

Improving the Osseointegration Properties of Biocompatible Plasma-Sprayed Coatings Based on Hydroxyapatite and Al_2O_3



I. P. Melnikova, A. L. Nikolaev, and A. V. Lyasnikova

Abstract A new technique of biocompatible coatings spraying on the surface of implants was developed. This technique is based on a special preparation of powders before plasma spraying, namely, the use of immobilization techniques and thermo-mechanical processing (TMP) of powders. We investigated coatings based on Al_2O_3 and Hydroxyapatite (HAp) obtained with different parameters of TMP. Compression tests and thermal cycling tests have shown that Al_2O_3 powders subjected to TMP at 1200–1250 °C have the highest resistance to mechanical and thermal influences. It was also shown that coatings obtained from HAp powders subjected to TMP at 800 °C have a more uniform morphology. At the same time, coatings based on powders obtained with TMP at 1000 °C are more crystalline. The roughness and average size of the open pore channel on these coatings is greater than on coatings obtained with other TMP temperatures. XRD and IR-spectroscopy showed the formation of a new phase of β -tricalcium phosphate, $\beta\text{-Ca}_3(\text{PO}_4)_2$, in HAp powders obtained using TMP at 1000 °C. The results achieved in this work will help to obtain biocompatible coatings based on Al_2O_3 and HAp, which will increase the osseointegration properties of implants.

Keywords Hydroxyapatite (HAp) · Al_2O_3 · Plasma spraying · Thermomechanical processing (TMP) · Coatings

1 Introduction

Modern dentistry and traumatology widely uses biocompatible materials based on Al_2O_3 and calcium phosphate ceramics to replace bone tissue with defects of various etiology. The main limitation of these implants is low mechanical stability. One of the

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solutions to the problem is plasma spraying of Al_2O_3 powder and calcium phosphate materials used for the formation of ceramic coatings on the surface of implants. The coatings should have specific mechanical, physicochemical and biochemical properties to interact with the environment of the host organism. It is well known that size of the pores in the porous scaffold is associated with the size of the constituent particles [1].

We have developed and applied a new technology of plasma spraying of ceramic coatings on intraosseous titan implants with porous titan sublayer formed by particles 250 μm . To achieve high homogeneity of the porous structure of the coatings and sufficient pore size for the effective growth of blood vessels and bone tissue into an implant, we use biocompatible powder with the particle size of 40–100 μm [2]. HAp powder has binding properties complicating its sifting, which makes usage of smaller particles inefficient due to significant material losses.

This work is aimed at the development of functional characteristics of biocompatible plasma-sprayed coatings, in particular, improvement of their mechanical properties by homogenization of the porous structure and stabilization of the crystalline structure.

2 Experimental Details

We have developed a method of assessment of processing quality for Al_2O_3 powder. The main criterion of the quality is compressive strength of test tablets formed from the powder. Tablets of 8 mm size are formed from Al_2O_3 powders and their mixtures with plasticizers (2% of the tablet mass) in press forms under 0.32 GPa pressure. Tablets are sintered in hydrogen furnaces of continuous pushing-type with temperature controlled by optical pyrometer LOP-72 at 1750 °C for 10 min. Finally they are tested by compression on tensile machine. We used the “BV-22” as a plasticizer.

During the experiments, aluminum oxide coarse powders with 40–60 μm particles of spherical form and electrovacuum Al_2O_3 powders with 1–3 μm particles were mixed in $\frac{1}{4}$ proportion in ceramic evaporation chamber for 15–20 min. Loosely packed mixtures of Al_2O_3 powders were annealed at 1100–1500 °C in hydrogen for 3 h, and then grinded in a ceramic mortar for 20 min. Thermal cycling was carried out by sintering mixtures of Al_2O_3 powders in hydrogen atmosphere at 1750 °C for 10 min. Testing was carried out in glass vacuum diodes (in vacuum of 3×10^{-7} mmHg or higher) in cycles ($U_N = 9$ V for 3 min on 7 min off) at 1470 °C.

