

# Functional Coating of Biocompatible Powder Composites Obtained by the Method of Detonation-Gas Spraying

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**Abstract.** In this paper we investigate the structure of composite biocompatible coatings with the composition: calcium hydroxyapatite - titanium nickelide, obtained by the method of detonation-gas spraying.

## Introduction

Skeletal system of a living organism is formed and maintained as a result of complex biochemical reactions. The loss or destruction of bone leads to the use of implants for replacement. Implants consist generally of metallic materials based on alloys, stainless steel or titanium.

The use of implants, when physico-chemical and mechanical properties of metallic substrates and bone differ greatly can lead to an active rejection of the implant. To reduce the negative influence of these factors it is necessary to create a transition zone between the bone and the implant, which, along with the strong bond with the implant surface and the bone tissue should have acceptable for organism macro-and microstructure [1-2]. Such a zone can be obtained by coating with a specific porosity and it may have a composite structure. It is assumed that the elemental and phase composition of the coating should match the composition of natural bone and/or promote formation of bone tissue on its surface. Hydroxyapatite (HA) -  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  is usually applied as a starting material for bioactive coatings. When you create a biocompatible coating, special attention is paid to the formation of a topography (roughness) on the implant surface.

There are various methods of forming the calcium-phosphate coating on metal surfaces: plasma spraying, slip method, the method of micro-arc oxidation, magnetron sputtering, the method of detonation-gas spraying (DGS), etc. [3-4]. The development of new coatings requires their full certification (surface morphology, roughness, phase and elemental composition, etc.). The method of detonation-gas spraying has good prospects for the production of biocompatible coatings due to the identity of the phase composition of sprayed material and the coating [5-7].

The task of creating a solid biocompatible coatings can be solved by the introduction of the powder mixture of hydroxyapatite calcium hyperelastic material with high biochemical and biomechanical compatibility [8]. In this work, as such material titanium nickelide was used, which positively recommended itself in medical implantology. High porosity coatings of titanium nickelide (80-90%) promotes good ingrowth of hard and soft tissues of the body. In these composites, one component (titanium nickelide) has superelasticity, and the other HA — retains the properties of bioceramics. This will allow us to obtain a class of materials possessing high mechanical properties [9].



In a research experiment composite coatings were obtained with the composition: hydroxyapatite-calcium – titanium nickelide by the method of detonation-gas spraying.

### The experimental procedure

In experimental studies powdered mixture of composition HA +TiNi was used as a material. The average particle size of the biological powder of calcium hydroxyapatite was 150-300  $\mu\text{m}$ , the average particle size of powder of titanium nickelide brand PNi55Ti45 – 50-100  $\mu\text{m}$ .

To obtain a laminated composite consisting of HA+ TiNi the method of mechanical alloying treatment (MA) was used as an effective method for producing composite materials. Preliminary mechanical activation (MA) of the initial mixtures of HA + TiNi in the ratio: 50HA +50 wt., % (25 vol.,%) TiNi and 70HA +30 wt., % (15 vol., %) TiNi was carried out in planetary ball mill AGO–2 with water cooling. Time of mechanical activation is selected on the basis of analysis of literary sources and amounted to 3, 7, 15 and 30 min [8].

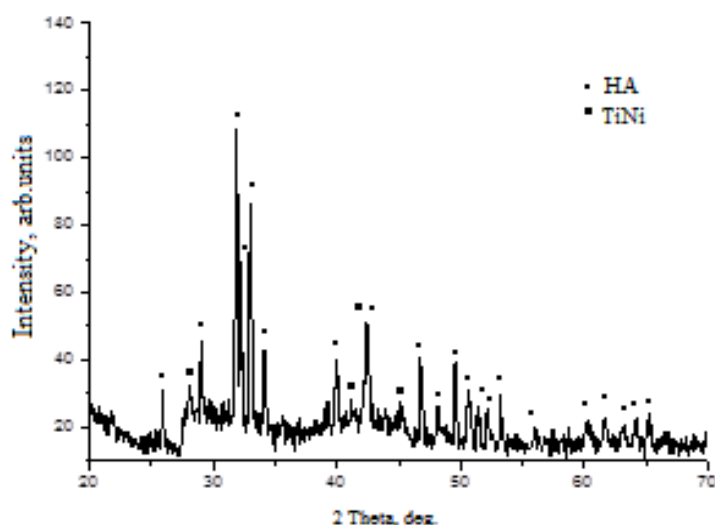
As a substrate for deposition a titanium plate (W-1.0) of size 20×20×3 mm was used. The surface of titanium plates was pre-treated with air-abrasive mixture at the blasting installation. Processing quality was determined visually according to the degree of dullness of the surface [9].

