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Sintering Behaviors and Microstructure of Apatite-based Materials under a High Magnetic Field

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Abstract : In the present study, the compactions of hydroxyapatite-based materials were fabricated by the *in-situ* process by the pressureless sintering method at 1273 ~1373 K for 2 h under a high magnetic field of 10 tesla. The microstructures of sintered bodies for these hydroxyapatite-based materials were evaluated. It was found that hydroxyapatite and hydroxyapatite with an additive fabricated by the *in-situ* process through the pressureless sintering method with a high magnetic field in an air atmosphere possessed higher relative density than ones by the normal process through the pressureless sintering method under 0 tesla. Also, the results of SEM observation indicated the significant grain growth for hydroxyapatite and hydroxyapatite with an additive prepared by the *in-situ* sintering process with a high magnetic field, compared to the samples prepared by the normal sintering process without a high magnetic field. The effect of a high magnetic field of 10 tesla on microstructure of hydroxyapatite and this hydroxyapatite-based ceramics was mainly investigated.
Key words: hydroxyapatite, additive, bioceramics, high magnetic field, in-situ sintering

1. INTRODUCTION

Sintering behaviors of inorganic materials, such as grain growth, and densification behaviors, are generally dependent on many factors, for example, temperature, pressure, and concentration etc [1]. Also, other factors in the electric, magnetic and maicrogravity fields is thought to be influenced to that grain growth and precipitation behaviors, which might often lead to the development of new material synthesis techniques [2]. For example, Yamashita et al reported the interesting results of the effect of electric poling on the acceleration and deceleration of bone-like crystal growth on hydroxyapatite and osteogenetic ability [3]. According to their results, the accelerated crystal growth of bone-like hydroxyapatite were observed on the negatively charged surface of various bio- and electro-ceramics [3]. Recently the results about magnetic fields effect on precipitation and crystal growth of metals were reported by some researchers, which might result in the development of novel material synthesis [4-5]. In addition, Yasuda et al reported the effect of a high magnetic field on the periodic microstructure formation in peritectic alloys and also refered to the possibility of magnetic processing using nonequilibrium microstructure for BiMn alloyes [6].

Here, the effect of a high magnetic field on the sintering behaviors of bioceramics, such as hydroxyapatite and its related calcium compounds, was evaluated for the development of high performance biomaterials. Hydroxyapatite is a main components of bone and teeth and considered to be one of biomaterial candidates as implants and bone fillers, because it possesses the good biocompatibility and the excellent biologically active properties [7-8]. Generaly, the bioactivity of hydroxyapatite depends on the presence of OH^- ions of its structures. Although the improvement of bioactivity of hydroxyapatite can be achieved by the inhibition of the decrease of OH^- on the microstructure of sintered hydroxyapatites, the deficiency of OH^- of sintered hydroxyapatites was imperative because of the dehydration on the hydroxyapatite sintered at high temperature [9]. Therefore, the sintering of hydroxyapatite at lower temperature is demanded to inhibit the deficiency of OH^- in hydroxyapatite structures for the developments of high bioactive bioceramics[10]. In this study, the possibility of densification of hydroxyapatites at lower sintering temperatures were confirmed using the *in-situ* process through the pressureless sintering method with a high magnetic field of 10 tesla (T). The purpose of this paper is to fabricate the hydroxyapatites bodies through *in-situ* process by pressureless sintering method under a high magnetic field of 10 T and evaluate their microstructure of the hydroxyapatites bodies prepared by *in-situ* process by pressureless sintering method under a high magnetic field of 10 T, compared to hydroxyapatites bodies prepared by a normal process through the pressureless sintering method with a magnetic field of 0 T.

2. EXPERIMENTAL PROCEDURES

In this experiment, hydroxyapatite and disodiuim hydrogenphosphaste ($Na_2HPO_4 \cdot 12H_2O$) as an additive were used as a starting material. Hydroxyapatite was rod-like with the average particle size of some hundreds nm. Their characteristic of hydroxyapatite powder is shown in Table 1. The powder of hydroxyapatite with 10wt% of $Na_2HPO_4 \cdot 12H_2O$ as an additive was mixed by a conventional ball milling method. Each compaction with the diameter of 20 mm and the thickness of 4 mm was prepared using the stainless mold and subsequently treated with a CIP equipment. The compacted bodies of hydroxyapatite and hydroxyapatite with $Na_2HPO_4 \cdot 12H_2O$ were set *in quartz tube and subsequently* fabricated by *in-situ* process by pressureless sintering method at 1273~ 1373 K under a high magnetic field of the 10 T order with using the experimental apparatus, in which the furnace was inserted into a room temperature bore of vertical type superconducting magnet [6]. For the comparison, the compactions of hydroxyapatite were heat-treated at 1273~ 1373 K for 2 hours in the air atmosphere through the normal process through the pressureless sintering method with the same furnace.