Obtained powder was plasma-sprayed onto samples of BT1-00 titan with sublayer of titan powder (particle size is 250 μm). Metallographic and fractographic analysis of the coating, performed with microscopes “MBS-10”, “MIM 8 M” and profilometer “model 170,623”. X-ray and phase analysis of powders was carried using diffractometer “DRON-3”. Morphology of the plasma-sprayed coatings and structure of the layers was carried out using scanning electron microscope (SEM) MIRA II LMU TESCAN (Czech Republic) at accelerating voltage in range of 20–30 kV. Samples

were covered by gold coating (10–20 nm) by magnetron deposition. The microstructure and open pore size of the coatings were demonstrated using an atomic force microscope (AFM) Nanoeducator (NT-MDT, Russia).

3 Results and Discussion

A widely used method to improve powder granulometric composition, that eliminates ultra dispersed and fine dispersed, is based on thermomechanical processing (TMP) with prolonged annealing followed by light milling [3]. During the annealing, the smallest and the most active particles of the processed powder attach to each other and to larger particles. These conglomerates withstand the light milling. Larger, less active conglomerates (60–70 μm) are fractioned into smaller particles during milling. Thus, pre-annealed and milled powder becomes less polydisperse which allows one to form porous scaffolds with more homogeneous structure.

During spraying, small particles (below 40 μm) are strongly heated, however, they have relatively low kinetic energy. The particles deform insignificantly when hitting the substrate, which results in their weaker adhesion. Above this size limit, increased mass allows them to gain sufficient kinetic energy, which results in stronger deformations, leading to increased contact area, and thus increased coating adhesion to the substrate.

Considering the abovementioned mechanisms, the newly developed TMP method for the powders of biocompatible materials, based on the synthesis of combined particles of source powder through spraying of small particles (40 μm) on larger ones, also leads to higher adhesion of the coating to the titanium scaffold with sublayer of titanium powder [4].

During plasma spraying in high spraying in a high-temperature jet, heat transfer from smaller particles to larger ones prevents a fraction of smaller particles from full melting. When hitting the substrate, combined particle is fractioned into larger single particle and a couple of smaller ones [5, 6]. One can speculate that smaller particles, having speed compatible to a larger one, will fraction into nanometer-sized particles. Introduction of the ceramic nanoparticles to the structure of biocompatible material improves its functional characteristics by increasing the contact area between implants and bones.

We have tested a method for the stabilization of aluminum oxide properties. It relies on homogenization of distribution of various size particles in the volume of material by prolonged thermal processing of Al_2O_3 powders and their mixtures, followed up by milling.

The results of the compression tests of the samples, shown in Table 1, prove that their strength increased after TMO. Maximal strength was reached for the samples of Al_2O_3 powders annealed at 1200–1250 $^\circ\text{C}$, which indicates the most optimal [7] and homogeneous packing [8] of particles (Table 1).

Pre-annealed, grinded mixture of Al_2O_3 powders becomes more homogeneous in granulometric composition. It is associated with elimination of ultra dispersed

Table 1 Testing results of samples from mixtures of Al_2O_3 powders, annealed at various temperature

Mixture annealing temperature, T °C	Compressive strength, σ_v , kg/mm^2
No annealing	17.4
1100	22.2
1200	35.5
1250	35.4
1300	28.5
1400	25.6
1500	24.8

fraction (1 μm and less) [9], which is fixed on microgranules, after the powder mixture processing (Fig. 1).

We performed additional mechanical strength and durability tests of Al_2O_3 powder mixtures by thermocycling. Then we coated the surface of the vacuum diodes with these suspensions and annealed them at 1750 °C in hydrogen atmosphere. Measurements were carried out in a high vacuum at 1470 °C. The experimental results are present in Table 2. To do that we prepared a suspension and subjected it to heating (Table 2).

