Comparison of Microstructural and Mechanical Properties of Hydroxyapatite-Al$_2$O$_3$ Composites with Commercial Inert Glass (CIG) Addition

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Hydroxyapatite (HA) is one of the most widely used biomaterials for orthopedic and dental applications. However, HA is a brittle and weak material and this constrains its orthopedic applications. There are several methods for the improvement of mechanical properties of the HA. One of these methods is to strengthen the HA material by a secondary phase (i.e polymer, metal or ceramics), to make a stronger composite material. Alumina (Al$_2$O$_3$) is a bioinert material, which has been widely investigated as a reinforcing agent for HA. The aim of this study is to compare the microstructural and mechanical properties of HA-Al$_2$O$_3$ composites with the addition of 5 and 10 wt.% of commercial inert glass (CIG). The grain samples were produced according to BS 7253 at 350 MPa. Then, they were sintered at temperatures between 1000–1300 °C for 4 hours. The samples were also analyzed by SEM + EDS to determine microstructural properties, phase analysis was done by X-ray diffractometer (XRD), mechanical properties were measured by compression and hardness tests. Results show that HA-Al$_2$O$_3$ composites with addition of 5 and 10 wt.% CIG have reached high density values and high mechanical properties, such as compression strength and hardness at 1300 °C. The compression strength and hardness of composites has increased with the increasing CIG content.

1. Introduction

Hydroxyapatite is a kind of calcium phosphate that has generated a great interest as an advanced orthopedic and dental implant candidate [1, 2]. Although HA has excellent biocompatibility, its poor mechanical properties limit its use as an implant material [1, 3]. There have been many investigations aimed on the improvement of mechanical properties. The way of improving mechanical properties is to make composite materials [4]. The goal for development of such materials has been to achieve a combination of properties not achievable by any of the elemental materials acting alone [5].

Alumina, which is also classified as a bioinert material, has been widely investigated as a reinforcing agent for HA [6]. Alumina (Al$_2$O$_3$) has been used in orthopedic applications due to its excellent wear resistance, high hardness and high abrasion resistance [7, 8]. Bioactive glasses and glass ceramics are highly bioactive biomaterials due to formation of a strong bonding between them and the neighboring bone [5, 8]. The glass ceramic has superior mechanical properties, good biocompatibility, bioactivity and no toxicity, making it useful as a biomaterial in artificial bone and dental implants [8].

There are some studies that have worked on HA-Al$_2$O$_3$ and HA-CIG composites. Ayed et al. [7] had studied sintering of tricalcium phosphate-fluorapatite (TCP-Fap) composites with addition of alumina. In that study, the effect of alumina addition on the densification of TCP-Fap composites were reported. The TCP-Fap composites' apparent porosity of about 13% was reached without alumina. With the addition of alumina, the composites' apparent porosity was decreased and mechanical properties were enhanced. Xihua et al. [1] had studied fabrication of hydroxyapatite/alumina/diopside composites. These ceramic composites were fabricated by hot pressing and the diopside was composed of SiO$_2$, CaO and MgO. In that study, the addition of alumina provided an increase in mechanical properties. Demirkol et al. [4] had studied influence of commercial inert glass (CIG) addition (5 and 10 wt.%) on the mechanical properties of commercial synthetic HA (CSHA). The mechanical properties of composites have decreased with the increasing CIG content. The highest mechanical properties and the highest density were obtained in CSHA-5 wt.% CIG composites sintered at 1300 °C.

2. Materials and methods

2.1. Materials

Commercial synthetic hydroxyapatite (Acros Org.,BE) was used as the major material. Alumina (α-corundum) (Seranit Org,TR) and commercial inert glass (CIG) were

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selected as additives. The CIG, obtained from conventional window glass, has the same chemical composition as the one in Demirkol's et al. study [4]. The HA-Al$_2$O$_3$ (90 wt.% HA, 10 wt.% Al$_2$O$_3$) powders were mixed for 24 h and then the powders were separately mixed with 5 and 10 wt.% of CIG powders for 4 h using ball milling. The powders were pressed at 350 MPa and the pressed samples were sintered at 1000, 1100, 1200, 1300 °C for 4h (+5 °C min^{-1}).

