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Obtaining hydroxyapatite coatings by mechanochemical interaction

¹ Mamaeva A. A., ^{1*} Kenzhegulov A. K., ¹ Panichkin A. V., ² Shah A.

¹ Satbayev University, Institute of Metallurgy and Ore Beneficiation JSC, Almaty, Kazakhstan

² Faculty Technical and Vocational, Sultan Idris Education University, 35900 Tanjung Malim, Perak Malaysia

* Corresponding author email: kazakh_1403@mail.ru, a.kenzhegulov@satbayev.university

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Abstract. The research represents a newly-developed simple method to apply hydroxyapatite by gas-dynamic spraying. The hydroxyapatite coating formed on VT1-0 titanium were obtained following the mechanochemical interaction of hydroxyapatite and titanium with gas-dynamic spraying. The article proposes the phase composition, surface morphology, and roughness of these coatings. The surface morphology of the hydroxyapatite coating had a porous structure. The transverse sections of coatings were researched to study the interaction of hydroxyapatite with a titanium base. It was shown that the coatings mainly form in the titanium bedding depressions. Analyzing the roughness parameter R_a of hydroxyapatite coatings made it possible to conclude that the samples obtained fell almost within the same limits. These data are within the roughness optimum ($R_a = 2-3 \mu\text{m}$) of artificial surfaces aimed to manifest the best human osteogenic properties. The analyzed phase composition enabled to establish the fact that the hydroxyapatite layer composition does not change significantly after spraying that is important for biomedical use.

Keywords: coating, powder, titanium, hydroxyapatite, implant, cold spraying, nozzle, sandblasting.

Information about authors:

Mamaeva Aksaule Alipovna, Candidate of physical and mathematical sciences, Head of the Laboratory of Metall Science, Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan. Email: ak78@mail.ru, ORCID ID: 0000-0002-9659-8152

Kenzhegulov Aidar Karaulovich, PhD, Researcher of the Laboratory of Metall Science, Institute of Metallurgy and Ore Beneficiation, Almaty, Kazakhstan. Email: kazakh_1403@mail.ru, ORCID ID: 0000-0001-7001-2654

Panichkin Aleksandr Vladimirovich, Candidate of Technical Sciences, Head of the National Scientific Laboratory, Institute of Metallurgy and Ore Beneficiation, E-mail: abpanichkin@mail.ru, ORCID ID: 0000-0002-2403-8949

Shah Arman, Professor, Dr., Faculty Technical and Vocational, Sultan Idris Education University, 35900 Tanjung Malim, Perak Malaysia. Email: armanshah@ftv.upsi.edu.my, ORCID ID: 0000-0002-4366-9156

Introduction

Titanium and titanium alloys are preferred materials for medical implants. They have favorable properties such as relatively low elasticity modulus, low density, and high strength. On the other hand, the biocompatibility of titanium alloys is much worse than that of calcium phosphate ceramics [1].

To improve the biocompatibility attributable to Ti and its alloys, a ceramic coating is applied to their surface. The main ceramics used in medicine is hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) marked with high biocompatibility, since its chemical and crystallographic structure is similar to the bone tissue structure [2-3]. To this date, various methods of applying the HA coatings have been employed

[4-8]. However, due to extremely high operating temperatures, some HA deposition methods usually stimulate the amorphous phase forming at the implant-coating interface that impairs osseointegration [9]. A more acceptable method of applying biologically active surfaces to orthopedic implants is plasma sputtering (PS) [10]. But, the main problems when using the PS coating technology include poor control over the phase composition, low applying reproducibility, and the use of expensive vacuum equipment. An interesting alternative to this method is the use of a relatively new gas-dynamic spraying (GDS) method [11] based on the mechanochemical fusion process. Compared to plasma sputtering, the GDS temperature is significantly lower than the melting points of the sputtered materials [12]. It overcomes some traditional thermospray “disadvantages”, such as unwanted phase transitions and decomposition [13].

GDS is a solid-state coating process where powder particles are accelerated at supersonic speeds and pass through a de Laval nozzle to a bedding but the powder particles do not reach their melting point unlike conventional processes. Very few attempts to obtain pure HA coatings by the GDS method is attributable to the difficulties in the ceramic particle cohesion [14]. If compared to the plasma sputtering methods, the ceramics GDS, in particular HA, is a more difficult task, but recent studies have shown that the mechanism of their deposition depends on the sprayed mixture characteristics [15-17]. In this regard, the study of HA coatings on titanium beddings obtained by the GDS method is an urgent problem in medical materials science.

The present study is focused on testing the modes of mechanochemical interaction between HA and VT1-0 grade titanium by the GDS method.

