

Fabrication of dense β -wollastonite bioceramics by MgSiO_3 addition

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Highly dense β -wollastonite (CaSiO_3) with good mechanical property and bioactivity was fabricated by pressureless sintering at 1250 ~ 1300 °C and phase transition of α to β -wollastonite with MgSiO_3 . Starting pure α -wollastonite powder were prepared by solid state reaction, and MgSiO_3 powder was added to α -wollastonite powder to induce the phase transition α to β -wollastonite over 1250 °C. Sintered wollastonite at 1250 °C with 5 and 10 wt% MgSiO_3 were $\alpha + \beta$ phase and β phase respectively, and showed higher densification rate than that of α or β -wollastonite, which are almost the same as the theoretical density. Hardness and Young's modulus of sintered wollastonite were dependent on the apparent density and the amount of β -wollastonite. Young's modulus (78 GPa) of β -wollastonite added 10 wt% MgSiO_3 was almost double time of sintered α -wollastonite. From the *in-vitro* test, β -wollastonite shows lower bioactivity in SBF solution and better mechanical property than α -wollastonite, and biphasic ($\alpha + \beta$) wollastonite with 5 wt% MgSiO_3 had good bioactivity in simulated body fluid solution.

Key words: β -wollastonite, High density, MgSiO_3 , Phase transition, Biocompatibility.

Introduction

Bioactive materials were defined as one that elicits a specific biological response at the interface of the material which results in the formation of a bond between the tissue and the materials [1]. Various kinds of ceramics have been studied as bioactive ceramics, which include 45S5 bioglass, hydroxyapatite (HA) and apatite-wollastonite glass ceramics (noted by A-W GC), etc [2-4]. Most of bioactive materials make a HA layer grow on their surfaces when put in simulated body fluid (SBF) or human body, which provides strong bonding with surrounding bones. Monophase bioactive ceramics, such as Bioglass® type glasses and sintered HA shows good bioactivity, but have poor mechanical properties than that of the human cortical bones. To enhance the poor mechanical properties of bioactive ceramics, Kokubo et al. fabricated A-W GC by the crystallization process of glass in 1982 [5]. The A-W GC is a bioactive glass-ceramic and consists of apatite (38 wt%), β -wollastonite (34 wt%) and glassy phases (28 wt%). Due to the high bending strength compared with HA and cortical bone, the A-W GC commercially called "Cerabone A-W" has been used in spine and hip surgery since 1983. In the A-W GC, β -wollastonite (β - CaSiO_3) consisting of chain structure was used as the reinforcing phase.

Besides the purpose for reinforcing the poor

mechanical properties in bioactive ceramics and glass ceramics, one of the reasons that wollastonite ceramics have drawn attention as bioactive ceramics, is the important role of Ca and Si ions in the formation mechanism of bone-like HA layer in SBF or human bodies. It has been widely known that Ca and P ions which are the main components of bones and hard tissues in mammals play an important role in bioactivity of materials [6, 7]. Recently, it was demonstrated by Ohura [8] and De Aza [9] that materials, which consist of Ca and Si ions and which are free of P ion, can also produce HA layer on the surface of bioactive materials. That is, the Ca ion dissolved from glass ceramics increases the ion activity product of the apatite in SBF, and hydrated silica provides favorable sites for apatite nucleation. Once the apatite nuclei are rapidly formed, they spontaneously grow by consuming Ca and P ions from SBF solution. Therefore many P-free CaO-SiO_2 based bioactive ceramics such as diopside ($\text{CaMgSi}_2\text{O}_6$), bredigite ($\text{Ca}_7\text{Mg}(\text{SiO}_4)_4$) and α -wollastonite, have been studied [10-12]. These P-free CaO-SiO_2 based bioactive ceramics induce apatite formation in SBF solution, closely bond to bone tissue when implanted, and show no toxicity in cell test. Among these materials, various forms of wollastonite ceramics (which include composite with other bioactive materials, for examples, bioeutectic, α -wollastonite + α -TCP) [13], coating material on the Ti-Al substrate [14] and reinforcing phase of A-W GC as previously stated have been widely studied for biomedical applications [4].

