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# Sand-blasting treatment as a way to improve the adhesion strength of hydroxyapatite coating on titanium implant

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**Abstract.** In the current study, the effect of corundum particle sizes (50 and 250–320 μm) used for sand–blasting on the structure, roughness, wettability, mechanical properties, and adhesion of radio frequency magnetron hydroxyapatite coating deposited on treated titanium substrate is studied. Morphology analysis revealed that pretreatment uniformly deforms the surface and induces the formation of pits, which size depends linearly on the grit size. The deposited coatings (Ca/P was in a range of 1.75-1.79) are homogeneous and repeat the relief of the substrate (mean roughness Ra is 1.9±0.1 (250–320 μm) and 0.8±0.1 μm (50 μm)). Texture coefficient calculations revealed the predominant (002) growth texture of hydroxyapatite coatings. The resistance of the coating to plastic deformation and the surface hardening were significantly higher for coatings formed on sand blasted with particle size of 50 μm. Scratch test have shown the significant improvement of wear resistance and lower friction coefficient of coatings for smoother samples. Dynamic contact angle measurements revealed the hydrophilic properties of the hydroxyapatite coating. Thus, sand–blasting of titanium with corundum powder having the size of 50 μm prior to the deposition of RF magnetron coating is recommended for the medical applications intended to improve the bonding between the substrate and coating.

## 1. Introduction

Since the early 1980s, the excellent mechanical properties of titanium (Ti) substrates have been commonly utilized in the biomedical field for the compensation of poor mechanical properties of porous bulk calcium phosphate (CaP) materials [1, 2], which are widely accepted as a biocompatible materials chemically similar to the mineral component of bones and hard tissues.

The CaP-coated Ti implants have been widely employed in the orthopedic and dental fields due to their excellent biocompatibility [3, 4], which in turn leads to the development of good interfacial strength between the implant and bone [3, 4].

However, in order to maintain long-term stability, CaP-coated Ti implants have to demonstrate not only the good bone regeneration process, but also the high bonding strength at the interface between the coating and metallic substrate. Bonding strength should be high enough to sustain possible fatigue stress during the surgical operation or after implantation.

Altering the metallic surface texture, namely, the implant roughness, via different pretreatment techniques or/and their combination is the most commonly used and relatively inexpensive way that can help in tackling above mentioned challenges as the substrate properties play an important role in obtaining stable coating, which in turn leads to the effective implant–tissue interaction and osseointegration.

It is known, that the mechanical properties of biomaterials are strongly governed by the film fabrication method and substrate characteristics. According to E. Mohseni et al, the sputtering technique has the highest adhesion of coating to the substrate as compared to other methods, which can be attributed to the sputter cleaning and ion bombardment processes [5].

The main sputtering technique employed today in the application of CaP coatings on medical implants is radio frequency (RF) magnetron sputtering. This technique allows producing thick, uniform, dense and pore-free films with high bonding strength to the metal implants [6, 7].

Nowadays, prior to RF-magnetron spray procedure, the Ti substrates are normally pretreated by grinding (GR), sand–blasting (SB) and acid–etching (AE) [7, 8] to remove the surface impurities and roughened the surface in order to improve the surface characteristics, such as hardness, Young's modulus and adhesion of the CaP coatings to substrate, thus increasing life expectancy of implants. Our previous study have assessed the effects of SB at different pressures on grain size, mechanical properties and surface wettability of RF magnetron silver-containing hydroxyapatite (HA) coating and revealed that the coating microstructure could be designed by controlling the pre-treated Ti surface topography [7]. However, the type, size and geometry of the sand particles are also important factors determining the result of the treatment. Therefore, in the current study, the effect of SB particle size (50 and 250–320 μm) on the surface structure, roughness, wettability, mechanical properties, and adhesion failure at the interface of RF magnetron deposited HA coating is studied.

## 2. Materials and methods

The commercially available technically pure Ti plates (10 x 10 x 2 mm) with the following chemical composition (in wt%): 0.30 Fe, 0.10 Si, 0.10 C, 0.05 N, 0.25 O, 0.0015 H and balance Ti were chosen as a material for the modification. Two groups of the Ti substrate were prepared using SB treatment with 250-320 μm and 50 μm of $Al_2O_3$ particles designated below as group 1 and group 2, respectively. Then all the samples were AE using a 1:2:2.5 mixture of HF (40 %), $HNO_3$ (66 %) and distilled water for 10 s in a laminar flow hood. Subsequently, the samples were washed using ultrasonic bath (Eurosonic Micro) sequentially during 10 min in acetone, ethanol and deionised water and dried in an autoclave at 70–80 °C.