2.2. Mechanical properties

Density, Vickers microhardness, and compression strength tests were performed consequently. The hardness measurements of the samples were done using Vickers microhardness testing system (HMV Shimadzu, JP), 200 g load for 15 s. The compression tests were performed using Universal Testing machine (Shimadzu, JP) at a crosshead speed of 3 mm/min.

2.3. Characterization techniques

X-ray diffraction (XRD) analysis was carried out using a Brucker D8-Advanced X-ray diffractometer with Cu K$_\alpha$ radiation. Scanning electron microscopy (SEM) (Jeol JSM-5910 LV–Low Vacuum Scanning) and energy dispersive spectroscopy (EDX) (Oxford Inca Energy 200) were used to characterize the microstructure of the composites.

3. Results and discussion

Table I summarizes density and porosity data of composites sintered at different temperatures. The highest density was obtained in HA-Al$_2$O$_3$-10 wt% CIG composite, sintered at 1300 °C.

TABLE I
Density and porosity values of HA-Al$_2$O$_3$-CIG (5 and 10 wt.%) composites sintered at different temperatures.

Temper. [°C]	Density [g/cm^3]		Porosity [%]	
	5 wt.%	10 wt.%	5 wt.%	10 wt.%
1000	1.79 ± 0.04	1.79 ± 0.03	40.9 ± 1.5	37.96 ± 0.8
1100	1.79 ± 0.01	1.83 ± 0.02	40.0 ± 0.2	37.5 ± 0.83
1200	1.87 ± 0.04	2.05 ± 0.083	37.9 ± 1.4	31.6 ± 1.24
1300	2.31 ± 0.050	2.47 ± 0.02	19.10 ± 2.8	5.49 ± 0.940

Table II summarizes product phases obtained in XRD diagrams for HA-Al$_2$O$_3$-CIG (5 and 10 wt.%) composites, sintered at 1000 and 1300 °C. Both composites sintered at 1000 °C include hydroxyapatite (HA), alumina (Al$_2$O$_3$) and whitlockite (beta-tricalcium phosphate) (W). HA-Al$_2$O$_3$-5 wt.% CIG composite sintered at 1300 °C includes hydroxyapatite (HA), alumina (Al$_2$O$_3$), whitlockite (beta-tricalcium phosphate) (W) and gehlenite (Ca2A$_{l2}$Si$_{O7}$). HA-Al$_2$O$_3$-10 wt.% CIG composite, sintered at 1300 °C, showed sodium calcium silicate (SC-Si) phase, in addition to the phases mentioned above.

Figure 1 presents the microstructure and EDS analysis of composites sintered at 1000 and 1300 °C. When Fig. 1a

TABLE II
Phases obtained in XRD diagrams of HA-Al$_2$O$_3$-CIG (5 and 10 wt.%) composites, sintered at different temperatures.

	1000 °C	1300 °C
HA-Al$_2$O$_3$-5 wt.% CIG	1) Ca$_{10}$(PO$_4$)$_6$(OH)$_2$(HA) 2) Al$_2$O$_3$(alpha-corundum) 3) Ca$_3$(PO$_4$)$_2$(W)	1) Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ 2) Al$_2$O$_3$ 3) Ca$_3$(PO$_4$)$_2$ 4) Ca$_2$Al$_2$SiO$_7$(Gehlenite)
HA-Al$_2$O$_3$-10 wt.% CIG	1) Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ 2) Al$_2$O$_3$ 3) Ca$_3$(PO$_4$)$_2$	1) Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ 2) Al$_2$O$_3$ 3) Ca$_3$(PO$_4$)$_2$ 4) Ca$_2$Al$_2$SiO$_7$ 5) Na$_2$CaSiO$_4$(SC-Si)

