HYDROXYAPATITE LANTHANUM OXIDE COMPOSITES

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Abstract. In the present study a commercially synthetic hydroxyapatite powders (CSHAp) were doped with lanthanum oxide (5 and 10 wt % La\textsubscript{2}O\textsubscript{3}). The composite powders were well homogenized and pelleted in an uniaxial mould at 350 MPa. Pelleted green bodies were sintered at five different temperatures. Finally, the effect of La\textsubscript{2}O\textsubscript{3} amount on the microstructural and mechanical properties of CSHA was investigated. Microstructural properties were detected by X-ray diffraction patterns (XRD) and scanning electron microscope (SEM). Mechanical properties of the sintered samples were determined by the density, hardness and compression strength measurements. Experimental results show that the mechanical properties of HA can be improved by the doping of La\textsubscript{2}O\textsubscript{3}.

Keywords: Hydroxyapatite, lanthanum oxide, mechanical properties

PACS: 87.85.jf
1. Introduction

The number of treated skeletal deficiencies steadily increases in a global scale due to accident/injury and/or bone defects. Although autogenous bone is most preferred for the treatment of bone defects, there are disadvantages and risks involved in using autogeneic bone such as post-operation pain, increased blood loss, secondary surgical wounds and risk of thrombosis. Allograft bone could overcome the above limitations, but it bears the risk of transmission of infection (e.g. HIV, Hepatitis, etc.). Another possible alternative is the use of effective and inexpensive biomaterials such as HA produces from different sources such as biologically derived and synthetic hydroxyapatite [1-3]. Despite of its desirable properties, the low fracture strength and poor fatigue resistance due to the instability of OH groups limit the use of its biomedical applications to non-load bearing applications. Low mechanical properties of HA can be improved by precise control of the microstructure and the use of various reinforcements [4-6]. One of the most commonly used methods to improve the mechanical properties of HA, reinforcements of its with oxide based ceramics such as ZrO₂ [7], TiO₂ [8], Al₂O₃ [9], MgO [10], BaTiO₃ [11] etc. In the present study, we doped a commercially synthetic hydroxyapatite powder with lanthanum oxide and the effect of lanthanum oxide on the microstructural and mechanical properties of CSHA was investigated.

2. Materials and Method

2.1. Materials

A commercial HA powder (5 µm, CAS Number: 1306-06-5, Across Organics/Belgium) was used as matrix material and doped with lanthanum oxide (5 µm, La₂O₃, 5 and 10 wt%, CAS Number: 1312-81-8, Sigma Aldrich, Germany). The powders were firstly well homogenized in Restch PM 100 ball milling device in a zirconia coated stainless steel container with 15 zirconia balls and enough ethyl alcohol at 180 rpm for 2h. Afterwards, they were pelleted at 350 MPa according to a British Standard for compression tests [12]. Finally, the compacted green samples were sintered at 900, 1000, 1100, 1200 and 1300 °C for 4h with the heating and the cooling rates of 5 °C/min.
2.2. Mechanical Properties

Density of the sintered samples were calculated using Archimedes method. Relative densities of the sintered samples were calculated by comparing the measured densities with the theoretical densities of samples. (HA: 3,156 gr/cm$^3$, HA–2.5La$_2$O$_3$: 3,197 gr/cm$^3$, HA–5La$_2$O$_3$: 3,239 gr/cm$^3$ and HA–10La$_2$O$_3$: 3,327 gr/cm$^3$) The compression strengths of the samples were measured using Devotrans Universal testing device at 2 mm/min speeds. Micro-vickers indentation method was used to determine the hardness of the sintered samples under the loads of 1.962 N for 20 s.

2.3. Microstructural Properties

XRD patterns were obtained at room temperature in an X’Pert MPD Philips diffractometer using Cu-Kα radiation in the range of 2$\theta$ (10-90$^\circ$). The microstructures of the samples were determined by scanning electron microscope (SEM, JOEL Ltd., JSM-5910 LV) after gold coating.

