

Electrophoretic Coating of Hydroxyapatite-Boron Nitride Nanocomposites on Titanium Implants

F. Bakan^{*}, M. Sezen^{*}, M. Gecgin^{***}, Y. Goncu^{**}, N. Ay^{***}

^{*}Sabancı University Nanotechnology Research and Application Center (SUNUM),
Istanbul, Turkey, feraybakan@sabanciuniv.edu

^{**}BORTEK Boron Technologies & Mechatronics Inc., Eskisehir, Turkey, yyuceturk@yahoo.com

^{***}Anadolu University, Materials Science and Engineering, Eskisehir, Turkey, nay@anadolu.edu.tr

ABSTRACT

Titanium (Ti) and its alloys have long been used as implant materials in dental and orthopedic applications. However, they can suffer certain disadvantages, such as poor osteoinductive properties and low corrosive-wear resistance. The potential of hydroxyapatite (HAp) coatings to enhance the long-term stability of the bond between metallic implants and the surrounding bone structure has been well documented. The HAp-coated implant can combine the high mechanical strength of the metal with the excellent biocompatibility and bioactivity of the ceramic and is therefore suitable for implants in high load-bearing applications. Recently, in order to improve the mechanical properties of the HAp coating itself, HAp composite coatings can be used. Accordingly, nano-sized hexagonal boron nitride (hBN)-HAp composites coated on Ti by Electrophoretic deposition (EPD) process and structural and morphological properties of coatings were investigated. For the structural characterization, XRD, Raman Spectroscopy and EDS were used, and for the identification of morphology and surface features, SEM and FIB analyses were conducted.

Keywords: hydroxyapatite, boron nitride, nanocomposite, electrophoretic deposition (EPD), characterization

1. EXPERIMENTAL

The starting powders used in the present work were nano sized hydroxyapatite (nHAp, Nanotech Advance Technology and Electric Electronic Systems Co. Ltd., Eskişehir, Turkey) and nano sized hexagonal boron nitride (nhBN; 120nm; Boron Technologies and Mechatronics Inc., Eskişehir, Turkey) powders. Commercial pure titanium (Ti-Gr4) plates used as substrate were provided from TIMET Metal&Medical, Izmit, Turkey.

Each powder was dispersed in absolute ethanol (Sigma-Aldrich, USA) under magnetic stirring and sonication. The suspensions were prepared by magnetically stirring (Heidolph MR Hei-Standart) of nHap-nhBN dispersions

certain ratios in absolute ethanol. Each suspension contains 1% nHAp. The concentration of nhBN was chosen 0-2.0-10.0 and 25.0 % (w) by the percentage of nHAp.

Commercial pure titanium sheet was used and cut in a way to have the same surface area (10x20x1.5 mm). Each sample was polished using SiC papers. Subsequently the samples were washed with detergent in ultrasonic bath and then ultrasonically cleaned with acetone. Substrates were washed with distilled water and kept in ethanol.

Titanium plates were used as working and counter electrodes. The distance between the electrodes was chosen 10mm. Experiments were performed at 100V using a D.C volt regulator (BioRAD Power Pac Basic). Voltages were applied on Ti plates for 5 seconds. After deposition, all of the samples were heat treated respectively in tube furnace 800°C, for 2h in argon atmosphere at a heating rate 1°C/min and cooling rate 1°C/min. Sample abbreviations are given in Table 1.

Notation	nhBN amount (w%)
HB0.0	0
HB5.0	5
HB10.0	10
HB25.0	25

Table 1: Description of the coated samples

For the examination of structural and morphological characteristics of the composites various complimentary analysis methods were performed. For the structural characterization, XRD and Raman Spectroscopy were used while, SEM and FIB techniques were carried out for revealing the morphological characterization.

To investigate the phase composition, XRD analyses were performed at a Bruker AXS Advance D8 using a CuK α radiation with the step scanning mode, applying a tube voltage of 40 kV and a tube current of 40 mA. The XRD patterns of BN/HAp composites sintered at 1100°C for 2 h are shown for different BN amounts. Phase

analyses were performed using PDF card no 009-0432 for HAp, 09-169 for Ca_3PO_4 (β -TCP) and 034-421 for BN.

Raman Spectroscopy measurements were taken by Renishaw Raman inVia Spectrometer couoled with a laser source of 532 nm and a Leica microscope (measurements performed using 50x objective).