Table 1 Impurities of starting hydroxyapatite powder

Impurities (ppm)				
Cl	Fe	As	Mg	Mn
20	10	1	50	20

The density of hydroxyapatite with an additive and monolithic hydroxyapatite samples fabricated by the *in-situ* process through pressureless sintering method with a high magnetic field of the 14 T and by the normal sintering process without a high magnetic field was measured by the Archimedes method. The components of all sintered samples were identified by the X-ray diffraction method (XRD) with Cu-Kα radiation (Rigaku, RINT-2500). The microstructures of sintered bodies were observed by scanning electron microscopy (SEM) (Hitachi: S-800).

3. RESULTS AND DISCUSSION

XRD results of monolithic hydroxyapatites fabricated by the normal process through pressureless sintering method without a high magnetic field at 1273 and 1373 K showed that the components of their XRD patterns were identified as a hydroxyapatite from JCPDS and no other phases were observed. Hydroxyapatites bodies with Na_2HPO_4 sintered by the normal sintering techniquse with 0 T, at 1273 and 1373 K were composed of mainly hydroxyapatite without any other phase. On the contrary, hydroxyapatites bodies with Na_2HPO_4 sintered at 1273 K with 10 T had mainly hydroxyapatite and secondly β-TCP and little $NaCaPO_4$. Also, hydroxyapatites with Na_2HPO_4 sintered at 1373 K with 10 T were composed of mainly hydroxyapatite and partly β-TCP, and $NaCaPO_4$ and $Na_3Ca_6(PO_4)_5$.

The results of relative density of monolithic hydroxyapatite and hydroxyapatite with disodium hydrogenphosphaste as an additive fabricated by the *in-situ* process through pressureless sintering method with and without a high magnetic field of 10 T in air at 1273 to 1373 K for 2 h are shown in Fig.1. For monolithic hydroxyapatite, in the case of in-situ sintering under a high magnetic field of 10 T, relative densities were 83 % at 1273 K and 86 % at 1373 K, respectively. On the other hand, monolithic hydroxyapatite bodies sintered at 1273 K and 1373 K by the normal sintering process under 0 T showed 65 % and 75% of relative density, respectively. These results of density for monolithic hydroxyapatite prepared by normal sintering process are consistent with the previous results. In the case of Na_2HPO_4 addition into hydroxyapatite, samples fabricated by the *in-situ* process through pressureless sintering method with 10 T had 5 % higher relative densities, compared to ones by the normal sintering process without a high magnetic field at both 1273 and 1373 K. In this Na_2HPO_4 addition system as an additive, the formation of liquid phase was reported by Doi et al [11]. Obviously it was found that the *in-situ* process through pressureless sintering method with a high magnetic field of 10 T enhanced the densification of monolithic hydroxyapatite and hydroxyapatite with Na_2HPO_4 addition and obtained approximately 5 to 10 % higher relative density than the normal sintering process with 0 T at 1273 and 1373 K.

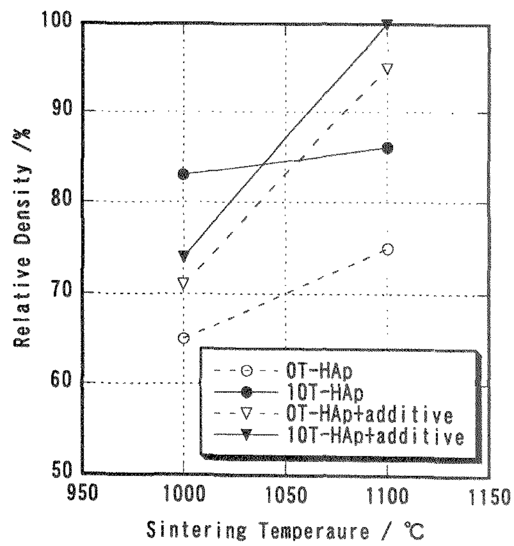


Fig.1 Relative density of monolithic hydroxyapatite and hydroxyapatite with disodium hydrogenphosphaste as an additive.

