

Fabrication and Characterization of Hydroxyapatite/Mullite and Tricalcium Phosphate/ Al_2O_3 Composites Containing 30 wt% of Bioactive Components

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ABSTRACT

Mullite-matrix and Al_2O_3 -matrix composites were fabricated with 30 wt% hydroxyapatite (HA) and tricalcium phosphate (TCP), respectively, as additives to give bioactivity. A diphasic gel process was employed to lower the densification temperature of the mullite matrix to 1320°C. A polymer complexation process was used to synthesize a TCP powder that was fully densified at 1250°C, for application to the matrix. For the HA/mullite composite, HA decomposed during sintering by reactions with the matrix components of Al_2O_3 and SiO_2 , resulting in a mixture of Al_2O_3 , TCP, and other minor phases with a low densification of less than 88% of the theoretical density (TD). In contrast, the TCP/ Al_2O_3 composite was highly densified by sintering at 1350°C to 96%TD with no reaction between the components. Different from the TCP monolith, the TCP/ Al_2O_3 composite also showed a fine microstructure and intergranular fracture, both of which characteristics are advantageous for strength and fracture toughness.

Key words : *Hydroxyapatite, Mullite, Tricalcium phosphate, Al_2O_3 , Composites*

1. Introduction

Hydroxyapatite (HA) and tricalcium phosphate (TCP) are chemically similar to the inorganic components of bones and teeth, and so their bioactivity is excellent. Hence they can react with biological tissues for direct bonding, which makes them very suitable materials as hard tissue substitutes. Particularly, TCP can be used as a scaffold for bone regeneration due to its bioresorbable property. However, sintered bodies of these materials are so low in strength that they are only limitedly used in orthopedic and dental fields, which require a high load-bearing capability.¹⁾

Therefore, previous studies have focused on improving the mechanical properties of these materials, mainly through a conventional composite approach. That is, a mechanically strong material like Al_2O_3 ,²⁻⁶⁾ ZrO_2 ,⁷⁻⁹⁾ or mullite¹⁰⁾ is added to the bioactive materials as reinforcement. In this approach, however, HA partly decomposes to TCP during sintering and this lowers the mechanical properties.^{4,8,9)} On the other hand, the mixture of HA and TCP resulting from the decomposition is called BCP (biphasic calcium phosphate) and this material has a positive aspect in that it can be a bioresorbable bone substitute.¹¹⁾

Another approach to making a strong bioactive material is to incorporate HA or TCP into strong materials as an additive to impart bioactivity.¹²⁻¹⁵⁾ Shen *et al.*¹²⁾ fabricated 10 - 50 vol% HA/ ZrO_2 composites using pressure-aided spark plasma sintering (1150°C, 5 min, 50 MPa)

to avoid HA decomposition. Fully densified composites were obtained with strength of 439 - 657 MPa (3-p bending) and fracture toughness of 2.5 - 4.2 $\text{MPa}\cdot\text{m}^{1/2}$ (Vickers indentation). Kong *et al.*¹³⁾ synthesized a ZrO_2 -20 wt% Al_2O_3 (ZA) nanocomposite powder using the Pechini process and used the powder to fabricate 10 - 40 vol% HA/ZA composites by hot pressing (1400°C, 30 MPa, 1 h). HA decomposed by reacting with ZrO_2 , and BCP formed as a result. The density was close to the theoretical value with 10 vol% HA but decreased for higher levels of HA. The strength also decreased with the content and reached 720 MPa (4-p bending) for 30 vol% HA. The composition was considered to be optimal for load-bearing biological applications because of its sufficient bioactivity, which was confirmed by in vitro tests, and also because of its high strength. Sakka *et al.*¹⁴⁾ fabricated 25 wt% TCP/ Al_2O_3 composites by sintering (1550°C, 2 h) and obtained a density of 64%TD and a strength of 8.6 MPa (Brazilian test). In another study,¹⁵⁾ the same researchers made 10 - 50 wt% TCP/ Al_2O_3 composites by sintering (1400-1600°C, 30 - 90 min) and reported that the optimum result was obtained with 10 wt% TCP with a strength of 13.5 MPa (Brazilian test); however, no density data was presented.

