THE EFFECT OF COLD ISOSTATIC PRESSING ON THE SINTERABILITY OF SYNTHESIZED HA

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ABSTRACT

The effect of cold isostatic pressing (CIP) on the sinterability of a laboratory synthesized hydroxyapatite (HA) powder was investigated. The starting powder was initially uniaxially die-pressed at about 6 kN force to form disk and rectangular green compacts. Two batches of green samples were prepared, i.e. one batch was in the as-compacted state (Un-CIP) and another batch samples was subjected to cold isostatic press at 200 MPa (CIP). The latter samples exhibited a linear shrinkage of ~16% prior to sintering. All the samples were sintered in air at temperatures ranging from 700°C to 1400°C. The densification behaviour of HA was evaluated in terms of linear shrinkage, phase stability, bulk density, Vickers hardness and Young's modulus. The results revealed that green samples subjected to cold isostatic pressing exhibited better sinterability and possessed excellent mechanical properties. This effect is more pronounced particularly for the low temperature sintering regime i.e. $\leq 1100^\circ\text{C}$.

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1. INTRODUCTION

Hydroxyapatite (HA) or $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, with its excellent biocompatibility due to its chemical similarity with the mineral portions of hard tissues as well as its ability to form chemical bonding with surrounding tissues [1-4], makes it an ideal synthetic ceramic for clinical application. The widespread utilization of HA as an implant material especially in load-bearing application (tensile nature) is however

hampered mainly due to the low fracture toughness ($\sim 1 \text{ MPam}^{1/2}$) as compared to $2\text{-}12 \text{ MPam}^{1/2}$ for the human bone [2, 5] and the low fracture strength ($< 120 \text{ MPa}$) [6] of the material.

In applications where HA powders are sintered to form ceramic components, the mechanical properties of HA will be very much dependent on the sintered density and microstructure of the final sintered product. As such, concerted effort has been directed towards improving the reliability of HA such as the use of sintering additives [7] and microwave processing [8]. Powder characteristics such as particle size and distribution, agglomeration and surface area are some of the main features that controls the sintered properties of the HA body [9]. In general, fine powder with greater surface area allows higher sinterability that leads to the use of lower densification temperature. On the other hand, the presence of agglomerates, especially of the hard form, tends to disrupt the

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densification process resulting in the formation of defects (e.g. porosity, grain growth, microcracks, etc.) in the microstructure and thus limiting the strength of the sintered material.

In the present work, the effect of cold isotatic pressing (CIP) on the sinterability/densification of HA powder that was produced in the laboratory by a wet chemical technique was investigated. Sintering under ambient conditions was carried out at temperatures ranging from 700°C to 1400°C.

2. EXPERIMENTAL PROCEDURES

2.1 Starting Powder and Sample Preparation

A stoichiometric HA was prepared using the precipitation reaction between 1 moles calcium hydroxide and 0.6 moles orthophosphoric acid. In general, the precipitation reaction was carried out at room temperature and the pH was maintained above 10 by the addition of ammonium hydroxide solution. After complete mixing of the reactants, the suspension was aged overnight. The resulting precipitate was filtered, washed, dried and then ground to a powder of high purity which composed of single phase stoichiometric HA [10].

The as-received powder was die-pressed at about 6 kN into disc and rectangular green compacts. Higher pressing loads were found unfavourable as it resulted in lamination of the powder on the die surface. Two batches of green samples, i.e. in the as-compacted condition (Un-CIP) and samples that were CIP at 200 MPa (Reiken Seiki Japan), were prepared. The compacts were sintered in a Superburn furnace, in air atmosphere at temperatures ranging from 700°C to 1400°C, at ramp rates of 2°C/min and a holding time of 2 hours.

2.2 Body Characterisation

The phase compositions of the synthesized powder and the sintered compacts were analysed by X-ray diffraction (XRD) (Rigaku GeigerFlex, Japan) using Cu-K α as the radiation source with a scan speed and step scan of 0.5°/min and 0.02° respectively to determine the phases present in the samples. Identification of phases was achieved by comparing the diffraction patterns of HA with ICDD (JCPDS) standards [11].

