Characterization of boron nitride-reinforced hydroxyapatite composites prepared by spark plasma sintering and hot press

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Hydroxyapatite (HA) has been introduced as a bone grafting material due to its similar composition to that of natural bone, along with its lack of toxicity and high chemical stability, which prevent inflammatory or antigenic reactions. However, the high porosity of HA leads to increased osteoconductive capacity to the implant, while reducing its mechanical resistance and hence limiting its clinical use. Research on the mechanical properties of HA such as superplasticity has been necessary to solve these disadvantages. In this study, boron nitride (BN; 0, 2, 4 wt %) was added as the second phase reinforcement to increase the bone strength and improve the mechanical combination. The BN was added using the appropriate sintering method in order to control the grain size and reduce the chances of HA being dissociated into tricalcium phosphate (TCP) due to the shorter exposure at high temperature.

The microstructures of the samples with various percentages of BN-reinforced HA demonstrated some variation. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were conducted to determine the elemental composition of the materials and observe the microstructural transformation. As a result, the various percentages of BN-reinforced HA combined with hot press (HP) and spark plasma sintering (SPS) methods demonstrated the improved consolidation of the HA composites with BN, which is a promising result for the development of bioactive load bearing ceramic bone substitution with improved mechanical properties.

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1. Introduction

Many types of calcium phosphates possess remarkable biocompatibility and bioactivity due to their great chemical similarity with the biological calcified tissue.1) In the area of biomaterials (specifically materials for bone repair, substitution or augmentation), the perceived similarity between bone apatite and hydroxyapatite (HA) provided the impetus for the development of commercial and non-commercial calcium phosphate materials. Among the calcium phosphate types, the most stable phase is HA.2)

The processing of HA is reviewed from the previous observations of past crystallochemical, geochemical, and phase stability studies and ongoing investigations on the processing of ideal fine crystals for ceramics. The formulation of apatite is usually Ca10(PO4)6(OH)2.

The use of dense HA ceramics in orthopedic and dental clinical applications is difficult due to its intrinsically poor mechanical properties.3)4) Furthermore, a dedicated effort is required to reduce the secondary phase that is formed during sintering.3)–5) Dense HA has been fabricated via various sintering methods, including conventional sintering,3) hot press (HP) method,5) and aligning the crystal orientation via pulse electric current sintering by using spark plasma sintering (SPS).3)

Boron nitride (BN), which is usually used as the dental cement and cosmetics for its unique characteristics profile, has also been used as an additive. Research and development in BN-containing products are brought together for improvement that is enabled by the material in existing processes and in the materials itself. One of the essential advantages for BN application is the improvement of mechanical properties.6)

The aim for this study is increase the mechanical strength of HA by adding BN, in order to obtain a fine grained microstructure and to investigate the effects of BN on the microstructure and phase transformation during the sintering process by comparing SPS and HP for feasible superplastic improvement in HA and BN-added HA.

2. Experimental procedure

2.1 Sample preparation

HA powders (Junsei Chemical, Japan) with a particle size of 1.5μm and hexagonal BN (Sonderkeramik) with an average particle size of 1μm were used in this study. After weighing the samples (0, 2 and 4 wt% of BN) and adding ethanol as a solventing agent, the mixture was subsequently ball milled for 12 h and placed in an oven at 60°C for 1 day, followed by oven drying for 24 h. The sample was mechanically ground to produce a new reaction surface between particles.

Two types of sintering were used in this study: SPS (S-825, SPS Syntex, Japan) and HP (ThermVac Engineering Inc., Korea). The SPS and HP units were similar, and both were loaded into a pressure die in which the powder was submitted to uniaxial pressure.

Both were performed under vacuum condition in a chamber where the water was cooled. In both, the pressure was maintained...
at 40 MPa with a temperature range between 900–1000°C, but with a holding time of 5 min for SPS and 1 h for HP as shown in Table 1.

The heating rate of 100°C per min and the uniaxial pressure level were both maintained in the SPS method. The actual densification took place during the resistance-sintering step when the high-DC current was applied. The electric power was then turned off after reaching and holding the sintering temperature in SPS.

The densities of the samples were measured in the water according to the Archimedes principle, assuming a theoretical density of 3.16 and 2.28 g cm⁻³ for HA and BN, respectively. The closed pores of the samples influence the density, and mechanical properties.¹⁸) X-ray diffraction (XRD) patterns of each sample were recorded in a PANalytical XRD instrument using Cu Kα radiation. The XRD patterns were also used to verify any HA decomposition during the sintering process.