It is well known that the wollastonite has two main phases, i.e. α and β . β -wollastonite (wollastonite-2M; the low temperature phase of CaSiO_3) is stable below

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1125 °C, and it transforms into α -wollastonite (pseudowollastonite; the high temperature phase of CaSiO_3) above 1125 °C. α -wollastonite can be fully-densified at temperatures over 1300 °C [15-17], but it is hard to obtain the pure β -wollastonite ceramics with high density because it is transformed into α -phase over 1125 °C, in which the temperature is too much lower to obtain full densification rate. So, it was difficult to compare the bioactivity and mechanical properties of sintered α - and β -wollastonite ceramics directly, because β -wollastonite shows poor densification rate on sintering below the β to α transformation temperature. Fortunately, β -wollastonite ceramic has a solid solution with diopside ($\text{CaMgSi}_2\text{O}_6$) ceramic and it shifts the transformation temperature of β to α from 1125 to 1350 °C [18]. So, dense β -wollastonite with Mg solid solution can be prepared by the sintering at high temperature over 1200 °C.

Mg-containing calcium silicates have also revealed attractive results from the point of view of their bioactivity and biocompatibility [19, 20]. From the results of *in vitro* and *in vivo* experiments, these materials have been shown to promote cell adhesion, proliferation, spreading, and differentiation [21, 22]. Mg can substitute easily for Ca site, because two atoms have same valence, and the atomic radius of Mg ion is smaller than that of Ca ion [23]. It was recently reported that the Mg ion plays positive effects on the mechanical strength and sintering process of bioactive calcium phosphate ceramics, especially tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$, TCP) [24, 25]. TCP is also a bioactive and biodegradable material, and has polymorphs like wollastonite: β , α , α' . β -TCP phase is stable below 1125 °C, α -TCP phase is stable from 1125 °C to 1430 °C, and α' -TCP phase becomes the stable phase above 1430 °C [26]. β -TCP has been investigated intensively as a bioactive bone graft material because α -TCP has a problem of rapid degradation in SBF. Studies on Mg-doped TCP reported that cell volume of the β -TCP structure decreases with increasing Mg ion contents, and Mg substituted for Ca sites. The sintering of Mg-containing TCP can be performed at much higher temperatures than the phase transition temperature without undergoing the β to α phase transformation [25].

Wollastonite bioactive ceramic is one of the promising bioactive materials due to its outstanding bioactivity [12, 27-30], however, the mechanical properties of the wollastonite ceramics are not satisfied because of its low density and high resorption or high dissolution rate. The relative densities of the sintered β -wollastonite and α -wollastonite reported up to date are below 90% and the low bending strengths (≥ 70 MPa) [31-34]. Difficulties in preparing dense wollastonite ceramic with improved mechanical properties might limit its potential application as bioactive implants [35]. Rapid resorption rate of α - or β -wollastonite ceramics is not ideal in the experiment of *in vitro* or *in vivo* [36, 37], which might

result in the loss of mechanical support during the early stage of bone regeneration. By the previous study showed that the Mg content in bioactive calcium silicate ceramics plays an important role in determining their dissolution, and the dissolution rate of the ceramics can be tailored by adjusting the Mg content [38]. The dissolution rate of calcium silicate bioceramics decrease with Mg content.

Given the biological relevance of magnesium, many research teams have worked on the preparation of apatite and calcium phosphate implant materials containing low levels of Mg, which has been shown to improve their bioactivity [39, 40]. In practice, magnesium is an important trace element in bone and teeth. Indeed, despite its low concentration (generally between 0.5 and 1.5 wt%), it plays a key role in bone metabolism, in particular during the early stages of osteogenesis where it stimulates osteoblast proliferation [41].

So we suggested that highly dense β -wollastonite ceramics with MgSiO_3 should have good properties in the biological and mechanical aspects. By the phase diagram between wollastonite and enstatite, highly dense β -wollastonite ceramics can be fabricated by MgSiO_3 addition and sintering at high temperature above 1200 °C [18, 42, 43]. β -wollastonite have a solid solution up to 22 wt% of diopside, and phase transition temperature of β to α -wollastonite increases with diopside mole fraction from 1150 °C to 1363 °C.

