % TiO₂). a = Ca₁₀(PO₄)₆(OH)₂; b = CaO; d - α-Ca₃(PO₄)₂.

Fig.44 - Microstructure of a HA coating sprayed on a sample from technically pure nanocrystalline titanium

Fig. 45 - Microstructure of a HA coating sprayed on a sample from nanocrystalline composite material (Ti + 5 % TiO₂)

Fig.46 - Microstructure of a HA coating sprayed on a sample from nanocrystalline composite material (Ti + 10 % TiO₂)

study of sprayed nanocrystalline surface is not required. At the same time, a comparative analysis of modifications occurring in structures of sprayed substrate from nanocrystalline titanium and associated compositions is of interest.

The structure is investigated in specimen cross-section, perpendicular to the coating. When preparing the cross-section, the latter is grinded, polished, etched. The grinding is done with abrasive paper with SiC of 180, 240, 320, 600 units in graininess. The polishing is carried out in two steps: rough polishing and finishing. Rough polishing is done using "dp-cloths" with additives of diamond pasts type ACM 7/5, 5/3, 2/1 as well as "metadi fluid" liquid manufactured by "Buchler" (Switzerland). The finishing is conducted in distilled water using a "microcloths" nappa with $\alpha\text{-Al}_2\text{O}_3$ of 0,3 μm in graininess. The etching is realized by the following reagent: 50 ml of HCl, 2 g of CuSO_4 , 50 ml of alcohol, 50 ml of H_2O .

Study of the cross-section is conducted using a "Nanolab-7" scanning electron microscope manufactured by "Opton" (Germany), magnification being x 500, x 2500, x 5000; "Unimet" light microscope (Japan), magnification being x 200, x 1000.

Fig. 47...52 present photos of microstructures of nanocrystalline substrates from titanium and associated compositions in initial state as well as after plasma spraying with HA. Technically pure titanium (Fig. 47, 48) is produced at Ufa State Technical University for Aircraft in accordance with technology of equichannel angular compaction (ECAC) of corresponding powders having grain size about 36 μm . Compaction and annealing of the compacted powder is made in vacuum (10^{-2} mm Hg). Compaction modes are as follows: temperature - 823 K; pressure - 0,8 HPa. Annealing modes are as follows: temperature - 1073 K; duration - 1 hour. Said technology provides intensive plastic deformation and titanium particle milling up to the nanocrystalline level (grain size being about 300 nm). As shown in Fig.47,48, the substrates in initial state and after spraying are similar in many respects. For example, said substrates are characterized by the presence of hydrides, oxides, nitrides (white zones in photos). These substances result from interaction of titanium with hydrogen, oxygen, nitrogen containing in air, as well as technological gases of HA spraying. Aforemen-

x 2500

x 5000

Fig. 47 - Microstructure of nanocrystalline technically pure titanium
before spraying with HA

Fig.48 - Microstructure of nanocrystalline technically pure titanium after spraying with HA

tioned substances are presented both within the limits and along boundaries of metal grains. The surface of sprayed titanium base is characterized by higher content of hydrides, oxides, nitrides in comparison with initial substrate. However, the thickness of surface layer with excessive hard and brittle inclusions is insignificant (5...12 μm) and does not effect operation properties of the sprayed implant. Analysis of Fig.47, 48 shows that there is observed no principled modifications of titanium structure after spraying.

Titanium composition with 5 % of TiO_2 (Fig. 49, 50) is produced by ECAC of a mixture consisting of corresponding powders. Titanium particle size is about 36 μm , TiO_2 is used as a nanopowder. Compaction and annealing of the compacted material is made in vacuum (10^{-2} mm Hg). Compaction modes are as follows: temperature - 773 K; pressure - 0,55 HPa. Annealing modes are as follows: temperature - 773 K; duration - 30 minutes. Then the compact material is subjected to special treatment with supplementary plastic deformation. In accordance with Fig.49, 50, the composite substrate is enough homogeneous, there is observed no significant nonuniformity of TiO_2 particle distribution. It is to be stated that the negative effect of excessive hard and brittle inclusions is increased because of analogous phases presenting in base material. At the same time, the significance of said effect at brittle layer thickness about 10 μm may be lower in comparison with the effect of base material reinforcing by TiO_2 phase.

Titanium composition with 10 % of TiO_2 (Fig. 51, 52) is produced by ECAC of a mixture consisting of corresponding powders. Titanium particle size is about 36 μm , TiO_2 is used as a nanopowder. Compaction and annealing of the compacted material is made in vacuum (10^{-2} mm Hg). Modes of compaction, annealing and plastic deformation are practically the same. In accordance with Fig. 51, 52, the composite substrate is enough homogeneous, there is observed no significant nonuniformity of TiO_2 particle distribution. However, total amount of inclusions is significantly increased due to the phase presenting in base material. For the structure of the kind, the factor of base material reinforcing by TiO_2 may be ineffective when using an implant

x 200

x 1000

Fig.49 - Microstructure of nanocrystalline composite material (Ti + 5 %
TiO₂) before spraying with HA

x 200

x 1000

Fig. 50 - Microstructure of nanocrystalline composite material (Ti + 5 %
TiO₂) after spraying with HA

x 200

x 1000

Fig. 51 - Microstructure of nanocrystalline composite material (Ti + 10 % TiO₂) before spraying with HA

x 200

x 1000

Fig. 52 - Microstructure of nanocrystalline composite material (Ti + 10 % TiO_2) after spraying with HA

at alternating loads. Fatigue fractures appearing on substrate surface may free-progress into the base material thanks to excessive hard and brittle TiO_2 phase. However, above assertion requires supplementary experimental checking.

