MATERIALS FOR HUMAN LIFE SUPPORT
AND ENVIRONMENTAL PROTECTION

Adhesion of Hydroxyapatite Plasma Coatings

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Abstract—Hydroxyapatite (HA) coatings were sprayed by an arc plasma gun with argon-nitrogen plasma at the power of 25 kW from the powder with particle size of 25–63 μm at the distance of 95 mm. Before spraying of the coatings, the samples were preheated in a resistance furnace in air to the temperatures within the range from 20 to 600°C. Adhesion of the HA plasma coating to a titanium substrate was determined on pin samples. The maximum mean value of adhesion was observed when the titanium substrate was preheated to the temperature of 550°C. The results of the study were discussed by reference to the way of increase in activity of the titanium substrate at its preheating for increase in the HA coating adhesion and formation of an equilibrium phase state in the HA coating necessary for long-term usage of the implants. The obtained results will be used for formation of the optimal structure of the bioactive coating consisting of a three-dimensional capillary-porous titanium coating (3D CP Ti) in the form of crests and hollows with porosity of 50% and HA coating sprayed on its surface at the temperature of 550°C. Such mode of the spraying provides formation of a dense, strong, and stable HA coating on endosseous implants.

Keywords: hydroxyapatite coatings, adhesion, pin method, plasma spraying, titanium substrate, heating
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INTRODUCTION

The system "endosseous titanium (Ti) implant—bone" is a complicated version of composite material in which the "implant–bone tissue" boundary forms itself already in the living body. The tenfold difference in elastic moduli of Ti and bone tissue and the absence of a strong chemical bond between them necessitates formation of a developed (porous) and bioactive surface of the implant. In the majority of cases, the plasma composite Ti–hydroxyapatite (HA) coatings whose elastic modulus has an intermediate value [1] are sprayed for this purpose. Porous Ti sublayers consisting of lightly deformed particles and HA coatings on them are considered to be unreliable owing to their poor mechanical properties [1]. That is why, in recent times, the coatings are formed of dense Ti sublayers and HA coatings, but the pores on the surface of HA are necessary for the most suitable interaction with new bone tissue [1]. However, transmissions of cyclic force through the HA coating also cannot be considered as reliable [2]. The three-dimensional capillary-porous (3D CP) Ti coatings with porosity less than 50%, consisting of crests and hollows, in which a new type of surface porosity is implemented, were developed. The porosity in the 3D CP Ti coatings is aggregated in the hollows and on the walls of crests [3]. Functional separation of the dense and porous volumes makes it possible to form crests with strength similar to the strength of solid material, and open volumes of the hollows are the most suitable for integration and functioning of new bone tissue. In this case, the HA coating sprayed on 3D CP Ti coating can be formed dense and strong, while the high-surface area of the 3D CP Ti coating, which is 6 times that of traditional coatings, makes it possible to decrease the mechanical stress on the HA coatings. To obtain such HA coatings, the modes of spraying with completely melted particles are used; however, the arc plasma gun power is limited in order to decrease the changes in phase composition [1]. Increase in the magnitude of the adhesion, cohesion, and density of HA coating is achieved at preheating of the Ti substrate to 300°C [4].

The objective of this research is determination of the dependence of adhesion of HA coatings to Ti substrate on the temperature of its preheating within the temperature range from the room temperature to 600°C.

MATERIALS AND METHODS

The standard procedure of tearing off taper pins from the sprayed coating, which were made of titanium VT1-00 and where the diameter of the end face of the pin was 2.3 ± 0.2 mm, was used to determine adhesion of the HA coating to the Ti substrate. The pins which were seat against retainers exercised the function of substrate at spraying (Fig. 1). The samples
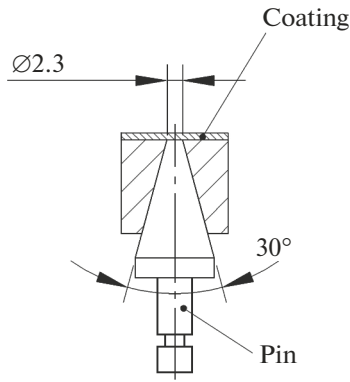
Fig. 1. Pin sample for testing of adhesion of coating.

were fastened three each on the steel guide plates for subsequent combined sandblasting and spraying.