The thin coatings (<800 nm) were deposited using a commercially available setup with an RF generator COMDEL (USA, 13.56 MHz). The samples were rotated in the deposition chamber. The precursor-powder of HA ($Ca_{10}(PO_4)_6(OH)_2$, $Ca/P = 1.67 \pm 0.02$) was synthesized using a mechanochemical activation method. The preparation and investigation of the target are reported in detail elsewhere [6].

Optical ellipsometry (Ellipse 1891-S AG) was used to determine the thickness of the deposited coatings. Surface morphology and chemical composition were investigated via scanning electron microscopy (SEM) using a Quanta 400 instrument (FEI, USA) equipped with an energy-dispersive X-ray analysis (EDX analysis system Genesis 4000, SUTW-Si (Li) detector) operated under high vacuum. The surface roughness was studied by Dektak 6M Stylus Surface Profilometer (Veeco Instrument Inc., USA). Surface phase composition was investigated by X-ray diffractometer (XRD) (D8 Advance, Bruker, Germany). The wettability of the samples was studied via the static and dynamic drop method using deionized water (Easy Drop Instrument (Kruess, Germany)). Mechanical properties of the samples were studied by Nano Hardness Tester «NanoScan-3D» using a Berkovich indenter at the load of 2 mN. For each sample, 30 indentations were performed. Based on the elastic deformation theory, Young′s modulus ($E$) and nanohardness ($H$) values were determined in accordance with Oliver–Pharr method. Wear resistance was evaluated using the plastic resistance parameter ($H/E$ ratio) as well as resistance of the material to plastic deformation ($H^3/E^2$ ratio).

Adhesion properties of the coatings were determined by Micro-Scratch Tester (Micro-Scratch Tester MST-S-AX-0000).

## 3. Experimental results and discussion

The appearance of the Ti surface was significantly altered by multi-surface pretreatment for all the groups, as shown in Figures 1a and 1b. SEM analysis of pretreated Ti substrates revealed that the modification via the combination of SB and AE uniformly deforms the surface and induces the formation of homogeneously distributed micro-pits, which size depends linearly on the grit size of corundum powder. Thus, the combination of these pretreatment methods leads to the formation of textured micro-relief on Ti surface, which application as a substrate for the deposition of nanostructured coatings can decrease micro-tension and increase the effective surface area, which in turns is very promising for osseointegration.