Experimental procedure

The need to study the mechanochemical interaction of HA powder and a titanium bedding during mechanical fusion resulted in developing a GDS unit. The analysis covered three modes for applying the HA powders on the surface of VT1-0 titanium beddings with a size of 25x40x1 mm with and without a carrier. The modes are presented in Table 1. The beddings were preliminarily cleaned from the oxide layer with a sandblaster using an abrasive material.

Testing of modes 1 and 2 included using a SBS 350 sandblaster that has a box and a sand supply system equipped with a W-0.9/8 compressor enabling to create a pressure of up to 10 atm. with a productivity of 1121 l/min (Figure 1). The sprayed

mixture for the sandblaster was prepared with the addition of 5% HA powder by the carrier weight. The carrier was intensively mixed with HA powder and distilled water in an amount of 250 ml per 3 kg of the mixture in a volumetric glass for this purpose. Then the mixture was placed in an oven to evaporate the water. The mixture dried in this way was placed in the sandblaster storage device, then titanium beddings were processed with a pistol.

Table 1 Modes for applying HA coatings

Modes	No.1	No.2	No.3
Sprayed mixture	HA and garnet sand powder (<150 μm)	HA and SHH15 steel powder (<50 μm)	HA powder (<5 μm)
Mixture flow pressure	8-10 atm.	8-10 atm.	50 atm.
Distance between the nozzle and bedding	10 mm	10 mm	10 mm
Processing time	approx. 20 sec	approx. 20 sec	approx. 20 sec

Mode 3 testing applied the developed unit that had a box, a nozzle, and a powder supply system with valve cocks making it possible to supply a gas flow at a pressure of up to 100 atm. (Figure 2). The sprayed material flow pressure was measured using a monometer located in the nozzle. The working gas was pure argon (99.99%) supplied from the cylinder at a pressure of at least 100 atm. The GDS took place without a carrier using pure HA powder loaded into the hopper. The nozzle was specially designed to accelerate the sprayed particle to supersonic speeds.

The surface morphology was studied by scanning electron microscopy (SEM) on a JXA-8230 (JEOL) microscope at an accelerating voltage of 20 kV and an electron beam current of up to 7 nA. For all areas of the samples selected for the SEM study, the backscattered electron mode (COMPO) was used. The obtained samples were studied by X-ray phase analysis (XPA) using a D8 Advance (BRUKER) diffractometer with α -Cu radiation ($\lambda \approx 1.54 \text{ \AA}$), $U = 40 \text{ kV}$, $I = 40 \text{ mA}$, the recording rate was 0.1-1 deg./min, the angle interval – 2θ 4-90° with a scanning step 0.01°. The X-ray recording applied focusing according to Bragg-Brentano. For the phase analysis, the PDF 2 base was used. A Diavite DH-5 profilometer helped to measure the surface roughness. Each sample was measured 5 times with the average of five measurements chosen upon obtaining the results. The measurement length was 4 mm. SEM and XPA

studies took place at the National Research Laboratory for Collective Use in the priority direction "Technologies for the hydrocarbon and mining and metallurgical sectors and related service industries of the Institute of Metallurgy and Ore Beneficiation JSC.



Figure 1 Sandblaster (SBS 350 brand)

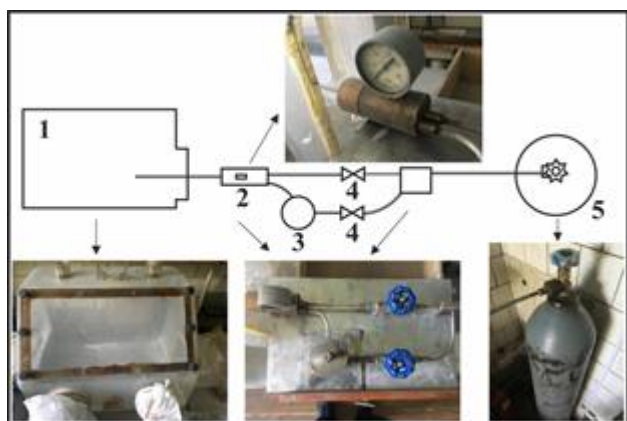


Figure 2 Diagram for the unit used with GDS HA coatings: 1 – a box, 2 – a nozzle with a monometer, 3 – a hopper for sprayed powder, 4 – valve cocks, 5 – an argon cylinder

Results and discussion

To determine the relationship between the coating and bedding, transverse sections of the obtained HA coatings were prepared. With this in view, two samples were fixed on a single table in such a way that their surfaces (the sprayed side) were located on top of each other. In this position, the two samples were ground and polished simultaneously. Next, the polished surface was explored followed by determining how HA was formed on titanium, and the coating thickness was also measured.

Figure 3 shows the titanium surface morphology and transverse sections of the obtained HA coatings. According to the SEM studies, HA coatings on titanium obtained in modes 1 (Figures 3a and 3d)

and 2 (Figures 3b and 3d) are similar in appearance and have a porous structure. As shown in Figure 3d, the HA coating is formed mainly in the titanium bedding depressions.