In this study, we were tried to fabricate the fully densified β -wollastonite ceramics with high bioactivity and low dissolution rate by solid state reaction at sintering temperature above 1200 °C and investigated the effect of MgSiO_3 addition on the β -phase formation during sintering. And then, the bioactivity, sintering and mechanical properties of dense β -wollastonite were also studied and compared each other.

Experimental

Pure α - and β -wollastonite were synthesized by a conventional solid state reaction. The starting materials were highly pure CaCO_3 (99.99%, high purity chemical, Japan) and SiO_2 (99.99%, high purity chemical, Japan) to avoid impurity and to produce materials suitable for biomedical use. CaCO_3 and SiO_2 powders were prepared by 1 : 1 molar ratio, mixed and ball-milled in an ethanol media using zirconia balls for 24 hours. Two powder mixtures were prepared. One was calcined at 1300 °C for 3 hours, and the other at 1050 °C for 48 h in platinum crucible. The calcined powders were pure α - and β -wollastonite phases, respectively from the powder X-ray diffractometry (XRD, M18XHF, Mac Science instruments, Japan; 50 kV, 100 mA). The resulting powders were pulverized again in polyethylene bottle with ethanol media for 24 hours. α -wollastonite powder was mixed with different amounts of MgSiO_3 powder (5 and 10 wt%). MgSiO_3 powder was used instead of

MgO powder in order to maintain $\text{Ca}_x\text{Mg}_{1-x}/\text{Si}$ ratio in the wollastonite. Mixed powders were ball-milled in an ethanol media using zirconia balls for 24 hours. The samples with 5 and 10 wt% MgSiO_3 were named W5MS and W10MS, respectively. Samples prepared from pure β -wollastonite were prepared in order to investigate the effect of the β to α phase transition on the densification and sintering properties. The samples prepared from pure α - and β -wollastonite powders are called α W and β W samples, respectively.

The powder was uniaxially pressed at 10 MPa into pellet shape 8 mm in diameter before being isostatically pressed at 100 MPa. Pressed pellets were placed on Pt plate and sintered at temperature range of 1000 °C to 1300 °C with a heating rate of 5 °C/min for 2 hours and slowly cooled to room temperature by shutting off the current to investigate the effect of MgSiO_3 addition on the phase formation and the sintering behavior of wollastonite ceramics. To investigate the formation of second phases which are not shown in XRD pattern, the samples were examined by Raman spectrometry (T64000, HORIBA Jobin Yvon, France).

The shrinkage of the specimens during heating was measured using a horizontal-loading dilatometer with Al_2O_3 rams and boats (DIL 420C, Netzsch Instruments, Germany). Crystalline phases of the sintered specimens were identified by powder XRD. The bulk densities of the sintered specimens were measured using Archimedes' principle, in ethanol media and vacuum to prevent from hydration of samples. Polished and thermally etched (1200 °C for 30 min) surfaces of sintered specimens were examined using scanning electron microscopy (SEM: JSM 5600, JEOL Co., Japan). Hardness and Young's modulus of pure α , β -wollastonite, W5MS and W10MS samples were measured by Vickers micro hardness testing (AIS 3000, Frontics, Korea) with a load of 5N. 12 measurements were carried out for each specimen.

In-vitro bioactivity of specimens was observed by soaking the WMS samples in SBF solution, and the formation of the HA layer on the surfaces of samples was examined. The SBF solution has ion concentration nearly equal to those of human blood plasma. The mirror-polished samples were soaked in the SBF solution at 36.5 °C for different periods of 1, 3, 7 days. The changes in surface were examined by XRD (incident angle of X-ray was fixed to $1\theta^\text{TM}$ to collect diffracted intensities from thin top layer of the samples) and SEM.