The objective of the present study is to fabricate 30 wt% HA/mullite and 30 wt% TCP/ Al_2O_3 composites, following the latter approach using HA and TCP as bioactive additives. The reason for choosing the figure of 30 wt% is that this amount was found through cell proliferation rate measurements to be enough to impart bioactivity in the HA/ZA composites.¹³⁾ Previously, the HA matrix was reinforced with mullite¹⁰⁾; however, no study has been done in the reverse direction. Sintering temperatures of commercial mullite powders are usually as high as 1700°C.¹⁶⁾ Hence, it is very important to reduce the sintering temperature of the mullite-matrix composite containing HA in order to suppress the decomposition of HA, which occurs significantly above 1300°C.¹⁰⁾ In the present study, as a solution to this issue, a

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mullite powder for the matrix was prepared using a diphasic gel process,¹⁷⁾ and thereby an attempt was made to reduce the sintering temperature of the HA/mullite composite to nearly 1300°C. In the diphasic gel process, retarded mullite crystallization enhances densification through viscous-phase sintering. In the case of the TCP-added Al_2O_3 composite, the previous study¹⁴⁾ obtained a very low sintered density of 64%TD, and this seems to have caused the low strength. In addition, the sintered density of TCP alone was only 78%TD, suggesting a very low sinterability of the TCP powder that presumably caused the low sintered density of the composite. In the present study, a highly sinterable TCP powder was synthesized using a polymer complexation process¹⁸⁾; this powder was used to fabricate the composite. In the process, polymer molecules with long chains adhere to the metal ions or sol particles in solution to form organic/inorganic complexation. This not only inhibits segregation or precipitation of the ions and particles but also reduces their tendency to agglomerate. In addition, the polymers can be an internal heat source via combustion during heat treatment. As a result, pure and fine ceramic powders can be obtained at a low temperature.¹⁸⁾ Densification behavior of the TCP/ Al_2O_3 composite was investigated and compared with densification using a commercial TCP powder.

2. Experimental Procedure

2.1. Preparation of mullite powder and sintering of mullite and HA powders

In order to prepare the mullite matrix powder via the diphasic gel process¹⁷⁾ (hereafter named SGM), a boehmite powder (AlOOH ; 80 wt% Al_2O_3 , 30 nm; Dispal 11N7-80, Sasol, Germany) and a SiO_2 sol (30 wt% SiO_2 , 10 - 20 nm; Silifog 45AK, Ace Nanochem, South Korea) were used as starting materials for Al_2O_3 and SiO_2 . First, the boehmite powder was weighed to make 6 wt% solid content and added to distilled water with stirring to prepare a boehmite sol. Then, the SiO_2 sol was added according to the stoichiometric ratio to form mullite, and the mixed sols were stirred with heating until gelling. The gel was dried at 60°C and ground into powder using an alumina mortar. In order to determine the material's densification behavior, disc specimens 13 mm in diameter were uniaxially compacted at 116 MPa and sintered at 1320°C for 1 h. HA powder (3 μm ; HA-10, Sun-koo, South Korea) was used as the bioactive additive for the composite. To determine the densification behavior, bar specimens (35 × 8 mm) were isostatically compacted at 200 MPa and sintered at 1200-1300°C for 1 h.

2.2. Synthesis and sintering of TCP powder

In the synthesis of the TCP powder using the polymer complexation process,¹⁸⁾ calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, reagent grade, Junsei, Japan) and phosphoric acid (H_3PO_4 , 85%, reagent grade, Samjeon, South Korea) were used as the sources of Ca and P. PVA (MW 146000-186000, 87-89% hydrolyzed, Aldrich, USA) was used as the polymer for complexation. First, the calcium nitrate and phosphoric acid were dissolved in deionized water. The amount of phosphoric acid used was 20 wt% excess over the stoichiometric level for TCP, because some portion of phosphoric acid evaporates during the subsequent drying step.¹⁸⁾ The PVA, in a 5 wt% aqueous solution, was

added to the solution with adjustment such that the proportion of the negative charges of the OH functional groups from PVA to the positive charges from Ca and P ions was 1 to 4.¹⁸⁾ Stirring the resulting solution with heating for 4 h led to a gel precursor for TCP. After drying, the precursor was ground, calcined at 1000°C for 1 h, and then ball-milled with isopropyl alcohol for 12 h to obtain the TCP powder (hereafter named TCP-S). In order to determine the densification behavior, disc specimens (13 mm diameter) were uniaxially compacted at 36 MPa and sintered at 1200 and 1250°C for 1 h each. For comparison, the commercial TCP powder (Sigma-Aldrich, USA; hereafter named TCP-P) was compacted as above and sintered at 1200-1400°C for 1 h.