For application of composite coatings on a titanium base the installation of detonation-gas spraying of powder materials "Katun M" was used [10-11]. The thickness of the sprayed layer was measured after 50 spraying cycles for each sample. The deposition ended when reaching the coating of 150 microns.

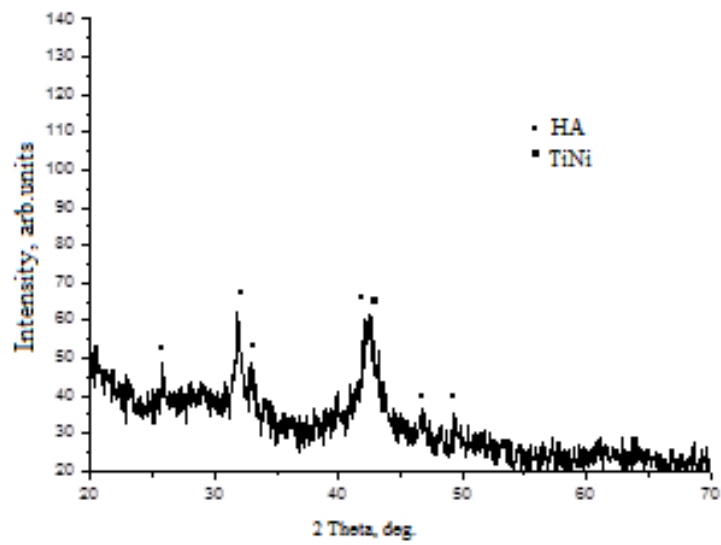
The study of surface morphology was carried out on an optical microscope Carl Zeiss AxioObserver Z1m. Spectral analysis was performed on scanning electron microscope Carl Zeiss EVO50 equipped with microprobe EDS X-Act (Oxford Instruments) with a Si-drift detector. The study of the phase composition and structural parameters of mechanically activated composites was carried out using x-ray diffraction x-ray on General purpose DRONE-6 diffractometer.

### Experimental results and discussion

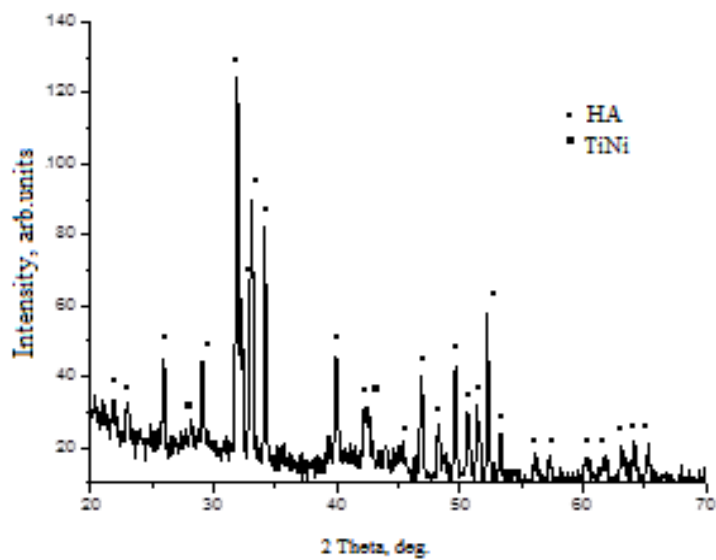
At the stage of activation processing of the powder mixture to 3 min MA the mixing and dispersion of components take place. After 3 minutes of mechanical activation there is a significant broadening and decrease of intensity of diffraction peaks of reflections of hydroxyapatite and intermetallic compound, indicating the increase of non-equilibrium defects in the product of grinding and reducing the size of the crystallites, with the transition to the nanocrystalline state. With increasing MA time up to 15 min the diffraction reflections of the intermetallic compound virtually disappear, a transition of TiNi into x-ray amorphous state can be observed. Additional compounds in the process of mechanical activation are not formed (Fig.1 b, d).