Scanning electron microscopy (SEM) examinations were done for investigating the morphology of the composites using a JEOL 4601F MultiBeam Platform with FEG-SEM, equipped with an energy dispersive spectrometer (EDS-Xmax^N SDD Oxford Instruments). An electron probe at low acceleration voltages (3-5 kV) were applied. Prior to morphologic characterization, all of the samples were coated with a thin layer of Pt/Pd by sputtering (Cressington, USA). For the gallium ion milling, 30 keV ion energy was used at intermediate milling currents (0.1-1 nA), while the SE images were acquired by the FEG-SEM column of the platform at low electron energies vaying from 3 to 5 keV.

2. RESULTS AND DISCUSSION

2.1 X-ray diffractometry (XRD)

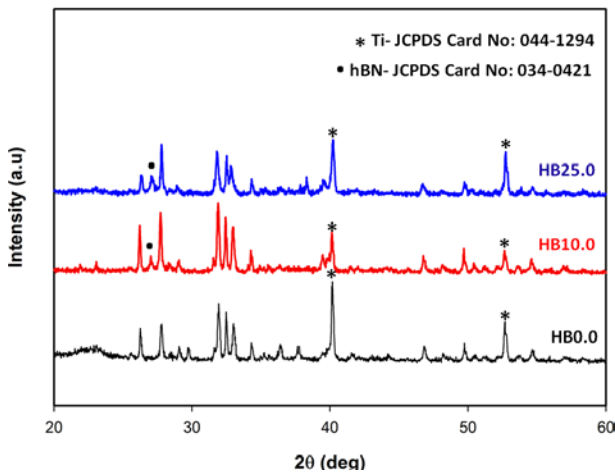


Figure 1: XRD patterns of HAp-hBN coatings on Ti-Gr4.

XRD patterns of samples sintered at 800°C under Ar atmosphere is shown in Figure 1. Phase analysis was performed using PDF card no. 009-0432 for nHAp, 034-0421 for hBN and 034-0421 for Ti, providing information in the 2θ range of 20° – 60° . Phase analysis revealed that all major peaks of HAp were present for all the samples.

2.2 Raman Spectroscopy

Figure 2 shows the Raman spectra of the samples. All bands have been assigned to internal vibrational modes of the phosphate groups. The strong peak at 960 cm^{-1} is

assigned to the totally symmetric stretching mode (ν_1) of the tetrahedral PO_4 group (P–O bond) [1-3]. Triply degenerate bending mode (ν_4) of the PO_4 group (O–P–O bond) was observed at 590 cm^{-1} and 578 cm^{-1} . Triply degenerate asymmetric stretching mode (ν_3) of the PO_4 group (P–O bond) was observed at 1046 cm^{-1} [4-5]. For structural characterization of hBN in the composites, the peak observed at 1368 cm^{-1} can be attributed to the characteristic adsorption of in-plane B–N stretching vibration mode of hBN [6-8].

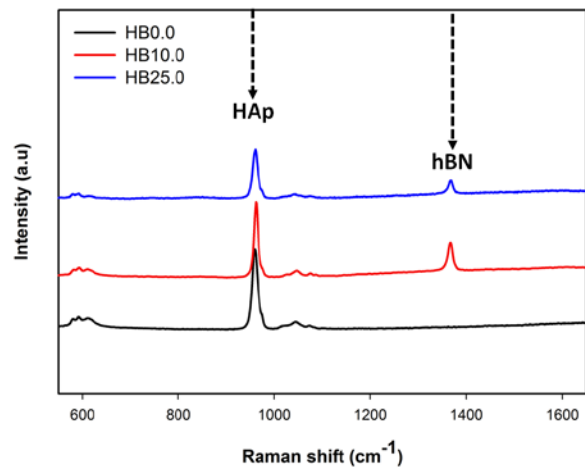


Figure 2: Raman spectra of the HAp-hBN coatings on Ti.

2.3 Morphology

Figure 3 shows the secondary electron (SE) images of the coatings. Increasing the BN amount in the composite caused structural change from spherical-like to plate-like form. Also the highest porosity was observed for HB10.0 compared to other structures.

In addition, cross-sections from each sample were acquired by means of gallium ion milling at the FIB/SEM platforms. The cross-sections revealed the nanocomposite coating layer as well as the Ti substrate, while the interfaces between those layers could also be observed. The related SE images from the cross-sections are given in Fig. 4, Fig.5 and Fig. 6 respectively.

