

The Effects of Zirconia Additions on the Sintering Behaviour and Phase Stability of Hydroxyapatite Ceramics

Muralithran G. Kutty¹ & Ramesh Singh²

¹Advanced Materials Research Centre, SIRIM Berhad, Shah Alam, Malaysia

²Ceramics Technology Centre, SIRIM Berhad, Shah Alam, Malaysia

ABSTRACT

Hydroxyapatite-zirconia composites with different ratios were prepared by using the conventional ball-milling technique. Ceramic pellets prepared from these powders were compacted and sintered without distorting or cracking. The sintering behaviour (at 1250°C, 1400°C and 1600°C) of the composites were studied in terms of phase stability, densification and microstructural evolution. By X-ray diffraction, tetragonal zirconia as well as HA was identified as the major phases in the composites. In addition, small diffraction peaks corresponding to α -TCP was evident indicating sign of HA decomposition. Reaction between the zirconia and HA to form CaZrO_2 was also detected in the composite system containing up to 20 wt% zirconia throughout the sintering regime employed. SEM examination of the sintered composites at room temperature suggested the involvement of a reactive liquid phase during sintering. The presence of zirconia phase in hydroxyapatite matrix played an important role in the stability of the HA phase.

Keywords: Composites, sintering behaviour, bioceramics, hydroxyapatite, zirconia, Y-TZP

INTRODUCTION

Hydroxyapatite (HA) with the chemical constituent $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ is considered as one of the most promising candidate for orthopedic implants due to its excellent biocompatibility which is attributed mainly to its chemical and crystallographic similarities with the mineral portion of bone and teeth (Jarcho *et al.* 1977).

Synthetic HA is increasingly being considered in clinical applications due to its excellent bioactivity which encourages bonding between body tissues and the implant surface (Ogiso *et al.* 1992a). In addition, the similar calcium-to-phosphorus ratio of HA and bone, promotes bone growth directly on the implanted HA surface (Liu *et al.* 1997; Ogiso *et al.* 1992b).

However, one of the major factors that hampered the full exploitation of HA ceramics in bio-applications is the brittle nature of the material (Muralithran and Ramesh 1999). As a result, implantation of this material is limited to unstressed regions of the body (Ogiso *et al.* 1996). This is because of the low fracture toughness (0.8 to 1.2 MPam^{1/2}) and the low flexural strength (< 130 MPa) of the material (Liu *et al.* 1997; Wang and Chaki 1993).

In contrast, yttria-tetragonal zirconia polycrystal ceramics (Y-TZP) has been considered in many structural applications due to its excellent resistance to wear, high bending strength (> 1000 MPa) and high fracture toughness (5 - 12 MPam^{1/2}) (Ramesh *et al.* 1996).

These improved mechanical properties of Y-TZP ceramics have been attributed mainly to a mechanism known as transformation toughening i.e. the tetragonal particles in the zirconia matrix transformed to the monoclinic symmetry under the application of external stress which is accompanied by 3-5% volume expansion and as a result suppress crack propagation (Lange 1983).

In addition, the excellent chemical inertness and bioinert properties of Y-TZP ceramics have realised its potential uses in the medical field as an implant material, replacing metallic component such as femoral heads in hip-joint prostheses (Cales and Stefani 1994).

In theory, combination of the two ceramic systems to form a composite would yield the ideal properties suited for bio-applications. In this case, the biocompatibility is assured by HA while the necessary strength and toughness is provided by the bioinert tetragonal zirconia phase.

The objective of this work was to study the effect of zirconia additions on the sintering characteristics and phase stability of hydroxyapatite. Evaluation of the materials involved sintering studies conducted at a range of temperatures, with the compositions assessed in terms of densification, phase stability and microstructural evolution.

MATERIALS AND METHODS

Powder Preparation and Densification

The as-received commercially available materials : Y-TZP powder containing 3 mol% yttria (Kyoritsu Co. Ltd. Japan) and HA powder (Merck Germany) were used in this study. The calcium content of the HA powder was determined by Inductive Coupled Plasma (ICP) method after dissolving in nitric acid whereas titration method of standard EDTA solution was used to determine the phosphate content. Varying amounts of Y-TZP powder (5, 10, 20 and 50 wt%) were mixed with the HA powder in a polyethylene container containing Y-TZP milling media. Mixing was achieved by ball milling the mixture for 3 hours and subsequently sieved through a 50 μm sieve. A description of the powders are given in Tables 1 and 2.