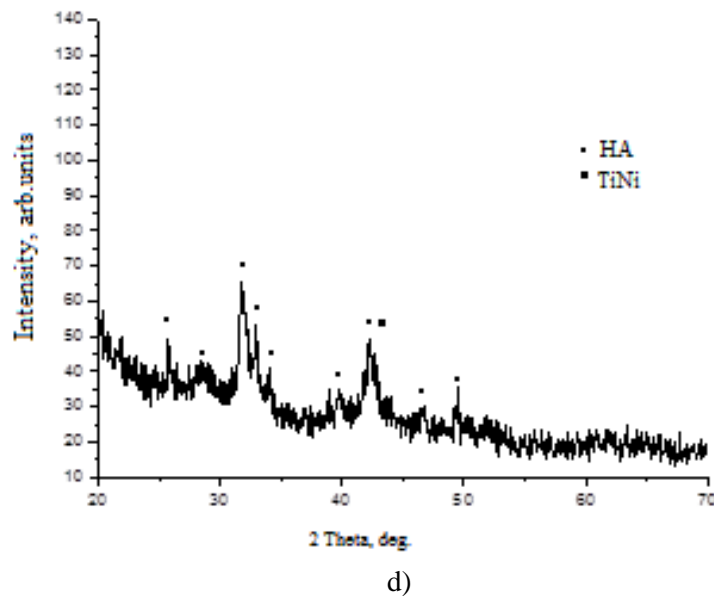
a)



b)

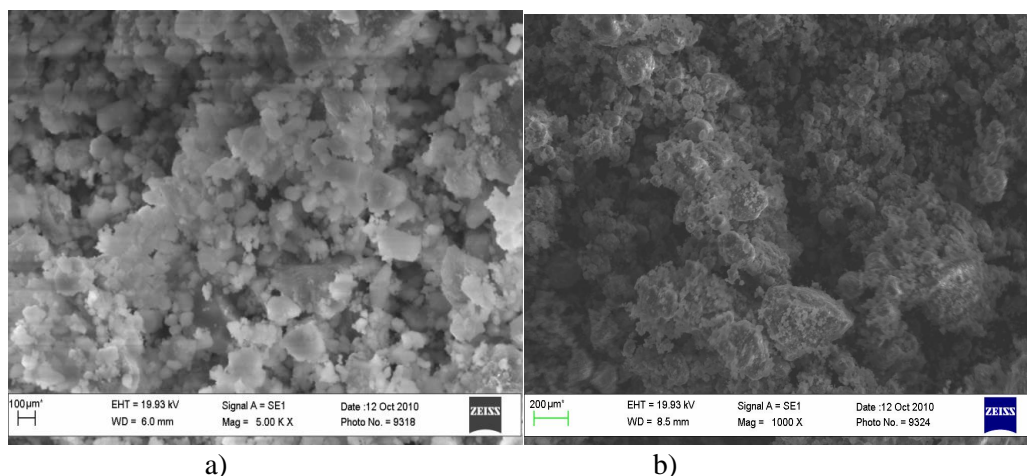


c)



d)  
Figure 1. Diffractograms of the powder mixtures: a - initial powder mixture 50HA +50TiNi (mass, %); b - 50HA +50TiNi (wt, %) min at 15 min. MA; c - the original powder mixture 70HA +30 TiNi(mass, %); d - 70HA +30 TiNi(wt, %) at 15 min MA.

Fig. 2 shows the SEM images of composites 50HA +50TiNi (wt.,%) at 15 and 30 min of MA. Fig. 2 shows the SEM images of composites 50HA +50TiNi (wt.,%) at 15 and 30 min of MA. At 15 min MA, particles of composite HA and TiNi conglomerate in integrated composition. The bulk of the particles fall within the range 50-100  $\mu\text{m}$  (Fig. 3a), the average particle size of composite is 112.5  $\mu\text{m}$ . With longer MA time (30 min.) there is a significant consolidation of conglomerates, the average particle size is 196.4  $\mu\text{m}$  (Fig. 3b). Composites of such large size groups (over 200  $\mu\text{m}$ ) is not recommended for use in the process of detonation-gas spraying according to the technological requirements. For the mixture with the composition 70HA +30TiNi (wt.,%) the agglomeration of particles in conglomerates with prolonged (more than 15 min) time MA take place as well. Therefore, the most efficient activation time of the mixtures 50HA +50TiNi (wt.,%) and 70HA +30TiNi (wt.,%) before detonation-gas spraying should be considered as 15 minutes.



a) b)  
Figure 2. SEM images of mechanically activated mixture of HA/TiNi:  
a – 50HA +50TiNi (wt.,%), time of activation – 15 min;  
b – 50HA +50TiNi (wt.,%), time of activation – 30 min