The harder and more brittle HA powder particles form microroughness upon colliding with titanium, and HA is fixed in further deepened areas. Processing in modes 1 and 2 results in the HA coating thickness ranging from 9 to 20 μm . Also under these conditions, the coating has significant roughness, and for this reason, high waviness is noticeable. On the contrary, the coating obtained in the third mode (Figures 3c and 3f) forms occasionally relatively smooth and continuous coatings (with a thickness of 23.06 μm) with small microcracks. Decreasing roughness of the HA layer surface occurs due to the replenishment of the deeper Ti surface. The GDS mode using the starting HA powder without a carrier leads to a morphology consisting of submicron grains (Figure 3c).

The elemental composition of the coating shows the presence of the main HA elements and bedding: Ca, P, O, and Ti. At the same time, given the microprobe analysis data, the Ca/P ratio was 1.7 meeting the biocompatibility conditions. No obtained coatings had pores, delamination, or any defects near the coating/bedding interface pointed at a good quality of the sprayed coating. In the future, it would be useful to try and make it possible to obtain a uniform coating on the VT1-0 titanium. Works [8, 13, 17-18] describe obtaining coatings on the implant surface that is already in progress.

Upon processing by the GDS modes, the following crystalline phases are present on the titanium surface: HA, titanium, calcium hydrogen phosphate, and titanium hydrogen phosphate. This is confirmed by the XPA results shown in Table 2.

The X-ray diffraction results (Figure 4) show that for the three types of GDS coatings, the main coating phases were practically the same. However, small peaks were observed attributed to the phases $\text{Ca}_3(\text{PO}_4)_2\text{H}_2\text{O}$, $\text{Ca}_3(\text{PO}_3)_6\text{10H}_2\text{O}$, $\text{Ti}(\text{HPO}_4)_2$, although the low intensity of these peaks indicates a limited number of such phases. The $\text{Ti}(\text{HPO}_4)_2$ phase formation is usually caused by titanium interacting with phosphate groups in the HA composition. Large broad bands were not observed due to the absent amorphous phases. It should be noted that the TiO_2 and CaO phases were not identified either on the raw material powder or on the Ti-HA surfaces deposited by the GDS sputtering. Also, no carrier phases (sand, tungsten) were detected in the coatings obtained under modes No. 1 and No. 2.

The surface roughness evaluation included the values of the vertical profile irregularity parameters using the measuring system of the profilometer.

Table 2 Phase compositions obtained in all coating application modes

Modes	Phase fractions, %				
	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$	Ti	$\text{Ca}_3(\text{PO}_4)_2\text{H}_2\text{O}$	$\text{Ca}_3(\text{PO}_3)_6\cdot 10\text{H}_2\text{O}$	$\text{Ti}(\text{HPO}_4)_2$
No.1	17.9	82.1	–	–	–
No.2	17.9	72.5	9.6	–	–
No.3	33.7	41.7	–	7.1	17.5

