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Effect of Space Holder Content on Pore Morphology and Mechanical Properties in HA/β-TCP Composites Consolidated by SPS

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Abstract **-**Biomaterials of ceramics are useful as implant materials in orthopedic surgery. In this study, porous HA(hydroxyapatite)/β-TCP(tricalcium phosphate) composite biomaterials were successfully fabricated using HA/β-TCP powders with 10-30wt% NH_4HCO_3 as a space holder (SH), 2wt%TiH_2 as a foaming agent (FA) and as binder of 1wt% MgO powder. The HA/β-TCP powders were consolidated by spark plasma sintering (SPS) process at 1000 ℃ under 20MPa pressure. The effect of SH content on the pore size and distribution of the HA/β-TCP composite was observed by scanning electron microscopy (SEM) and micro-focus X-ray computer tomorgraphy system(SMX-225CT). These microstructure observations revealed that the volume fraction of pores increased with increasing SH content. The pore size of the HA/β-TCP composites is about 400-500μm. The relative density of the porous HA/β-TCP composite increased with decreasing SH content. The porous HA/β-TCP composite fabricated with 30%SH exhibited similar elastic modulus to cortical bone, but compression strength of this composite is higher than that of cortical bone.

Keywords: biomaterials, SPS, porous materials, hydroxyapatite, tricalcium phosphate

1. Instruction

Recently, the artificial bone has been widely used due to the growth of senior citizen's population. However, bones in the human body are hard to be substituted because of its specific structure and mechanical properties. For these reasons, a variety of research about Hydroxyapatite [Ca_{10} $(PO_4)_6(OH)_2$; HA] as a biomaterial has been carried out [1]. Because HA has been known for its similarity with structure of the bone as a hard tissue. On the other hand, biodegradation in the human body is also one of the important factors to be used for restoration of the bone. Therefore, in this study, β-TCP [$Ca_3O_8P_2$; tricalcium phosphate] known for high degradable materials in human body was used. However, in the case of using β-TCP as an implant exclusively, one problem is present; β-TCP was degraded before bone ingrowth [2]. Therefore, it is need to control the composition of β-TCP to recover bone defects. So, in this study, HA/β-TCP biomaterials were fabricated. Moreover, stress shielding phenomenon has also been considered because of Young's modulus difference between human bone and implant [3]. In order to control Young's modulus of composites, porous HA/β-TCP composites were fabricated with NH_4HCO_3 as a space holder(SH) and TiH_2 as a forming agent(FA) by Spark plasma sintering(SPS) is one of the rapid sintering. In addition, MgO as a binder was added into mixed powders to promote sintering. MgO was reported that make bio-ceramics which hard to be sintered restrict unusual coarsening and facilitate sintering [4].

In this study, HA/β-TCP composites were fabricated with NH_4HCO_3 (SH), TiH_2 (FA) and MgO (Binder) by SPS. Furthermore, the effect of SH contents on microstructure, mechanical properties of porous HA/β-TCP biomaterials has been investigated.

2. Experimental Procedure

Table. 1. The chemical composition of specimens. wt%

Sample No.	HA	β-TCP	NH_4HCO_3	TiH_2	MgO
A	79.2	19.8	X	X	1
B	77.6	19.4	10	2	1
C	77.6	19.4	20	2	1
D	77.6	19.4	30	2	1

The HA and β-TCP powders were mixed to 80 : 20 ratio (wt%). The NH_4HCO_3 as space holder(SH) was added with 10wt%, 20wt% and 30wt% in mixed HA/β-TCP powders respectively. And TiH_2 as a FA and MgO as a binder were added in the mixed powder at 2g and 1g respectively as listed in Table 1. The powders were mixed for 24h using mechanical mixer (ABB ACS100) with polyethylene bowl.

Table. 2. SPS condition.