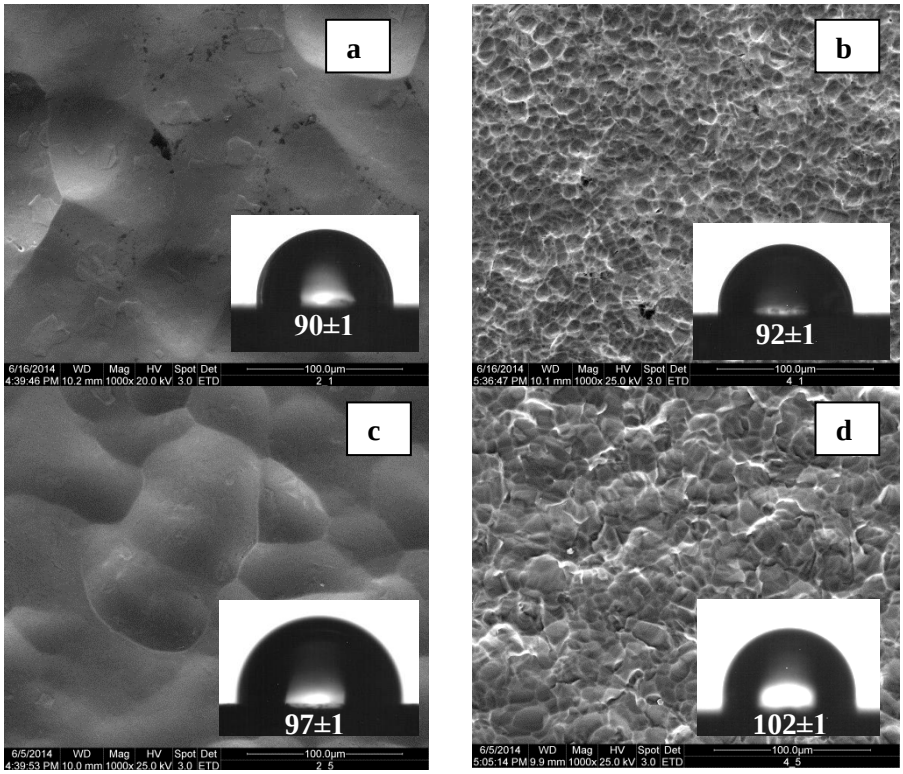


**Figure 1.** Typical SEM images showing the Ti surface morphology after SB and AE (a–b) (the insets are optical images of a water droplet), and after the deposition of the HA coatings on the nano-patterned Ti substrates (c–d) (the insets are optical images of a water droplet). For the surfaces (a, c) and (b, d), the grit size of $Al_2O_3$ were 250-320 μm and 50 μm, respectively.

Different powder size at SB also resulted in obtaining various surface roughness characteristics of substrates. A significantly higher surface roughness of group 1 compared with group 2 was observed after SB (Table 1). Chemical etching of the titanium surface was selective and led to the smoothing of initial blasted topography, which in turn led to the decrease in roughness (Table 1).

The resulting deposited coatings are homogeneous with unclear grain boundaries and repeat the relief of the initial Ti substrate (Figures 1c and 1d). HA coatings have no significant influence on the parameters of surface roughness. The mean roughness $R_a$ of HA-coated Ti substrates was 1.94±0.14 and 0.76±0.02 μm for group 1 and group 2, respectively (Table 1).

**Table 1.** Effect of the surface treatment procedure on the surface roughness parameters and mechanical properties of the samples.

| Parameters | SB | | SB + AE | | SB + AE + HA coating | |
|---|---|---|---|---|---|---|
| | Group 1 | Group 2 | Group 1 | Group 2 | Group 1 | Group 2 |
| $R_a$, (μm) | 6.6 ± 0.5 | 1.3 ± 0.4 | 1.8 ± 0.1 | 0.96 ± 0.04 | 1.94 ± 0.14 | 0.76 ± 0.02 |
| $R_q$ (μm) | 8.4 ± 0.6 | 1.8 ± 0.1 | 2.4 ± 0.2 | 1.21 ± 0.04 | 2.57 ± 0.23 | 0.97 ± 0.03 |
| $R_z$ (μm) | 36.7 ± 2.4 | 12.2 ± 1.8 | 12.4 ± 1.2 | 7.43 ± 0.20 | 14.61 ± 1.96 | 5.57 ± 0.25 |
| $H$ (GPa) | 5.8 ± 0.3 | 3.9 ± 0.3 | 3.1 ± 0.2 | 3.09 ± 0.19 | 12.23 ± 0.61 | 15.20 ± 0.66 |
| $E$ (GPa) | 108.7 ± 11.7 | 86.8 ± 13.5 | 74.6 ± 0.2 | 80.87 ± 11.47 | 118.41 ± 5.85 | 147.11 ± 15.93 |
| $H/E$ | 0.053 | 0.044 | 0.041 | 0.038 | 0.101 | 0.101 |
| $H^3/E^2$ (GPa) | 0.016 | 0.008 | 0.005 | 0.005 | 0.131 | 0.164 |
| $h_c$ (nm) | 101 ± 6 | 127 ± 10 | 145 ± 6 | 130 ± 5 | 74 ± 2 | 71 ± 3 |

EDX analysis revealed that the Ca/P ratio of the coatings for both regimes of SB was in a range of 1.75-1.79, which is close to that reported for CaP coatings deposited via RF magnetron sputtering [7].

XRD patterns for all of the coatings are mainly composed of crystalline HA with (002), (211) and (300) Bragg peaks and several peaks corresponding to the substrate (Figure 2). Blasting with 50 and 250-320 μm corundum particles resulted in lesser average crystallite sizes of HA estimated from the XRD patterns and were 66±1 and 96±2 nm, respectively (Table 2). The formation of HA grains with c-axis is preferentially aligned in the direction perpendicular to the substrate. This is evidenced by the calculations of the texture coefficient (*TChkl)* [8], which revealed the predominant (002) growth texture for all groups of HA coatings (Table 2). The determined unit cell parameters were in good agreement with that of HA standard (ICDD, #09-432, $a = b = 0.9418$ nm, $c = 0.6884$ nm (space group *P63/m*) (Table 2).