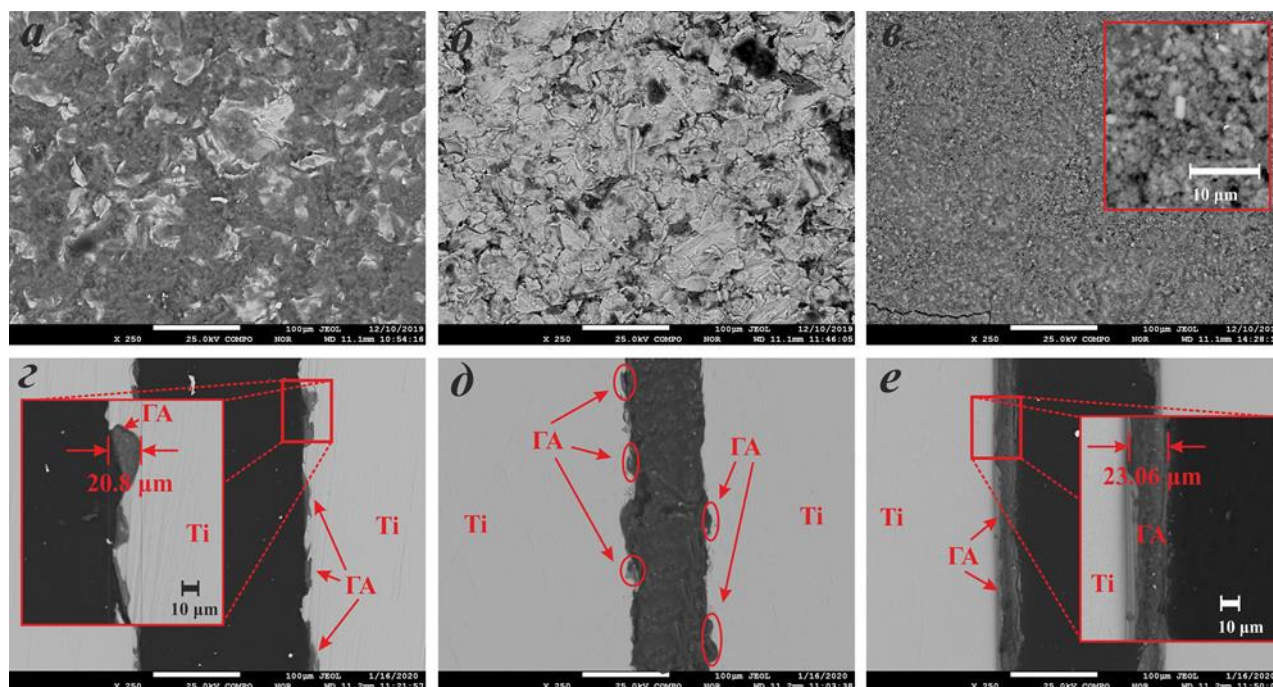


Figure 3 SEM micrographs of morphology and transverse sections of the obtained HA coatings by the GDS method in all production modes

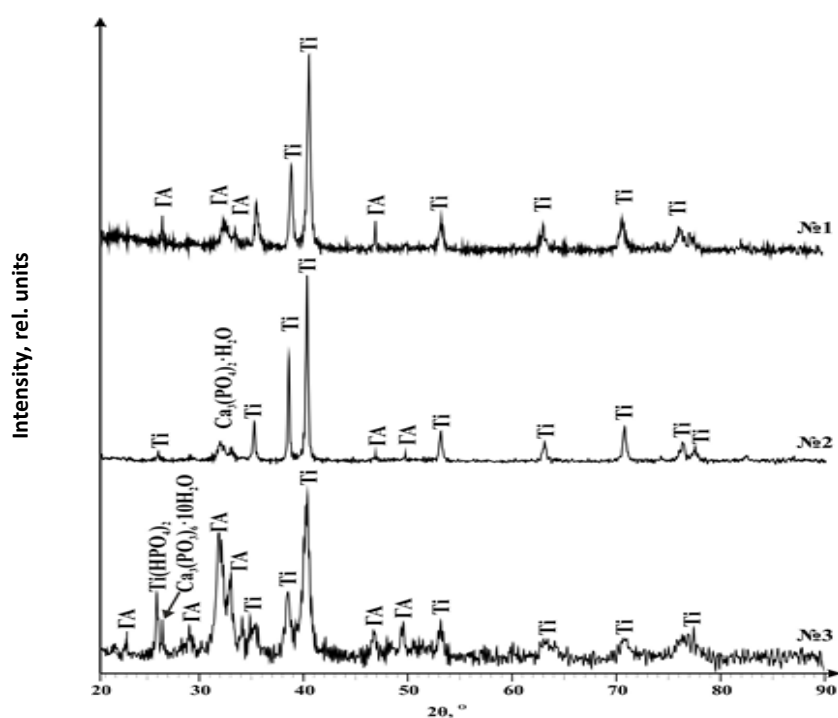


Figure 4 X-ray diffraction pattern of a sample obtained after mechanochemical interaction by the GDS method

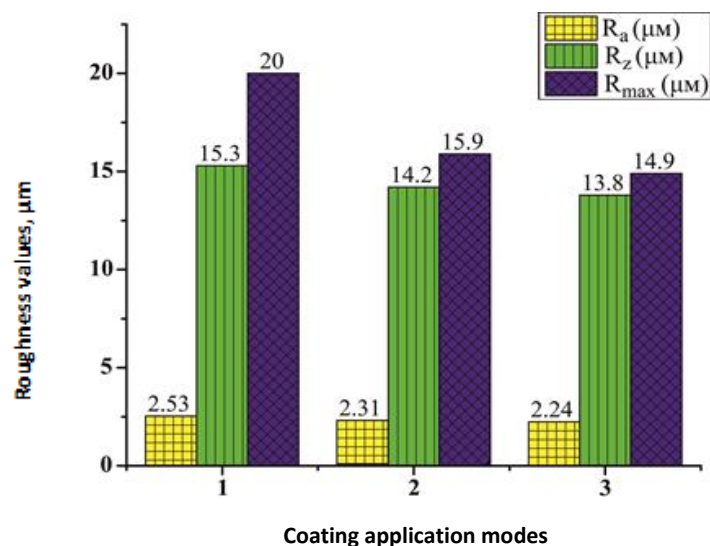


Figure 5 Roughness parameters of the HA coatings on titanium obtained in all application modes

The HA coating surface on titanium was measured within several areas. Analyzing the roughness parameter R_a of HA coatings made it possible to conclude that the samples obtained fell almost within the same limits. Figure 5 shows the main values of the roughness parameters for all the coatings obtained (the average deviation of the profile, R_a (μm), the height of the profile irregularities at ten points, R_z (μm), the maximum profile height, R_{max} (μm)). These data are within the roughness optimum ($R_a = 2\text{-}3 \mu\text{m}$) of artificial surfaces aimed to manifest the best human osteogenic properties [19].