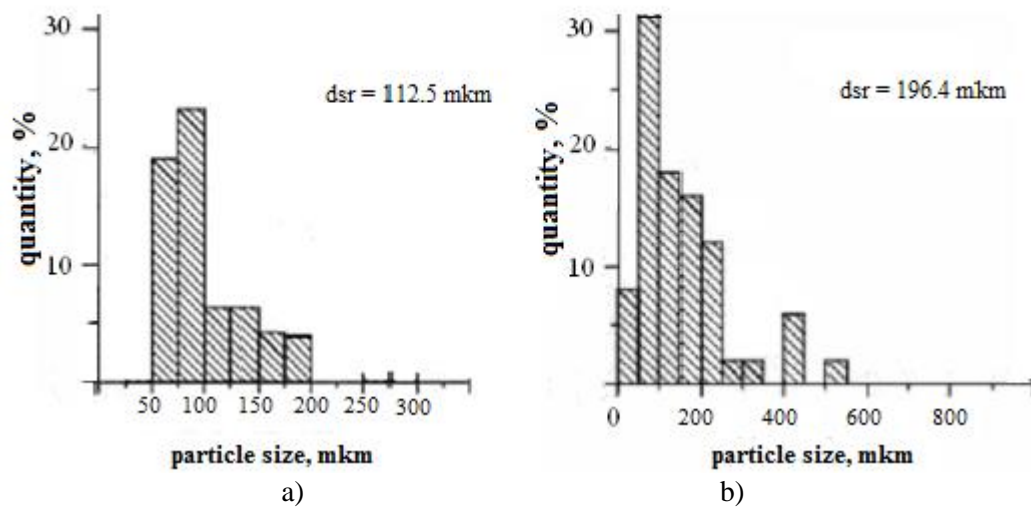


Figure 3. Histograms of size distribution of particles of composite:  
 a – 50HA + 50TiNi (wt.,%), time of activation – 15 min;  
 b – 50HA + 50TiNi (wt.,%), time of activation – 30 min.

Fig. 4 shows the SEM image of the coating based on the composite caused by the detonation-gas method. It is seen that the coatings have a porous structure and a very pronounced relief, the nature of which does not change at different ratio of components in composite. The coatings consist of particles of composite HA+TiNi (wt.,%), in some cases these particles are fused under the influence of the stream flow detonation. The size of pores is from 2 to 16 microns.

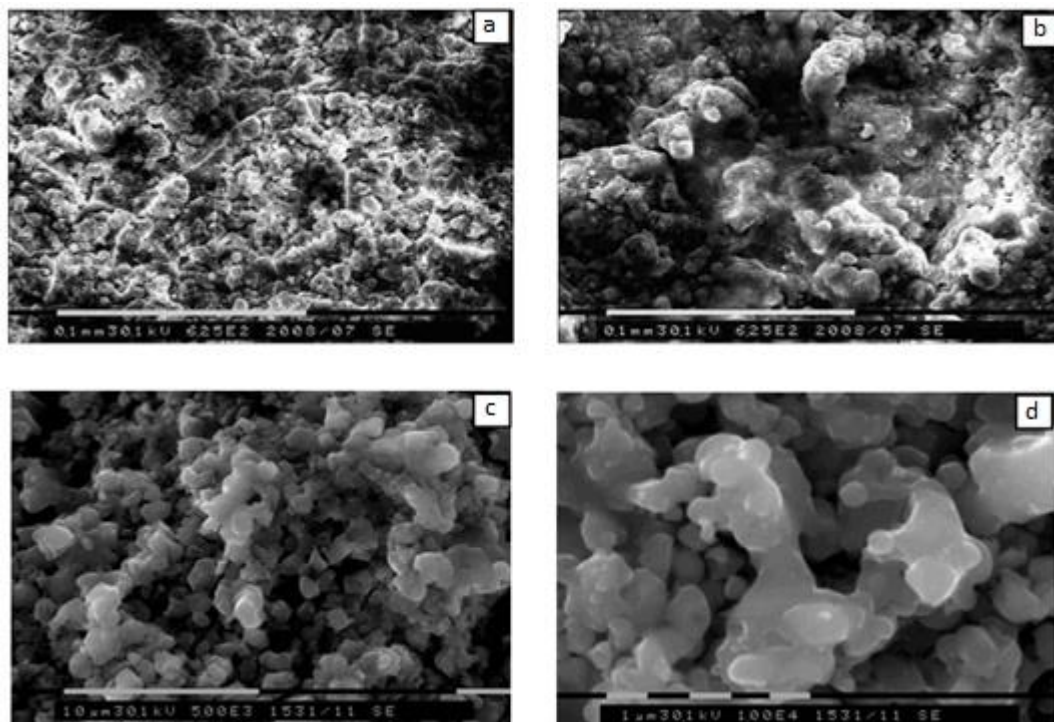


Figure 4. SEM image of the coating based on the composite HA+TiNi caused by the detonation-gas method: a, c – 50HA + 50TiNi (mass., %);  
 b, d – 70HA + 30TiNi (mass., %)

Elemental composition analysis showed that the coatings consist of calcium, phosphorus, Nickel, titanium, and oxygen with a small admixture of carbon, i.e. the composition of the coating corresponds to the powder composite.