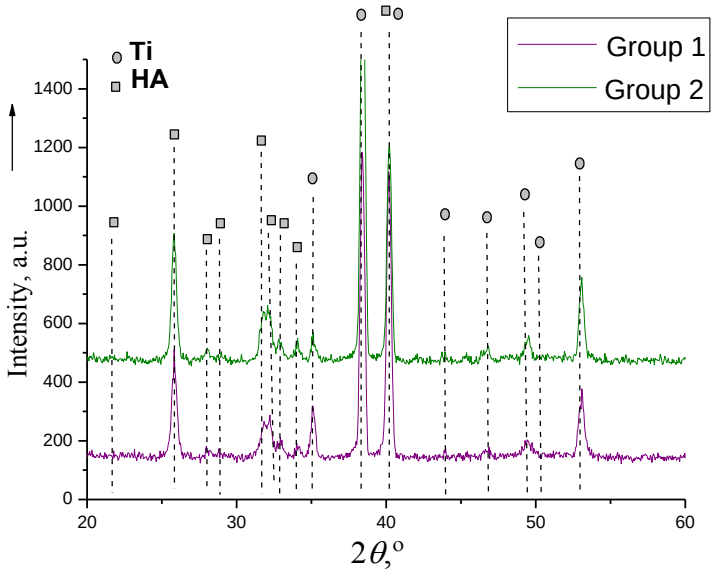


**Figure 2.** The typical XRD patterns of HA coatings deposited onto the surface of sand blasted and acid etched Ti substrates. The size of $Al_2O_3$ at SB was: a) 250-300 μm and b) 50 μm.

Nanoindentation results indicated intensive surface hardening after nanocrystalline HA coating deposition (Table 1). Nanohardness of the HA films in the case of substrate treated with the smaller particle size was 15.20±0.66 GPa, while with the higher particle size it was 12.23±0.61 GPa. Based on the data obtained before for pure HA coatings deposited on the surface of untreated Ti (nanohardness ~10 GPa [9]), we can assume that the substrate surface microstructure strongly affected the mechanical properties of HA films. It can be seen from the obtained data that $H/E$ ratio correlated with the mechanical performance under load (i.e., deformation for tribological applications) [10] was significantly higher as compared with the non-coated samples, due to an increased hardness of the HA coating. The resistance of the material to plastic deformation for the coating ($H^3/E^2$ parameter proposed by Johnson [11]) in the case of smaller abrasive particle size (0.164 GPa) was significantly higher than for the larger one (0.131 GPa) (Table 1). Thus, it can be concluded that the mechanical properties of the coating can be enhanced via variation of the particle size during blasting.

**Table 2.** Effect of Ti surface treatment on the phase composition, lattice parameters, crystallite size, element composition, texture coefficient of deposited coatings and wettability, where $\theta_{adv}$ is advancing contact angle.

| Group | Phases | Lattice parameters ($\AA$) | Crystallite size (nm) | Ca/P | $TC_{002}$ | $TC_{112}$ | $TC_{300}$ | $\theta_{adv}$ (°) | $\Delta\theta$ (°) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Ti | a = 2.931, c = 4.646 | 214 | 1.75 | 1.7 ± 0.1 | 0.7 ± 0.1 | 0.5 ± 0.1 | 85 ± 2 | 35 |
| | HA | a = 9.468, c = 6.787 | 66 | | | | | | |
| 2 | Ti | a = 2.949, c = 4.691 | 335 | 1.79 | 2.1 ± 0.1 | 0.6 ± 0.1 | 0.4 ± 0.1 | 87 ± 1 | 36 |
| | HA | a = 9.411, c = 6.876 | 96 | | | | | | |

In the present paper, the main task in the pretreatments of Ti surface prior to coating deposition was to enhance the bonding strength of the coating to substrate. Therefore, the adhesion strength at the interface was the most important characteristic, which was measured via scratch test method. Scratch test results revealed that the deposited HA coatings exhibited improved wear resistance and lower friction coefficient, especially in the case of 50 μm corundum particles.

Figures 3a and 3b show the typical scratch test diagram of the friction coefficient change as a function of the scratch length for the HA-coated sample. The clear jumps of the friction coefficient from ~0.29 to ~0.65 and from ~0.40 to ~0.70 in arbitrary units are visible for group 1 and group 2, respectively (Figures 3a and 3b). The evolution of the coating failure can be divided into three stages. At low loads (under ~2.6 N), cracking on the coating trackside was evident (Figures 3e and 3f, insets). As the load gradually increased, delamination at the trackside occurred. Eventually, the coating was delaminated from the substrate along the scratch path when the load increased up to ~2.60 and to ~3.14 N for group 1 and group 2, respectively.