Conclusions

The developed new simple method to apply HA is distinguished by the possibility to obtain HA coatings with the composition that fully corresponds to human bone tissue. Mechanochemical interaction produced HA coatings on VT1-0 titanium using GDS. The article proposes the phase composition, surface morphology, and roughness of these coatings. As it can be seen from the results obtained

while analyzing the phase and elemental composition, no significant change in the HA composition was revealed after spraying.

The coating morphology had a porous structure. Studying the interaction between hydroxyapatite and a titanium base included examining the transverse sections of coatings.

To detail the morphology and structure of the samples obtained, it is necessary to perform additional studies using atomic force and transmission electron microscopy. It is planned to study the adhesion properties of HA coatings in the future using sclerometry.

Conflict of interest

The author declares that there is no conflict of interest on behalf of all authors.

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Механохимиялық әрекеттесу арқылы гидроксипатиттен жабындылар алу

¹ Мамаева А. Ә., ¹ Кенжеғұлов А. Қ., ¹ Паничкин А. В., ² Шах А.

¹ Сәтбаев университеті, Металлургия және кен байыту институты, Алматы, Қазақстан

² *Техникалық және кәсіптік факультеті, Сұлтан Идрис атындағы білім беру университеті, 35900 Танджунг Малим, Перак Малайзия*

Түйіндеме. Газ-динамикалық бүрку әдісімен гидроксипатитті жалатудың жаңа қарапайым әдісі жасалды. Газ-динамикалық бүрку әдісімен гидроксипатит пен титанның механохимиялық өзара әрекеттесуінен кейін BT1-0 маркалы титанда гидроксипатит жабындылары алынды. Олардың фазалық құрамы, беткі морфологиясы және кедір-бұдырлығы келтірілген. Гидроксипатиттің беткі қабатының морфологиясы борпылдақ құрылымға ие болды. Гидроксипатиттің титан негізімен өзара әрекеттесуін зерттеу үшін жабындардың көлденең қималары зерттелді. Жабындылардың қалыптасуы негізінен титан төсенішінің ойықтарында жүретіні көрсетілді. Гидроксипатит жабындыларының кедір-бұдырлық параметрін R_a зерттеу нәтижесінде алынған үлгілердің бірдей шектерде екендігі анықталды. Бұл деректер адамның ең жақсы остеогендік қасиеттерін көрсететін жасанды беттердің кедір-бұдырлығының оңтайлы шегінде ($R_a = 2-3$ мкм) жатыр. Фазалық құрамның нәтижелері бойынша жалатудан кейін гидроксипатит қабаты құрамының айтарлықтай өзгеруіне ұшырамайтындығы анықталды, бұл биомедициналық қолдану үшін маңызды.

Түйін сөздер: жабынды, ұнтақ, титан, гидроксипатит, имплантат, газ-динамикалық жалату, шүмек, құм төгу арқылы өңдеу.

Получение покрытий из гидроксипатита путем механохимического взаимодействия

¹ Мамаева А. А., ¹ Кенжегулов А. К., ¹ Паничкин А. В., ² Шах А.

¹ *АО «Институт металлургии и обогащения» при НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева», Алматы, Казахстан*

² *Факультет технического и профессионального образования, Университет Султана Идриса, 35900 Танджунг Малим, Перак, Малайзия*

Аннотация. Разработан новый простой способ нанесения гидроксипатита методом газодинамического напыления. После механохимического взаимодействия гидроксипатита и титана методом газодинамического напыления получены гидроксипатитовые покрытия на титане марки BT1-0. Представлены результаты их фазового состава, морфология поверхности и шероховатость. Морфология поверхности покрытия из гидроксипатита имела рыхлую структуру. Исследованы поперечные шлифы покрытий для изучения взаимодействия гидроксипатита с титановой основой. Показана, что формирование покрытий происходит преимущественно в углублениях титановой подложки. В результате исследования параметра шероховатости R_a гидроксипатитовых покрытий было выявлено, что полученные образцы находились почти в одинаковых пределах. Эти данные лежат в пределах оптимума шероховатости ($R_a = 2-3$ мкм) искусственных поверхностей для проявления наилучших остеогенных свойств человека. По результатам фазового состава установлено, что после напыления слой гидроксипатита существенного изменения состава не претерпевает, что важно для биомедицинских применений.

Ключевые слова: покрытие, порошок, титан, гидроксипатит, имплантат, газодинамическое напыление, сопло, пескоструйная обработка.