Comparing the results of testing samples for compression and thermal cycling (Tables 1 and 2), one can see that usage of homogeneously structured mixtures of Al_2O_3 powders, which is achieved by their thermal processing at 1250 °C, corresponds to maximal durability of coating formed from these mixtures, as well as their increased mechanical strength in cyclic tests. Thus, thermomechanical processing of Al_2O_3 powders at 1200–1250 °C leads to the homogenization of the granulometric composition, which improves functional characteristics of the biocompatible material of plasma-sprayed coatings by corresponding homogenization of their porous structure.

Fig. 1 Mixture of Al_2O_3 powders of different grain size composition after TMP. The image was obtained using optical microscopy

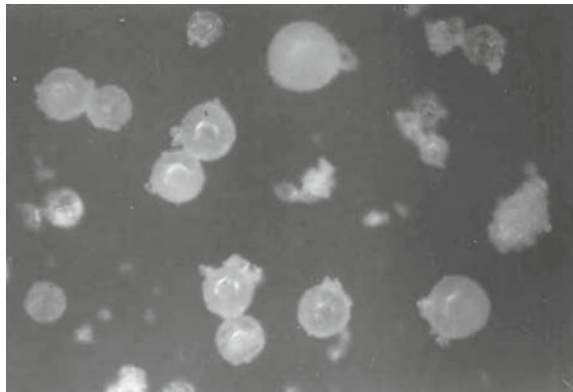


Table 2 Thermal cycling results for Al₂O₃ films of different grain size composition, annealed at different temperatures

Annealing temperature of Al ₂ O ₃ powders, <i>T</i> , °C	Number of cycles (<i>N</i>)		
	Shrinking	Destruction	
		Cracks	Delamination
Without burning	450	1500	–
1200	800	–	4100
1250	790	–	4200
1300	150	–	3500
1500	100	Burnt out after 250 cycles	

The developed method of thermomechanical processing of Al₂O₃ powders may be applied for the preparation of calcium phosphate ceramic biocompatible powders prior to their plasma spraying. Thermomechanical processing of polydisperse HAP powders prior to plasma spraying, performed for homogenization of the granulometric composition, was carried out at 800–1000 °C. Powders were annealed in furnace for 3 h. Then they were grinded in a ceramic mortar for 20 min. Temperature was controlled by the thermocouple. Metallographic and fractographic analysis of coatings from powders obtained by this method showed that thermomechanical processing at 800, 900 and 1000 °C lead to the formation of more homogeneous structure with larger pores (Fig. 2). The size of the pores increases with the increase of annealing temperature in accordance with variation of the surface morphology (Table 3).

With the increase of the TMO annealing temperature, increase of the particle size, characteristic of TMO, leads to the more developed surface morphology of the coating and increase of the open pore channel size (Table 4). The size of open pore channels and the value of the surface roughness of the sprayed coatings can be estimated from Fig. 3.

We also performed studies of the influence of TMO annealing temperature on the structure of GA powders, their structure, crystallinity, phase composition, binding properties by X-ray diffractometric and electron microscopic analysis (Figs. 4, 6). The crystallinity was determined from the ratio of the XRD reflections area to the total area of the reflections and the background in the 2θ angle range from 39° to 44°.

TMP of HAP powders at temperature in the range of 800–900 °C does not change phase composition of powders but changes its crystallinity and lowers inner stress (Table 5). In initial state, HAP is amorphous and its structure is unstable. During annealing between 800 and 1000 °C, it crystalizes and reliefs stress. Annealing at 1000 °C results in the formation of new phase of β-Ca₃(PO₄)₂ (β-tricalcium phosphate) [10], which is reflected by the new line in the XRD of HAP (Fig. 4). Moreover, a change in the character of absorption lines in the IR-spectra indicates the appearance of β-tricalcium phosphate (Fig. 5) [11].