As stated earlier, formation of hydrides, oxides, nitrides when spraying titanium with HA at the optimal modes is stabilized in thin surface layer of the substrate ($\approx 10 \mu\text{m}$). Temperature effect for stabilization of the kind is shown in Fig. 53, presenting photos of overheated structure of nanocrystalline technically pure titanium. In accordance with Fig. 53, grain of structure is going big. Absorption of hydrogen, oxygen, nitrogen by the base material is intensified when overheating. The thickness of base material surface layer comprising excessive hard and brittle inclusions is significantly increased. That negatively effects operation capacity of the sprayed product.

$\times 200$

$\times 1000$

Fig. 53 - Microstructure of overheated nanocrystalline technically pure titanium

5. Theoretical generalization of the results obtained when investigating bioceramic coatings spraying on titanium substrate

Relatively low mechanical strength (compression strength, bending at alternating loads, etc.) is considered to be a weak point of bioceramic materials. Said characteristics of the latter are inferior to corresponding ones of titanium and stainless steels. That is why the process of bioceramic plasma spraying on metal implant surface is widely used last years in the USA, Japan, Germany, Sweden, Russia.

Constructions of the kind are characterized by combination of mechanical strength characteristic for metal implants with biological characteristics of bioceramic materials. It provides perspectives for wide clinical use of said materials. At the same time, realization of aforementioned perspectives is possible only in case of continuous improvement of both bioceramic coating material and metal substrate. Optimization of spraying modes is an important problem.

When improving sprayed material, there are carried out investigations of HA - Al_2O_3 composition, with various Al_2O_3 content as well as HA from natural bone tissue. Aluminium oxide as compared with HA is designed for bioceramic coating reinforcing (fig.54).

x 100000

x 100000

x 100000

a

b

Fig. 54 – Electronic and microscopic photos of HA powder provided with 20 % of Al_2O_3 after thermal treatment at 1073 K (a); electronograms (b).

Results of investigation of HA - Al_2O_3 composition designed for plasma spraying reveals that the produced coatings are unhomogeneous and are characterized by non-uniform distribution of aluminium oxide(fig. 55). In this case, the latter cannot be used as reinforcing frame as planned. Moreover, coating fracturing in the area of boundary with base material occurs.

HA powder from natural bone tissue is approved as well. Powder material represents a well crystallized product. X-rayogram of the latter corresponds to ASTM Standard. Specific weight of particle material is higher as compared with synthetic HA. X-ray phase- and structural analysis of coatings sprayed with the use of HA from natural bone tissue shows that said coatings are characterized by required quality (decomposition products quantity makes up about 20 % from all phases, porosity is 16...19 %, open porosity - 1,4...4,6 %). But these coatings are less active with respect for living bone tissue where an implant is put. This fact is explained by stable crystalline state of sprayed particles. Diffusion of calcium and phosphate ions in living tissue is obstructed, intergrowth of implan and human bone is slower.

A nanocrystalline substrate, produced by ECAC of corresponding powders (titanium and Ti- TiO_2 composition), is developed at Ufa State Technical University for Aircraft to improve operation properties of the implants. Compaction and annealing of compact material are conducted in vacuum (10^{-2} mm Hg). When investigating structure of the material it is determined that the structure is practically not changed in comparison with initial state in the process of spraying at the optimal modes. Insignificant modification consists of forming excessive hydrides, oxides, nitrides in thin ($\approx 10 \mu\text{m}$) surface layer of the substrate; but this formation does not effect operation properties. Comparison of traditional and nanocrystalline structures confirms that the latter are characterized by the same degree of surface layer saturation by excessive hard and brittle phase.

When investigating nanocrystalline substrate from technically pure titanium, (Ti+5% TiO_2) and (Ti+10 % TiO_2) there is observed increase in total amount of hard and brittle phase due to titanium oxide presenting in base material. For Ti+5% TiO_2 the

x 200

x 1000

Fig. 55 - Microstructure of the coating from hydroxiapatite and Al_2O_3 produced by APS-method

significance of negative effect resulted from said structure modification may be less important than the effect of base material reinforcing with TiO_2 phase. At the same time for $\text{Ti}+10\% \text{TiO}_2$ composition the factor of reinforcing may be low-effective at alternating loads when using implant. Fatigue fractures appearing on substrate surface may free-progress into base material thanks to excessive hard and brittle TiO_2 phase. However, this assertion is to be supplementary checked.

Results of our investigations, experimental data and theoretical generalization presented in provide the possibility to offer mechanisms of forming HA coatings at plasma spraying. Coating formation is caused by the processes occurring during the following stages:

- heating and acceleration of sprayed particles in plasma jet;
- collision between particles and product surface;
- plastic deformation and increase in dimensions of particles on product contact surface;
- interaction on contact surface between deformed particles and product and formation of adhesion binders between coating and substrate;
- collisions between particles and boundary sprayed layer;
- plastic deformation and interaction between particles and previously sprayed material, formation of cohesion binders in the coating

The sizes and energy state (temperature, velocity) of HA particles moving in center and periphery of plasma jet are different. It causes nonuniformity of the structure considered as a single whole as well as nonuniformity of layers formed during one step of the plasmatron. For example, the phases of crystalline HA, decomposition products (tribasic calcium phosphate and CaO) as well as microporosity are irregularly distributed in a coating. The authors [9] consider that a thin layer of amorphous HA joins to the boundary between the coating and substrate from titanium alloy. But we have not discovered such an amorphous layer in the process of our investigations. It may be related to merits of produced coatings because considerable amount of aforementioned amorphous material reduces life stability of the implant.