The composites were pressed into cylindrical disc samples (20 mm die) followed by cold isostatic pressing at 200 MPa. The green pellets were sintered at three different temperature i.e. 1250°C, 1400°C and 1600°C, at a furnace ramp rate of 2°C/min and holding time of 2 hours.

The notation used to characterise the samples were HAZX, where HAZ denotes the composite hydroxyapatite zirconia (Y-TZP) and X represent the content of Y-TZP added (% wt/wt).

TABLE 1
Properties of the as-received starting powders

Starting Powder	Specific surface area (m^2/g) *	Mean particle diameter (μm)
HA	70	~ 27.4
Y-TZP	~ 9 - 12	~ 0.3 - 0.4

* Determined by the Brunauer-Emmett-Teller (BET) method.

Characterisation and Properties Evaluation

The relative density of the composites was measured by water immersion method. For this purpose the theoretical densities of the composites were calculated from a simple mixture rule (the theoretical density of HA and Y-TZP were assumed to be 3.156 gcm^{-3} and 6.09 gcm^{-3} , respectively).

Phase analysis by X-ray diffraction (XRD) of samples was carried out at room temperature using $\text{Cu-K}\alpha$ as the radiation source. The crystalline phases present in the samples were identified by comparing to standard JCPDS files available in the system. In addition, microstructural evolution of the composites was examined by scanning electron microscopy (SEM).

TABLE 2
Compositions of the materials studied

Code	Composition	Theoretical density (gcm ⁻³)
HA	undoped HA	3.156
HAZ5	95% HA + 5% Y-TZP	3.303
HAZ10	90% HA + 10% Y-TZP	3.449
HAZ20	80% HA + 20% Y-TZP	3.743
HAZ50	50% HA + 50% Y-TZP	4.623
Y-TZP	undoped 3 mol% Y-TZP	5.730

RESULTS & DISCUSSION

Relative Density

The effects of sintering temperature on the relative densities of composites are presented in Table 3. As expected, the undoped HA samples exhibited 99% theoretical density when sintered at 1250°C and 1400°C. However, the relative density of the HA sintered at 1600°C could not be measured due to melting of the material.

In contrast, the additions of Y-TZP was found to be detrimental and the relative densities of the composites decreased with increasing Y-TZP content, see Table 3. This was unexpected since as predicted in Table 1, the relative density of the composites were expected to increase with increasing Y-TZP content.

The low bulk density of the composite materials could be attributed to several factors such as the method employed to mix the starting powders, the sintering schedule, sintering atmosphere and residue porosity. In addition, decomposition of HA to form other calcium phosphate phases such as α -TCP and β -TCP that usually occur when sintered at temperatures above 900°C (Hench and Wilson 1993) could also have contributed to the variation in bulk density.

TABLE 3
Relative density versus sintering temperature

Sample	1250°C	1400°C	1600°C
HA	99%	99%	melted
HAZ5	88%	87%	melted
HAZ10	70%	72%	70%
HAZ20	59%	60%	62%
HAZ50	49%	54%	61%

Phase Retention

The XRD analyses revealed some important aspects related to the behaviour of different powders. The room temperature XRD patterns of HA containing varying amounts of Y-TZP, sintered at 1250°C, 1400°C and 1600°C are presented in Figures 1–3 respectively. The formation of a composite material with peaks corresponding to both starting powders was evident.

It has been found that the additions of Y-TZP significantly influenced the stability of hydroxyapatite in the composite system. In general, the HA phase decreases with increasing Y-TZP content in the system regardless of sintering temperature employed.

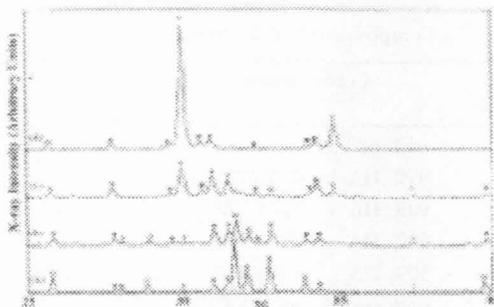


Fig. 1. XRD patterns of HA containing (a) 5 wt%, (b) 10 wt%, (c) 20 wt% and (d) 50 wt% Y-TZP respectively. All samples were sintered at 1250°C. (Key : = HA ; ▼ = α-TCP ; + = CaO ; T = ZrO₂ ; * = CaZrO₂ ; ● = β-TCP).