The samples were sandblasted with the Al_2O_3 particles with the mean size of 700 μm for formation of the relief on the sprayed surface. Before the spraying, the assemblies with the pin samples were preheated in a resistance furnace in air and were held at the preset temperature for 20 min. Spraying on the samples at the temperatures of 25, 150, 300, 450, and 550°C was carried out at the initial stage of the investigations, and the number of samples for each of the heating temperatures was 12, 6, 3, 3, and 3 respectively. In the second set of experiments, the initial results obtained at the heating temperatures of 450, 500, 550, 570, and 600°C, were determined more precisely (the number of samples was 3, 3, 3, 6, and 9). The HA powder with the particle sizes of 25−63 μm was deposited by a UPU3d unit with a PP-25 direct current plasma gun at arc voltage of 66 V and current strength of 400 A; the plasma-supporting gas was an argon-nitrogen mixture, with total flow rate of 32.2 L/min; the spraying distance was 95 mm. Optimization of the spraying modes was carried out in preparatory experiments on the material utilization rate (MUR). During the spraying, the pin samples were transferred toward the plasma gun with velocity of 300 mm/s. After the spraying, the samples were cooled in Al_2O_3 powder to decrease the cooling rate. The thickness of the sprayed coatings was 0.3 mm. Before examination, metal plates 1 mm in thickness were attached to the surface of the coating by cyanoacrylate gel with strength of the glue joint up to 200 kgf/cm^2 to decrease the influence of stress concentration from bowing of the coating during the testing. Tearing off the pin from the coating was implemented by an Instron 5882 testing machine at the loading speed of 1 mm/min. After examination, the true diameter of the end face was measured by an IMC 100×50,A engineer microscope.

RESULTS

In the coatings sprayed on the substrates without preheating, the MUR was 64.7%, while after the preheating to 600°C, the MUR increased to 66.1%. Upon testing of the coatings, the fracture occurred along the interface between the Ti pin and the HA coating. In viewing in the optical microscope, only discrete impregnations of the HA are detected on the Ti surface, which indicates adhesion behavior of the fracture. The maximum dispersion of the values of the HA adhesion to the Ti substrate, equal to 42 MPa, was obtained at preheating of the samples to the temperature of 300°C; the values varied from 28 to 87 MPa. At all other temperatures of the substrates, the standard deviations were no more than 20 MPa. Owing to the significant difference of the results obtained at the heating to the temperature of 550°C (in favor of greater values) from the samples with the other heating temperatures, in the second set of experiments, the coatings to the samples were repeatedly sprayed at the temperatures of the substrates of 450 and 550°C and additionally at the temperatures of 500, 570, and 600°C. In the second set, at the same temperatures of heating of the substrates, the obtained values of adhesion strength were similar to the values obtained in the first set of the samples. With the consideration of two sets, the maximum mean values of 170.7 ± 19.7 MPa were obtained at the temperature of heating of the substrates of 550°C (Fig. 2). At similar values of temperatures of heating of the substrate of 500 and 570°C, the value of adhesion was much less, 33.6 ± 5.2 and 43.7 ± 13.4 MPa, respectively. The mean value of adhesion was 63 MPa for all the experiments, while the minimum values of 36.9 and 33.6 MPa were obtained in the cases of heating of the substrates to 450 and 500°C. Taking into consideration that the experiments with heating to 500 and 550°C were repeated (spraying of the coatings and testing of mechanical properties) and yielded similar results, at standard deviations of 16 and 12% of measured quantity, the obtained values cannot be considered as incorrect.

DISCUSSION

At the present time, the problem of increase in adhesion and cohesion of the bioactive HA coatings cannot be considered as solved, especially when formation of the coatings with porosity less than 50% are needed. At use of the 3D CP Ti coating, whose porosity amounts to 50%, as a metal sublayer, the HA coating can be sprayed dense, strong, and in an equilibrium state [3]. The sprayed HA particles are in an active energy state by the effect of the high temperature, which exceeds the melting temperature by 450—865°C, and of the rate, up to 200 m/s [5]. To increase density and adhesion strength of the HA coating, it is possible to increase the plasma jet power and increase the temperature of the particles, but it results in change in phase composition of the coating, and the

amorphous phases of TTCP, TCP, and calcium oxide are formed [1]. The substrate at room temperature is not sufficiently active for the chemical interaction (and wetting) with the sprayed HA particles. The activity of the surface of the substrate can be increased by the effect of its preheating to the temperature of 600°C [1]. Increase in the temperature of the Ti substrate from 20 to 550°C increases the microhardness of the interface between the HA coating and Ti substrate from 2.32 to 3.07 GPa (to the hardness of the HA coating) [6]. These results were taken into account in these experiments at selection of the temperatures of preheating of the Ti substrate.