The microstructures were characterized by scanning electron microscopy (SEM, Hitachi S-4800 using 15 kV and 10 μA). The samples were then etched with 0.05 N HCl solution and coated with Osmium. The Vickers hardness of the sintered samples was measured by Vickers hardness test technique by first preparing a high quality, smoothly polished, test specimen surface with no precracking. Then, the polished specimens were indented by a Vickers pyramidal microhardness indenter (MVK-H1, Akashi, Japan) at a load of 1 kg for 10 s.

3. Results and discussion
3.1 Phase characterization and thermal stability

The typical sintering temperature for dense HA bodies is ~1200°C for micrometer-sized powders in conventional sintering.⁶⁻⁹) However, a lower temperature sintering of 1000°C through carrying pressure along heating was proposed in this study.

Figure 1 shows the XRD analysis of the dense HA samples sintered by HP in vacuum with BN contents of 0, 2, and 4 wt. The crystallinity was unchanged but the BN peak became stronger with increasing BN content. Figure 2 clearly reveals HA and BN as the main phases of the composites. The XRD pattern matched with JCPDF no. 02205 for the HA sample and no. 024644 for BN, in both the HP and SPS samples. On the other hand, another secondary phase was observed in the HP sample, which also contained tricalcium phosphate (TCP) and CaO. The TCP phase was degraded too quickly in our body. The TCP phase was naturally produced when the HA temperature exceeded 900°C.¹⁰⁻¹¹)

No TCP phase was detected by the XRD analysis of the SPS sample. However, in the HP sample, a faint XRD pattern of a peak that was associated with TCP appeared at 2θ angles of 37 and 36°. The CaO phase was also detected. HA did not significantly dissociate into TCP during the SPS processing for all compositions. The HA decomposition resulted from dehydroxylation beyond a critical point. For temperatures below the critical point, the HA crystal structure is retained, despite the dehydroxylation process, and the HA rehydrates on cooling.¹²) The faster heating rate in SPS has prevented long exposure of HA at high temperature and the dissociation into TCP. HA decomposition must be avoided since it generates enhanced in-vitro dissolution rates.¹³)

3.2 Densification and microstructure

Very high density of each samples were achieved until exceeded 99%, Table 3 shows the density by both SPS and HP method. SPS and HP have both been applied to densify HA powders, as this technique offers benefits from the simultaneous application of pressure and efficient heating process.

Figure 3 shows the microstructure of the six samples, with the grain size decreasing with increasing BN content. From Table 2, it is observed that the addition of BN suppressed the grain growth. Interestingly, the HP samples tended to have smaller grain size compared to the SPS samples, although the mechanism is yet to be elucidated and awaits further study.

3.3 Hardness measurement

The Vickers indentation method was used to determine the hardness of the samples. In Fig. 4, the increase in hardness with decreasing grain size in metals and ceramics could be explained through the Hall-Petch equation:¹⁴)

\[ \sigma_f = \sigma_0 + k_0 \left( \frac{1}{d} \right) \]

(1)

The significant improvement in the hardness for the BN-reinforced HA sample was also attributed to its fine grain size. The HP samples had smaller grain size than the SPS samples,
indicating that the HA matrix ceramics produced by HP exhibited significant improvement in mechanical properties compared to the SPS samples.

During Vickers indentation, with increasing indentation loads, a transition occurs during the development of the cracks about the impression.15) As shown in Fig. 5, two different types of crack were observed on the materials: lateral cracking with often considerable spalling about the impression for the higher indentation test loads, and multiple cracking because of the indentation transitions in the complex residual stress state inside the samples.
The presence of BN causes grain size refinement and strong bonds in the HA matrix, the hexagonal BN (h-BN) is a structural analogue with graphite. In the area of biomaterials, carbons with a graphite structure are usually used as implants.16) Within each layer of boron and nitrogen atoms, they are bound by strong covalent bonds, whereas the layers are held together by weak Van der Waals forces, such as in graphite. The planar hexagonal arrays in both hexagonal BN and graphite are formed with strong covalent bonds. The bonding between layers is stronger than the Van der Waals force, which suggests the presence of cross-linking between them.17,18)

4. Conclusions

In summary, HA was observed to dissociate into CaO and TCP in the HP samples. However, the SPS samples were not used to observe in the experiment. This means that the shorter exposure in SPS can hinder the formation of the secondary phase.

Dense HA was successfully prepared by typical sintering methods of HP and SPS at 1000°C with a holding time of 1 h in HP and 5 min in SPS. The as-sintered HA had an average grain size of 700 nm and a relative density of more than 99%. The densification was attributed to the extremely high heating rate, which activated the diffusion mechanism.

Due to the smaller grain size, the HP samples were harder than the SPS samples by the Hall-Petch relationship. Further study is needed in order to fully understand this observation such as an effect of h-BN content in HA.

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