Heat conductivity of dense particle material of thermally treated HA powder provides uniform heating of a particle in plasma jet. Heat accumulation by particle surface as well as local decomposition of the latter followed by tetrabasic calcium phosphate formation are obstructed. That results in providing minimal quantity of HA decomposition products at the optimal spraying modes, thus providing thereby higher biocompatibility of implant coating.

Production of coatings by successive application of multiple deformed particles inevitably leads to formation of microcavities among particles. When producing coatings by plasma flow, said microcavities are filled by gas thus making worse thereby boundary properties, especially, this is characteristic for boundaries among layers because these boundaries are maximally saturated by absorbed gases. Defects and cavities over the area of contacts with previously applied particles result from considerable roughness of coating and very intensive spreading and hardening of particles as well as release of gases dissolved in melted particles.

Surface relief of coating is formed when spraying last coating layer. Said formation occurs because of open porosity and hardened particles of HA, presenting on the surface. The porosity, open one including, as well as whole surface relief of coating sprayed at the optimal modes (Fig.56) provides the reliable fixation of the implants. It is achieved by mechanical adhesion between bone tissue and sprayed coating surface.

As to formation of bonds between coating and base material, this is to be stated that said bonds result from mechanical binder (chemical interaction is possible). Mechanical binder is provided by blasting surface to be sprayed as well as preceding application of adhesive as rough sublayer. As mentioned earlier, we use in the process of our investigations electrocorundum jet; sublayer is formed by titanium powder plasma spraying. Rough porous sublayer has lower heat conductivity in comparison with this one of the same compact material. Heat accumulation along boundaries between coating and sublayer material is increased, chemical interaction between HA and sprayed titanium sublayer is activated, adhesion strength is increased and, as a

Fig. 56 - Fractogram of HA coating surface

result, implant quality is improved. However, the idea of chemical interaction is to be checked because of contradictory information. In particular, chemical interaction between coating and base material has been estimated in the process of preceeding study with respect for interaction products in transition zone between the coating and the base. X-ray analysis of HA coating as well as transition zone has been fulfilled using a DRON-3.0 diffractometer. However, there were observed no interaction products. It means that there are no phases of the kind or amount of the latter is insignificant ($< 5\%$). The authors [9] consider that there are no analysed phases. But [10, 11, 12] show that the chemical interaction between HA and titanium base, resulting is production of CaTiO_3 and TiP_3 , is possible.

6. Development and investigation of the process of applying nanocrystalline multilayer metal-oxide coatings

6.1. Physical bases of selection and estimation of the base technological process

The majority of modern technologies based on ion-beam spraying (IBS) may be presented as a combination of the following processes: 1 - transportation of the ion beam from ion source to sprayed target or substrate; 2 - mass transfer and chemical reaction in surface layer of a target or substrate; 3 - material emission from the surface and transportation of said material in vacuum; 4 - condensation of emitted material. An adequate phenomenological model of the processes accompanying IBS provides the possibility to significantly reduce expences for determinating optimal technological modes.

The IBS processes are often used in technologies designed to apply oxide- and nitride films. In practice, the technology is realized in two versions. The first one consists of a target made from pure material, for the second one, the target is from oxide (nitride) of required stoichiometrical composition. In both cases, the main technological problem is to determine active gas ion concentration in the beam in order to produce a film of required stoichiometrical composition with good physical parameters. At the same time, the productivity should be maximal.

When considering a model of ion-beam spraying of a two-component target, this is to be expected that not only selective spraying process caused by difference in coefficients of component spraying, but also intensive mass transfer to the surface due to generation of a number of vacancies by ion beam and diffusion of these vacancies into the target significantly effect the composition of target sprayed layer. As the model supposes that the component condensation coefficients are similar as well as actual technology conditions (operation gas pressure in a chamber equals to 16×10^{-2} Pa, distance "target - substrate" is 0,25...0,3 m max.) practically exclure reciprocal particle collisions during transportation, the composition of a film is effected by phenomena occuring in a pre-surface layer only.

In the case where IBS of metal targets is used for oxide film application, the situation becomes more complicated. Although it is possible to ignore interactions during transportation, it is necessary to take into account the fact that a volatile chemically active component (oxygen) appears in spraying ion beam and condensed flow.

As the condensation coefficient for the majority of metals is about 1 and condensation coefficient for oxygen atoms (molecules) is within $0,1 < \alpha_s < 1$, the film is more depleted by oxygen in comparison with composition of condensing flow. The situation is also more complicated in sprayed pre-surface target layer. Active component of the beam interacts with target material as well as physical processes of mass transfer because spraying and diffusion occur. It is to be noted that just the active gas diffusing particles participate in chemical reactions and, therefore, in changing composition of target surface layer. Chemical interaction should occur at the depth of $d \geq D/V_p$, where D - diffusion coefficient for oxygen atoms, V_p - velocity of displacement of a surface to be sprayed. Chemical process on implantation depth may be neglected because the instantaneous velocity of surface displacement exceeds much times said depth.

In the case where there occurs IBS of pure metal (Me) by combined beam of j_i ions which includes argon ion components j_{iAr} and oxygen ion components j_{iO_2} , the following sprayed flow of the material is formed:

$$j_p = j_{pMe} + j_{pO_2}, \quad (7)$$

where j_{pMe} and j_{pO_2} - sprayed flows of Me and oxygen atoms in shares. When considering flow j_p sprayed on a substrate, a film of MeO_x composition is produced. Both kinds of ions (j_{iAr} and j_{iO_2}) participate in direct atom spraying from target surface layer as well as in introducing and diffusing in this target. Atoms of inert argon practically do not effect chemical composition of the material and may be dissolved in metal lattice in insignificant amount.