is compared with Fig. 1c, grain growth, which occurred with increasing sintering temperature, is evident. When Fig. 1a is compared with Fig. 1b, it is also evident that composite's porosity has decreased and a more compact microstructure occurred with the increasing CIG content.
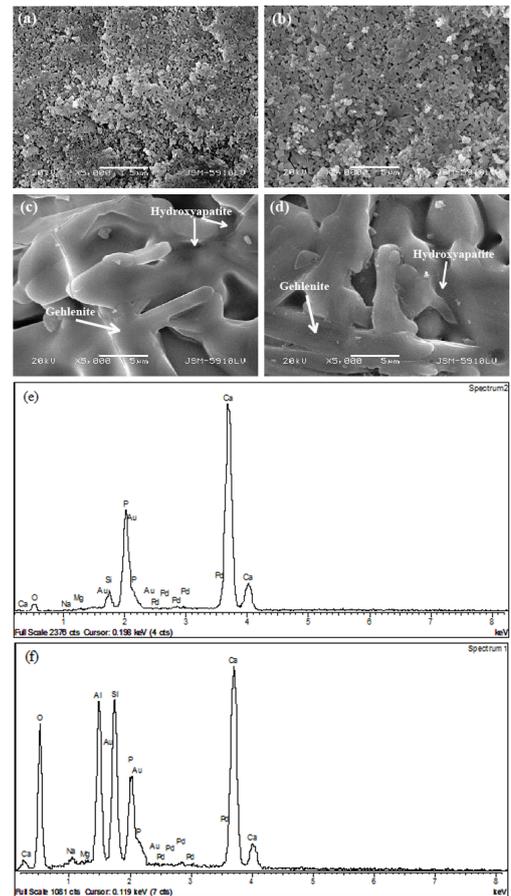

Fig. 1. (a) Microstructures of HA-Al$_2$O$_3$-5 wt.% CIG at 1000 °C, (b) microstructures of HA-Al$_2$O$_3$-10 wt.% CIG at 1000 °C, (c) microstructures of HA-Al$_2$O$_3$-5 wt.% CIG at 1300 °C, (d) microstructures of HA-Al$_2$O$_3$-10 wt.% CIG at 1300 °C, (e) EDS analysis results of hydroxyapatite phase, (f) EDS analysis results of gehlenite phase.

Table III summarizes the experimental results of compression strength and Vickers microhardness of the samples sintered at different temperatures. The highest compression strength and Vickers microhardness values were obtained in HA-Al$_2$O$_3$-10 wt.% CIG composite, sintered at 1300 °C.

Compression strength and microhardness of HA-Al$_2$O$_3$-CIG (5 and 10 wt.%) composites sintered at different temperatures.

TABLE III

Temp. [°C]	Compression Strength [MPa]		Vickers Microhardness [HV]	
	5 wt.%	10 wt.%	5 wt.%	10 wt.%
1000	32.13 ± 8.66	40.58 ± 11.90	43.06 ± 13.14	39.73 ± 2.68
1100	34.64 ± 10.18	42.78 ± 6.81	31.2 ± 6.03	30.84 ± 3.59
1200	36.21 ± 9.47	43.55 ± 2.69	29.47 ± 4.43	36.90 ± 3.46
1300	47.34 ± 14.08	53.82 ± 16.25	56.76 ± 1.86	129.36 ± 9.8

HA-Al$_2$O$_3$ composites with additions of 5 and 10 wt.% CIG have reached high density and low porosity values with the increasing sintering temperature. Grain size has also increased with increasing sintering temperature. According to the results, the measured mechanical properties of composites have increased with the increasing CIG content. In the HA-Al$_2$O$_3$-10 wt.% CIG composite, a glassy phase (SC-Si) has formed above 1200 °C, which has caused an increase in hardness and strength values (129.36 HV, 53.82 MPa).

4. Conclusions

The findings of this study are summarized as follows:
The highest density, the lowest porosity and the highest Vickers microhardness and compression strength values were obtained in HA-Al$_2$O$_3$-10 wt.% CIG composites sintered at 1300 °C. The measured mechanical properties of composites (the compression strength and the microhardness) have increased with the increasing CIG content.

Acknowledgments

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