2.3. Fabrication of composites

In the fabrication of the 30 wt% HA/mullite composites (hereafter named HMC), an SGM sol was used rather than the SGM powder because the sol to powder process can provide more uniform mixing than can the powder to powder process. First, as described before, a mullite sol was prepared with the boehmite powder and the SiO_2 sol. Also, an HA slurry (solid content 50 wt%) was prepared by dispersing the HA powder in water with a dispersant. The mullite sol and the HA slurry were mixed by stirring and then heated on a hot plate to obtain a concentrate. The concentrated mixture was dried at 60°C and ground using an alumina mortar to give an HMC powder. Disc specimens (13 mm diameter) were uniaxially compacted with the powder at 116 MPa and sintered at 1320°C for 1 h.

To fabricate 30 wt% TCP/ Al_2O_3 composites (hereafter named TAC), the TCP-S powder and an Al_2O_3 powder (AKP-53, Sumitomo Chemical, Japan) were weighed and ball-milled with isopropyl alcohol for 12 h. Then, after removing the solvent by stirring on a hot plate, the resulting mixture was completely dried at 60°C in an oven. Using an alumina mortar, the dried mixture was ground into a powder. Then, disc specimens (13 mm diameter) were uniaxially compacted with the powder at 36 MPa and sintered at 1350°C for 2 h. The same procedure was also performed with the TCP-P powder to make TAC samples for comparison.

2.4. Characterization

The densities of the sintered samples were measured by the Archimedes method. Phases and microstructures of the powder and sintered samples were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

3. Results and Discussion

3.1. HMC (30 wt% HA/mullite composites)

3.1.1. Densification and phase of raw materials

First, experiments to determine the sintering conditions were performed on the HA and SGM powders. The optimum conditions were found to be 1200°C/1h for HA and 1320°C/1h for SGM, which had sintered densities of 99% and 95%TDs, respectively. Figs. 1 and 2 show the XRD results of the samples before and after sintering. HA retained the initial HA phase well after sintering, while SGM, comprised of boehmite (AlOOH) and amorphous SiO_2 before sintering, changed completely to mullite phase.

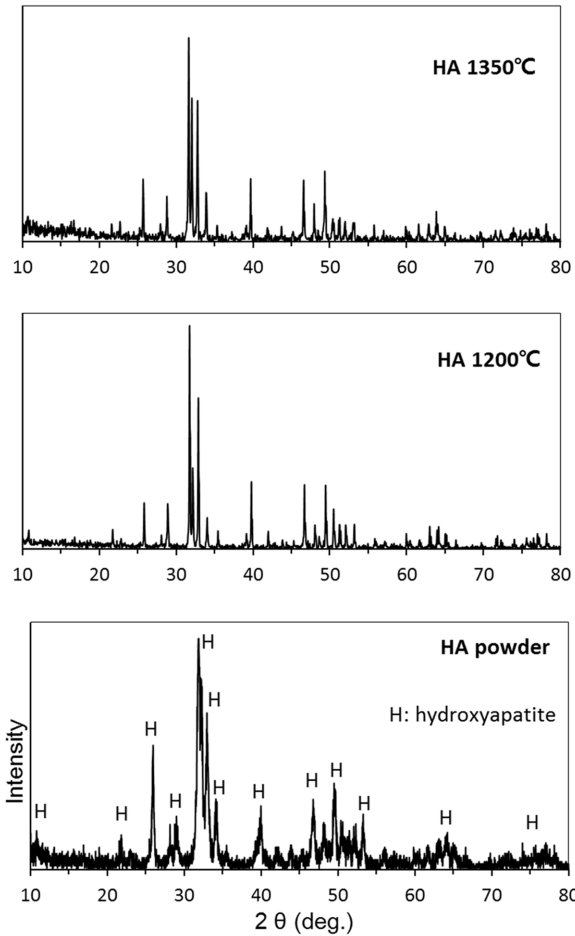


Fig. 1. XRD patterns of HA powder, HA sintered at 1200°C, and HA sintered at 1350°C.