Литература

- [1] Thian, E. S., Loh, N. H., Khor, K. A., & Tor, S. B. (2002). Microstructures and mechanical properties of powder injection molded Ti-6Al-4V/HA powder. *Biomaterials*, 23(14), 2927–2938. [https://doi.org/10.1016/s0142-9612\(01\)00422-7](https://doi.org/10.1016/s0142-9612(01)00422-7)
- [2] Surowska, B., Bienias, J., Walczak, M., Sangwal, K., & Stoch, A. (2004). Microstructure and mechanical properties of ceramic coatings on Ti and Ti-based alloy. *Applied Surface Science*, 238(1-4), 288–294. <https://doi.org/10.1016/j.apsusc.2004.05.219>
- [3] Khor, K. ., Gu, Y. ., Quek, C. ., & Cheang, P. (2003). Plasma spraying of functionally graded hydroxyapatite/Ti-6Al-4V coatings. *Surface and Coatings Technology*, 168(2-3), 195–201. [https://doi.org/10.1016/s0257-8972\(03\)00238-x](https://doi.org/10.1016/s0257-8972(03)00238-x)
- [4] Zheng, B., Luo, Y., Liao, H., & Zhang, C. (2017). Investigation of the crystallinity of suspension plasma sprayed hydroxyapatite coatings. *Journal of the European Ceramic Society*, 37(15), 5017–5021. <https://doi.org/10.1016/j.jeurceramsoc.2017.07.007>
- [5] Yessengazyev, A. M., Ultarakova, A. A., & Uldakhanov, O. H. (2019). Calcium nitrate generating out of nitrogen-acid solutions after breaking up slurries of titanium production. *Kompleksnoe Ispol'zovanie Mineral'nogo syr'a/Complex Use of Mineral Resources/Mineraldik Shikisattardy Keshendi Paidalanu*, 4(311), 74–81. <https://doi.org/10.31643/2019/6445.40>

- [6] Кенжегулов А.К., Мамаева А.А., Паничкин А.В. Исследование кальций-фосфатных покрытий, полученные методом ВЧ магнетронного распыления. // Вестник КазНУ. – 2018. – № 6. – С. 271-276.
- [7] Asri, R. I. M., Harun, W. S. W., Hassan, M. A., Ghani, S. A. C., & Buyong, Z. (2016). A review of hydroxyapatite-based coating techniques: Sol-gel and electrochemical depositions on biocompatible metals. *Journal of the Mechanical Behavior of Biomedical Materials*, 57, 95–108. <https://doi.org/10.1016/j.jmbbm.2015.11.031>
- [8] Балихин А.В., Симонов М.И., Получение титана, сплавов и композиционных материалов методом электролиза оксидов в расплаве хлорида кальция: ffc cambridge process. Обзор. // *Комплексное использование минерального сырья*. – 2017. – №. 4. – С. 12-20. www.kims-imio.kz
- [9] Guillem-Marti, J., Cinca, N., Punset, M., Cano, I. G., Gil, F. J., Guilemany, J. M., & Dosta, S. (2019). Porous titanium-hydroxyapatite composite coating obtained on titanium by cold gas spray with high bond strength for biomedical applications. *Colloids and Surfaces B: Biointerfaces*, 180, 245–253. <https://doi.org/10.1016/j.colsurfb.2019.04.048>
- [10] Harun, W. S. W., Asri, R. I. M., Alias, J., Zulkifli, F. H., Kadirgama, K., Ghani, S. A. C., & Shariffuddin, J. H. M. (2018). A comprehensive review of hydroxyapatite-based coatings adhesion on metallic biomaterials. *Ceramics International*, 44(2), 1250–1268. <https://doi.org/10.1016/j.ceramint.2017.10.162>
- [11] Noorakma, A. C. W., Zuhailawati, H., Aishvarya, V., & Dhindaw, B. K. (2013). Hydroxyapatite-Coated Magnesium-Based Biodegradable Alloy: Cold Spray Deposition and Simulated Body Fluid Studies. *Journal of Materials Engineering and Performance*, 22(10), 2997–3004. <https://doi.org/10.1007/s11665-013-0589-9>
- [12] Stoltenhoff, T., Kreye, H., & Richter, H. J. (2002). An Analysis of the Cold Spray Process and Its Coatings. *Journal of Thermal Spray Technology*, 11(4), 542–550. <https://doi.org/10.1361/105996302770348682>
- [13] Heimann, R. B. (2006). Thermal spraying of biomaterials. *Surface and Coatings Technology*, 201(5), 2012–2019. <https://doi.org/10.1016/j.surfcoat.2006.04.052>
- [14] Faucheux, N., Schweiss, R., Lützwow, K., Werner, C., & Groth, T. (2004). Self-assembled monolayers with different terminating groups as model substrates for cell adhesion studies. *Biomaterials*, 25(14), 2721–2730. <https://doi.org/10.1016/j.biomaterials.2003.09.069>
- [15] Cinca, N., Vilardell, A. M., Dosta, S., Concustell, A., Garcia Cano, I., Guilemany, J. M., ... Peiró, F. (2016). A New Alternative for Obtaining Nanocrystalline Bioactive Coatings: Study of Hydroxyapatite Deposition Mechanisms by Cold Gas Spraying. *Journal of the American Ceramic Society*, 99(4), 1420–1428. <https://doi.org/10.1111/jace.14076>
- [16] Vilardell, A. M., Cinca, N., Cano, I. G., Concustell, A., Dosta, S., Guilemany, J. M., ... Peiró, F. (2017). Dense nanostructured calcium phosphate coating on titanium by cold spray. *Journal of the European Ceramic Society*, 37(4), 1747–1755. <https://doi.org/10.1016/j.jeurceramsoc.2016.11.040>
- [17] Vilardell, A. M., Cinca, N., Garcia-Giralt, N., Dosta, S., Cano, I. G., Nogués, X., & Guilemany, J. M. (2020). In-vitro comparison of hydroxyapatite coatings obtained by cold spray and conventional thermal spray technologies. *Materials Science and Engineering: C*, 107, 110306. <https://doi.org/10.1016/j.msec.2019.110306>
- [18] Первушин Д.А., Шишковский И.В., Смуров И.Ю. Газодинамическое напыление гидроксипатита на медицинский инструментарий из титановых сплавов. // *Известия высших учебных заведений. Порошковая металлургия и функциональные покрытия*. – 2012. – №. 4. – С. 66-70.
- [19] Гнеденков С.В., Шаркеев Ю.П., Синебрюхов С.Л., Хрисанфова О.А., Легостаева Е.В., Завидная А.Г., Пузь А.В., Хлусов И.А. Кальций-фосфатные биоактивные покрытия на титане. // *Вестник ДВО РАН*. – 2010. – №. 5. – С. 47-57.