That is why desorption flows of such particles from the target may be neglected. At the same time, argon from the ion beam contributes to V_p velocity when spraying. It is easy to show that the diffusion coefficient D is changed when changing composi-

tion of initial ion beam j_i because of changing middle weight of bombarding particles. Thus, modifications in composition of the initial ion beam ($j_i = j_{iAr} + j_{iO_2}$) leads to changing diffusion layer depth ($d = D/V_p$).

Diffusion coefficient is proportional to the full concentration of vacancies in conditions of radiation. Said coefficient may be presented as follows:

$$D = D' = K/\alpha_v \quad (8)$$

where D' - heat component of the diffusion coefficient; K - velocity of vacancies formation, proportional to ion current density; α_v - concentration of vacancies $\sigma_{\text{ок}}$. It is expedient to consider $D = f(j_i) = \text{const.}$ at densities of ion current characteristic for IBS processes, where V_p exceeds much times the depth of ion beam implantation. So, as a result of solving classical diffusion equation for constant surface concentration,

$$C(x, t) = C_{sO_2} \operatorname{erfc}(x / 2\sqrt{Dt}) \quad (9)$$

Concentration of ion beam active component in pre-surface layer is proportional to the value of surface concentration $C_{sO_2} \approx j_{iO_2}$. Therefore, the concentration of the active component in the spraying layer is increased proportional to j_{iO_2} increase. It occurs until the concentration of oxygen atoms in the sprayed layer has achieved the limit value, determined by chemical formula of the highest oxide of target material. Film composition should correspond practically linear to the composition of the highest oxide due to proportional $j_{pO_2} \approx C_{sO_2} \approx j_{iO_2}$ value. However, in case the composition of the sprayed target layer corresponds to the composition of the highest oxide, the oxygen in the film should be in slight deficiency due to increased desorption of oxygen in comparison with Me atoms.

Further increase in j_{iO_2} part of the initial ion beam leads to formation in the sprayed layer of a second phase representing accumulation of non-reacted oxygen atoms. Said atoms coalesced into microbubbles or migrate to target surface and desorb with the latter in conditions of high mobility. As the sprayed surface is moving, gas bubbles are open. Thus, j_{pO_2} flow with characteristic particle energy on the desorption level is added to the sprayed flow. Particles with energy of the kind cannot be chemi-

cally sorbed on the surface and, therefore, do not participate in chemical processes of oxide film formation. In counterbalance to that, sprayed Me and O atoms from surface oxide have energies which are as a rule higher than threshold energy of chemical sorption ($\approx 0,4$ eV). That is why just the sprayed particles may correspond the most in energy parameters to form an oxide film on substrate surface. Thus, excessive increase in j_{iO_2} part in the initial ion beam practically do not effect film composition. At the same time, desorbed particles of j_{dO_2} flow may be physically sorbed with the surface of a growing film and be easily desorbed with the latter. As supposed that the defects of film structure appear on the place of desorbed atoms, so the excessive growth of j_{iO_2} should lead to worsening film quality (for example, micropores appear) observing the same stoichiometrical composition.

Thus, in case the highest oxide for the given target may be presented as MeO_x , so when increasing oxygen ion part in the beam, oxygen concentration is as follows:

$$C_{sO_2}^0 = Ki \cdot j_{iO_2}^0 \leq x/(1+x) \quad (10)$$

where $C_{sO_2}^0 = C_{sO_2} / (C_{sMe} + C_{sO_2})$; $j_{iO_2}^0 = j_{iO_2} / (j_{iAr} + j_{iO_2})$; $K_i < 1$ - proportionality factor to characterize incomplete participation of all oxygen ions in oxide forming on target surface. So, oxygen atoms part $C_{O_2 fl.}$ in oxide film of the surface will correspond to the following expression as j_{iO_2} value is increasing

$$C_{O_2 fl.}^0 = a_s \cdot j_{pO_2}^0 = a_s \cdot Ki \cdot j_{iO_2}^0 \cdot S_o^0 < x/(1+x) \quad (11)$$

Because $0,1 < \alpha_s < 1$. In (6) the S_o^0 - value is oxygen atom spraying coefficient in shares.

The aforementioned fact results in obtaining dependence of film composition on beam composition for $0 \leq j_{iO_2} \leq 1$ interval (Fig.57).

Fig. 57 - Calculated dependences of compositions of sprayed flow consisting of metal atoms $j_{P_{Me}}^0$ and oxygen $j_{P_{O_2}}^0$ as well as oxide $j_{i_{O_2}}^0$ film composition $C_{O_{2n.}}^0 = a_s \cdot j_{P_{O_2}}^0$ on oxygen share in ion beam

The analysed technological process requires careful maintenance of composition of gas mixture supplied to ion source. This is necessary for reproducibility. As a result, rigid demands should be made on proportional systems and units to control consumption and pressure of gases. The technology is unavailable for industrial application in case of non-guaranteed possibility to maintain gas mixture composition with accuracy of $\pm 5\%$, or the technology requires supplementary informational parameters providing the possibility to control, for example, composition of target sprayed surface. IBS of previously sprayed oxide target is a way alternative to the considered technological process of producing oxide films type TiO_2 . Reproducibility of the process of the kind should be much higher in comparison with IBS of metal target. However, difficulties in manufacturing such oxide targets of enough large dimensions are often insuperable obstacle for industrial application in production of large-dimensional products.