3.1.2. Densification, microstructure, and phase of composites

The sintered density of HMC, fabricated using the same conditions as were used for SGM, was 88%TD. It was expected that the sintered density would be at least higher than that of SGM, but it was in fact much lower. Fig. 3 provides the SEM results for the etched surface of HMC. It can be seen that the microstructure was not dense, having large pores with sizes of 5-30 μm and small pores between the grains. This is consistent with the low sintered density.

Figure 4 shows the XRD results for HMC, indicating the presence of no mullite or HA phases, which is different from the expectation. Namely, Al_2O_3 was the major phase, along with minor phases such as TCP, tridymite, quartz, gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$), and CaO. Therefore, the low sintered density was considered to be due to HA decomposition. The density of 88%TD mentioned before is a relative density determined from the nominal theoretical density, stemming from the supposition that HMC consists of HA (TD 3.16 g/cm^3) and mullite (TD 3.17 g/cm^3) phases. This is because the exact amounts of the phases actually present could not be determined. Al_2O_3 , whose theoretical density (3.98 g/cm^3) is higher than that of mullite (3.17 g/cm^3), was the major phase; the other phases, except for CaO (3.35 g/cm^3), have lower theoretical densities than those of HA and mullite. Hence,

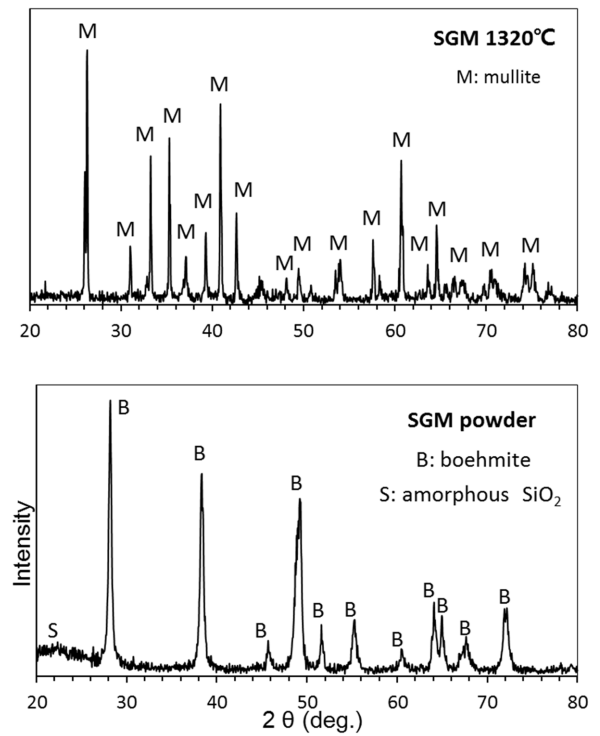


Fig. 2. XRD patterns of SGM powder and SGM sintered at 1320°C.

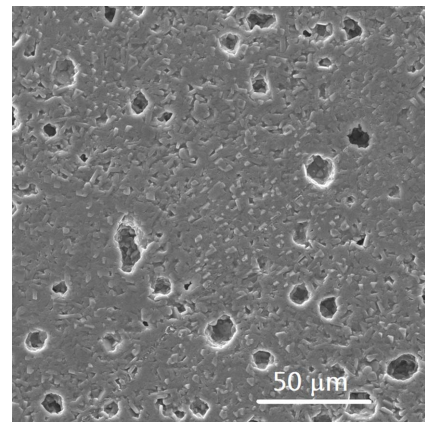


Fig. 3. SEM micrograph of the etched surface of HMC sintered at 1320°C.

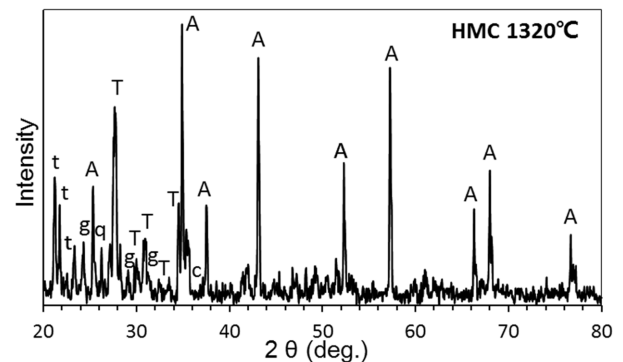


Fig. 4. XRD pattern of HMC sintered at 1320°C. The notations A, T, t, q, g, and c indicate Al_2O_3 , TCP, tridymite, quartz, gehlenite, and CaO, respectively.