Reference

- [1] Thian, E. S., Loh, N. H., Khor, K. A., & Tor, S. B. (2002). Microstructures and mechanical properties of powder injection molded Ti-6Al-4V/HA powder. *Biomaterials*, 23(14), 2927–2938. (In Eng.). [https://doi.org/10.1016/s0142-9612\(01\)00422-7](https://doi.org/10.1016/s0142-9612(01)00422-7)
- [2] Surowska, B., Bieniaś, J., Walczak, M., Sangwal, K., & Stoch, A. (2004). Microstructure and mechanical properties of ceramic coatings on Ti and Ti-based alloy. *Applied Surface Science*, 238(1-4), 288–294. (In Eng.). <https://doi.org/10.1016/j.apsusc.2004.05.219>
- [3] Khor, K. ., Gu, Y. ., Quek, C. ., & Cheang, P. (2003). Plasma spraying of functionally graded hydroxyapatite/Ti-6Al-4V coatings. *Surface and Coatings Technology*, 168(2-3), 195–201. (In Eng.). [https://doi.org/10.1016/s0257-8972\(03\)00238-x](https://doi.org/10.1016/s0257-8972(03)00238-x)
- [4] Zheng, B., Luo, Y., Liao, H., & Zhang, C. (2017). Investigation of the crystallinity of suspension plasma