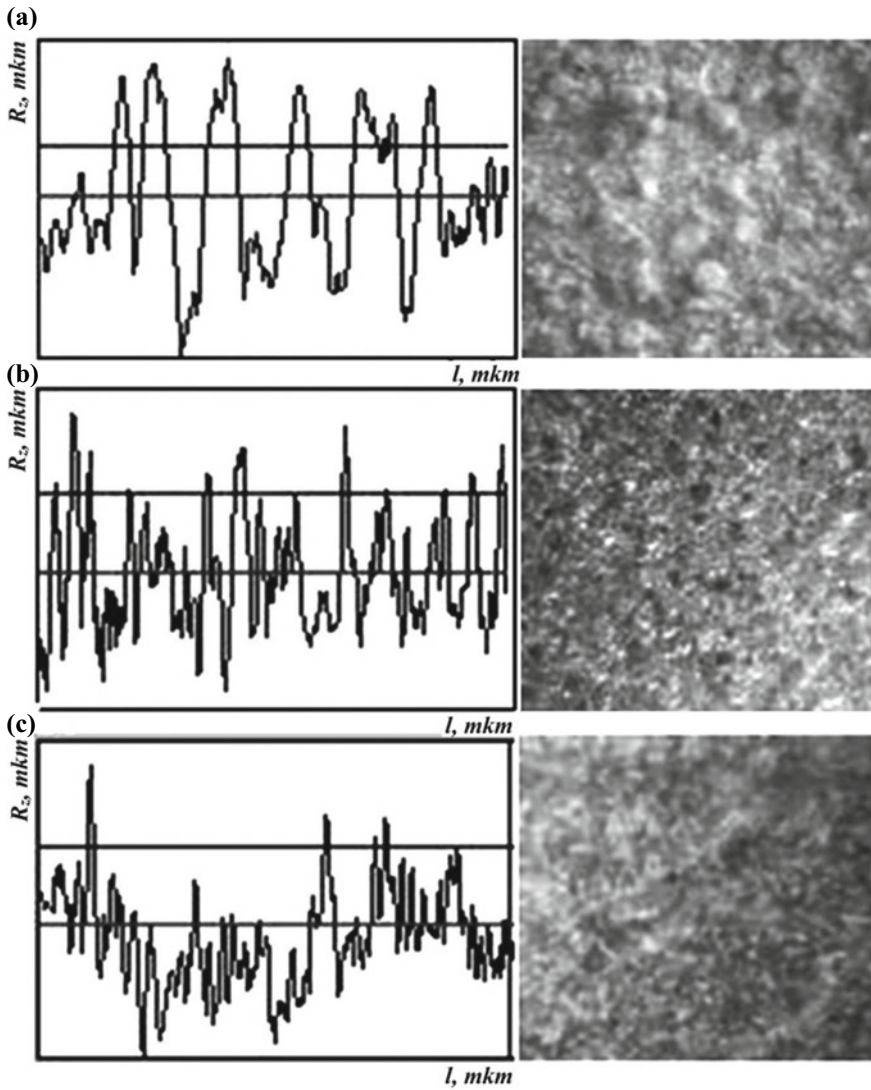


Fig. 2 Image and profile of the surface of a plasma-sprayed coating made of HAp on titanium with a sublayer of titanium powder after TMP at 1000 °C (a); 800 °C (b); and without TMP (c)