Thus, the IBS of metal targets in gas mixtures ($\text{Ar} + \text{O}_2$) is considered to be the main technological process.

6.2. Special features of the design of ion-spraying source

An axis-symmetric ion source with discharge in $E \times H$ crossing fields, capable to form two independent ring ion beams, is used for realization of ion beam deposition. One of the independent beams is used for spraying target, the other one is designed for processing substrate surface. The work of every accelerators channel is provided by supplying high voltage and portioned flow of operation gas as well as by magnetic field formed by a united magnetic system of the device. A system for substrate displacement is designed to provide uniformity of film properties over the coating area when applying materials as well as at ion processing.

The units of the kind are characterized by relatively simple design, reliability and wide range of functional capacities. A special design of a solenoid and magnetic circuit provides the possibility to produce maximally elongated power lines in the area of discharge. As a result, the outer face packing is out of direct discharge and is not

sprayed by beam ions. Reciprocal location of magnetic circuit, anode and cathode-neutraliser provides 1) minimal energy to transport electrons to discharge layer, 2) generation of ion beams with large divergence and 3) negative gradient of anode surface magnetic field intensity in the direction of ion acceleration.

6.3. Technological features of coating forming by ion-beam spraying

There are determined dependences of film application velocity V_n on main technological parameters:

- target current value (Fig.58)
- discharge voltage (Fig.59)
- value for magnetic coil solenoid current (Fig.60)
- content of oxygen in gas mixture, % (Fig.61)

Said work is done in order to determine optimal technological parameters of ion source operation. Said parameters are as follows:

- discharge voltage - 5 kV;
- target ion current - 200 mA;
- Argon pressure in the chamber - $3,2 \times 10^{-2}$ Pa.

Fig. 58 - Dependence of titanium film application velocity on target current value

Fig. 59 - Dependence of titanium film application velocity on discharge voltage

Fig. 60 - Effect of current of a solenoid of ion source magnetic system on titanium film application velocity.

Fig. 61 - Effect of oxygen content in operation gas on the velocity of film deposition when spraying titanium target.

6.4. Methods to determine element concentration using the dependence of line intensity on accelerating voltage and a "Cameca MS-46" microanalyser

The main advantage of micro X-ray structural analysis consists of the possibility to locally determine chemical composition of inclusions, phases, grains; to study distribution of separate elements among structural components.

The dependence of line intensity on accelerating voltage is used to determine concentration using a MS-46 microanalyser.

This method provides the possibility to determine concentration of analysed element using values obtained in the process of one experiment only. The method consists of the following:

Measured is relationship of intensities of the analysed line in an object to be investigated and in a standard at various accelerating voltages; revealed is dependence $I_A/I_{(A)}$ on accelerating voltage E . Having elongated said curve up to E_0 line, we find element concentration in question.

It means that X-ray radiation, excited in surface layer which thickness is determined by the length of electron free path with E_0 energy, is leaving the object without absorption. There is also no fluorescence excitation of the analysed radiation caused by stronger characteristic radiation of other elements, because the energy of falling electrons is insufficient. Number of electrons exciting X-ray radiation in the analysed object and standard may be different because different processes of electron interaction with the sample and the standard.

6.5. Investigation of the structure of composite multilayer Ti-TiO₂ coating

An angle lap (10°) is prepared in order to study the possibility to widen coating area. A thin gold layer (100 Å) is applied to provide electrical conductivity of composite material oxide layer. It does not result in absorption of titanium X-ray radiation.

Fig. 62, 63 show concentration curves of Ti distribution in a sample with multilayer Ti-TiO₂ coatings, layer thickness being about 50 nm. Total thickness of the coating makes up about 2 µm.

Fig. 62 shows titanium distribution in a sample when moving probe from titanium substrate perpendicular to the coating. The analyser registers 100 % of Ti in the area of substrate; 60 % of Ti in the area of coating, evidently, 40 % are related to oxygen, that corresponds to Ti-TiO₂ multilayer composition.

The concentration curve of titanium distribution in a multilayer coating (Fig.63) is made at an oblique angle ($1 \div 2^\circ$). Slight difference in % content of titanium in the coating testifies about the complication of the latter, but it is impossible to exactly measure layer size because the diameter of the probe of a MS-46 microanalyser is commensurable with coating size in total.

Fig. 62 - Ti distribution in a sample to be investigated (the probe is moving perpendicular to the film surface)

Fig. 63 - Ti distribution in a composite multilayer coating (the probe is moving along the coating surface at an angle of $1 \div 2^\circ$).

Investigation of composite coating structure is conducted using a "Nanolab-7" scanning electron microscope.

Fig. 64 (a, b), 66 (a, b, c) and 67 (a, b, c) present various sections of sample fracture (coated base), magnification being x2500, x5000, x10000. Fig. 65 (a, b) shows coating fracture.

