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# Nanocrystalline Structure of the Surface Layer of Plasma-Sprayed Hydroxyapatite Coatings Obtained upon Preliminary Induction Heat Treatment of Metal Base

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**Abstract**—Biocompatible nanocrystalline hydroxyapatite (HA) coatings for intrabone titanium implants have been obtained by plasma spraying. The HA coatings have an average grain size within 10–30 nm and are characterized by improved characteristics of morphological heterogeneity that is acquired due to the induction heat treatment (IHT) of substrates prior to plasma spray deposition. Based on the data of scanning electron microscopy with computer-aided processing of images, it is established that the average grain size depends on the IHT temperature.

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Intrabone implants represent artificial supports for teeth and jaw system and locomotor apparatus, which are made of biocompatible materials, mostly titanium alloys. Numerous experimental and clinical investigations in Russia and abroad showed that bioceramic calcium–phosphate coatings on the surface of metal implants most actively stimulate their osteointegration (engraftment), thus offering an effective solution of the problem of intrabone structure rejection. Of course, the implant coatings must occur in a required structural-phase state and possess a definite combination of properties, including high mechanical strength and developed morphological heterogeneity (in particular, on a nanometer scale).

The implant base is most frequently made of a metal (e.g., titanium and its alloys) and then coated by spraying calcium–phosphate materials such as hydroxyapatite (HA) and tricalcium phosphate. These coatings, supported on metal implants with a proper surface microrelief, actively stimulate osteogenesis. The rate of implant engraftment is determined by its chemical and phase composition and depends on the dimensions of fine structure elements in the surface layer of coatings (in particular, on the presence of nanodimensional grains) [1]. Indeed, it is commonly accepted that the interaction between a biocompatible coating material and biological structures of the organism takes place on a nanometer scale level of collagen fibrils. The data of atomic force microscopy for the surface of bone trabeculae show that their structural components (collagen fibrils) are covered by mineral (HA) plates of medium size (30–200 nm) [2]. Compatibility with biostructures of the bone bed is determined by the characteristics of developed morphological heterogeneity, in particular, the average grain diameter. In this context, it is a topical task to establish the influence of the regime of preliminary induction heat treatment (IHT) of the titanium base on the average grain size $D$ in plasma sprayed bioceramic HA coatings, which in turn affects the rate of splat cooling and the character of crystallization.

Well-known disadvantages of coatings obtained by the traditional thermal spraying include a significant spread of the dimensions of nanograins relative to the average value, high degree of amorphization, and the related nonuniformity of the physical properties. In many cases, the underestimation of these factors leads to a significant decrease in the quality of coatings, which is manifested by insufficient reliability and working life of intrabone implants [3].

One of the most important properties of thermally deposited coatings on intrabone implants is the developed morphological heterogeneity (i.e., combination of the surface structure elements with a large number of dimensional modes) and uniformity of the distribution of nanodimensional grains. It should be noted that the essential elements do not include dusty particles of the uppermost surface layer with weak cohesion. The plasma spraying of HA coatings involves structural phase transformations, which change the structure of deposit as a result of incongruent melting and amorphization during solidification on a metal substrate. These undesired phenomena can be eliminated by ensuring conditions for facilitated spreading of deposited splats over the base surface and by decreasing the rate of cooling, which is determined by

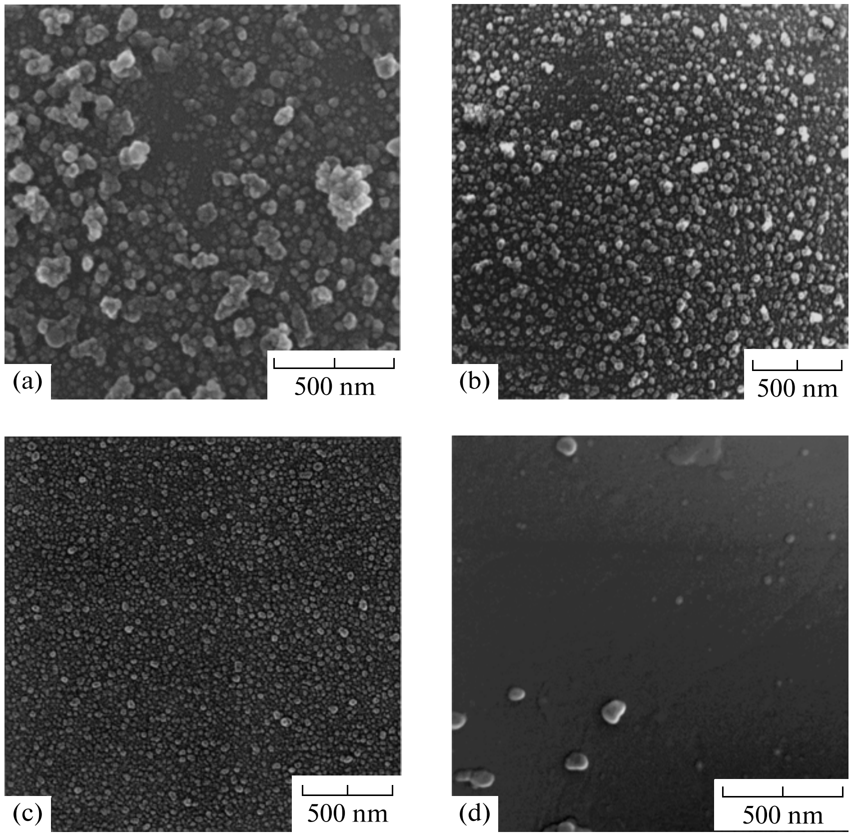


**Fig. 1.** SEM images of the surface of plasma sprayed HA coatings obtained on titanium substrates upon IHT in regimes (a) 0, (b) 4, (c) 6, and (d) 8.

the contact temperature. The latter temperature depends on the IHT conditions and the spraying distance.

