

The Effect of Sintering Conditions on the Formation of Hydroxyapatite-Boron Nitride Nanocomposites

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ABSTRACT

Being the main inorganic constitution of hard tissues (bone and teeth), calcium phosphates has been applied in medical and dental applications for hard tissue repairment. Hydroxyapatite (HAp) based ceramics are attracting attention because of their excellent osteoconductive and bioactive properties. Although having sufficient biocompatibility, HAp cannot perform the expected mechanical properties of a hard tissue. It is considered that, the production of composites by adding variety of materials to nHAp would improve mechanical properties and by controlling important parameters such as particle size and shape, particle distribution and agglomeration also affect the mechanical properties. Accordingly, in this study, nano-sized hexagonal boron nitride (hBN) having different compositional percentages was added to the nHAp to form novel composites with expected properties and the effect of sintering process on microstructure and morphological properties of sintered composites were investigated. For the structural characterization, XRD, Raman Spectroscopy and EDS were used, and for the identification of morphology and surface features, SEM, FIB and AFM analyses were conducted.

Keywords: hydroxyapatite, boron nitride, nanocomposite, sintering, characterization, electron microscopy

1. EXPERIMENTAL

In this study, nano HAp powder was provided by Nanotech Advance Technology and Electric Electronic Systems Co. Ltd., Eskişehir TURKEY, nano hexagonal boron nitride powder (nano hBN) was supplied from BORTEK Inc., Eskişehir, TURKEY and Poly Vinyl Alcohol (PVA) was used as binder. Samples that included 0 wt. %, 2.5 wt. %, 5.0 wt.% and 10.0 wt % nano hBN were prepared and named as HB0.0, HB2.5, HB5.0 and HB 10.0 respectively. Raw materials were mixed in ball mill under wet conditions using zirconia ball for 6 hours, dried at 80°C for 24 hours (MMM, EcoCell), then dried powders were grounded and screened. Samples were shaped by uniaxial pressing (Gabrielli, 40t) at room temperature under the pressure of 50 bar to produce disk-shaped samples (7.6 mm

diameter, about 2 mm thickness). The binder removal of samples were carried out heating rate of 2°C/min until 600°C, dwell time 2 hours, then cooling rate 5°C/min to room temperature in a electrical furnace (RETA, electro mechanic ceramic furnace). All samples were sintered by heating at 1100 in a laboratory tube furnace (Protherm Furnace), dwell time of 1 hour peak temperature under N₂ and atmospheric conditions. Sample abbreviations are given in Table 1.

Notation	BN amount (w%)	Sintering atmosphere
HB0.0	0	Air
HB0.0N2	0	N ₂
HB2.5	2.5	Air
HB2.5N2	2.5	N ₂
HB5.0	5	Air
HB5.0N2	5	N ₂
HB10.0	10	Air
HB10.0N2	10	N ₂

Table 1: Description of the nanocomposite 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 AFM, SEM, 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 2h are shown for different BN amounts. Phase analyses were performed using PDF card no 009-0432 for HAp, 09-169 for Ca₃PO₄ (β -TCP) and 034-421 for BN.

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

Dynamic mode AFM measurements were performed using a Bruker Multimode AFM to investigate the surface roughness of the composites. The cantilever has a spring constant $k=42 \text{ N.m}^{-1}$ and guaranteed tip radius of curvature $< 10\text{nm}$ (PPP NCHR-Nanosensors) was used.

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) was applied. Prior to morphologic characterization, all of the samples were coated with a thin layer of Pt/Pd by sputtering (Cressington, USA).

2. RESULTS AND DISCUSSION

2.1 X-ray diffractometry (XRD)

XRD patterns of samples sintered at 1100°C under air and N_2 atmosphere are shown in Figure 1 and Figure 2, respectively. Phase analysis was performed using PDF card no. 009-0432 for nHAp and 29-0359 for Ca_3PO_4 (β -TCP) and 034-0421 for hBN, providing information in the 2θ range of 20° – 60° . Phase analysis revealed that all major peaks of HAp were present for the samples that were sintered both under air and under N_2 . Atmosphere. hBN peaks could not be tracked for the samples that were sintered under air. This could be attributed to the thermal decomposition of hBN at the corresponding sintering temperature.

