MICROWAVE SINTERING OF HYDROXYAPATITE-BASED COMPOSITES

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ABSTRACT

Composites of hydroxyapatite/partially stabilized zirconia (HAp/PSZ) and hydroxyapatite/silicon carbide whiskers (HAp/SiC) were sintered at 1100-1200°C by microwave at 2.45 GHz. Characterization of the sintered composites was carried out by density, microstructure, phase composition, and fracture toughness measurements. The results show that although not yet fully densified, a much higher sintered density in the HAp/PSZ composite was achieved by microwave sintering than by conventional sintering at the same temperature. A relative density of 93% was achieved by 20 min. microwave processing at 1200°C. Comparatively, 2 h conventional sintering of the same material at 1200°C led to only 75.5% relative density. KIC of this microwave sintered HAp/PSZ of 93% density was found to be 3.88 MPa√m, which is 250% of the value for pure HAp of the same density. A further increase in KIC could be expected if full or nearly full densification was achieved. Sintering of PSZ particles in the HAp/PSZ composite was also observed in the microwave processed sample. Microwave sintering of HAp/SiC was not successful in the current study due to the oxidation of SiC in air at high temperature.

INTRODUCTION

Hydroxyapatite has a stoichiometric composition of Ca10(PO4)6(OH)2. Due to its similarity in both composition and structure to the main inorganic component of the mammalian teeth and bones, HAp shows the best compatibility in biomaterials with human hard tissues and thus has been considered an excellent material for biomedical applications, i.e., implantation or repairing of the hard tissues.

In the last two decades, much work has been done to develop a fundamental understanding of various aspects of HAp. HAp ceramics have now been used clinically for nonload-bearing applications. However, pure HAp ceramic is

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The fracture toughness of dense HAp ceramics is about 1 "mp which is only a quarter to a half of that of bones. Because of this, HAp ceramics could not be used for any load-bearing implantation unless its toughness is antially improved. Therefore, toughening of HAp is an important subject, and research work carried out in this area is very limited. The reported include HAp dispersed with ZrO2 particles and α-Si3N4 whiskers.

1 preparing HAp/ZrO2 composites, sintering has to be carried out at high rates which could lead to decomposition of HAp [1, 2]. Wu and Yeh [2] described conventional sintering of HAp/ZrO2 composites containing 20 wt. % of ZrO2, while the post-sintering HIP at 100 MPa showed only 1-2% increase in density. Compared to the pure HAp which can be easily sintered to around or over 99% of the theoretical density, it is obvious that the addition of ZrO2 to HAp sinterability of the mixture very poor under the conventional conditions. The decomposition of HAp at temperatures becomes worse, it seems impossible to achieve a dense HAp/ZrO2 composite without decomposition of the ambient pressure. Using hot pressing followed by HIP at 200 MPa, imura et al. [4] could make a dense HAp/ZrO2 composite without decomposition of HAp. They also prepared HAp/α-Si3N4 by hot pressing at 3000°C and obtained a dense composite, but they observed a reaction between HAp and α-Si3N4. Through the dispersion of ZrO2 particles or α-Si3N4 whiskers in the fracture toughness, KIC, had been improved by these investigators to 3 MPaVm.

The other hand, fabrication of regular, porous, and transparent HAp ceramics has been achieved by Fang et al. [5-8] recently. Microwave sintering has a heating anisotropy totally different from that of the conventional method. The sintering density in microwave processing is material dependent. Materials that have a dielectric loss factor absorb microwave energy efficiently and are easy to heat from the inside out, while those of low dielectric loss absorb microwave energy less efficiently and are hard to heat. Because of this, selective sintering is possible processing multi-phase materials. The success in microwave sintering of indicates that the microwave absorption of HAp is good enough at least at typical temperatures, while the very high microwave absorption of zirconia is well known. It is expected that good sintering of HAp/PSZ composite can be achieved by microwave processing. Silicon carbide is also a good microwave absorber, so there is a possibility that HAp/SiC composite could sinter better in a microwave field.

In the current study, microwave sintering of HAp-based composites, i.e., HAp/PSZ and HAp/SiC, was attempted.