3. Results and Discussion

The XRD patterns of CSHA and CSHA-La$_2$O$_3$ composites are shown in Fig. 1. All peaks are compatible with HA (JCPDS file no.: 98-006-0428) and no other phases were detected for CSHA samples sintered between 900 $^\circ$C and 1100 $^\circ$C. But, the samples sintered at higher temperatures beta-tetracalcium phosphate ($\beta$-TCP, at 1200 $^\circ$C) and beta/alphaTCP and also calcium oxide ($\beta$-TCP, $\alpha$-TCP and CaO, at 1300 $^\circ$C) phases were determined in addition to HA as shown in Fig 1(a). For all CSHA-La$_2$O$_3$ composites were detected HA, lanthanum hydroxide (La(OH)$_3$) and La$_2$O$_3$ phases sintered at 900 $^\circ$C. However, new phases were also detected as summarized in Table 1 and also shown in Fig. 1 (b), (c) and (d) in addition to the specified phases. Same phases were also detected by F. Oktar et al [13].
FIGURE 1. XRD patterns of (a) pure CSHA, (b) CSHA–2.5La₂O₃ (c) CSHA-5La₂O₃ and CSHA-10La₂O₃ composites.

TABLE 1 Phases occurred during sintering process into CSHA-La₂O₃ composites.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>CSHA-2.5La₂O₃</th>
<th>CSHA-5La₂O₃</th>
<th>CSHA-10La₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>HA (La(OH)₃) and La₂O₃</td>
<td>HA, La₂O₃, calcium phosphate hydrate (Ca₁₀(OH)₆(PO₄)₁₀)</td>
<td>HA, lanthanum (III) hydroxide (La(OH)₃) and whitenkite (Ca₉(PO₄)₆(PO₃OH))</td>
</tr>
<tr>
<td>1100</td>
<td>HA, La₂O₃ and lanthanum dihydrogenphosphate (H₅La₂O₇P₃)</td>
<td>HA, La₂O₃, calcium phosphate hydrate (Ca₁₀(OH)₆(PO₄)₁₀) and porlandite (Ca(OH)₂)</td>
<td>HA, lanthanum (III) hydroxide (La(OH)₃) and whitenkite (Ca₉(PO₄)₆(PO₃OH))</td>
</tr>
<tr>
<td>1300</td>
<td>HA, La₂O₃, (Ca(OH)₂)</td>
<td>HA, La₂O₃, (Ca(OH)₂) and CaO</td>
<td>CaO, La₂O₃ and (Ca₉(PO₄)₆(PO₃OH))</td>
</tr>
</tbody>
</table>

As shown in Fig. 2 that necks started to form and grow between particles at 900 °C (Fig 2a1, a2 and a3), tubular pores appeared along the grain boundaries at 1100 °C (Fig 2b1, b2 and b3) and the tubular pores break up into isolated quasi-spherical pores typically located at the triple points of grains at 1300°C (Fig 2c1, c2 and c3). However, grain size decreases by increasing La₂O₃ rates so porous microstructures occurred for CSHA-10La₂O₃ composites compared to other La₂O₃ reinforced samples.
As shown in Fig. 3, the density of all sintered samples increase by ascending sintering temperatures. While the lowest density value was obtained for CSHA-10La$_2$O$_3$ samples (1.82±0.04 gr/cm$^3$) sintered at 900 °C, the highest density value was obtained for CSHA-2.5La$_2$O$_3$ samples (3.06±0.03 gr/cm$^3$) sintered at 1300 °C. It is also seen that density values of CSHA-2.5La$_2$O$_3$ composites are higher than other CSHA-La$_2$O$_3$ composites. For all sintering temperatures density of CSHA-La$_2$O$_3$ composites decrease by increasing La$_2$O$_3$ rates which may related to at higher La$_2$O$_3$ values diffusion rates. This situation causes the formation of higher porosity. This may be related to particle size of starting powders, milling time, speed and also ball diameters and numbers used during ball milling process.
As shown in Fig. 4, the compressive strength of all samples increase by increasing sintering temperatures until 1100 °C and then decrease at higher sintering temperatures. While the highest compressive strength was obtained to CSHA-5La2O3 composites sintered (151±5.56 MPa), the lowest density value was obtained to pure CSHA sintered at 1300 °C (65±5.59 MPa). Compressive strength of pure CSHA decrease at 1200 and 1300 °C because of the formation of TCP, whitlockite and CaO phases, respectively. These formations were also detected to CSHA-La2O3 composites, but they have generally higher strengths.
compared to pure CSHA which may explain by the decreasing of second or third undesirable phase’s rates via La$_2$O$_3$ reinforcement and due to its reducing effect on the grain growth of HA. Hardness of the sintered ceramics are affected by average grain size, porosity rates and second and/or third phases. As shown in Fig. 5, the hardness values of the samples increase by ascending sintering temperatures. For all sintering temperatures, the highest microhardness values were measured for CSHA-2.5La$_2$O$_3$ samples which may explain by lower porosity values, higher grain sizes and lower glassy phases.

