Formation and Characterization of Crystalline Hydroxyapatite Coating with the (002) Texture

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Abstract. This study reports the effect of titanium (Ti) microstructure on the mechanical properties and surface wettability of thin (<800 nm) hydroxyapatite (HA) coating deposited via radio-frequency (RF) magnetron sputtering. It was revealed that the sand-blasting (SB) and acid etching (AE) of Ti prior deposition led to a wide range of surface roughness in nano/micro scale. After nanostructured HA coating deposition such physico-mechanical characteristics as nanohardness H, Young's modulus E, H/E ratio and H^3/E^2 were significantly improved. Moreover, HA coatings exhibited improved wear resistance, lower friction coefficient and ability of the coating to wetting.

1. Introduction

Permanent implants based on Ti and its alloys are clinically used this time due to their good mechanical properties and a high corrosion resistance [1-3]. Unfortunately, a wide application of such materials is limited due to insufficient wear resistance, high friction coefficient and lack of osteoconductivity. Recently, there is increasing interest to the investigations of different ways of surface modification to enhance their physico-chemical, mechanical and biocompatible properties [4].

Crystalline HA thin films is the best choice for bone repair and replacement [5-7]. However, a low ductility of HA limits its load bearing applications. In order to fabricate high quality bone implants with rapid healing the combination of good mechanical properties of Ti based metals with excellent biocompatibility and bioactivity of HA have been applied. Nevertheless, the long-term stability of HA coating in body environment is still a subject for investigations.

In order to maintain long-term stability of Ti implants with HA coating, several requirements are usually should be met. First, HA coating itself should have good mechanical properties (high hardness, low friction etc.); second, the bonding strength of the interface between HA coating and Ti substrate should be high enough to sustain possible fatigue stress during surgical operation or after implantation. In this study, two ways have been studied to overcome the above mentioned challenges. One is to use

RF magnetron sputtering, which allows to prepare dense, pore-free films with high adhesion strength [8]. The other is to increase the bonding strength via several surface pretreatment methods, such as SB and AE prior a coating deposition procedure.

Table 1. Effect of the titanium surface treatment procedure on the surface roughness, local physico-mechanical characteristics and wettability

Sample type	R_a	H	E	H/E	H^3/E^2	h_c	θ_{adv}	$\Delta\theta$
	(µm)	(GPa)	(GPa)		(GPa)	(nm)	(°)	(°)
SB	1.3±0.4	3.9±0.3	87±14	0.044	0.008	126.5±9.6	63.7±0.4	28.18
SB+AE	1.0±0.1	3.1±0.2	81±12	0.038	0.005	130.1±4.5	69.4±2.7	31.03
SB+AE+HA	0.8±0.1	15.2±0.7	147±16	0.101	0.164	71.1±2.9	87.1±0.2	36.55

2. Materials and methods

The commercially pure Ti substrates were used in the study. The samples were prepared via SB with Al_2O_3 particles (50 µm) for 10 s at the pressure P=1 MPa Pressure was measured using a pressure gauge via a coaxial compressor Fini SUPER TIGER 245. Then the samples were AE using 1 ml HF + 2 ml HNO_3 + 2.5 ml H_2O solution for 10 s. Finally, after AE, the samples were thoroughly cleaned with acetone in an ultrasonic bath (Eurosonic Micro, Euronda SPA, Italy) for 10 min followed by ethanol and deionised water. The coatings were deposited using a commercially available apparatus with an RF generator COMDEL (13.56 MHz). The precursor-powder of HA ($Ca_{10}(PO_4)_6(OH)_2$) was synthesized using a mechanochemical activation method. Preparation and investigation of the target was described elsewhere [8, 9].

Surface morphology and chemical composition of the biocomposites were investigated via scanning electron microscopy (SEM) using a Quanta 400 instrument equipped with an energy-dispersive X-ray analysis (EDX analysis system Genesis 4000, SUTW-Si (Li) detector) operated under high vacuum. The phase composition of the coating was identified by X-ray diffraction (Bruker D8 Advance XRD). Lattice parameters, crystallite size and the texture coefficient (TC_{hkl}) were calculated. To calculate the average crystallite size and the lattice parameters, Rietveld refinement (using the Le Bail method) with the program package TOPAS 4.2 from Bruker was performed. The calculations of TC_{hkl} were performed using the following HA reflexes: 25.8 ° (002), 31.7 ° (211) and 32.9 ° (300) according to the study [10]. Wettability and contact angle hysteresis of the samples were studied using Easy Drop Instrument (Kruess, Germany) with the use of deionized water.

The surface roughness of the samples was investigated using a Dektak 6M Stylus mechanical profilometer. Mechanical properties of the samples were studied via a Nano Hardness Tester «NHT-S-AX-000X» using a Berkovich indenter at the load 2.5 mN. Young′s modulus (E) and nanohardness (H) were determined in accordance with the Oliver–Pharr method [11]. Wear resistance was evaluated using the plastic resistance parameter (H/E) as well as resistance of the material to plastic deformation (H^3/E^2 factor). Adhesion of the coatings was investigated via Micro-Scratch Tester "MST-S-AX-0000". Optical ellipsometry (Ellipse 1891-S AG) was used to determine the thickness of the deposited coatings [12].