- sprayed hydroxyapatite coatings. *Journal of the European Ceramic Society*, 37(15), 5017–5021. (In Eng.). <https://doi.org/10.1016/j.jeurceramsoc.2017.07.007>
- [5] Yessengazyev, A. M., Ultarakova, A. A., & Uldakhanov, O. H. (2019). Calcium nitrate generating out of nitrogen-acid solutions after breaking up slurries of titanium production. *Kompleksnoe Ispol'zovanie Mineral'nogo syr'â/Complex Use of Mineral Resources/Mineraldik Shikisattardy Keshendi Paidalanu*, 4(311), 74–81. (In Eng.). <https://doi.org/10.31643/2019/6445.40>
- [6] Kenzhegulov A.K., Mamaeva A.A., Panichkin A.V. *Issledovanie kal'tsij-fosfatnyh pokrytij, poluchennye metodom VCH magnetronnogo raspylenia* (Investigation of calcium phosphate coatings obtained by HF magnetron sputtering). *Vestnik KazNITU = Bulletin of Satbayev university*. 2018. 6, 271-276. (in Rus).
- [7] Asri, R. I. M., Harun, W. S. W., Hassan, M. A., Ghani, S. A. C., & Buyong, Z. (2016). A review of hydroxyapatite-based coating techniques: Sol–gel and electrochemical depositions on biocompatible metals. *Journal of the Mechanical Behavior of Biomedical Materials*, 57, 95–108. (In Eng.). <https://doi.org/10.1016/j.jmbbm.2015.11.031>
- [8] Balihin A.V., Simonov M.I., *Poluchenie titana, splavov i kompozitsionnyh materialov metodom elektroliza oksidov v rasplave hlorida kal'tsia: ffc cambridge process. Obzor* (Obtaining titanium, alloys and composite materials by electrolysis of oxides in a calcium chloride melt: ffc cambridge process. Review) *Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. = Complex Use of Mineral Resources*. 2017. 4, 12-20. (in Rus).
- [9] Guillem-Marti, J., Cinca, N., Punset, M., Cano, I. G., Gil, F. J., Guilemany, J. M., & Dosta, S. (2019). Porous titanium-hydroxyapatite composite coating obtained on titanium by cold gas spray with high bond strength for biomedical applications. *Colloids and Surfaces B: Biointerfaces*, 180, 245–253. (In Eng.). <https://doi.org/10.1016/j.colsurfb.2019.04.048>
- [10] Harun, W. S. W., Asri, R. I. M., Alias, J., Zulkifli, F. H., Kadirgama, K., Ghani, S. A. C., & Shariffuddin, J. H. M. (2018). A comprehensive review of hydroxyapatite-based coatings adhesion on metallic biomaterials. *Ceramics International*, 44(2), 1250–1268. (In Eng.). <https://doi.org/10.1016/j.ceramint.2017.10.162>
- [11] Noorakma, A. C. W., Zuhailawati, H., Aishvarya, V., & Dhindaw, B. K. (2013). Hydroxyapatite-Coated Magnesium-Based Biodegradable Alloy: Cold Spray Deposition and Simulated Body Fluid Studies. *Journal of Materials Engineering and Performance*, 22(10), 2997–3004. (In Eng.). <https://doi.org/10.1007/s11665-013-0589-9>
- [12] Stoltenhoff, T., Kreye, H., & Richter, H. J. (2002). An Analysis of the Cold Spray Process and Its Coatings. *Journal of Thermal Spray Technology*, 11(4), 542–550. (In Eng.). <https://doi.org/10.1361/105996302770348682>
- [13] Heimann, R. B. (2006). Thermal spraying of biomaterials. *Surface and Coatings Technology*, 201(5), 2012–2019. (In Eng.). <https://doi.org/10.1016/j.surfcoat.2006.04.052>
- [14] Faucheux, N., Schweiss, R., Lützwow, K., Werner, C., & Groth, T. (2004). Self-assembled monolayers with different terminating groups as model substrates for cell adhesion studies. *Biomaterials*, 25(14), 2721–2730. (In Eng.). <https://doi.org/10.1016/j.biomaterials.2003.09.069>
- [15] Cinca, N., Vilardell, A. M., Dosta, S., Concustell, A., Garcia Cano, I., Guilemany, J. M., ... Peiró, F. (2016). A New Alternative for Obtaining Nanocrystalline Bioactive Coatings: Study of Hydroxyapatite Deposition Mechanisms by Cold Gas Spraying. *Journal of the American Ceramic Society*, 99(4), 1420–1428. (In Eng.). <https://doi.org/10.1111/jace.14076>
- [16] Vilardell, A. M., Cinca, N., Cano, I. G., Concustell, A., Dosta, S., Guilemany, J. M., ... Peiró, F. (2017). Dense nanostructured calcium phosphate coating on titanium by cold spray. *Journal of the European Ceramic Society*, 37(4), 1747–1755. (In Eng.). <https://doi.org/10.1016/j.jeurceramsoc.2016.11.040>
- [17] Vilardell, A. M., Cinca, N., Garcia-Giralt, N., Dosta, S., Cano, I. G., Nogués, X., & Guilemany, J. M. (2020). In-vitro comparison of hydroxyapatite coatings obtained by cold spray and conventional thermal spray technologies. *Materials Science and Engineering: C*, 107, 110306. (In Eng.). <https://doi.org/10.1016/j.msec.2019.110306>
- [18] Pervushin D.A., Shishkovskij I.V., Smurov I.Yu. *Gazodinamicheskoe napylenie gidroksiapatita na meditsinskie instrumentarij iz titanovyh splavov* (Gas-dynamic spraying of hydroxyapatite on medical instruments made of titanium alloys). *Izvestia vysshih uchebnyh zavedenij. Poroshkovaiametallurgija i funktsional'nye pokrytia = Proceedings of higher educational institutions. Powder metallurgy and functional coatings*. 2012. 4, 66-70. (in Rus).
- [19] Gnedkov S.V., Sharkeev Yu.P., Sinebryuhov S.L., Hrisanfova O.A., Legostaeva E.V., Zavidnaia A.G., Puz' A.V., Hlusov I.A. *Kal'tsij-fosfatnoe bioaktivnoe pokretia na titane* (Calcium Phosphate Bioactive Coatings on Titanium). *Vestnik DVO RAN = Bulletin of DVO RAN*. 2010. 5, 47-57. (in Rus).