Fig. 68, 69, 70 show sections of structure and topography of coating surface at different magnification. Fig. 69, 70 let clearly seen coating lamination.

a

b

c

Fig. 64 - Structure of multilayer composite coating (fracture): a - coating with the base, b - coating with the base, c - coating surface

Fig. 65 - Structure of multilayer composite coating (fracture) at different magnifications

Fig.66 - Structure of multilayer composite coating and the base (fracture)

Fig. 67- Structure of multilayer composite coating and the base (fracture)

Fig. 68 - Structure of multilayer composite coating (the photo is made from surface side)

Fig. 69 - Structure of multilayer composite coating (the photo is made from surface side; angle lap)

Fig. 70 - Structure of multilayer composite coating (the photo is made from surface side; angle lap)

Conclusion

Investigations of the technology of HA plasma spraying on substrates from titanium and associated compositions of traditional and nanocrystalline structure have been carried out. Problems of HA powder production have been considered, parameters of the powder in initial state have been analysed, modes for spraying bioceramic coatings when manufacturing bone implants have been optimized, the effect of spray process on the substrate has been studied. The offered method included SEM, TEM, X-ray structural study, use of automatic and semi-automatic picture analysers.

When improving coating material, HA powder from natural bone tissue was used side by side with synthetic hydroxiapatite. Powder material from natural bone tissue represented a well crystallized product with X-rayogramme corresponding to the ASTM Standard. Specific weight of material particles was higher in comparison with synthetic HA. X-ray phase and structure analysis of coatings sprayed with HA from natural bone tissue has showed that said coatings were characterized by the required quality parameters (quantity of decomposition products of nanocrystalline material made up 20 % of total phase volume; porosity was 16...19 %, open porosity equaled to 1,4...4,6 %). However, these coatings were less active as related to living bone tissue where an implant has been located. This may be explained by the stable crystalline state of the sprayed particles. Diffusion of calcium and phosphate ions into the living tissue was hampered, intergrowth of the implant and human bone was realized slower.

Optimization of HA spray modes testified that these modes for titanium of traditional and nanocrystalline structure insignificantly differed in spray distance. The latter was by 5 mm longer when spraying HA on titanium and Ti-TiO₂ compositions of nanocrystalline structure. Study of X-rayogrammes of coatings produced at the optimal spray modes showed that total HA decomposition product quantity was on the level of 20 % of total HA phase volume. Photos of microstructure of coatings on sample brittle fracture confirmed the presence of pores of round shape as well as complicated one. Increased coating porosity corresponded to the nanocrystalline material of

a substrate, total and open porosities being 17,5...20,4 % and 4,1...6,3 %, respectively, thus providing thereby reliable fixation of the implant in the bone tissue because of mechanical adhesion.

Comparative analysis of substrates microstructure before and after spraying revealed that there are no principle differences. As for the nanocrystalline substrates, this is to be noted that the surface of said substrates was characterized by increased quantity of hydrides, oxides, nitrides in comparison with the initial state. However, the thickness of outer layer with excess hard and brittle inclusions was insignificant ($\approx 10 \mu\text{m}$). It did not effect perceptibly on operation properties of an implant from technically pure titanium and Ti+5%TiO₂ composition. At the same time, total quantity of the inclusions in a titanium sample with 10 % of TiO₂ was significantly increased due to the phase of the base material. A factor of reinforcing the base material with TiO₂ phase for such a structure may be low efficient for implant operation in conditions of alternating loads. Fatigue cracks occurring on substrate surface may free progress in the depth of the base material because of excess TiO₂ hard and brittle phase. But this suggestion requires additional experimental testing.

Important role of spray optimization has been confirmed by investigating overheated structure of the nanocrystalline technically pure titanium. Absorption of hydrogen, oxygen, nitrogen by the base material was appreciably intensified thus effecting negatively operation capacity of the sprayed product.

One of the chapters of the report was devoted to a technology of ion-beam spraying which is the most controlled, low-temperature and regenerable way of all ion spraying methods. Plasma generation, formation and acceleration of an ion beam occur in a separate unit independent on interchamber attachment - ion source. As a result, a target as well as a substrate were not functional electrodes; the space between said target and substrate was free of the effect of intensive electrical and magnetic fields.

A multilayered coating represented a combination of alternating Ti-TiO₂ layers of 2 μm in thickness on a titanium substrate. Should the coating thickness exceed 2 μm , the coating was peeled because of high stresses in the composite coating.

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Belorussian State Research and Production Powder Metallurgy Concern
Powder Metallurgy Research Institute with Pilot Plant

Approved by

Director

A.F. Ilyuschenko

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COATING APPLICATION ON TO IMPLANTS BY PLASMA SPRAYING
Technological Instruction

Department Manager

V.S. Ivashko

"24" 04 1998

Minsk 1998

The present Technological Instruction is designed for regulating processes of coating plasma spraying onto implants for dental prothesis.

1. Characterization of Initial Materials.

1.1. Technical requirements for powders used for coating application.

1.1.1. Powders to be sprayed should be controlled in order to correspond to the accompanying documents.

1.1.2. Titanium powder of 40...63 μm (analogous to Vactex 22-00 manufactured by Plasma-Technik AG company) should be used for sublayer application

1.1.3. HA powder of 63...100 μm (analogous to Amdry 6021 manufactured by Plasma-Technik AG company) should be used for spraying coating main layer;

1.2. Operation gases used for spraying are as follows:

1.2.1. Gaseous argon, Standard 10157-79;

1.2.2. Gaseous hydrogen, Standard 3022-80;

1.2.3. Gaseous nitrogen, Standard 9293-74;

1.3. The following materials are used for degreasing part surface before blasting and spraying:

- acetone, Standard 2768-84;
- ethanol, Standard 17299-78;
- cotton napkins, Technical Terms 63-178-77-82;
- zirconium electrocorundum with grains of 0,1-0,2 mm.