Results and Discussion

Phase analysis

Fig. 1 shows XRD data of α W, β W and WMS samples sintered at 1200 and 1250 °C for 2 hours. After sintering at 1200 °C and 1250 °C, α W and β W samples can be identified as the α -phase. W5MS sample with 5 wt% MgSiO_3 consists of mixture of α -

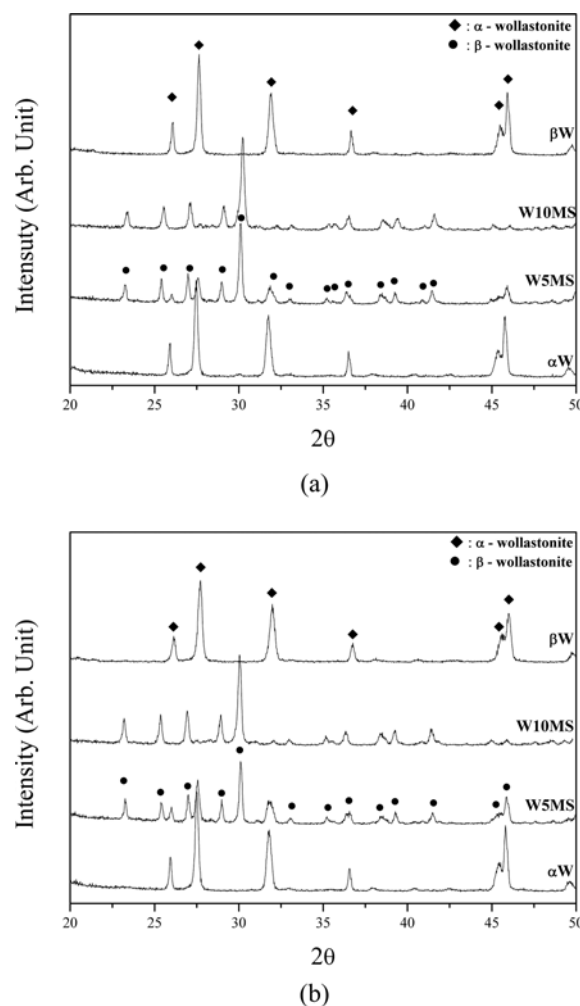


Fig. 1. XRD patterns of α W, β W (starting material is β -wollastonite phase), WMS (α -wollastonite + MgSiO_3) sintered at (a) 1200, (b) 1250 °C for 2 hours.

and β -phase, W10MS sample 10 wt% MgSiO_3 can be identified as pure β -phase. But in the case of sintering at 1300 °C, β -phase is not observed in both of WMS sample, and α phase is the main phase with a small amount of diopside phase.

It was reported that the phase transition temperature of wollastonite is 1125 °C [17]. It was found that pure α -wollastonite is not transformed into β -phase by heat treatment (that is β to α phase transition is irreversible by only heat treatment), while α -wollastonite can be transformed into β phase with Mg addition from our results. W10MS sample was sintered in temperature range of 1000 ~ 1300 °C with intervals of 50 °C. It was found from XRD results of W10MS sample (Fig. 2) that it consisted of α -wollastonite and diopside when sintered at 1000 ~ 1100 °C and β -wollastonite when sintered at temperatures higher than 1150 °C. By the previous experiment, the presence of Mg is solid solution in wollastonite ($\text{Ca}_{1-x}\text{Mg}_x\text{SiO}_3$; $0 \leq x \leq 0.17$) shifts the transition temperature from 1125 °C to 1350 °C [42]. Therefore, the β -phase in W10MS sample was formed by solid solution between α -

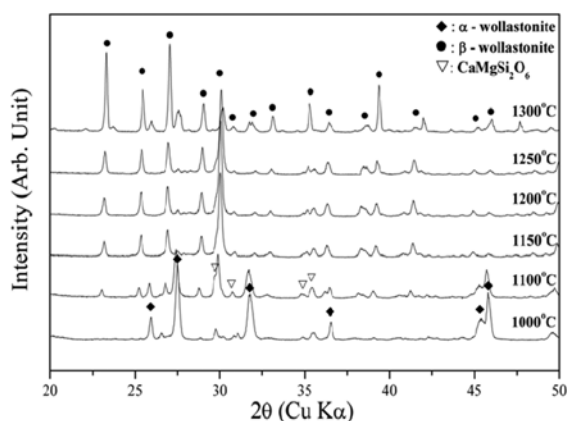


Fig. 2 XRD patterns of W10MS ceramic (α -wollastonite + 10 wt% MgSiO_3) sintered at 1000 ~ 1300 °C for 2 hours.