The growth of bone tissue at the implant osseointegration is significantly affected by phase composition of the coatings. X-ray analysis of coating of calcium hydroxyapatite showed that the coatings revealed no other lines besides the main phase of HA, which indicates its homogeneity. The study of phase composition of coatings of composites showed that composite coatings applied by the detonation-gas spraying method are in the x-ray amorphous state.

## Conclusions

1. The amorphous composite calcium-phosphate coatings were obtained by the detonation-gas spraying method.
2. The coating contains only chemical elements of the initial HA powder and TiNi.
3. As a result of experimental studies of the morphology of the coating, the size of pores from 2 to 16 microns was determined.

## References

- [1] B. I. Beletskiy, V. I. Shumskiy, A. A. Nikitin, E. B. Vlasova, Biocomposite calcium-phosphate materials in bone-plastic surgery, *Steklo i keramika*, [Glass and ceramics], 9, (2000) 35-37. (in Russian)
- [2] V. N. Lyasnikov Properties of plasma coated powder coatings, *Perspektivniye materialy* [Advanced materials], 4(1995) 61-67. (in Russian)
- [3] J. Delecrin, N. Passuti, J. Poyer, G. Daculsi, Y. Maugars, Biphasic calcium phosphate as a bone graft substitute for spine fusion: stiffness evaluation, 4th World Biomaterials Congress, Berlin Abstract,(1992), 644-645.
- [4] V. F. Pichugin, *Poverkhnost. Rentgen., Sinkhrotron., Neitron. Issled.* [Surface. X-ray, synchrotron and neutron studies], 11, (2007), 67–72 (in Russian)
- [5] A. A. Popova, V. I. Yakovlev, E. V. Legostaeva, A. A. Sitnikov, Yu. P. Sharkeev Influence of the granulometric composition of the powder of calcium hydroxyapatite on the structure and phase composition of coatings deposited by the method of detonation-gas spraying, *Izvestiya vuzov. Physics*, 55, 11 (2012) 41-45. (in Russian)
- [6] M. Kh. Shorshorov and Yu. A. Kharlamov, *Physical-Chemical Fundamentals of Detonation Gas Spraying of Coatings*, M. Kh. Shorshorov, ed., Nauka [Science], Moscow (1978). (in Russian)
- [7] A. A. Sitnikov, V. I. Yakovlev, A. A. Popova Preparing an initial powder of calcium hydroxyapatite for detonation-gas spraying on a titanium base, *Polzunovskii vestnik*, [Polzunovskii Bulletin], 1/1(2012) 269-272. (in Russian)
- [8] A. A. Popova, V. I. Yakovlev, A. A. Sitnikov, M. V. Loginova, A.V. Sobachkin Structural-stress state of mechanocomposite "hydroxyapatite-titanium nickelide" designed to create biocompatible coatings on medical implants, *Fundamentalniye problem sovremennogo materialovedeniya*, [Fundamental problems of modern materials science], 12,2 (2015) 179-183. (in Russian)
- [9] V. I. Itin, O. G. Terekhova, T.E. Ulyanova, V. A. Kostikova, N.A. Shevchenko, D. V. Berdnikova, The influence of mechanoactivation on regularities of sintering of Nickel-titanium and composites "bioceramics-titanium nickelide", *Pisma v JTP*, [Technical physics Letters], 26,10 (2000) 73-79. (in Russian)
- [10] L. I. Tushinskii, *Methods of Investigation of Materials: Inorganic Coating Structure, Properties, and Deposition Processes*, Mir [Peace], Moscow (2004). (in Russian)
- [11] V. I. Yakovlev, *Experimental-Diagnostic Complex for Physical Investigations on SHS Powder Materials in Detonation Spraying*, Author's Abstract of Cand. Engineering Scie. Dissertation, Altai State Technical University, Barnaul, Russia (2003), 19. (in Russian)