2. List of Technological Equipment.

2.1. Plasma spraying control system type ALLGAS, consisting of:

2.1.1. Spraying process control desk;

2.1.2. Power source type PT-800;

2.1.3. Plasmotron type F4-HB;

- 2.1.4. Plasma spraying semi-automatic machine type 15BБ provided with sound absorbing chamber;
- 2.1.5. Blasting chamber type MicroOS, provided with a system of compressed air pressure adjustment;
- 2.1.6. Water cooler of closed cycle type FC-250;
- 2.1.7. Powder feeder type TWIN-10C;
- 2.1.8. Screen analysis unit, model 029.

3. Technological process.

Technological process of coatings plasma spraying onto titanium implants consists of the following operations:

- 1. Powder preparation.
- 2. Preparation of the surface to be sprayed.
- 3. Coating application.
- 3.1. Powder preparation.

To separate big as well as adhered powder particles for syblayer and coating layer, the powders are screened through a set of screens of a 029 screen analysis unit. The screens are placed as a stack in accordance with cell size increasing, and fixed on a vibration table of the unit. Weight of 1 kg is screened during 20-30 minutes. Having completed the screening, the powder is removed from the screens, the latter are cleaned from jammed particles by a compressed air jet.

3.1.2. Powder drying.

The screened powder should be dried before spraying at 323 K min. (for HA powder) or 373 K (for titanium powder) to remove absorbed moisture. Powder layer thickness on a pan should be 20 mm max.

3.2. Preparation of a surface to be coated.

3.2.1. Surface control before blasting. The blasted surface should have no hollows, pits, cavities. If some defects present, the latter are to be removed.

3.2.2. Sample degreasing before blasting is made by cotton napking moistened with acetone. After acetone degreasing, washing with hot and cold water containing salts according to Standard 2874-33 should be done. Sample drying after the washing is made in a drying oven at 100-150°C.

3.2.3. Sample surface blasting is conducted in a MicroOS chamber to remove oxide film and activize operation surface. Processing modes are as follows:

- compressed air pressure, MPa - 0,3...0,4;
- distance between a torch and a surface to be treated, mm - 100...120;
- angle between the jet and part surface, ° - 70...90;
- abrasive material - zirconium corundum, particle size being 100-200 µm.

Metal lustre of the surface subjected to the processing is not acceptable. Area of sample surface to be not sprayed should be protected against blasting. After the latter the sample is to be treated with dry compressed air to remove abrasive particles from the surface. If a part has cavities and pits after the blasting, such a part is rejected.

3.2.5. Storage of samples to be sprayed.

Time interval between surface preparation and spraying should be minimal as far as possible and do not exceed one hour. It is prohibited to touch a prepared surface by hands or dirty tools. All operations with the prepared parts are to be made in pure gloves or with cotton napkins. Should a surface be soiled it is required to clean this surface with a wad moistened with ethanol type A, Standard 17299-78. If transportation is required, the samples should be packed in paper to avoid soiling.

3.3. Coating application.

The following work should be carried out before spraying to avoid spallings, fractures, peelings:

- check the presence of oil and moisture in compressed air for cooling samples when spraying;

- check the system of powder feeding into the plasmotron;
- check all spraying equipment.

3.3.1. Application of the sublayer and coating layer.

3.3.1.1. Place a mandrel with samples onto manipulator guides. Open pressure regulator of vessels to feed plasma-forming as well as transportation gases to the control desk, open regulators of compressed air pipe-line. Switch on the control desk. Provide the feeder with powder to be sprayed as sublayer and coating layer.

3.3.1.2. Adjust sublayer application parameters on the spraying control desk as follows.

- plasmotron arc current, A - 360;
- arc voltage, V - 62;
- spraying distance, mm - 100;
- consumption of plasma-forming gas (argon), SLPM - 35;
- consumption of plasma-forming gas (hydrogen), SLPM - 10;
- consumption of transportation gas (argon), SLPM - 9;
- consumption of titanium powder, RPM - 20.

Having completed application of a 0,05 mm sublayer, powder feeding is off, the plasmotron is out of the mandrel.

3.3.1.3. Adjust parameters of main layer application on spraying control desk.

- plasmotron arc current, A - 550;
- arc voltage, V - 62;
- spraying distance, mm - 80;
- consumption of plasma-forming gas (argon), SLPM - 45;
- consumption of plasma-forming gas (hydrogen), SLPM - 12;
- consumption of transportation gas (argon), SLPM - 9;
- consumption of HA powder, RPM - 30.

Having completed coating layer spraying, the plasmotron is out of the mandrel; plasma spraying unit is off.

After sample cooling, this is to control coating quality.

4. Coating quality control.

4.1. The coating should have colour uniform surface.

4.2. Separate point inclusions as well as sprayed material drops are not acceptable on the surface.

4.3. The sprayed layer should have no fractures, spallings, peelings, etc.

4.4. Any liquids being not required according to the technological process are not acceptable on the sprayed surface.

4.5. The sprayed layer is not a subject of impacts and hard loads.

4.6. Control of coating quality in order to the latter corresponds to technical requirements is made by visual inspection and comparison with a standard.

5. Safety and Sanitary Requirements.

5.1. The operators of plasma spraying unit should fit with the following requirements: 18 years old min.; medically checked up, trained for operation on coating application, passed the safety examination, having 2nd qualification class min. in electric safety.

5.2. The persons involved in operating with plasma spraying unit should be subjected to periodical medical check up.

5.3. The persons involved in operating with plasma spraying unit should be trained and admitted as unit operators; they should pass examination on "Design and Operation Rules for Vessels Operating Under Pressure"; they should have side breifing as well.

5.4. Said persons should be provided with special cloths and footwear as well as individual protective means.

5.5. At plasma spraying, hearing organs of the operator should be protected against high-frequency noise by antiphones or earphones.