Here it should be noted that, the vertical lines are formed due to the uneven topography of the sample surface, resulting in milling lines caused by curtain effect of ion milling.

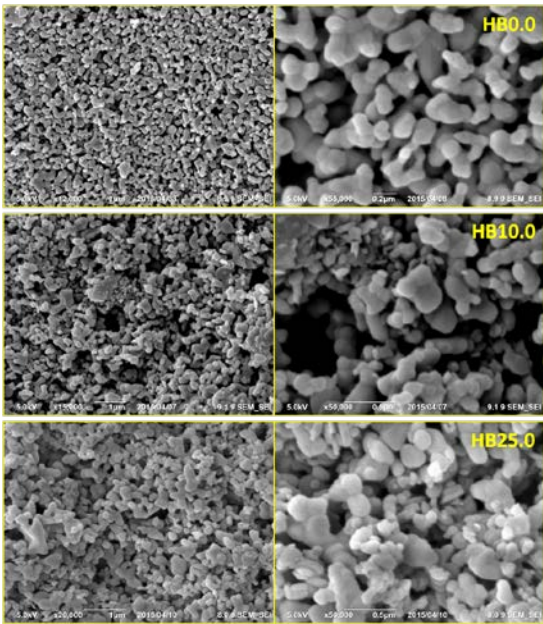


Figure 3: FEG-SEM images of HAp-BN composite coatings on Ti substrate.

According to FIB cross-section analyses, it can be observed that the coatings have different adhesion behaviour on to the substrates as well as the altered morphologies, such as porosity and packing. Moreover, with the increasing amount of hBN, there seems to be more integration with the Ti matrix as the interface between the substrate and the coating becomes less in thickness. This can be obviously tracked via the EDS line profile analysis which will be given in Fig.7.

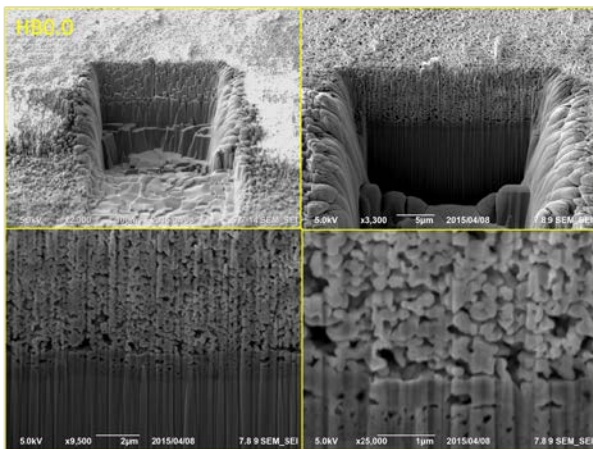


Figure 4: SE images of FIB cross-section which belongs to HB 0.0 sample.

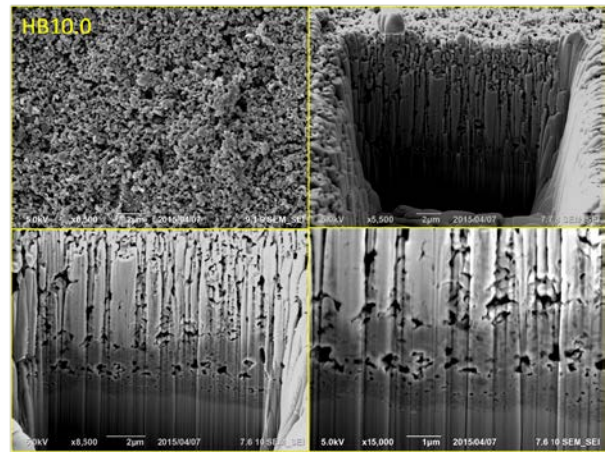


Figure 5: SE images of FIB cross-section which belongs to HB 10.0 sample.