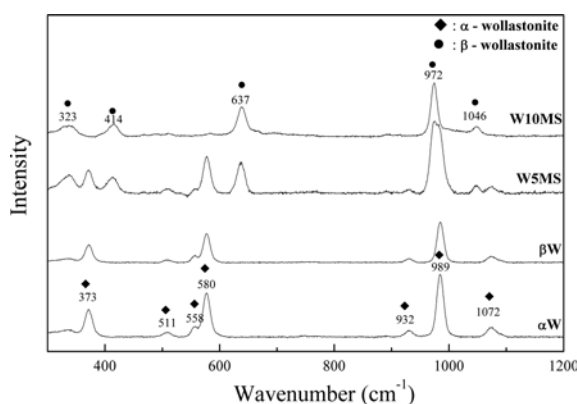


Fig. 3 Raman spectra of α W, β W, W5MS and W10MS sintered at 1250 °C for 2 hours.

wollastonite and diopside above 1150 °C after the compounding of diopside between α -wollastonite and enstatite below 1000 °C.

As the amount of MgSiO_3 addition to pure α -wollastonite increases, the phases observed at 1250 °C change as follows; pure α -wollastonite $\rightarrow$ solid solution of α -wollastonite and β -wollastonite $\rightarrow$ pure β -wollastonite $\rightarrow$ solid solution of β -wollastonite and diopside, which is consistent with the information from the phase diagram of wollastonite-diopside system [18, 42].

Raman spectrometer can be used to investigate the phase evolution and to identify the presence of minor phases which are difficult to identify in the XRD pattern. Moreover probing short-range order, Raman spectroscopy has been known to be a more sensitive technique than XRD which can be used to detect minute structural changes [43]. The results from Raman spectroscopy of samples sintered at 1250 °C reveals the phase present in WMS samples, but not the phase evolution. Fig. 3 shows a diagram of a Raman spectroscopy of α W, β W, W5MS and W10MS samples sintered at 1250 °C. α W sample sintered at 1250 °C shows strong bands at 989, 580, 373 cm^{-1} which correspond to α -wollastonite [44], and β W sample

sintered at the same temperature also shows peak distribution similar to that of α W without any second phases. This means that β W sample which was prepared from pure β -wollastonite, had been entirely transformed into α phase at 1250 °C. Similar to XRD data, W10MS sample shows β -wollastonite peak distribution [44] (which is also called natural wollastonite) which has strong bands at 972 and 637 cm^{-1} . It can be clearly observed that W10MS sample maintains β phase at 1250 °C from Raman spectroscopy. On the other hand, it can be confirmed by the overlapped peaks near 980 cm^{-1} that W5MS sample contains both α and β phases at 1250 °C. Shrinkage behavior of samples was analyzed in order to investigate the effect of delayed phase transition from β to α phase by MgSiO_3 addition on the sintering behavior.

Densification and microstructure

The densification behavior of α W, β W, W5MS and W10MS samples are shown in Fig. 4. A drastic change in the slope of the curve of β W sample was found at about 1150 °C, but the curves of α W, WMS samples were smooth without a drastic change. This means that β to α phase transition occurs in β W sample at about 1125 which is the phase transition temperature in the phase diagram [17]. In addition, the shrinkage ratio of W5MS and W10MS samples is about 23%, and those of β W and α W samples are about 17%. W5MS and W10MS ceramics start to shrink at temperature of 800 °C which is lower than that of pure α -wollastonite ($\approx$ 1000 °C).