3. Experimental results and discussion

Typical SEM-images of the investigated surfaces of treated Ti and thin (500-800 nm) HA coating are presented in figure 1. The roughness parameters after abrasive blasting were as follows R_a=1.3±0.4 µm. The chemical etching of Ti surface was selective and led to the smoothing of the initial microscale topography, which in turn led to decrease of the roughness to R_a=1.0±0.1 µm (table 1).

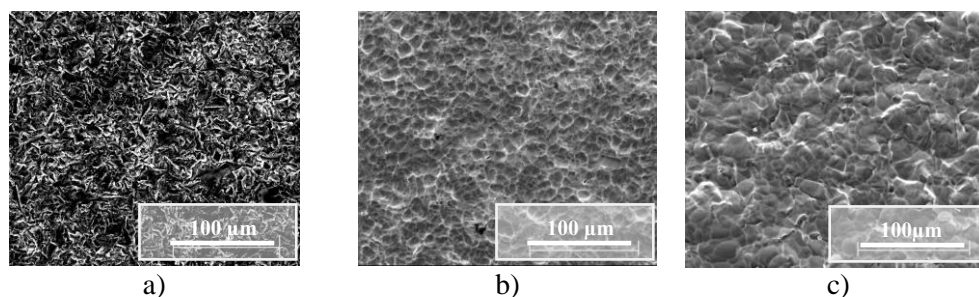|		
a)	b)	c)

Figure 1. SEM-images of the SB Ti surface (a), SB+AE Ti surface (b) and HA coating surface (c).

SEM micrographs of HA coating are shown in Fig. 1c. The samples were rotated in the deposition chamber. The resulting coatings are deposited without any cracks and repeat the relief of the initial Ti substrate (figure 1c). It can be seen a homogeneous coating with the unclear grain boundaries. Deposition of the HA coating resulted in surface smoothing in a nanometer range (R_a=0.8±0.1 μm).
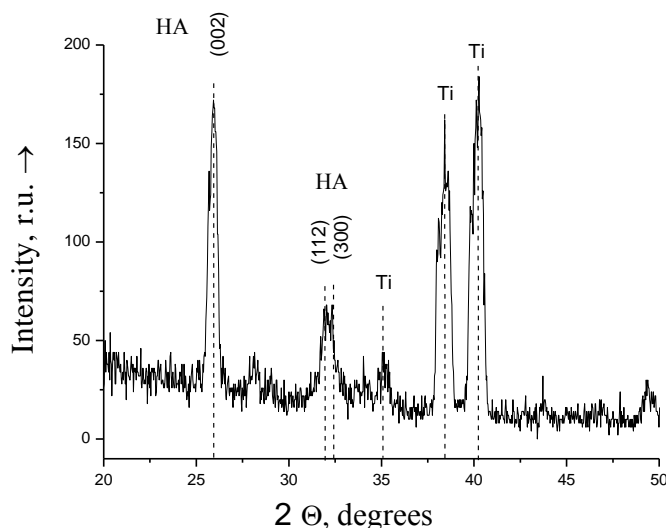

Figure 2. XRD-patterns of the HA-coated Ti substrate.

EDX analysis revealed that the Ca/P and O/P ratios of the coatings were 1.79 and 3.36, respectively, which were close to that reported for CaP coatings deposited via RF magnetron sputtering [8].

It can be seen from the figure 2 that the HA coating is crystalline with (002), (211) and (300) Bragg peaks of HA and several peaks corresponding to the substrate. Other phases such as CaO and (α, β) - TCP were not observed. An average crystallite size estimated from the XRD patterns was 96±2 nm. The calculations of TC_{hkl} revealed the predominant (002) growth texture of the HA coating (TC_{002}=1.40±0.01, TC_{112}=0.80±0.05, TC_{300}=0.75±0.05), which is common phenomenon for RF magnetron sputtering [13, 8-9]. This reveals the formation of HA grains with the c-axis preferentially aligned in the direction perpendicular to the substrate. The determined unit cell parameters were a=b=0.9430 nm and c=0.6893 nm, which were in good agreement with that of HA standard (ICDD, #09-432, a=b=0.9418 nm, c=0.6884 nm (space group $P6_3/m$).