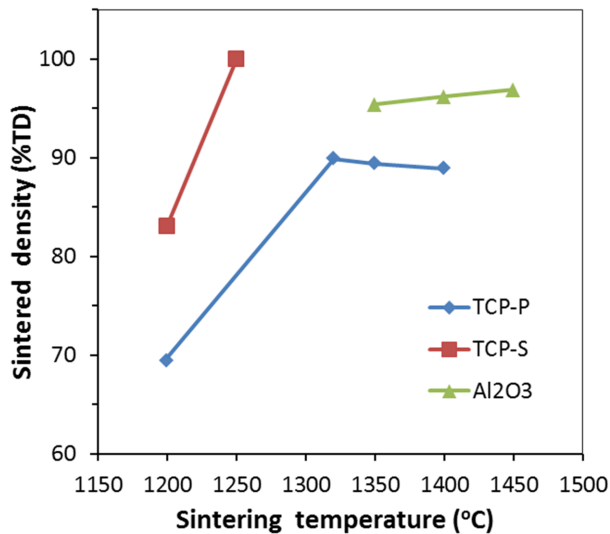
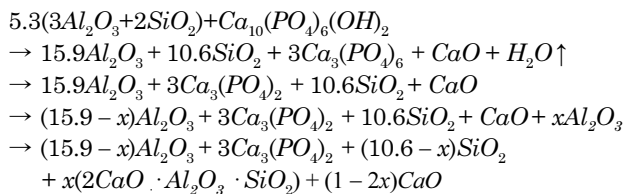


Fig. 5. Sintered densities for TCP-P, TCP-S, and Al_2O_3 powders at various temperatures.

both Al_2O_3 and CaO decrease the relative density, while the other materials increase it. Due to this offset effect, the actual relative density of the composite is presumably close to that determined from the nominal theoretical density. In the case of the HA monolith, HA phase was retained well even after sintering at 1350°C (Fig. 1). This suggests that the absence of HA phase in the composite sample was not due to the decomposition of HA itself but due to the decomposition induced by its reactions with Al_2O_3 and SiO_2 in SGM powder. The previous report¹⁰ also showed that in HA composites reinforced with 20 and 30 wt% mullite, HA decomposition occurs at a temperature much lower than that at which it occurs in the HA monolith. Based on the XRD results, possible chemical reactions involved in the sintering can be written as follows; in all reactions, the coefficients were determined by converting the weight percentages of HA and mullite to mole ratios:



3.2. TAC (30 wt% TCP/ Al_2O_3 composites)

3.2.1. Densification, microstructure, and phase of raw materials

Figure 5 shows the sintering results for TCP-P, TCP-S, and Al_2O_3 powders, performed first to determine the sintering temperature of TAC. In the case of TCP-P, the density reached its highest value of 89.9%TD at 1320°C and then decreased slightly with increase of the temperature to 1350°C and 1400°C . In contrast, TCP-S exhibited density values of 83.1% and 100%TDs at 1200 and 1250°C , respectively, indicating that its sinterability was superior to that of TCP-P. The Al_2O_3 powder showed a value of 95.4 - 97%TDs in the range of 1350 - 1450°C . Fig. 6 shows the SEM results for the TCP-P and TCP-

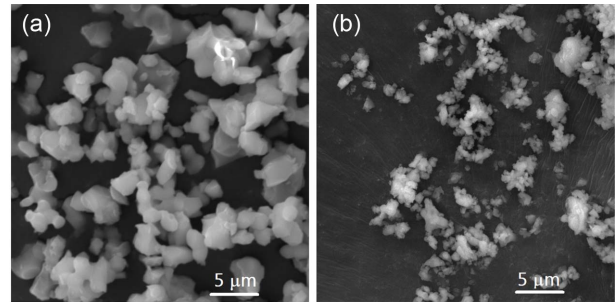


Fig. 6. SEM micrographs of (a) TCP-P and (b) TCP-S powders.