The sharp increase and subsequent decrease in adhesion in the results can be explained by occurrence of several competing processes that have an effect on formation of a sound connection of the substrate and coating. Increase in the temperature in the area of contact between the sprayed particle and the substrate results in intensification of chemical interaction and, as a consequence, better wetting by sprayed particle of the Ti substrate, which must increase the adhesion and cohesion of the coating [4]. At the same time, the value of adhesion is influenced by the increase in thickness of the Ti layer coming into interaction with oxygen at the stage of preheating in air. It is well known that the process of interaction of Ti with oxygen is extremely complicated, which occurs owing to great solubility of oxygen in it. At the temperature of 20°C, the TiO_2 film forms on the Ti surface [7, 8] whose thickness in [9] was 32 nm at heating to 250°C and 3 μm at 700°C. In this case, high values of adhesion obtained on the substrates preheated to 270°C in [9] were explained by occurrence of the TiO_2 layer. At heating to 600°C, the kinetics of oxidation is determined by a parabolic dependence on time [10]. According to increase in the film thickness, the amount of oxygen entering the interface region decreases, while the supply of Ti remains constant. As the result of this, when the oxidized layer reaches a certain thickness, correlation of the amounts of Ti and oxygen in the reaction zone becomes such that a TiO layer forms between TiO_2 and Ti. Its appearance diminishes the adhesion of the oxide to Ti. The oxide film, being subjected to compressive stresses, is distorted and flakes off, laying open the Ti surface, which results in a jumplike increase in the oxidation rate. Then, flaking off of the oxide results in TiO oxidation to TiO_2, and the process described above is repeated. Complementary to oxidation from the surface, also diffusion of oxygen into Ti takes place, a solid solution is formed, and, as a result, the hardness and brittleness of the layer close to the surface increase sharply [11].

It can be assumed that, at preheating of the Ti substrate (coating) in an inert atmosphere, the dependence of the value of adhesion on temperature can be different. The maximum values of adhesion of 62−65 MPa were found at vacuum plasma spraying of the HA coatings
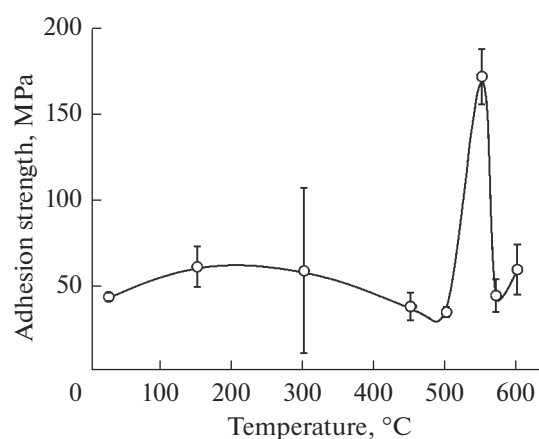

Fig. 2. Adhesion of HA coating at tearing off, depending on the temperature of preheating of Ti substrate.

with Ti sublayer [12]. The maximum value of adhesion of 170 MPa obtained in this investigation exceeds these values, which is probably due to the thermal activation of the Ti substrate at its heating to 550°C before the spraying. The obtained maximum value of adhesion of 170 MPa correlates to the values of shearing strength of 90.8 MPa obtained by us earlier [13]. The data for the HA coating are known from [14]: the tear strength $\sigma \sim$ 50.8 MPa, shearing strength $\tau \sim$ 22 MPa, the ratio $\tau/\sigma = 0.43$ [14]. In our experiments, the ratio $\tau/\sigma = 90.8/170 = 0.53$ is close to this value.

Preheating of the Ti substrate before spraying of the HA coating is of additional essence for survivability of the implants in bone tissue at long-term implantation. At the spraying onto the substrate preheated over 500°C, the amorphous phase, which dissolves in the living body with the rate higher than the crystalline phases, does not form [1]. That is why considerable attention, also at the present time, is paid to investigation of the content of amorphous and nanocrystalline phases at plasma spraying. At spraying of the HA coating on the Ti substrate at room temperature, the crystallinity of the HA coating decreases from 90% to 65% at increase in the arc current of the plasma gun from 400 to 700 A [15], which is the factor constraining the plasma jet power. In this case, heating of the substrate is the main method making it possible not only to increase adhesion of the HA coating but also to simultaneously increase the content of equilibrium phases in it, and our additional investigation will be devoted to this. At spraying of HA in the form of thin films, the amorphous state is recorded at the temperatures of preheating of the substrate to 400 or 450°C. The nanocrystalline structure is formed at temperatures of the substrate of 650°C. The amorphous phase in the HA coating is not recorded at spraying on the Ti substrate heated to 800°C, but in this case additional phases of TTCP and TCP are formed [16]. The mode of spraying which was used in this set of experiments makes it