In case of β W sample, the drastic change of shrinkage curve and small shrinkage ratio can be caused by phase transition from β - to α -wollastonite at about 1125 °C. Once β to α phase transition occurs, it induces the lattice volume expansion during phase transition and it may be affected to the densification rate of wollastonite. On the other hand, in case of WMS samples, added MgSiO_3 can play a role of flux material in the wollastonite structure, which can reduce the starting temperature for shrinkage of sintered body compared to pure α -wollastonite. Sintering with flux

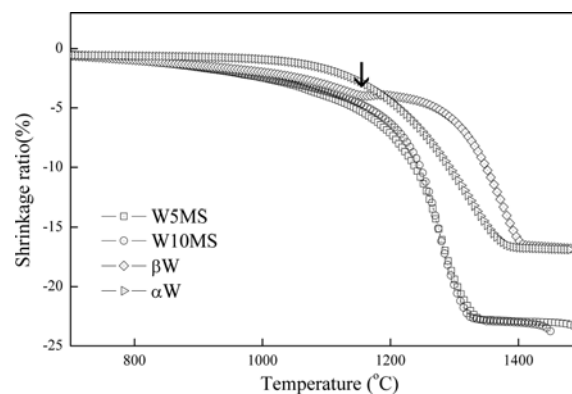


Fig. 4 Shrinkage ratio of α W, β W, W5MS and W10MS as a function of temperature.

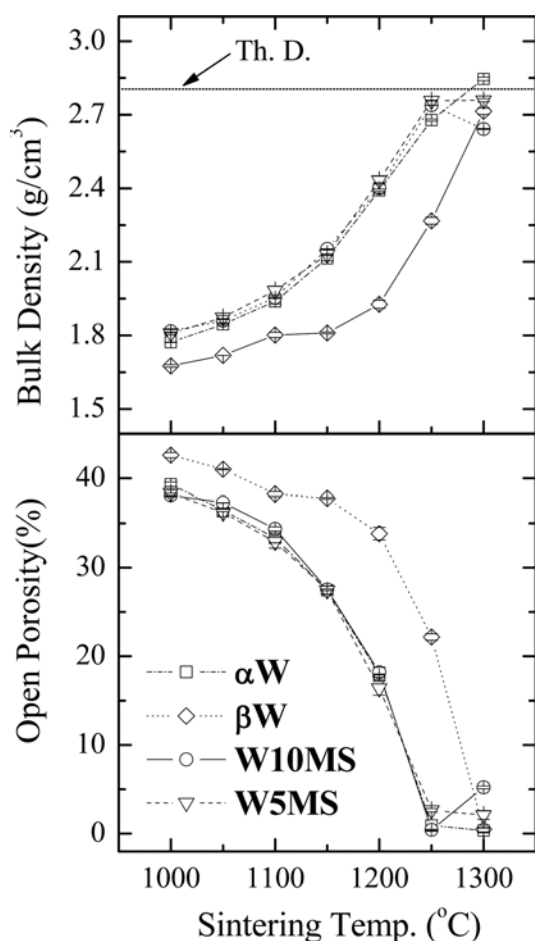


Fig. 5. Open porosity and apparent density of α W, β W, W5MS, and W10MS after sintered at various temperature.

material has been widely used to obtain the high densification rate in low temperature with additional advantages such as simple control of size and morphology [45, 46]. It is clear from the dilatometric study that sintered β -wollastonite ceramics from starting α -wollastonite powder with Mg addition has higher densification rate than that of α W or β W samples due to the suppression of phase transition by Mg addition.

Fig. 5 shows apparent densities and open porosities of α W, β W, W5MS and W10MS samples sintered at various temperatures. At 1250 °C, WMS samples have higher sintered density and lower open porosity than those of β W sample. Open porosity of W5MS sample is about 2.6%, but that of W10MS sample is nearly 0%. At 1250 °C, α W, W5MS and W10MS samples reach almost full densification rate, which density are almost the same as the theoretical density of CaSiO_3 , but β W sample shows the slightly low apparent density and the high open porosity. It means that wollastonite solid solution by Mg addition has an effect on the prevention of the β to α phase transition and continues the driving force for densification to high temperature and produces fully dense β -wollastonite ceramics.