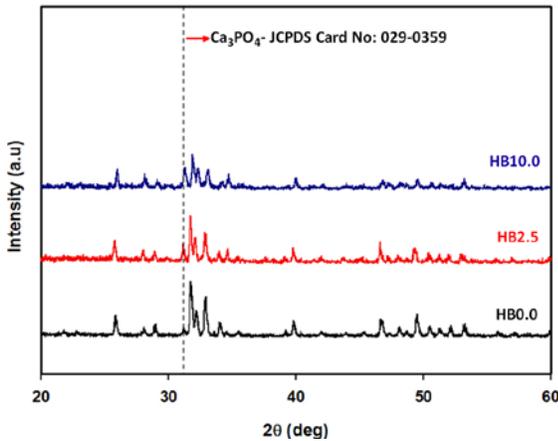


Figure 1. XRD patterns of samples sintered at 1100°C under air atmosphere.

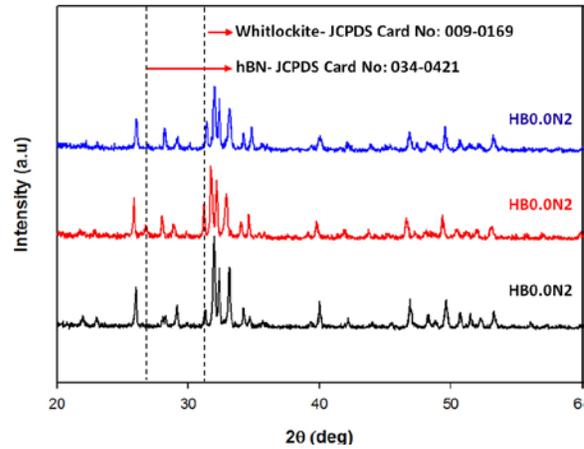


Figure 2. XRD patterns of samples sintered at 1100°C under N_2 atmosphere.

2.2 Raman Spectroscopy

Figure 3 shows the Raman spectra of the samples sintered at 1100°C under air (left) and N_2 (right) atmosphere, respectively. All bands have been assigned to internal vibrational modes of the phosphate groups. Librational modes of the hydroxyl groups belonging to water molecules were not observed at 630 cm^{-1} . 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 593 cm^{-1} and 581 cm^{-1} . Triply degenerate asymmetric stretching mode (ν_3) of the PO_4 group (P–O bond) was observed at 1048 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].

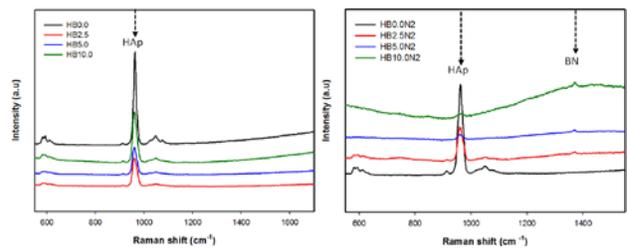


Figure 3. Raman spectra of the samples sintered under air (left) and N_2 (right).

2.3 Morphology

Figure 4 shows the secondary electron (SE) images of composites sintered at 1100°C in air and N_2 . It is very clear that increasing the hBN amount drastically affects the morphology of the samples sintered under air. The samples sintered under N_2 atmosphere have spherical regular shape whereas the samples sintered in air have elongated

hexagonal rod-like shape. The morphology change was observed in HB 5.0 and the structure changed from plate to hexagonal rods and it is suggested that a vitreous matrix phase is surrounding the crystals increases the strength. When the amount of hBN was increased to 10% (HB 10.0), the rods become more packed and a denser structure was obtained.

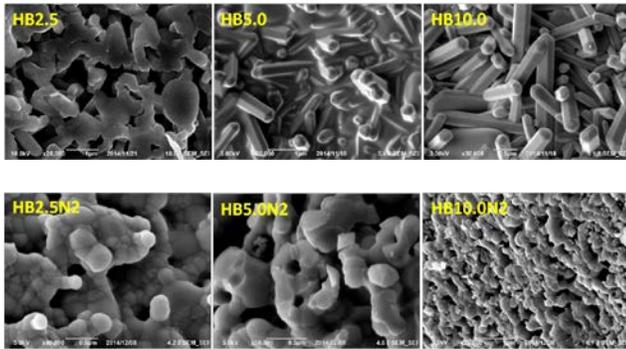


Figure 4: FEG-SEM images of composite surfaces sintered at 1100°C in air (above) and N₂ (below).