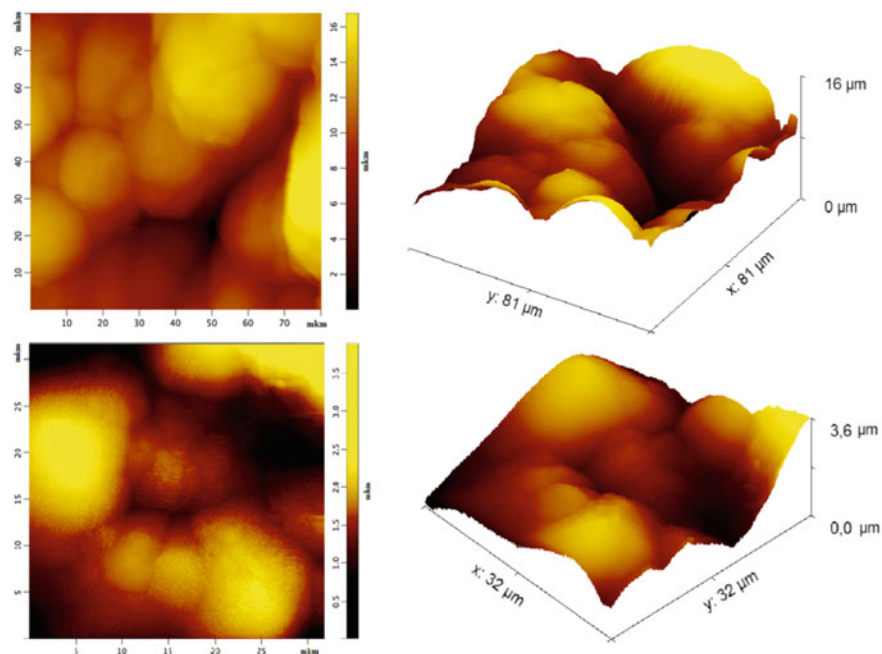
Substantial increase of the particle size of biocompatible HAp-based material at TMP annealing temperature of 1000 °C, leads to the decrease of the spraying quality due to the formation of large open pore channels (Table 4) and consequently substantial uncoated areas of the sublayer. Thus, recommended temperatures for

Table 3 Influence of the annealing temperature of HAp-powder on roughness of plasma sprayed coatings

Annealing temperature of TMP T , °C	Roughness parameters, μm			
	R_a	R_z	R_{max}	S_m
Without TMP	5.5	45.8	54.9	58.7
800	5.9	49.9	62.6	121
1000	16.7	104	125	237

Table 4 Influence of the TMP annealing temperature of source powder on the size of the open pore channel in HAp-based coatings

Powder composition	Annealing temperature of powder, °C	Size of open pore channel, μm
HAp (40–100 μm)	Without TMP	5–7
HAp (40–100 μm) + HAp (< 40 μm)	800	7.8–19.6
HAp (40–100 μm) + HAp (< 40 μm)	1000	39.2