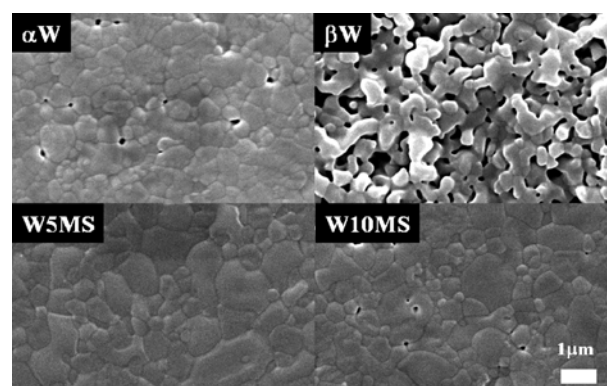


Fig. 6. Microstructures of α W, β W, W5MS and W10MS sintered at 1250 °C for 2 hours.

Fig. 6 shows SEM images of α W, β W, W5MS and W10MS samples sintered at 1250 °C. W5MS, W10MS, α W samples show dense microstructures, while many pores were observed on the surface of β W sample. As previously discussed in density and dilatometric experimental results, it means that β W sample was not fully densified at 1250 °C. Full densification rate and dense microstructure were obtained in W5MS, W10MS and α W samples sintered at 1250 °C. Also, large grain rounded by many of small grains was observed in WMS samples compared to that of α W sample. Compared with the microstructure of α W sample, it was seen that WMS samples have the positive effects for densification by the α to β -phase transition and solid solution between wollastonite and diopside during heat treatment.

Hardness and Young's modulus

The hardness values of α W, β W, W5MS and W10MS samples are listed in Table 1, which is directly dependent on the sintered density. The values of hardness in α W and β W samples which had relatively low density are lower values of about 114 and 121, respectively. On the other hand, highly densified W5MS sample which was composed of α and β -phases, shows higher hardness value of about 180. The highest hardness value is about 310 in W10MS sample which is nearly three times higher than that of α W sample. It is suggested that high hardness of W10MS sample is caused by dense microstructure and β -phase composition.

Table 1. Mechanical properties of α W, β W, W5MS and W10MS sintered at 1250 °C.

Sample	Vickers hardness	Young's modulus (GPa)	Phase
α W	114 ± 12	40 ± 3	α -phase
β W	121 ± 5	26 ± 1	α -phase
W5MS	180 ± 23	39 ± 3	α -phase + β -phase
W10MS	310 ± 24	78 ± 4	β -phase

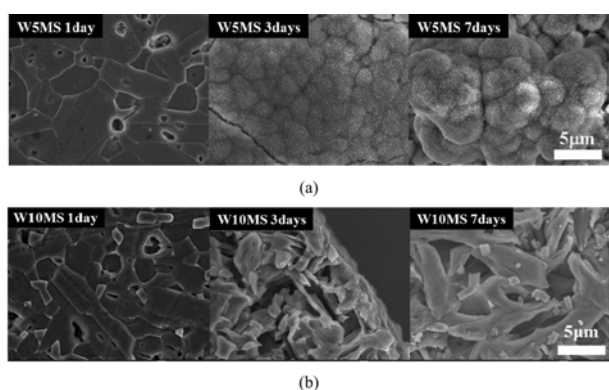


Fig. 7. Microstructures on the surfaces of W5MS (a) and W10MS (b) soaked in SBF solution for 1 day, 3 days, and 7 days.

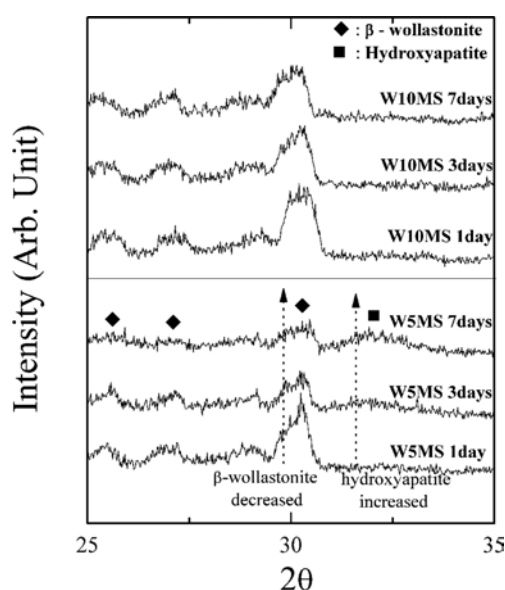


Fig. 8. XRD patterns of the W5MS and W10MS soaked in SBF solution for 1, 3, and 7 days. Incident angle of X-ray was fixed to 1° to collect diffracted intensities from thin top layer of the samples.