EXPERIMENTAL

Starting Materials

Two HAp powders were used in the current study. HAp-A was synthesized by hydrothermally treating the precipitate from solutions of Ca(NO3)2·4H2O or solution A, and NH4H2PO4, or solution B. The precipitate was then hydrothermally treated at 200℃ for 24 h. The resulting product was nanocrystalline fine HAp powder. The powder was dried at 80℃, then 120℃, and finally 550℃. The dried HAp was then sintered by grinding in an agate mortar and pestle. The BET surface area of the fine HAp powder was about 40 m2/g. HAp-B was prepared by hydrolysis of brushite (CaHPO4·2H2O) followed by ripening treatment [5] at 70℃ and pH 8.5. The BET surface area of this powder was 47 m2/g. The powder was sieved to -325 mesh and dried at 550℃ before use.

For the HAp/PSZ composite, the volume proportion of HAp-A:PSZ was 90:10. The SiC whiskers were of an average thickness 0.5 μm with varying lengths up to 25 μm. The whiskers were added to the precipitate slurry of HAp-A by magnetic stirring. The mixture of precipitate and whiskers was then subjected to the same hydrothermal, drying, and disagglomeration processes as HAp-A.

For the HAp/SiC composite, the tetragonal phase zirconia stabilized by 3 mol% yttria [Zirconia Sales (America), Inc., Atlanta, GA] of sub-micrometer particle size was used. The volume proportion of HAp-B:PSZ was 90:10. The two powders were then mixed in a plastic jar mill using zirconia balls as mixing media. The mixture was then sieved to -325 mesh to further improve homogeneity.

Compaction

The 12.7 mm diameter (~5 mm thick) pellets of HAp, HAp/PSZ and HAp/SiC powders were compacted uniaxially for both microwave and conventional sintering. The compaction pressure for all pellets was 350 MPa, except that in the case of HAp/PSZ, 420 MPa was also used.

Sintering

A 500 W, 2.45 GHz commercial microwave oven (GE, Model JE 43) was used for sintering. Only one pellet was used in each run. The arrangement inside the microwave oven is schematically shown in Fig.1. The pellet was placed on a board of Fibermax insulation (Carborundum Co., Niagara Falls, NY) in the center of the cavity. In the microwave oven, then vertically surrounded by two co-axial porous zirconia insulating cylinders of 30 mm in height, and then further insulated with the
boards. An end-open Pt-Pt10Rh thermocouple, sheathed with alumina, red from the bottom of the microwave oven, with the tip touching the to monitor the temperature during sintering. The processing temperature rolled by on-and-off operation of the microwave power. Heating started room temperature. After sintering, the system was allowed to cool down to room temperature.

parison, conventional sintering of some pellets with the same green was carried out at 1200°C in a 5 kW programmable box furnace, with cooling and cooling rates at 5°C/min. A HAp/SiC sample was uniaxially boran vacuum at 1200°C and 36.6 MPa for 15 min in a graphite mold of 12.7 meter.

![Microwave oven diagram]

**Figure 1.** The arrangement inside the microwave oven.

ized samples were characterized to determine density, phase composition, acture, and fracture toughness. Density was determined by weight and measurements. Phase composition was analyzed by powder X-ray (XRD) using a Scintag diffractometer (Scintag Inc., Sunnyvale, CA), structures were examined with a scanning electron microscope (SEM, ISI-DS iki Beam Technology Corp., Japan). Fracture toughness was measured indentation using a Vickers indenter.

TS AND DISCUSSION

he heating curve for microwave processing in the current study is shown in usually took 20 to 50 min. to trigger thermal runaway. Because of the high microwave absorption and relatively large mass of the ZrO₂ cylinders over that of the sample, the thermal runaway behavior here had much to do with the porous zirconia cylinders used to vertically shield the sample.

![Temperature vs. Time graph]

**Figure 2.** A typical heating curve for microwave processing of HAp (HAp-B) and HAp-based composites, where porous zirconia was used as accelerator.