The typical loading/unloading curves performed at the load of 2.5 mN recorded for uncoated Ti substrate and the HA coating are shown in Fig. 3a. The penetration depth of the indentor decreased significantly in the case of the deposited coating compared with that of the treated Ti. This was expected as the average coating nanohardness is superior to that of the uncoated Ti substrate. The

nanohardness of the HA films was 15.2±0.7 GPa while Young′s modulus was 147±16 GPa. On the other hand, the nanohardness of the treated Ti substrate prior deposition was 3.1±0.2 GPa while Young′s modulus was 81±12 GPa (figure 3a, table 1). 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 substrate surface microstructure affected the mechanical properties of HA films. The HA coated samples exhibited better mechanical resistance. The maximum penetration depth h_c was 130.10±4.47 nm before deposition and decreased to 71.11±2.87 nm after HA coating fabrication.
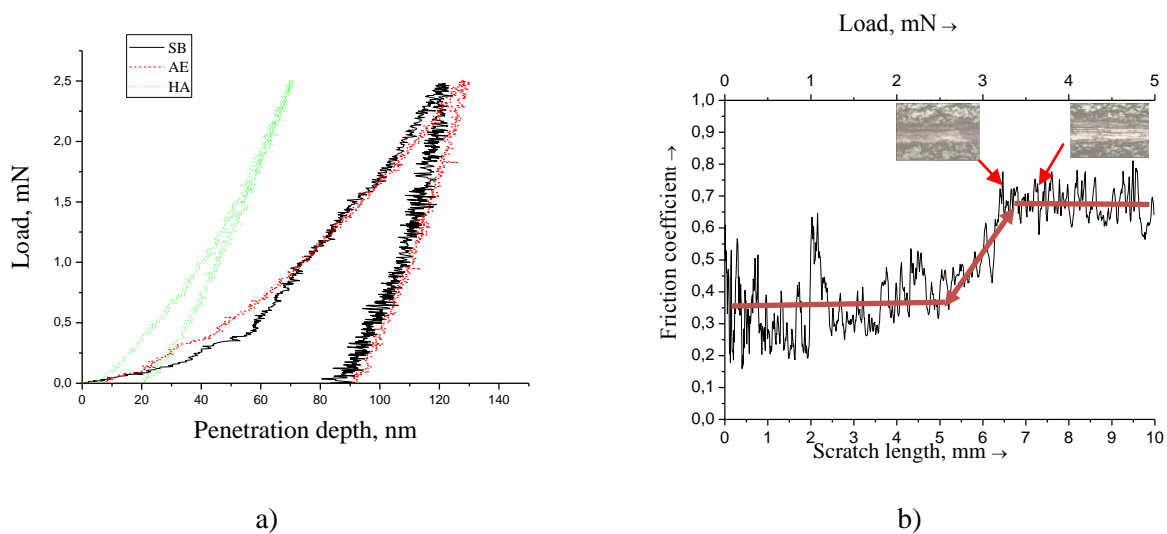

Figure 3. Loading/unloading curves (a) and results of the HA coating scratch test (b).

The coating wear resistance and adhesion can be estimated taking into account H and E values. The ratio between H and E is called elastic strain to failure and it was used for the first time as a materials ranking parameter by Oberle [14, 15]. The H/E ratio of the composite increased from 0.038 up to 0.101 after the HA coating deposition, which indicated the improvement of the wear resistance. The similar trend was observed in the case of the H^3/E^2 factor (table 1).

Figure 3b shows the typical scratch test diagram of the friction coefficient change as a function of the scratch length for the HA-coated sample. A clear jump of the friction coefficient from ~0.4 to ~0.7 is visible (figure 3b). We conclude that the HA coating resists against failure better at the loading than uncoated Ti substrate. For the deposited HA coatings, the evolution of the coating failure can be divided into three stages. At low loads (under 2.6 N), cracking on the coating's trackside was evident. As the load gradually increased, delamination at the trackside occured. Eventually, the coating was delaminated from the substrate along the scratch path when the load increased up to ~3.14 N.

Contact angle hysteresis $\Delta\theta$ was used to study the properties of the HA coating and uncoated Ti [9]. Analysis of the results obtained for the samples after SB and AE showed an increase in the hysteresis (table 1). The HA coatings were hydrophobic ($\theta_{advancing}$ = 87.1 ± 0.2°), while receding contact angle had a tendency to decrease which resulted in increase in hysteresis up to $\Delta\theta$ = 36.55°. Thus, dynamic contact angle measurements indicated the hydrophilic properties of the deposited HA coating: a high hysteresis led to better wetting of the coating.

4. Conclusion

The HA coatings with the (002) texture were deposited on the surface of SB and AE Ti substrates via RF magnetron sputtering. Nanoindentation results indicated an intensive surface hardening after nanocrystalline HA coating deposition. Nanohardness H and Young's modulus E of the coatings

prepared on Ti at the penetration depth of h_c =71.11±2.87 nm are 15.2±0.7 and 147±16 GPa, respectively. The values of H/E and H^3/E^2 for the HA coating (0.101 and 0.164 GPa, respectively) were significantly higher than that of the uncoated substrate after SB+AE treatment (0.038 and 0.005 GPa). Scratch test results revealed that the deposited HA coatings exhibited improved wear resistance and lower friction coefficient. Dynamic contact angle measurements revealed the hydrophilic properties of the deposited HA coating due to a higher hysteresis 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.

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