Vacuum (Torr)	Pressure (MPa)	Heating rate (°C/min)	Holding time (min)	Temperature (°C)
10^{-2}	20	100	10	1000

The mixed powders were placed in a 10 mm-diameter cylindrical graphite die of the SPS equipment. The chamber was evacuated down to 10^{-2} torr and a uniaxial pressure of 20MPa was applied. The powders were sintered in two steps. The first step was carried out at 393K with 5 minutes to burn out SH. In the second step, the powders were heated up to 1273K with 5 minutes of holding time and instantly cooled in chamber is shown in Table 2.

The density of sintered HA β-TCP composites were measured by Archimedes' method. The porosity and mean pore size were observed by Micro-focus X-Ray device (SMX-225 CT) with 100kV and 130μm of condition. The CT images were captured at 20μm intervals. The morphology of pores was observed by scanning electron microscope (JMS: SEM). The mechanical properties were measured by compression test using universal testing machine at high temperature and high velocity (UTM) at strain rate of 0.5 mm/min.

3. Results and Discussion

Pore distribution of HA/β-TCP composites increased with increasing SH contents as shown in Fig.1. In the 20% SH added composite, compacted pores were observed. Composites were fabricated by SPS under axial pressure (20Mpa). Therefore, interconnectivity of the pores was improved as shown in Fig.2. Mean pore size of HA/β-TCP composites also increased from 2 to 525 μm with increasing SH contents (Table 3). Mean pore size and interconnectivity of the pores are important factors as porous implants. Because porous implant for hard tissue scaffolds generally applied for cell loading, drug releasing agent until bone repair [5]. Considering the minimum pore size for bone in-growth (100~150μm [6]), fabricated composites in this study may be having a good biocompatibility.

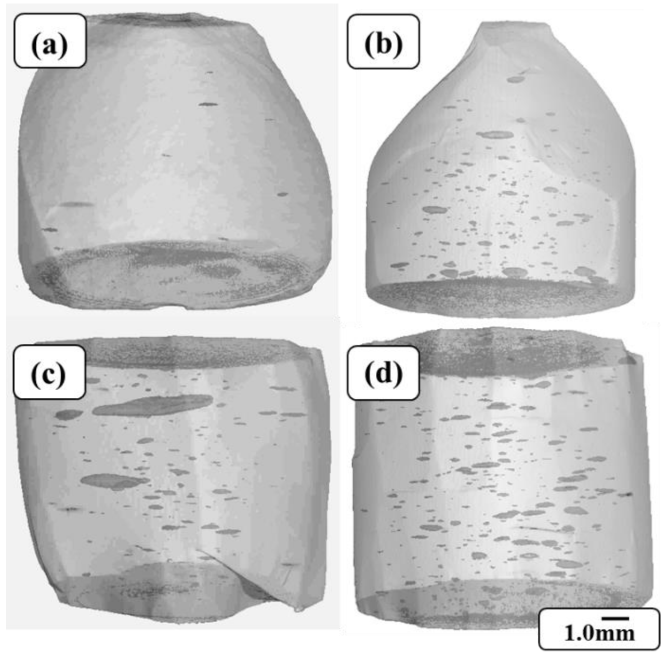

Fig. 1. 3D-CT images of HA/β-TCP composites: (a) Sample A; (b) Sample B; (c) Sample C; (d) Sample D.

Table. 3. The mean pore size of HA/β-TCP composites.