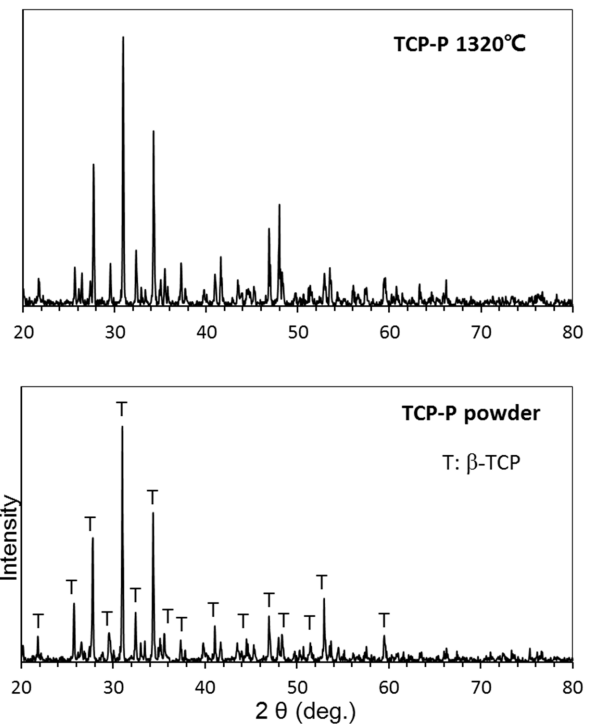


Fig. 7. XRD patterns of TCP-P powder and TCP-P sintered at 1320°C .

S powders. The average particle sizes were about 3 - 5 μm for TCP-P and 0.5 μm or less for TCP-S. Thus it can be seen that the outstanding sinterability of TCP-S should be attributed to the fine particle size. Figs. 7 and 8 show the XRD results for TCP-P and TCP-S, respectively, before and after sintering. TCP-P retained the initial β -TCP phase even after sintering. TCP-S exhibited only TCP phase after sintering, although a small amount of $\text{Ca}_2\text{P}_2\text{O}_7$ existed along with TCP in the calcined state before sintering.

3.2.2. Densification, phase, and microstructure of composites

The sintering condition of $1350^\circ\text{C}/2\text{ h}$ was used to fabricate TACs with TCP-P and TCP-S powders. These conditions were chosen because it was thought that they would simultaneously lead to considerable densification of the Al_2O_3 matrix, inhibition of the $\beta \rightarrow \alpha$ phase transition of the TCP, and maximum densification of the composites. The sintered density of TAC obtained with TCP-P was only 73.8%TD. In contrast, a much higher density of 96.2%TD was

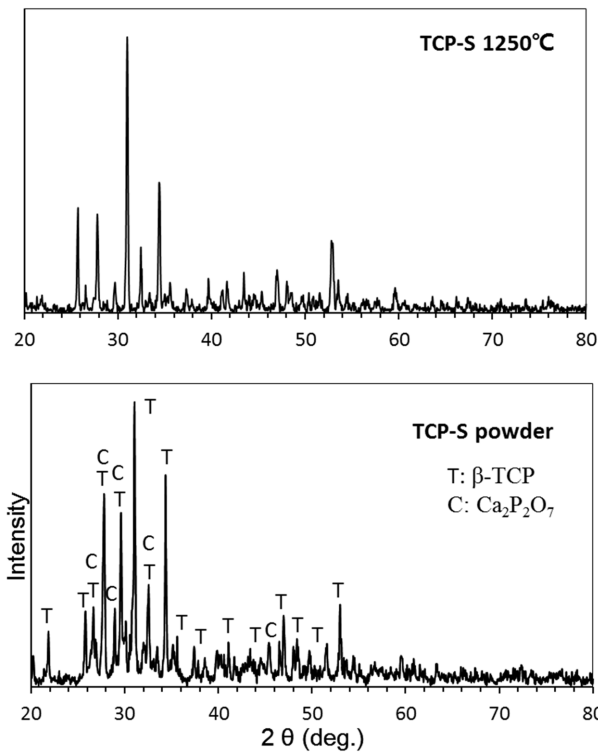


Fig. 8. XRD patterns of TCP-S powder and TCP-S sintered at 1250°C.