The value of Young's modulus in W10MS sample is 78 GPa which is almost double time than that of α W or W5MS sample. It has similar density to that of W5MS, but it composed of β -phase only. So it was seen that the obtainment of only β -phase might be improved the mechanical properties (hardness and young's modulus) of wollastonite.

Bioactivity

To investigate the bioactivity of MgSiO_3 added wollastonite ceramics, W5MS and W10MS samples sintered at 1250°C were soaked in SBF for 1, 3, and 7 days. Fig. 7 (a) shows the microstructural change on the surface of W5MS samples during soaking in SBF solution. After 1 day soaking, grains started to dissolve, which leads to the formation of rough surface, and there was no HA-like layer observed on the surface of W5MS sample. But HA-like layer, after 3 days, covered the surface of the sample, which was fully

covered with HA-like layers after 7 days. Fig. 7 (b) is SEM images of surfaces of W10MS after soaking in SBF solution after 1, 3 and 7 days, respectively. More detached grains on the surface were observed in W10MS than W5MS sample after 1 day soaking in SBF solution. There was no HA-like layer observed on the surface of W10MS specimen even after 7 days of soaking, which is different from the result of W5MS where most surfaces were covered by HA-like layer after 3 days of soaking. The presence of HA-like layer on the surface of W5MS was verified by XRD (Fig. 8). The amount of HA phase increased, and that of β -wollastonite decreased with soaking time in W5MS. In W10MS, however, no trace of HA phase could be found from XRD data, and the intensity of β -wollastonite peak ($2\theta \approx 30^\circ$) remained constant when soaking time was stretched.

HA-like layer on the surface of WMS samples by soaking in SBF solution was formed by the dissolution of wollastonite and after the precipitation of HA crystallite on the specimen surface. Therefore, the velocity of HA-like layer formation is dependent on the solubility of wollastonite phase. According to previous report¹⁸, the solubility limit of wollastonite in SBF at 37°C solution is set at $\sim 3.4 \times 10^{-5} \text{ g/l}$ for α -wollastonite, at $\sim 1.9 \times 10^{-5} \text{ g/l}$ for β -wollastonite ceramics. In the case of short immersion time in SBF solution, the formation of HA-like layer on the surface can be affected by the solubility limit of wollastonite phase, but both of wollastonite phases have good formability of HA-like layer on the specimen surface after soaking over 2 weeks in SBS solution. In our study, better formability of HA-like layer on the W5MS sample after soaking 1 week than that of W10MS sample was mainly due to the solubility difference between α and β -phases. But it is interesting to note that less solubility of β -wollastonite is suitable to sustain a good biostability in SBF solution or in body.

Conclusions

Highly densified β -wollastonite ceramics was fabricated by MgSiO_3 addition and α to β -phase transition during sintering. The phase transition of β to α -wollastonite ceramics at temperature range 1125°C to 1300°C was suppressed by MgSiO_3 addition. β -wollastonite ceramics with near theoretical density were prepared by the addition of 5 ~ 10 wt% MgSiO_3 and sintering at 1250°C for 2 hours, which shows higher densification rate and lower open porosity than those of pure α - or β -wollastonite which were sintered at the same temperature. Additionally, we found that β -wollastonite shows lower bioactivity in SBF solution from in vitro test and better mechanical property than α -wollastonite. Also, fully densified biphasic wollastonite ceramics composed of α and β phases could be fabricated by the control of

MgSiO₃ content which is added to starting wollastonite powder.

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