The samples were prepared using 2-mm-thick plates of VT1-00 titanium alloy, onto which HA coatings were plasma sprayed in air from a distance of 90 mm using a BPEC 744.3227.001 setup operating at an electric power of 16 kW, a plasmatron arc current of 540 A, and HA powder with particle sizes within 2–30 μm. The substrates were subjected to preliminary IHT at a temperature varied from 20 to 1000°C. The dependence of the average size of nanodimensional grains in the plasma sprayed coating on the IHT temperature has been studied.

The structural-phase state (average grain diameter $D$, dispersion, structural uniformity) of plasma sprayed HA coatings was studied by scanning electron microscopy (SEM) with computer-aided processing of images. The SEM measurements were performed on a MIRA II (Tescan) instrument at the Center of Collective Equipment Usage of the Saratov State University. The scanned area size was varied from 1.0 to 2.3 μm with a magnification of (117–200) × $10^3$. The samples were numbered 0–10 (with a step of 2) in accordance with the preliminary IHT regime (heating temperature $T$), so that regime 0 corresponded to unheated sample, regime 2—to a sample heated to 200°C, and so on up to regime 10 in which the sample was heated to 1000°C.

The HA coating structure on a nanometer scale is determined by the process of splat crystallization [1]. The samples obtained without preliminary heating (regime 0, Fig. 1a) are characterized by an average grain size of about 11 nm. The sample surface contains numerous aggregates with dimensions from 150 to 300 nm, which consist of agglomerated nanograins. Thus, the surface of these coatings is characterized by significant structural nonuniformity. On a substrate preliminarily treated at 200°C (regime 2), the structure of plasma sprayed HA coatings changed rather insignificantly: the average grain size increased to 26 nm and the number of agglomerates decreased. The subsequent increase in the IHT temperature to 400°C (regime 4, Fig. 1b) imparted an almost homogeneous structure to the coatings, whereby agglomerates were rare and consisted of a small (4 to 8) number of grains, while the average grain size reached a maximum value of 31 nm. A plot of the average grain size $D$ versus HT temperature $T$ in the interval from 20 to 400°C showed evidence of the linear growth of nanograins (Fig. 2, line $D_1$).

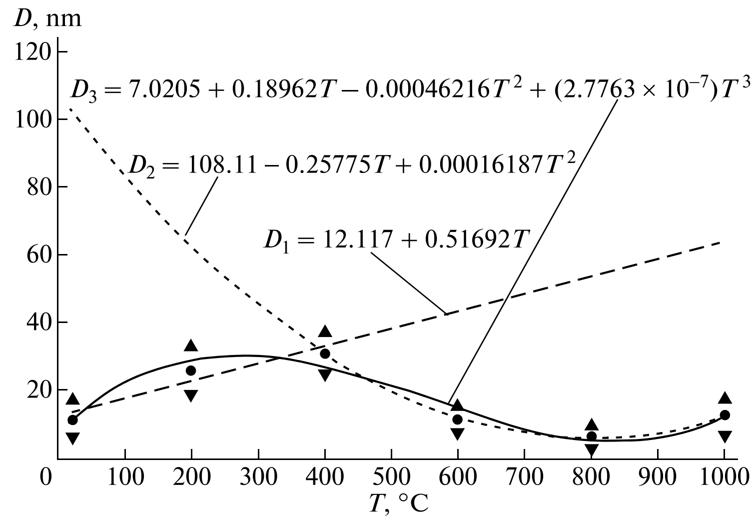


**Fig. 2.** A plot of average grain size $D$ versus IHT temperature $T$.

The heating to 600°C favored a decrease in the viscosity of deposited splats, which led to their better spreading on the substrate surface. The corresponding decrease in the average grain size $D$ to the initial level of 11 nm seems to be natural and fits to a parabolic law (Fig. 2, curve $D_2$). This structure is characterized by a high degree of homogeneity, with single agglomerates not exceeding 70–90 nm in size. It is especially important to note that the SEM image of a coating formed under these conditions (regime 6) reveals separate crystalline grains and subgrains with dimensions of 3–8 nm, the fraction of which amounts approximately to 48% (Fig. 1c).

Significant changes were observed when the temperature of preliminary heating was increased to 800–1000°C. In these regimes, separate agglomerated particles with dimensions ranging from 30 to 90 nm occur on a "smoothed" surface of the HA coating, the morphological heterogeneity is significantly reduced, and the average grain size decreases to 6 nm in regime 8 and is twice as large in regime 10 (Fig. 1d).

An analysis of the results of SEM investigation on the HA coating structure on a nanometer scale showed that, using the preliminary IHT of titanium substrates and a thermokinetic action on sprayed material in the plasma jet (controlled by the spraying distance), it is possible to impart a desired uniform nanocrystalline structure to the obtained HA coatings. A generalized law of variation of the average particle size (Fig. 2, curve $D_3$) in the optimum IHT regimes has been found and it was established that the morphology of HA coatings obtained in these regimes can approach the morphology of bone trabeculae, which improves the biomechanical compatibility of implants [1]. According to the results of experimental investigations, plasma sprayed coarse splats forming the bearing base of the HA coating acquire a uniform nanocrystalline structure with an average grain size of 31 ± 6 nm upon the IHT at 400°C, while the IHT at 600°C reduces the average grain size to 11 ± 3 nm.

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