The surface of Ti after SB followed by AE revealed almost the same static contact angle values (figure 2 c–d insets). The water contact angles for groups 1 and group 2 treated surfaces were 90 ± 1° and 92 ± 1°, respectively. The HA coating deposition process resulted in an increase in the water contact angle, that is, 97± 1° and 102 ± 1° for groups 1 and 2, respectively (Figures 2e and 2f, insets). Although the XRD patterns for all groups of the coatings are mainly composed of HA phase, some differences in the morphology of the HA films were observed. Therefore, surface chemistry gives the most contribution to the wettability of the HA coating than the surface texture. Thus, the deposited film is hydrophobic in static because of the formation of the multi-scale surface. However, dynamic contact angle measurements revealed the hydrophilic properties of the deposited HA coating due to a

higher hysteresis as compared with uncoated Ti surface. In this respect, we assume that HA coating can decrease stress-shielding effect and improve the fixation of an implant in bone.

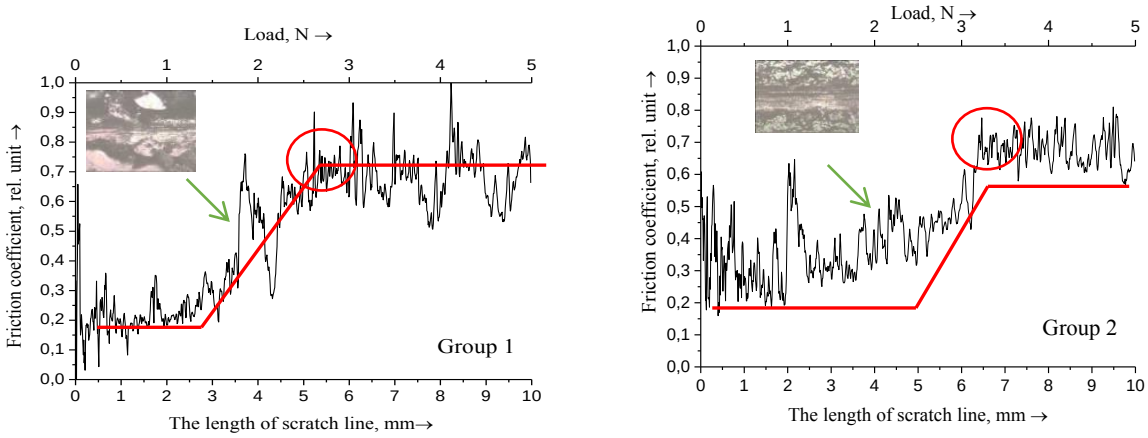


**Figure 3.** Results of scratch testing the HA coating deposited on the treated Ti substrates. The size of $Al_2O_3$ at SB was: a) 250-300 μm and b) 50 μm.

## 4. Conclusion

The results of the present study demonstrate that the predetermined surface texture of Ti substrates plays a crucial role in achieving the desired mechanical properties of RF magnetron deposited HA coatings (800 nm). Combination of SB and AE pretreatment methods led to the formation of the textured micro-relief on Ti surface with the mean roughnesses $R_a$ of 1.94±0.14 and 0.76±0.02 μm, for group 1 and group 2, respectively. Nanoindentation results indicated an intensive surface hardening after nanocrystalline HA coating deposition with the (002) texture. Nanohardness and Young's modulus of the coatings were 12.23±0.61 GPa, 118.41±5.85 GPa and 15.20±0.66 GPa, 147.11±15.93 GPa for groups 1 and group 2, respectively. The resistance of the material to plastic deformation ($H^3/E^2$ ratio) for the HA coating corresponding to group 2 (0.101 and 0.164 GPa, respectively) were significantly higher than that of the coated samples of group 1 (0.101 and 0.131 GPa). Scratch test results revealed that the deposited HA coatings exhibited improved wear resistance and lower friction coefficient.

Eventually, the coatings were delaminated from the substrates along the scratch path when the load increased up to ~2.60 and to ~3.14 N for group 1 and group 2, respectively. Obtained data revealed that HA surface chemistry gives more contribution to the wettability of the HA coating, than the surface texture. Dynamic contact angle measurements have shown the hydrophilic properties of the deposited HA coating due to a higher hysteresis as compared with uncoated Ti surface. Thus, SB of Ti with corundum powder having the particle size of 50 μm prior to the deposition of RF magnetron coating is recommended for medical applications intended to improve the bonding between the substrate and coating, which in turn can decrease stress-shielding effect and improve the fixation of an implant in bone.

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