Figure 5 shows the EDS maps of the samples sintered at 1100°C in air (right) and N₂ (left) Although boron has been tracked in each of the EDS maps, nitrogen was only detected in the maps that belong to the samples which were sintered under inert atmosphere (N₂). This can be attributed to hBN oxidation in air atmosphere.

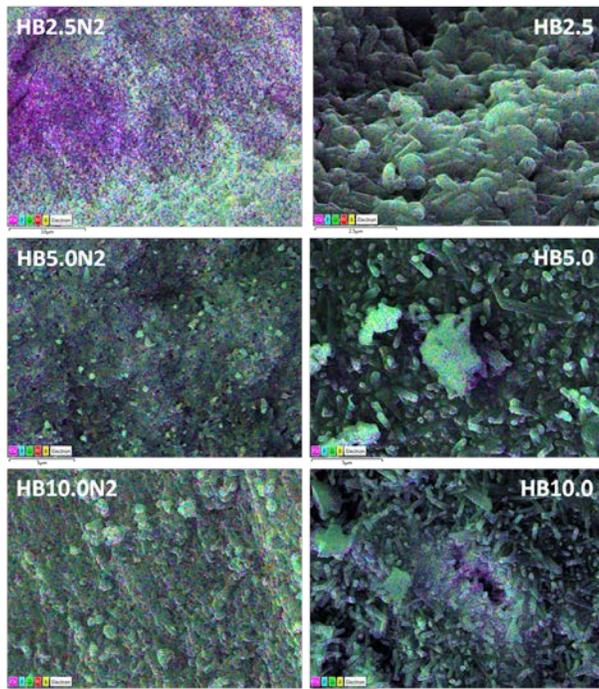


Figure 5: EDS maps of the samples sintered at 1100°C in air (right) and N₂ (left).

2.4 Atomic Force Microscopy (AFM)

The roughness values measured by AFM are given in Table 2, revealing the Ra (arithmetic average of absolute values) and Rq (root mean squared-RMS) for each composite surface sintered in both air and N₂. The results clearly demonstrated the alterations in the surface morphology of composites due to the sintering atmosphere. Surface roughness values of the samples sintered under N₂ atmosphere were low compared to the samples sintered in air.

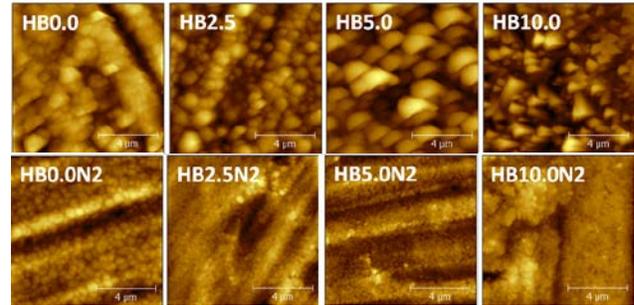


Figure 6: AFM images of composite surfaces sintered at 1100°C in air (above) and N₂ (below).

Sample	Ra (nm)	Rq (nm)
HB0.0	54.5	67.5
HB0.0	35	45.3
HB2.5	31.5	39.5
HB2.5	71.7	93.8
HB5.0	137.6	172.1
HB5.0	48.3	59.4
HB10.0	286	359
HB10.0	65.2	86.1

Table 2: Arithmetic average (Ra) and root mean square (Rq) surface roughness values of composite surfaces sintered in air and N₂.

3. CONCLUSION

In this study, ceramic composites with HAP matrix and nano-sized hexagonal boron nitride (hBN) having varying compositional percentages were developed for improved properties and the effect of sintering process on microstructure and morphological properties of sintered composites were investigated. For the structural characterization, XRD, Raman Spectroscopy and EDS were used, whilst for the identification of morphology and surface features, comprehensive SEM, FIB and AFM analyses were performed for a complimentary analysis. According to XRD results, all major peaks of HAP were present for the samples that were sintered both under air and under N₂ atmosphere. hBN peaks could not be tracked for the samples that were sintered under air. This could be attributed to the thermal decomposition of hBN at the

corresponding sintering temperature. 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. In addition, SEM images revealed the morphological alterations of various structures as when the amount of BN was increased to 10% (HB 10.0), the rods become more packed and a denser structure was obtained. Finally for the alterations in the surface morphology of composites according to the sintering atmosphere, AFM measurements were performed and it was tracked that the surface roughness values of the samples sintered under N_2 atmosphere were low compared to the samples sintered in air.

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