The sintered densities of the samples were obtained by water immersion technique for dense compacts (above 95% of the theoretical density) and from the measurement of geometric dimensions and sample mass for low density samples (below 95%). For low density samples, the former method allows water to penetrate the pores, resulting in an overestimate

value of the sample density. The relative density was calculated by taking the theoretical density of HA as 3.156 gcm⁻³.

The Vickers hardness (H_V) of the sintered polished samples was determined using a Matsuzawa microhardness indenter. A loading time of 10 seconds was employed and average hardness value was taken from at least five indents made for each sample.

The Young's modulus by sonic resonance was determined for rectangular samples using a commercial testing instrument (GrindoSonic: MK5 "Industrial", Belgium). The instrument permits determination of the resonant frequency of a sample by monitoring and evaluating the vibrational harmonics of the sample by a transducer; the vibrations are physically induced in the sample by tapping. The modulus of elasticity is calculated using the experimentally determined resonant frequencies, according to standard test method [12].

3. RESULTS AND DISCUSSION

The XRD analysis of the synthesized powder in this study exhibited peaks that corresponded to stoichiometric HA [11]. Thus, it is evident that the filtered crystals were mainly single-phase HA and is believed to be very small. Estimates of crystal size from peak broadening [13] for the synthesized powder gives about 110 Å from the (2 1 1) reflection and about 350 Å from the (0 0 2) reflection. In addition, the XRD pattern of the synthesized powder compared very favourably with that of a human tooth as shown in Fig. 1.

The XRD analysis of all the sintered samples, regardless of pressing conditions and sintering temperature, produced only peaks that correspond to stoichiometric HA. This results indicate that HA did not decompose to secondary phases upon sintering and the phase stability was not affected by the pressing conditions prior to sintering. In addition, phase decomposition was not observed for both batches of samples even when sintered at high temperature above 1300°C as typically shown in Fig. 2.

Decomposition of HA phase was not observed in the present material even for the high temperature (i.e. 1400°C) sintered samples. This observation is not in agreement with other workers, which have reported that decomposition of HA starts at about 1300°C [14-16]. The difference in result in the present work could in part be attributed to the relatively high humidity content present in the sintering atmosphere and the nature of the synthesized powder. It is believed that the high humidity content slows down decomposition rate by preventing dehydration of the OH group from the HA matrix [14].

Fig 1. Comparison of XRD patterns of synthesized HA with that of a human tooth (courtesy of Dr. S. Ramesh). All peaks correspond to stoichiometric HA phase.

Fig 2. XRD signatures of sintered (700°C-1400°C) CIP HA. Similar results were obtained for the Un-CIP HA. All peaks correspond to the hydroxyapatite phase.

In general, sintering HA can lead to the partial thermal decomposition of HA into tricalcium phosphate (TCP) and/or tetracalcium phosphate. The thermal decomposition is accompanied in two steps i.e. dehydroxylation and decomposition. Dehydroxylation to oxyhydroxyapatite proceeds at temperatures about 850°C to 900°C by the fully reversible reaction in accordance to equation 1 [15-16]:

The decomposition to TCP and tetracalcium phosphate occurs at temperatures greater than 900°C

according to the reaction given in equation 2 [15-16]:

Since both the dehydroxylation and decomposition reactions include water vapour as a product, the rates at which these reactions proceed depend on the partial pressure of H_2O in the furnace atmosphere. Thus, the secondary phase formation during sintering could be control by simply controlling the sintering atmosphere.

Since no attempt was made in the present work to control the sintering atmosphere, the present results indicate that the minimum moisture content for maintaining phase stabilization must be low. In addition, as the HA in the present work was produced by a wet chemical route and the powders were not calcined prior to sintering, a significant amount of absorbed water will probably remain. However, it is not clear if the loss of water during sintering plays a role in suppressing dehydroxylation.

The linear shrinkage based on length measurement of the bar samples with respect to sintering temperature is shown in Fig. 3. The results indicated that CIP HA exhibited higher linear shrinkage due to improved densification resulting from intimate powder particle contact from cold isostatic pressing. This was more evident for samples sintered below 1200°C. For example, the CIP HA recorded shrinkage of approximately 20% at 700°C, whereas the Un-CIP HA required a higher temperature of about 1150°C to achieve similar shrinkage value. The final linear shrinkages for both sets of HA, regardless of pressing condition, were between 34% - 35%.