Phase Composition

By XRD analysis, it was found that both the microwave and conventionally sintered HAp/PSZ composites were composed of HAp and tetragonal zirconia with trace amounts of α- and β-Ca₃(PO₄)₂. No CaZrO₃ was detected. Trace α- and β-Ca₃(PO₄)₂ were also detected in the pure HAp pellet after 1 h conventional sintering at 1200°C. This indicates that a partial decomposition of HAp took place during sintering, but the decomposition was due to the thermal stability of the starting HAp rather than the microwave processing or any reaction between HAp and ZrO₂.

In the case of the HAp/SiC system, the conventional sintering at 1200°C led to a slight oxidation on the surface of the pellet, while the microwave processing caused very extensive oxidation. A thick layer of oxidation product was observed on the surface of the HAp/SiC pellets after microwave sintering even without additional holding. A few minutes of microwave processing at 1200°C would lead to complete oxidation of the SiC in the HAp/SiC mixture. Microwave sintering of HAp/SiC in Ar gas was also attempted, but it did not help. It is believed that the lack of moisture in the sintering atmosphere caused HAp to decompose at lower temperatures, while the OH⁻ ion decomposition of HAp made the oxidation of SiC even worse. A complex mixture of SiO₂ phases was detected in the oxidation product. The hot-pressed HAp/SiC sample was composed of HAp and a large amount of α-Ca₃(PO₄)₂. The decomposition of HAp in this case was very serious.
use the sample was hot-pressed in vacuum. The hot-pressed HAp/SiC composite turned black due to the diffusion of graphite from the mold.

**Table 1. Summary of the processing conditions and some results measured on the red HAp and HAp-based composites.**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Processing</th>
<th>$\rho_{g, %}$</th>
<th>$\rho_{s, %}$</th>
<th>$K_{IC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAp</td>
<td>m/w</td>
<td>52.82</td>
<td>93.3</td>
<td>1.56</td>
</tr>
<tr>
<td>HAp/10%PSZ</td>
<td>m/w</td>
<td>54.33</td>
<td>87.0</td>
<td>1.18</td>
</tr>
<tr>
<td>HAp/10%PSZ</td>
<td>m/w</td>
<td>54.02</td>
<td>89.1</td>
<td>1.20</td>
</tr>
<tr>
<td>HAp/10%PSZ</td>
<td>m/w</td>
<td>59.79</td>
<td>92.7</td>
<td>3.88</td>
</tr>
<tr>
<td>HAp/10%PSZ</td>
<td>c/v</td>
<td>60.42</td>
<td>74.81</td>
<td></td>
</tr>
<tr>
<td>HAp/10%PSZ</td>
<td>c/v</td>
<td>59.86</td>
<td>75.08</td>
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<tr>
<td>HAp/10%PSZ</td>
<td>c/v</td>
<td>60.42</td>
<td>75.43</td>
<td></td>
</tr>
<tr>
<td>HAp/10%PSZ</td>
<td>c/v</td>
<td>60.06</td>
<td>75.2</td>
<td></td>
</tr>
<tr>
<td>HAp/10%SiC</td>
<td>HP</td>
<td>1200°C C 15 min.</td>
<td>72.5</td>
<td>2.85</td>
</tr>
<tr>
<td>HAp/10%SiC</td>
<td>c/v</td>
<td>1200°C Cx120 min.</td>
<td>66.83</td>
<td></td>
</tr>
<tr>
<td>HAp/10%SiC</td>
<td>m/w</td>
<td>1200°C no holding</td>
<td>58.5</td>
<td></td>
</tr>
</tbody>
</table>

$\rho_{g, \%}$ — Green density and sintered density, respectively.

**Red Density**

HAp/PSZ, conventional sintering at 1200°C led to a sintered density of only 72.5% of the theoretical (Table 1), and prolonging sintering time from ~30 min. to 4 h did not bring about any significant increase in sintered density. Under microwave sintering conditions, however, a 20 min. sintering at 1200°C led to a sintered density of 92.7% in the pellet of 59.8% green density, which was 24% more dense than the conventionally sintered sample. This substantial enhancement in density is attributed to selective heating in the microwave processing. Zirconia absorbs microwave energy much more effectively than HAp, so that it could promote sintering of a HAp/PSZ composite in microwave field when the amount of ZrO$_2$ is appropriate. This is just the reverse of the case in conventional sintering where the existence of ZrO$_2$ makes the sinterability of HAp/PSZ very low. This demonstrates the advantage of microwave processing for such a special system. It should be mentioned that the lower sintered densities of other two microwave sintered HAp/PSZ samples were due to their lower green densities.