Fig.2 shows the SEM photographs of monolithic hydroxyapatite prepared by the *in-situ* process through pressureless sintering method with a high magnetic field of 10 T and normal sintering process under 0 T at 1373 K. SEM observation of monolithic hydroxyapatites sintered at 1373 K by normal sintering process under 0 T showed porous structures with the average grain size of approximately 0.5 μm. Monolithic hydroxyapatites prepared by the *in-situ* process through pressureless sintering method at 1373 K with 10 T showed more densified microstructures.

Hydroxyapatites bodies with Na_2HPO_4 prepared by the *in-situ* process through pressureless sintering method with a high magnetic field of 10 T and the normal sintering under 0 T are shown in Fig.3. Hydroxyapatites bodies with Na_2HPO_4 samples prepared by the normal sintering at 1373 K without a magnetic field showed the average grain size of 1 μm. However, hydroxyapatites samples fabricated by the *in-situ* process through pressureless sintering method with 10 T had densified microstructure with larger grain

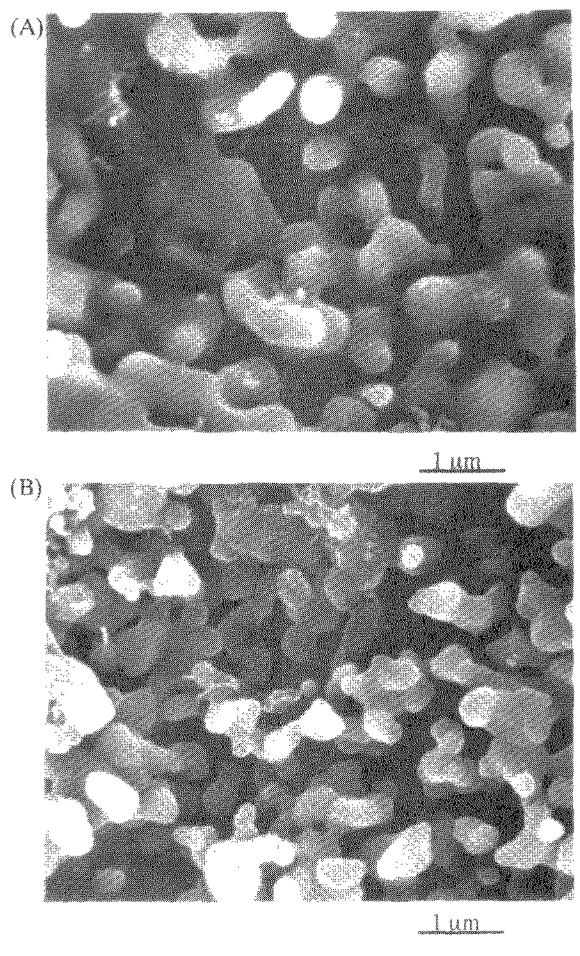
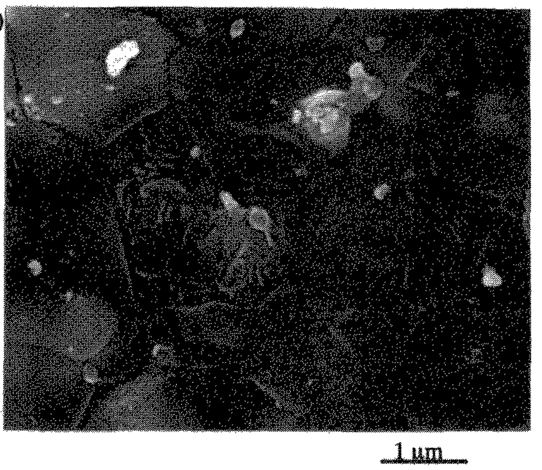


Fig.2 SEM photographs of monolithic sintered hydroxyapatites. (A) the *in-situ* process through pressureless sintering method with 10 T at 1373 K and (B) normal sintering process under 0 T at 1373 K.

(A)



(B)

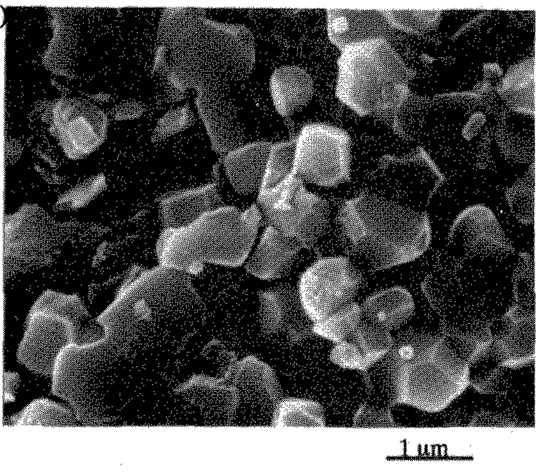


Fig.3 SEM photographs of sintered hydroxyapatite with Na_2HPO_4. (A) the *in-situ* process through pressureless sintering method with 10 T at 1373 K and (B) normal sintering process under 0 T at 1373 K.