possible to obtain the HA coating with content of the crystalline phase up to 98% [17]. At testing in vivo after 3 months, the HA coatings containing 56% of crystalline phases fragmented, while they remained integrated into the osseous system at 98% content; in this case, the coatings demonstrated the shearing strength of 27 and 40 MPa, respectively [18]. Behavior of the coatings containing 50 and 75% of crystalline HA phase is similar [19]. These results demonstrate that ceramic bioactive coatings with crystalline structure have the most suitable structure. The laminated bioactive coating must be taken as the best option. A lower layer of such coating adjacent to Ti should consist of the crystalline HA, which is more resistant to dissolution in the body, but on the surface, there should be the fast dissolving phase [1]. Such laminated composite TCP-(TCP/HA)-HA coating was proposed in [20].

Existence of the amorphous phase in the HA coatings was assumed in [21, 22] by occurrence of the halo in the X-ray pictures, by the thermal effect at DSC analysis, and also in [2] by the results of investigations by transmission electron microscopy. At the same time, there is a view [23] that it is not the amorphous phase but the combination of several phases, amorphous and nanocrystalline. In [24], the halo in the X-ray pictures of their own plasma coatings with thicknesses up to 536 μm was divided into three halos. The two of them, from the amorphous phases D_{max1} and D_{max2}, are placed between the angles of 29.4−29.8 and 31.0−31.4 degrees. The halo from the nanoscale phase D_{max3} is between 32.0 and 32.4 degrees. The size of crystallites <10 nm was calculated for the thickest coating. With increase in thickness of the coating, the volume of D_{max1} decreased quickly, while D_{max2} dominated in the coating 317 μm in thickness. In the coatings 373 and 536 μm in thickness, the presence of D_{max3} with decrease in D_{max2} and total disappearance of D_{max1} was observed. From there, the amorphous phase located in the HA coatings can have various structures and components, depending on the rate of cooling of the particles. At the testing in vitro, the amorphous phase (the D_{max1} component) dissolves, and the apatite from the solution deposits on the nanoscale phase (the D_{max3} component). In [24], it was concluded that the most suitable phase composition of the plasma coating for long-term use should consist mainly of the crystalline and nanocrystalline HA (D_{max3}) and certain amount of the amorphous phase on the surface to increase the biocomparability at the initial stage of implantation. The synthesized dried-up amorphous calcium phosphate (ACP) demonstrates two morphological shapes: spheroidal and discoidal [25]. After beginning of deposition, the ACP transforms into crystalline apatite. The crystalline phases were detected by transmission electron microscopy, while the X-ray spectra still demonstrated only the amorphous phase [25]. Clusters of HA nanoparticles give wide diffuse rings at analysis by the method of high-resolution transmission electron microscopy (HRTEM) [26]. At the use of a minimum spot size of 5−7 nm, the microdiffraction clearly demonstrates the crystal nature of the nanoparticles in this assembly. In the X-ray picture of natural bone tissue with sizes of crystallites of 19 nm, a halo similar to the amorphous phase is recorded [27]. In [28], only nanoscale phases were found by transmission electron microscopy in the powder of natural HA. As the result of the investigations of natural HA thermally treated within the temperature range of 700−800°C, the intense growth of the crystallites from 20 to 120 nm and decrease in specific surface area from 25 to 3 m^2/s were found. In this case, the DSC detects heat emission with a peak at temperature of 753.2°C [28]. The size of crystallites of 20 nm with high surface area in natural bone tissue provides continuous replacement of bone tissue during vital activity of the living body. Formation of HA with equilibrium crystalline structure at its spraying on the preheated substrate will increase the stability of the coating at long-term implantation, keeping in mind also its strong and dense structure. This mode of spraying is better because obtaining an equilibrium structure at the subsequent thermal treatment of the HA coating results in its cracking [1].

Preheating of the substrate up to 550°C increases adhesion of the HA coating and can increase the stability of the HA coating at long-term implantation by the effect of formation of an equilibrium crystalline rather than amorphous structure.

CONCLUSIONS

Adhesion of the plasma HA coatings to Ti substrate preheated within the range of 25−600°C was determined by the pin method. The mean value of adhesion under these spraying conditions is 63 MPa.

The anomalously high mean value of adhesion of the HA coating of 170 MPa was recorded at the temperature of the substrate of 550°C. The HA coating sprayed at this temperature of the substrate has a stable crystalline structure.

FUNDING

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