**Fig. 3** AFM of the surface of a plasma-sprayed HAp coating from a powder obtained using TMP at 800 °C

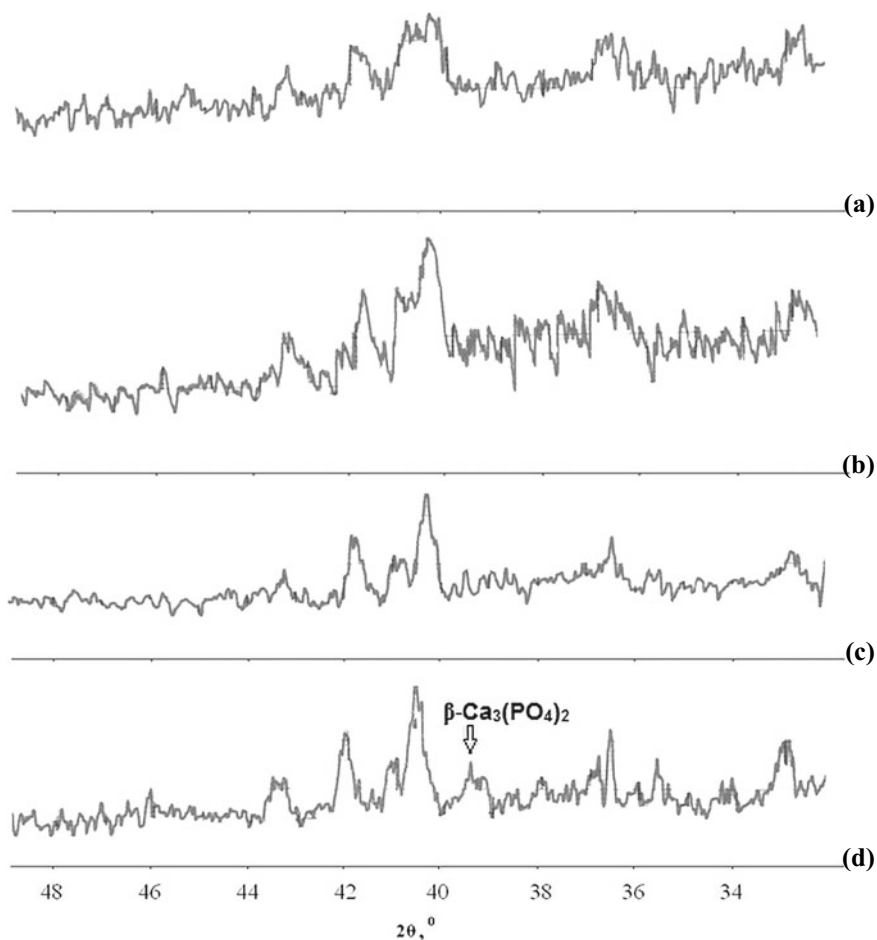
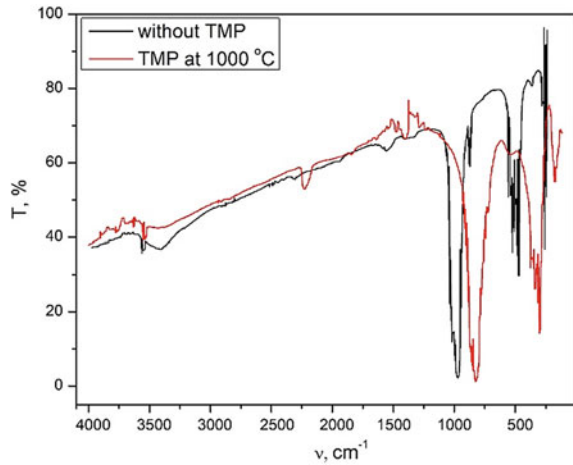


Fig. 4 XRD spectra of HAp powders obtained without TMP (a) and with TMP at 800 °C (b); 900 °C (c); 1000 °C (d)

Table 5 Influence of TMP temperature on HAp properties

TMP temperature, T , °C	Binding properties (adhesion of powders to the pestle)	Crystallinity, %	Presence of $\beta\text{-Ca}_3(\text{PO}_4)_2$ line with $d = 2.88 \text{ \AA}$ ($2\theta = 39.5^\circ$)
Without TMP	yes	33	–
800	yes	39	–
900	yes	45	–
1000	no (crumbly)	57	+

Fig. 5 IR-spectra of HAp powders without TMP (black line) and with TMP at 1000 °C (red line)



TMO powder annealing are 800–900 °C. Homogenization of the HAp coating structure after TMP at 800 °C is also confirmed by electron microscopy (Fig. 6 a, b) [12].

Figure 4 shows marks on the large particles, caused by the detachment of immobilized by TMP smaller particles in the moment of the collision with substrate. As a result, the structure of HAp coating contains not only 180 nm nanoparticles, whose size is defined by the fracture of the HAp particles on deposition, but also specific smaller 40–60 nm nanoparticles (Fig. 6, d). Fracture of HAp particles, prior subjected to TMP, is likely facilitated by their more crystallinity [13, 14].