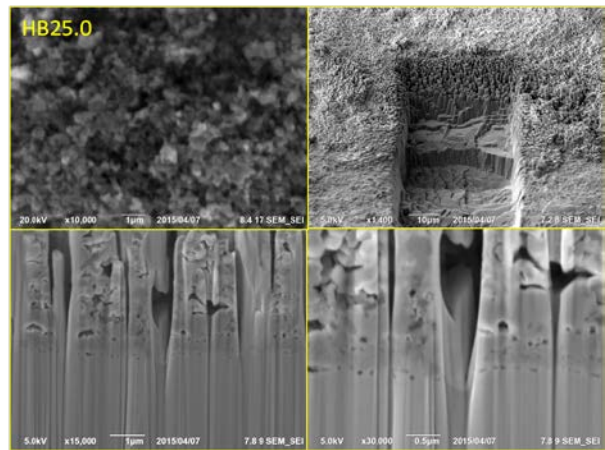


Figure 6: SE images of FIB cross-section which belongs to HB 25.0 sample.

EDS was used in order to track the changes in the chemistry through the cross-sections of 3 different materials. Figure 7 shows the elemental distribution within the line profiles acquired at the transition zones within FIB cross-sections of the samples that contains different percentages of hBN. The interface layer has found to be rich in oxygen when compared to other layers which can be due to native oxide layer formed by Ti substrate. However the thickness of this layer and the detected compositional percentage of O₂ varies by the hBN concentration of the nanocomposite coating. This can be attributed to the adhesion behaviour of the coatings on the Ti matrices.

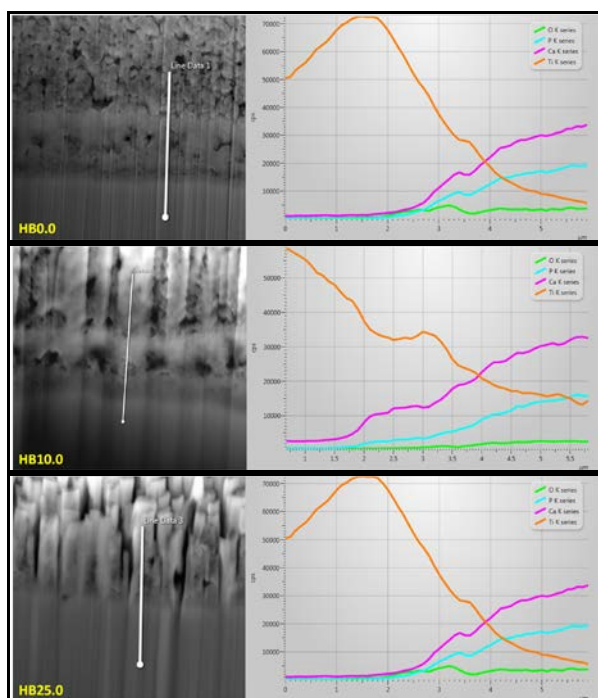


Figure 7: EDS line profiles through the FIB cross-sections of the samples

3. CONCLUSION

Titanium (Ti) and its alloys have long been used as implant materials in dental and orthopedic applications. However, they can suffer certain disadvantages, such as poor osteoinductive properties and low corrosive-wear resistance. In this study, ceramic composites with HAP matrix and nano-sized hexagonal boron nitride (hBN) having varying compositional percentages were coated on commercial pure titanium (Ti-Gr4) for improved properties and the effect of hBN amount on microstructure and morphological properties of the coatings were investigated. For the structural characterization, XRD, Raman Spectroscopy and EDS were used, whilst for the identification of morphology and surface features, comprehensive SEM and FIB analyses were performed for a complimentary analysis. According to XRD results, all major peaks of HAP were present for all samples. hBN and Ti peaks could also be tracked. For structural characterization of hBN in the composites, Raman measurements were done and the peak observed at 1368 cm^{-1} was attributed to the characteristic adsorption of in-plane B–N stretching vibration mode of hBN.

The FIB cross-sections revealed the nanocomposite coating layer as well as the Ti substrate, while the interfaces between those layers could also be observed. Via FIB-SEM and EDS analysis it was observed that the coatings have different adhesion behaviour on to the substrates as well as the altered morphologies, such as porosity and packing. With the increasing amount of hBN, there seems to be more

integration with the Ti matrix as the interface between the substrate and the coating becomes less in thickness, which was tracked via the EDS line profiles. The interface layer has found to be rich in oxygen when compared to other layers which can be due to native oxide layer formed by Ti substrate. However the thickness of this layer and the detected compositional percentage of O_2 varies by the hBN concentration of the nanocomposite coating. This can be attributed to the adhesion behaviour of the coatings on the Ti matrices.

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