The effect of sintering temperatures on the bulk density of HA is shown in Fig. 4. In general, the bulk density increases with increasing sintering temperature regardless of pressing condition. However, the beneficial effect of CIP in enhancing the bulk density of HA throughout the sintering regime employed has been revealed. The effect is more pronounced at lower temperatures $\leq 1100^\circ\text{C}$ where the density of the CIP samples was higher by more than 150% as compared to the Un-CIP samples when sintered at the same temperature. In addition, the CIP samples achieved > 95% of the theoretical density when sintered at temperature as low as 1050°C as compared to the Un-CIP HA which required a higher sintering temperature, above 1300°C.

The effect of sintering temperature on the Vickers hardness of HA is shown in Fig. 5. A linear relationship was observed for both sets of HA. The hardness of CIP HA decreases linearly with increasing sintering temperature whereas the opposite trend was observed for the Un-CIP HA.

Fig 3. Linear shrinkage of HA with respect to sintering temperature.

The relationship between the Young's modulus (E) of the HA (CIP and Un-CIP) and sintering temperature is shown in Fig. 6. Generally, it was found that the Young's modulus of the HA gradually increase with increasing sintering temperature up to about 1350°C. The variation in the Young's modulus is in good agreement with the bulk density as observed in Fig. 4. The CIP samples exhibited higher matrix stiffness than the equivalent Un-CIP samples, particularly at lower sintering temperatures. The results showed that the CIP HA achieved a Young's modulus above 100 GPa at approximately 1000°C, whereas the Un-CIP sample requires a sintering temperature of approximately 1250°C to reach a similar modulus of elasticity. This result further emphasize the importance of cold isostatic pressing prior to sintering of the HA product. However, this improvement is more pronounced at lower temperatures as the maximum Young's modulus obtained for both HA was almost similar, i.e. approximately 115 GPa (CIP HA) and 111 GPa (Un-CIP HA) sintered at 1300°C and 1350°C respectively.

Attempts to correlate the Young's modulus with bulk density revealed a different trend for the CIP and Un-CIP HA as shown in Fig. 7. It was found that Young's modulus varied almost linearly for the CIP HA as compared to the Un-CIP HA, which exhibited a polynomial relationship. Clearly, the use of cold isostatic pressing treatment prior to sintering of the green samples plays a significant role in determining the densification behaviour of the synthesized HA, more particularly when sintered at low temperature regimes.

Fig 4. The effect of pressing condition and sintering temperatures on the relative density of HA.

4. CONCLUSIONS

- * The synthesized HA powder produced in accordance to the present work is of single phase stoichiometric HA that possess a crystallographic phase pattern that is consistent with that of a human tooth.
- * The Synthesized HA powder is highly sinterable particularly at low temperature regimes below 1100°C.
- * Decomposition of HA phase to form tri-calcium phosphate, tetra tri-calcium phosphate and calcium oxide was not observed in the present work. In addition, the stability of the HA phase was not disrupted even when sintered at 1400°C.
- * The effect of cold isostatic pressing (CIP) on the sinterability of HA was reflected in the sintered

Fig 5. Effect of sintering temperatures on the Vickers hardness of HA.

Fig 6. The effect of sintering temperatures on the Young's modulus of HA.

Fig 7. Relationship between the relative density and Young's modulus of CIP HA and Un-CIP HA.

densities and Young's modulus values. The study revealed that CIP, among other parameters such as sintering temperature, plays an important role in enhancing the densification and stiffness of the HA matrix.

* Samples that were cold isostatic pressed at 200 MPa sinters more readily and required a much lower temperature ($\sim 1050^{\circ}\text{C}$) to achieve densities above 95% of theoretical value and a Young's modulus above 100 GPa, whereas the Un-CIP samples required a sintering temperature of above 1250°C to achieve similar results.

* In general, the present work revealed that the CIP samples exhibited superior properties than the equivalent Un-CIP samples and this effect is more pronounced when samples sintered below 1150°C .

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