5.6. Operators' eye protection against radiation should be provided by welding goggles with light filters.

5.7. Coating layer application at atmospheric pressure is done in special cabinets provided with ventilation of 4000 m³/hour in capacity for protection of the operator against aerosol effect. A breathing apparatus should be used for protection of respiratory ways. Plenum-exhaust ventilation should provide triple air exchange.

5.8. Plasma-spraying sector should be located in isolated rooms along building walls at the ground floor. Location in basements is prohibited. The room should have natural lighting; zones of aerosol, gas, dust accumulation, are To be avoided.

Belorussian State Research and Production Powder Metallurgy Concern
Powder Metallurgy Research Institute with Pilot Plant

Approved by

Director

A.F. Ilyuschenko

"24" 04 1998

Application of Multilayer Ti- and TiO_2 -based Coatings on Titanium Substrate
by Ion-Beam Spraying from Solid-Phases Materials.

Department Manager

V.S. Ivashko

"24" 04 1998

Minsk 1998

1. Characterization of Initial Materials.

1.1. All materials for spraying multilayer coatings consisting of alternating Ti and TiO_2 layers on a titanium substrate may be divided in main materials and auxiliary ones. The first group is required for realization of technological process, the second one - for equipment technological maintenance.

1.2. Base materials.

1.2.1. Titanium is designed for production of a target to be sprayed.

1.2.2. Argon is an operation gas.

1.2.3. Oxygen is used as a reaction gas.

1.2.4. Solvent designed for degreasing surface of a product to be sprayed.

1.2.5. Rectified ethanol for dehydration of the surface.

1.3. Materials designed for technological process realization directly in a vacuum chamber (titanium, argon, oxygen) should be as pure as possible to avoid quality worsening as well as coating peeling.

1.4. Auxiliary materials.

1.4.1. Vacuum oil (VO-1);

1.4.2. Petrol;

1.4.3. Rectified ethanol.

2. Technological process.

2.1. The technological process given below determines the main operation modes required for applying multilayer coatings from alternating Ti and TiO_2 layers on a titanium substrate, using a HHB-6,6-U1 unit provided with two-beam ion source.

2.2. Product preparation for spraying.

2.2.1. Process all surfaces of the product to be sprayed with cotton napking, moistened by a solvent (petrol, etc.).

2.2.2. Wash the product by running drinking water of 40-60°C during 2-3 minutes.

2.2.3. Fray surfaces with a cotton napking, moistened by rectified ethanol.

2.2.4. Visually control fraying quality (100 %). Do not accept visible impurities.

2.3. Coating application.

2.3.1. Place the product into the chamber of the HHB-6,6-U1 unit.

2.3.2. Fray the door gasket by alcohol.

2.3.3. Close chamber door.

2.3.4. Pump out air from the chamber up to $1,33 \times 10^{-3}$ Pa.

2.3.5. Provide the unit with technological gas (argon) from pipe-line or vessel. Technological gas pressure has to be within 0,8-1,5 atm.

2.3.6. Transport the argon into the top channel of the ion source with the help of a leak.

2.3.7. Adjust technological gas consumption to be corresponded to the pressure in operation chamber ($3,2 \times 10^{-2}$ Pa).

2.3.8. Provide the cap with cold water. Control the efficiency of ion source body cooling.

2.3.9. Switch on solenoid feeding source.

2.3.10. Adjust solenoid current as 3 A.

2.3.11. Connect a high-voltage source with the network.

2.3.12. Provide the top stage of the ion source with high voltage by slow turning of the handle "High Voltage" on the front pannel of a high-voltage supply unit. Adjust the following discharge parameters: $I=200$ mA, $V=5$ kV.

2.3.13. Open the valve of the ion source. Process substrate surface during 5-10 minutes. It is recommended to move substrate support to improve ion processing quality.

2.3.14. Stop argon supply in the top channel of the ion source. Lower high voltage of the top stage of the source.

2.3.15. Close the valve.

2.3.16. Supply the argon to the lower channel on the spraying stage of the source.

2.3.17. Provide the spraying stage of the ion source with high voltage by slow turning of the handle "High Voltage" on the front pannel of a high-voltage supply unit. Adjust the following discharge parameters: $I=200$ mA, $V=5$ kV. Note: Discharge current and voltage significantly depend on the pressure in the chamber. The pressure depends in tour on the capacity of pumping out facilities. That is why, should there be impossible to adjust the given values of current and voltage, the high voltage is to be off and the gas pressure is to be adjusted.

2.3.18. Spray a target during 3-5 minutes to clean the latter from impurities. Note: Adjust ion source modes (gas flow, magnetic field) to achieve relationship "target current/discharge current" within 0,8-1,1 at idle target spraying.

2.3.19. Open the valve. Apply titanium film untill the latter has achieved the required thickness.

2.3.20. Supply the oxygen into the chamber untill the pressure has been $1+2 \times 10^{-2}$ Pa.

2.3.21. Apply titanium oxide film during the period necessary for required thickness production.

2.3.22. Stop oxygen supply.

2.3.23. Close the valve.

2.3.24. Reiterate 2.3.4. - 2.3.23 untill a multilayer coating of required thickness has been produced.

2.3.25. Lower high voltage, switch off solenoid supply, close the regulator of technological gas supply.

2.3.26. Cool the product in the chamber at the pumping-out system being off during 15 minutes.

2.3.27. Fill the chamber with air up to atmospheric pressure.

2.3.28. Open the chamber door and back the products.