4 Conclusion

A new method for the processing of biocompatible aluminum oxide powders and HAp powders has been developed. It is based on their prolonged annealing followed by milling, which eliminates fine fraction of polydisperse powders, increases average particle size, and, as a result, an average size of the pore as well as homogeneity of porous structure. It has been demonstrated that the new method for homogenization of the structure increases strength and durability of coatings from biocompatible material aluminum oxide. It has been shown that TMO of HAp powder leads to the homogenization of the porous structure and formation of the stable crystalline structure of plasma-sprayed coating, which in turn improves its functional characteristics. To improve the functionality of biocompatible coatings based on Al_2O_3 and HAp, it is advisable to use the TMP process of powders to perform the process of immobilization of microparticles of Al_2O_3 and HAp on granules of these materials. This contributes to the nanostructuring of coatings during plasma spraying, as well as the improvement of the structural characteristics of the porous structure and the

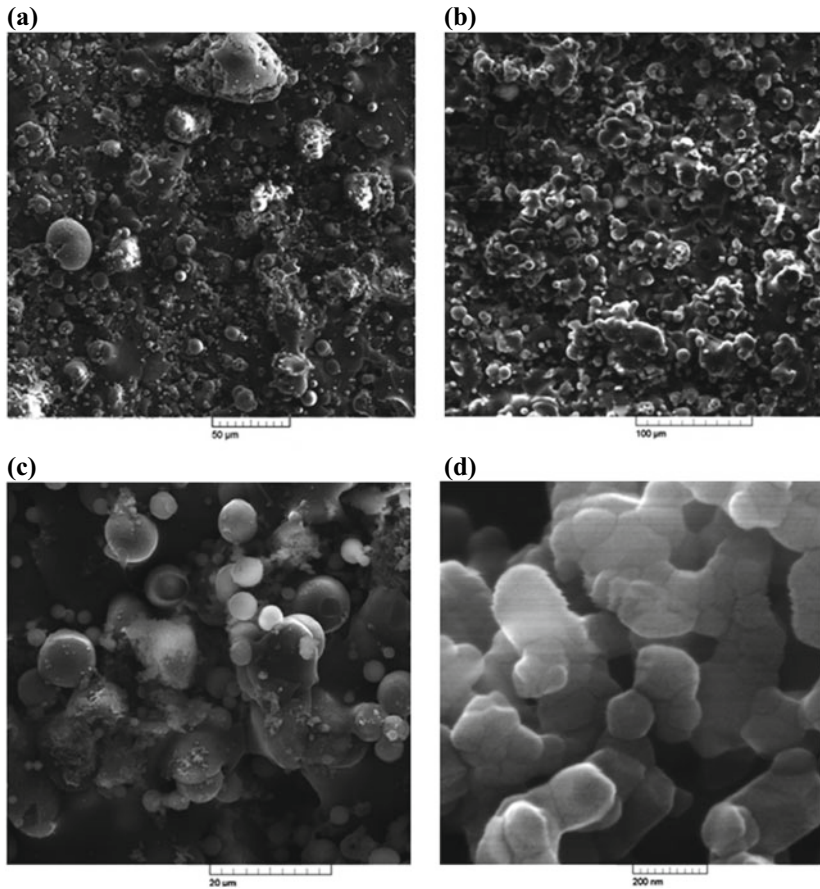


Fig. 6 SEM image of the plasma-sprayed HAp coating without TMP (a) and after TMP with annealing at 800 °C (b–d)

morphology of the implant surface. It is shown that the optimal temperature of TMP for immobilization of small particles of Al_2O_3 on Al_2O_3 macrogranules is 1200–1250 °C. Annealing of HAp powders during TMP in the temperature range from 800 to 1000 °C leads to the enlargement of particles without a significant change in the ratio of amorphous and crystalline phases. At a TMP temperature of 1000 °C and higher, the HAp crystallinity increases (by more than 50%) and $\beta\text{-Ca}_3(\text{PO}_4)_2$ forms. Application of the results obtained will significantly increase the osseointegration properties of implants with coatings based on HAp and Al_2O_3 .

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