In the case of HAp/PSZ, the conventional sintering at 1200°C for 2 h led to a density of 66.8%, and hot pressing, 72.5%. The density of the microwave sintered sample was not measured due to the serious oxidation on the surface after processing, but from SEM micrographs, which will be shown later, its density looks comparable to that of the hot pressed one. The low sintered density of HAp/PSZ was due to the morphology of the silicon carbide whiskers. Obviously, it is more difficult to achieve a high sintered density in a whisker dispersed system than in the particle dispersed one.

**Fracture Toughness**

$K_{IC}$ of 3.88 MPa m$^{-1}$ has been achieved in the HAp/10%PSZ composite of 92.7% dense sintered by microwave processing. Compared with 1.56 MPa m$^{-1}$ from the pure HAp of 93.3% density, a 150% net increase in $K_{IC}$ was realized. The significant improvement in $K_{IC}$ was attributed to the transformation toughening mechanism of tetragonal ZrO$_2$ dispersion. The toughening effect was not observed in the two other HAp/PSZ samples with density less than 90%. This seems to show that the transformation toughening could be realized only when density is over a certain value, most likely greater than 90%. Apparently, fracture toughness, $K_{IC}$, is a function of density. It increases with increasing density, but the relation is not linear. Since the densities of the HAp/PSZ samples sintered by the conventional method were well below 90% of the theoretical, no toughening was expected in these samples, and thus $K_{IC}$ was not measured for them.

In the case of the SiC-containing composite, although the density of the hot-pressed sample was only 72.5%, an obvious increase in fracture toughness was still observed. $K_{IC}$ of 2.85 MPa m$^{-1}$ was achieved in this sample, compared with the zirconia dispersed sample, where no toughening effect was achieved above 90% density. This is not surprising since the mechanism of whisker toughening is different from that of transformation toughening. Another factor which should be considered is that the $K_{IC}$ of this HAp/PSiC sample was measured on the plane perpendicular to the compaction direction and thus more whiskers had contributed to the toughening because of the preferred orientation of the whiskers due to the uniaxial compaction.

**Microstructure**

Fig. 3 shows the microstructures of the HAp/PSZ composite sintered by microwave at 1200°C. It can be seen that the distribution of PSZ particles was homogeneous (Fig. 3, A), and the microstructure of the composite was quite dense. The sintering of some PSZ particles is evident (Fig. 3, B). The microstructures of HAp/SiC composites, sintered by microwave as well as by hot pressing are shown in Fig. 4. Obviously, both were still very porous. The bonding between SiC whiskers and HAp matrix, however, looks good. If the oxidation of SiC could be avoided, and high densification could still be achieved, an improved toughening
The microstructure of microwave sintered HAp/PSZ composite, A) the distribution of zirconia particles and B) simultaneous sintering of HAp and PSZ particles (marked).

Figure 4. The microstructures of the fracture surfaces of the HAp/SiCw composites sintered by (A) microwave processing and (B) hot pressing (perpendicular to the compaction direction).
In both the cases of PSZ and SiC dispersed HA p ceramics, no cracks between the dispersion phase and the matrix were observed, indicating there was no significant mismatch in the thermal expansion coefficients between the toughening agents used and the HA p matrix.

**CONCLUSIONS**

Sintering of HA p/PSZ and HA p/SiC composites was carried out. The results show that the densification of HA p/PSZ was significantly enhanced in the microwave processing. The typical density of a HA p/PSZ composite sintered by microwave processing was 24% higher than that sintered by the conventional method; thus the fracture toughness of the microwave sintered sample was also higher. Fracture toughness of 3.88 MPa m$^1$ was achieved in the microwave sintered HA p/PSZ composite, compared with 1.56 MPa m$^1$ of the pure HA p without PSZ dispersion. Microwave sintering of HA p/SiC composite was successful in this study due to the oxidation of the SiC.

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