Samples	Mean Pore Size(μm)
A	2
B	466
C	492
D	525

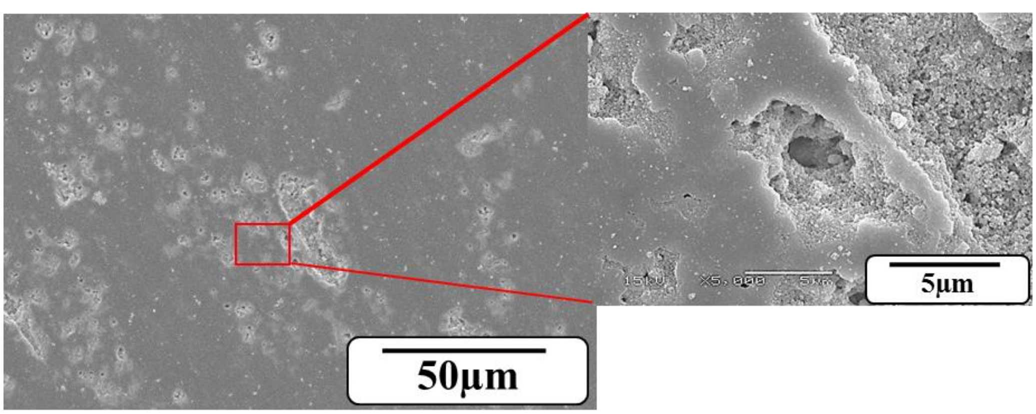

Fig. 2. The SEM images of cross sections of 20% S.H. added HA/β-TCP composite.

Fig.3. shows the SEM results of surface of HA/β-TCP composites. Pore size of composites increased with increasing SH contents and rough pores were observed. As TiH_2 in the mixed HA/β-TCP powders decompose at 723K, hydrogen ions floating on surface of composites [7]. Sintering temperature in this study is 1273K. For these reasons, HA/β-TCP composites have rough and open pores by adding TiH_2.

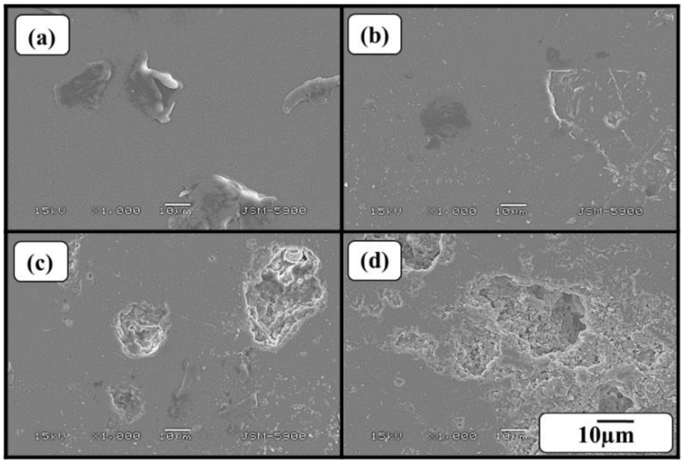

Fig. 3. The SEM images of surface area of HA/β-TCP composites: (a) Sample A; (b) Sample B; (c) Sample C; (d) Sample D.

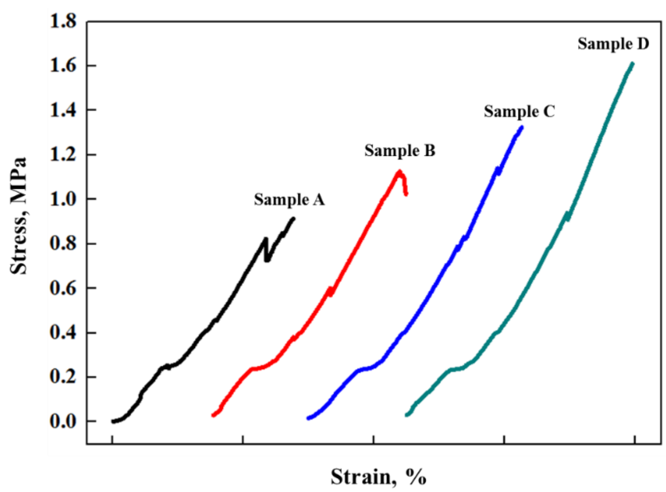

Fig. 4. The stress-strain curve of HA/β-TCP composites.

As a result of compression test, stress-strain curves of HA/β-TCP composites is shown in Fig. 4.

There is a regular stress area after yield point in the all of composites. When HA/β-TCP composites compacted by UTM (compression test machine), pores were fractured. It caused higher strain, but composites were given regular stress.

Table. 4. The mechanical properties of HA/β-TCP composites.