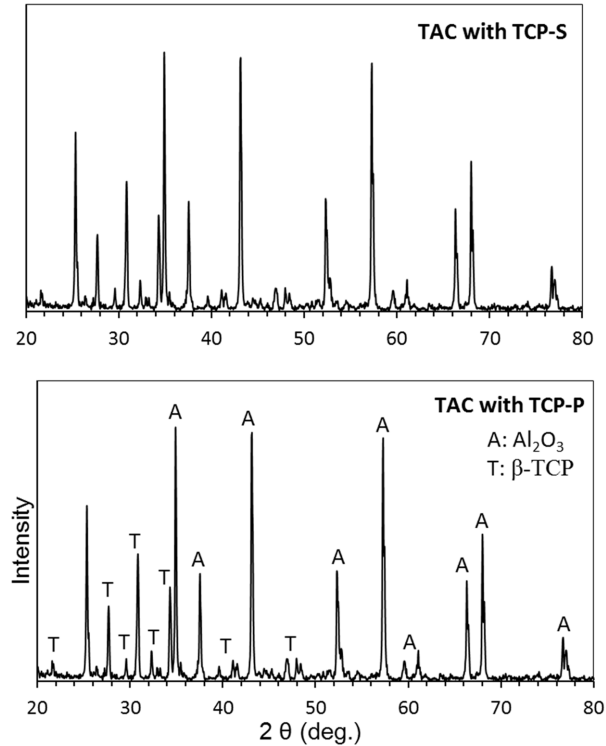


Fig. 9. XRD patterns of TACs sintered at 1350°C, prepared with TCP-P and TCP-S powders.

obtained with TCP-S. This indicates that the high sinterability of TCP-S, as mentioned earlier, also played a significant role in the densification of the composite. Fig. 9 shows the XRD results for the TACs fabricated with the two powders. It can be seen that both consisted of only Al_2O_3 and TCP phases, without any reaction, as intended. Fig. 10 shows SEM results comparing the fracture surfaces of the TCP-S sintered sample and the TAC fabricated with TCP-S powder. The TCP-S was fully densified, with almost no pores. The TAC was densified properly with a grain size ($2.5 \mu\text{m} \geq$) finer than that of the TCP-S ($5 \mu\text{m} \leq$). It can also be seen that the fracture modes were transgranular for TCP-S but intergranular for TAC. Intergranular fracture is advantageous for the fracture toughness because it involves a larger area of fracture surface and thus more fracture energy consumed than is the case for transgranular fracture.^{19,20} Therefore the strength and fracture toughness of TAC are expected to be high, and these characteristics will be investigated in a future work.

4. Conclusions

Fabrication of mullite and Al_2O_3 composites containing 30 wt% HA and TCP, respectively, as additives to impart bioactivity was attempted. To achieve this goal, the densification temperature of the mullite matrix was lowered to 1320°C and a TCP powder that was fully densified at 1250°C was synthesized and applied. For the HA/mullite composite, HA decomposed by reacting with the matrix components during sintering, so that no proper densification occurred, with no HA or mullite phases. On the contrary, for the TCP/ Al_2O_3

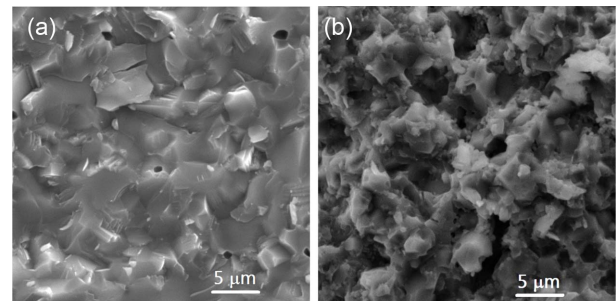


Fig. 10. SEM micrographs of the fracture surfaces of (a) TCP-S sintered at 1250°C and (b) TAC fabricated with TCP-S powder at 1350°C.

composite, a high densification was obtained without any reaction between the components at 1350°C. This composite also showed a fine microstructure and intergranular fracture, both of which characteristics are advantageous for strength and fracture toughness. Future work is necessary to evaluate the mechanical properties.