size. From these observation, especially, hydroxyapatites bodies with Na_2HPO_4 prepared by the *in-situ* process through pressureless sintering method with 10 T had the coarser microstructure, compared to samples prepared by the normal sintering with 0 T. The enhancement of densification and grain growth of monolithic hydroxyapatite and hydroxyapatite with disodiuim hydrogenphosphaste as an additive on the *in-situ* process through pressureless sintering method with 10 T was confirmed, compared to hydroxyapatites bodies prepared by a normal process through the pressureless sintering method with a magnetic field of 0 T. Yasuda et al reported the effect of a high magnetic field on the periodic microstructure formation in peritectic alloys and also refered to the possibility of magnetic processing using nonequilibrium microstructure for BiMn alloyes and superconducting compounds [6]. It is known that on the crystal growth a high magnetic field inhibits the convection of a melt and the segregation was suppressed for both single crystal and polycrystal and could result in homogenious microstructure. It is reported that the growth of some materials could be influenced by the anisotropic diamagnetic susceptibility of the crystal [12]. This enhancement of densification and grain growth of monolithic hydroxyapatite and hydroxyapatite with disodiuim hydrogenphosphaste in the present study may be thought to be caused by the anisotropic diamagnetic susceptibility of hydroxyapatite.

4. SUMMARY

Hydroxyapatites-based materials bodies were fabricated by the *in-situ* process by pressureless sintering method under a high magnetic field of 10 T and the normal sintering process without a high magnetic field. For these monolithic hydroxyapatite and hydroxyapatite with disodiuim hydrogenphosphaste as an additive, their microstructures were evaluated by SEM observation. The enhancement of densification and grain growth of monolithic hydroxyapatite and hydroxyapatite with disodiuim hydrogenphosphaste as an additive on the *in-situ* process through pressureless sintering method with 10 T was found, compared to hydroxyapatites bodies prepared by a normal process through the pressureless sintering method with a magnetic field of 0 T. Thus, in this study, the possibility of densification of hydroxyapatites at lower sintering temperatures were confirmed using the *in-situ* process through the pressureless sintering method with a high magnetic field of 10 T.

References

[1]. Y. Chiang, D. Birnie, and W. D. Kingery, Physical Ceramics, John Wiley & Sons, Inc., 1997.
[2]. Y. Ikezoe, N. Hirota, J. Nakagawa, K. Kitazawa, Nature 393, 749-50(1998).
[3]. K. Yamashita, N. Oikawa, and T. Umegaki, Chem. Mater. 8, 2697-2702(1996).
[4]. T. Kakeshita, T. Takeuchi, T. Fukuda, T. Saburi, R. Oshima, S. Muto and K. Kishio, Mater. Trans., JIM Vol.41, pp.882-887(2000).
[5]. S. Asai, Proc. Intern. Congress on Electromagnetic of Materials, 1997, Paris, Vol.1,PP.5-12.
[6]. H. Yasuda, I. Ohnaka, Y. Furukubo, H.J. Koh, S.Tozawa, and T. Fukuda, Materials Trans., JIM, Vol.41, pp.1005-1012(2000).
[7]. E. S. Ahn, N. J. Gleason, A. Nakahira, and J. Y. Ying, Nano Letters, 1, 149-53 (2001).
[8]. A.Nakahira, M.Tamai, H. Aritani, S. Nakamura and K. Yamashita, J. Biomed. Mater. Res., 62, 550-557(2002).
[9]. A. Nakahira, M. Tamai, K. Eguchi, S. Nakamura, K. Yamashita, Bioceramics 15., 551-555(2002).
[10]. A. Nakahira and K. Eguchi, J. Ceramic Processing Res., 2[3], 1-7(2001)
[11]. Y. Doi, T. Koda, N. Wakamatsu, T. Coto, H. Kamemizu, Y. Moriwaki, M. Adachi, and Y. Suwa, J. Dent Res., 72, 1279-84(1993).
[12]. M. Iwasaka, M. Takeuchi, S. Ueno, and H. Tsuda, J. Appl. Phys., 83, 6453 -5(1998).

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