Sample	Compressive Strength (MPa)	Modulus (GPa)	Theoretical Density (g/cm^2)	Relative Density (%)
A	165.61	30.43	3.514	88.8
B	204.29	26.88	4.424	72.3
C	240.04	23.73	4.502	69.7
D	291.84	23.54	4.74	64.6

On the other hand, none of SH added composite also shows the regular stress area. HA/β-TCP composites were fabricated using powder metallurgy. So, pores can be exist in the composites even though there is no space holder. However, relative density of none of SH added composite is around 90%(Table 4). It means that sintered composites were successfully fabricated by spark plasma sintering. Furthermore, MgO in the composites stimulated sintering by restricting abnormal coarsening particles of powders [8]. So, HA/β-TCP composites were successfully consolidated. In cases of other properties of composites, elastic modulus decreased from 30.43 to 23.54GPa and compression strength increased from 165 to 292MPa with increasing SH contents.

Table. 5. Characteristics of bone tissue and prosthetic bone materials.

Material	Density (g/cm^3)	Modulus (GPa)	Strength (Mpa)
Cortical bone [9]	1.6 – 2.0	12 – 20	150
Titanium [9]	4.4 – 4.7	106	780 – 1050
30% S.H. added composite (in this study)	3.06	23.5	291.8

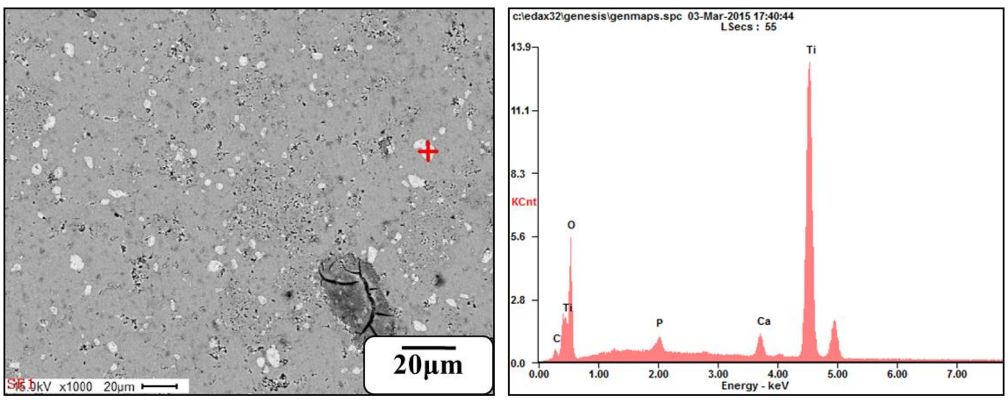

Fig. 5. The EDS results of 30% S.H. added HA/β-TCP composite.

Its mechanical properties are competitive compared to cortical bone shown in the Table 5. Generally, HA has been used in limited area of artificial bone implant such as coating materials, bone cements. Because HA has very low strength [1)] although it has good biocompatibility with the bone. However, 30% S.H. added composites fabricated in this study has similar elastic modulus (23.5GPa) and higher strength (291.8MPa) compared to cortical bone. Liu reported β-TCP particles improve mechanical properties of ceramic composites due to its good wettability with ceramic matrix [10]. And distributed TiO_2 particles were observed on the surface of composites as shown in Figure 5. It is because of effect of adding TiH_2 in the composites. For these reasons, its good strength is may be affected by TiO_2 and β-TCP particles.

Conclusions

1. The porous HA/β-TCP composites with the macro-pore size in range of 466-525μm were successfully fabricated by adding MgO as a binder using SPS.
2. The HA/β-TCP composites which have rough pores and interconnectivity with other pores were successfully fabricated by adding TiH_2.

3. The 30% S.H. added HA/β-TCP composites has similar elastic modulus (23.5GPa) and higher strength (291.8MPa) compared to cortical bone due to effect of β-TCP and TiO_2 on surface of composites.

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