Acknowledgments

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REFERENCES

1. W. Suchanek and M. Yoshimura, "Processing and Properties of Hydroxyapatite-based Biomaterials for Use as a

- Hard Tissue Replacement Implants," *J. Mater. Res.*, **13** [1] 94-117 (1998).
2. H. Y. Juang and M. H. Hon, "Fabrication and Mechanical Properties of Hydroxyapatite-alumina Composites," *Mater. Sci. Eng. C*, **2** 77-81 (1994).
 3. J. Li, B. B. Fartash, and L. Hermansson, "Hydroxyapatite-alumina Composites and Bone-bonding," *Biomaterials*, **16** 417-22 (1995).
 4. S. Gautier, E. Champion, and D. B. Assollant, "Processing, Microstructure and Toughness of Al_2O_3 Platelet-reinforced Hydroxyapatite," *J. Eur. Ceram. Soc.*, **17** 1361-69 (1997).
 5. B. Viswanath and N. Ravishankar, "Interfacial Reactions in Hydroxyapatite/Alumina Nanocomposites," *Scripta Mater.*, **55** 863-66 (2006).
 6. Y. X. Pang, X. Bao, and L. Weng, "Preparation of Tricalcium Phosphate/Alumina Composite Nanoparticles and Self-reinforcing Composites by Simultaneous Precipitation," *J. Mater. Sci.*, **39** 6311-23 (2004).
 7. E. Adolfsson, P. Alberius-Henning, and L. Hermansson, "Phase Analysis and Thermal Stability of Hot Isostatically Pressed Zirconia-hydroxyapatite Composites," *J. Am. Ceram. Soc.*, **83** 2798-802 (2000).
 8. R. R. Rao and T. S. Kannan, "Synthesis and Sintering of Hydroxyapatite-zirconia Composites," *Mater. Sci. Eng. C*, **20** 187-93 (2002).
 9. V. V. Silva, F. S. Lamerias, and R. Z. Dominguez, "Microstructural and Mechanical Study of Zirconia-hydroxyapatite (ZH) Composite Ceramics for Biomedical Applications," *Compos. Sci. Technol.*, **61** 301-10 (2001).
 10. S. Nath, K. Biswas, K. Wang, R. K. Bordia, and B. Basu, "Sintering, Phase Stability, and Properties of Calcium Phosphate-mullite Composites," *J. Am. Ceram. Soc.*, **93** [6] 1639-49 (2010).
 11. I. Manjubala and M. Sivakumar, "In-situ Synthesis of Biphasic Calcium Phosphate Ceramics Using Microwave Irradiation," *Mater. Chem. Phys.*, **71** 272-78 (2001).
 12. Z. Shen, E. Adolfsson, M. Nygren, L. Gao, H. Kawaoka, and K. Nihara, "Dense Hydroxyapatite Composites with High Strength for Biological Applications," *Adv. Mater.*, **13** [3] 214-16 (2001).
 13. Y. -M. Kong, C. -J. Bae, S. -H. Lee, H. -W. Kim, and H. -E. Kim, "Improvement in Biocompatibility of ZrO_2 - Al_2O_3 Nano-composite by Addition of HA," *Biomaterials*, **26** 509-17 (2005).
 14. S. Sakka, F. B. Ayed, and J. Bouaziz, "Mechanical Properties of Tricalcium Phosphate-alumina Composites," *IOP Conference Series: Mater. Sci. Eng.*, **28** [1] 012028 (2012).
 15. S. Sakka, J. Bouaziz, and F. B. Ayed, "Mechanical Properties of Biomaterials Based on Calcium Phosphates and Bioinert Oxides for Applications in Biomedicine," pp. 23-50 in *Advances in Biomaterials Science and Biomedical Applications*. Ed. by R. Pignatello, INTECH, 2013.
 16. A. Priya, S. Nath, K. Biswas, and B. Basu, "In Vitro Dissolution of Calcium Phosphate-mullite Composite in Simulated Body Fluid," *J. Mater. Sci.: Mater. Med.*, **21** 1817-28 (2010).
 17. J. -S. Ha and K. K. Chawla, "The Effect of Precursor Characteristics on the Crystallization and Densification of Diphasic Mullite Gels," *Ceram. Int.*, **19** 299-305 (1993).
 18. S. -J. Lee, S. -I. Ko, M. -H. Lee, and N. -S. Oh, "Fabrication of Nano-sized β -TCP Powder by an Organic-inorganic Solution Route," *J. Ceram. Proc. Res.*, **8** [4] 281-84 (2007).
 19. H. -J. Kleebe, G. Pezzotti, and G. Ziegler, "Microstructure and Fracture Toughness of Si_3N_4 Ceramics: Combined Roles of Grain Morphology and Secondary Phase Chemistry," *J. Am. Ceram. Soc.*, **82** [7] 1857-67 (1999).
 20. J. H. She and K. Ueno, "Effect of Additive Content on Liquid-phase Sintering on Silicon Carbide Ceramics," *Mater. Res. Bull.*, **34** [10/11] 1629-36 (1999).