![Microhardness values of the sintered samples as a function of sintering temperature](image)

**FIGURE 5.** Microhardness values of the sintered samples as a function of sintering temperature

4. Conclusion

The following conclusions can be drawn from the present study:

1- The mechanical properties of CSHA can be improved by the reinforcement of La$_2$O$_3$.

2- The optimum La$_2$O$_3$ rate was found % 5 for CSHA-La$_2$O$_3$ composites to obtain higher compressive strength.
3- The best compressive strengths for all samples were obtained at 1100 °C, however, at higher temperatures compressive strengths of the samples decreased due to occurred undesirable second and/or third phases such as CaO, TCP and whitlockite.

Acknowledgement

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5. References


Figures and Table Captions

FIGURE 1. XRD patterns of (a) pure CSHA, (b) CSHA-2.5La₂O₃ (c) CSHA-5La₂O₃ and CSHA-10La₂O₃ composites.

FIGURE 2. SEM micrographs of CSHA-2.5La₂O₃ composites sintered at 900 °C (a1), sintered at 1100 °C (a2), sintered at 1300 °C (a3), CSHA-5La₂O₃ composites sintered at 900°C (b1), sintered at 1100 °C (b2), sintered at 1300 °C (b3) and CSHA-10La₂O₃ composites sintered at 900 °C (c1), sintered at 1100 °C (c2), sintered at 1300 °C (c3).

FIGURE 3. The effect of sintering temperatures on the density values of the sintered samples.

FIGURE 4. Compressive strength of the sintered samples as a function of sintering temperature.

FIGURE 5. Microhardness values of the sintered samples as a function of sintering temperature.

TABLE 1 Phases occurred during sintering process into CSHA-La₂O₃ composites.
FIGURE 1. XRD patterns of (a) pure CSiA, (b) CSiA+2.5LaO₃, (c) CSiA+LaO₃, and CSiA+2.5LaO₃ compositions.
FIGURE 2. SEM micrographs of CSHA-2.5La$_2$O$_3$ composites sintered at 900 °C (a1), sintered at 1100 °C (a2), sintered at 1300 °C (a3), CSHA-5La$_2$O$_3$ composites sintered at 900 °C (b1), sintered at 1100 °C (b2), sintered at 1300 °C (b3) and CSHA-10La$_2$O$_3$ composites sintered at 900 °C (c1), sintered at 1100 °C (c2), sintered at 1300 °C (c3).

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</thead>
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<td>900</td>
<td>HA, lanthanum hydroxide (La(OH)₃) and La₂O₃</td>
<td>HA, lanthanum hydroxide (La(OH)₃) and La₂O₃</td>
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</tr>
<tr>
<td>1100</td>
<td>HA, La₂O₃ and lanthanum and hydrogenphosphatehydroxide (H₅La₁(O/P)₃)</td>
<td>HA, La₂O₃, calcium phosphate hydrate (H₃Ca₅O₈P₃) and porlandite ((Ca(OH))₃)</td>
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