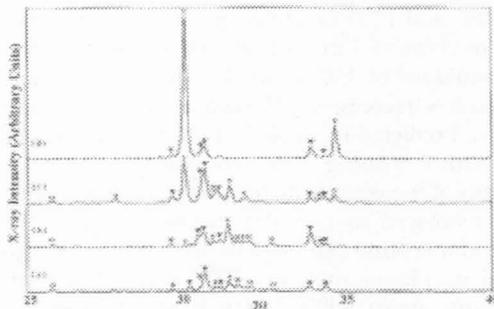


Fig. 2. XRD patterns of HA containing (a) 5 wt%, (b) 10 wt%, (c) 20 wt% and (d) 50 wt% Y-TZP respectively. All samples were sintered at 1400°C. (For key : refer to Figure 1). Note that the phase corresponding to β-TCP was only detected in HA containing 20 wt% Y-TZP.

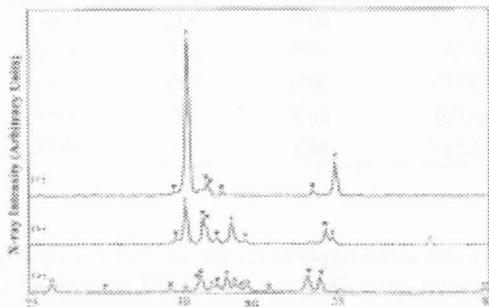


Fig. 3. XRD patterns of composites sintered at 1600°C containing (a) 10 wt%, (b) 20 wt% and (c) 50 wt% Y-TZP respectively. (For key : refer to Figure 1). Note that the phase corresponding to β-TCP was only detected in sample containing 10 wt% Y-TZP.

The presence of α -TCP, β -TCP and CaO peaks were detected in the composites indicating that HA has started to decompose at 1250°C. Also, small peaks corresponding to CaZrO_2 could be detected in composites containing up to 20 wt% Y-TZP.

For additions of 50 wt% Y-TZP and sintering temperature of 1250°C, HA has almost fully decomposed to form α -TCP and β -TCP (see Figure 1d). However, only α -TCP and ZrO_2 were detected when composite containing 50 wt% zirconia was sintered at higher temperatures (i.e. 1400°C and 1600°C), see Figures 2d and 3c.

In addition, from these XRD patterns, it can be noted that the CaZrO_2 phase was not detected in composites containing > 20 wt% Y-TZP throughout the sintering regime employed.

It has been reported by Fanovich and Lopez (1998) that the additions of certain additives in HA resulted in the formation of a liquid phase during sintering. The authors suggested that provided certain conditions have been met, the formation of liquid phase would reduce the β -TCP content in the sintered materials by dissolving it in the glassy phase.

In the present work, the additions of zirconia have resulted in the formation of some reactive liquid phase during sintering. This has been confirmed by SEM examination of un-etched composites containing 50 wt% Y-TZP, which revealed some remnant glassy phase remaining on the surface after cooling to room temperature (see Figure 4).

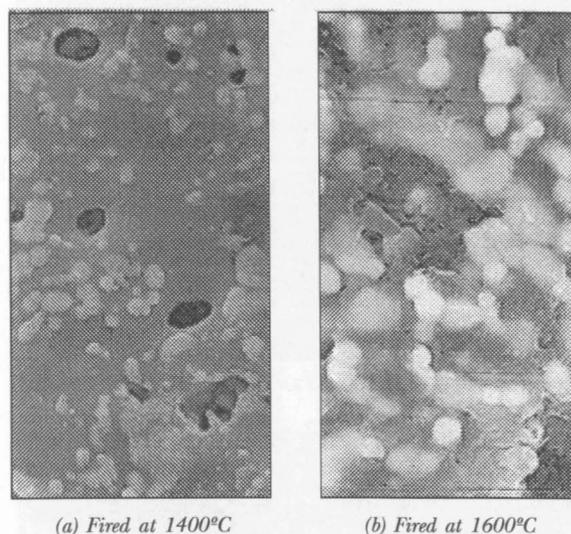
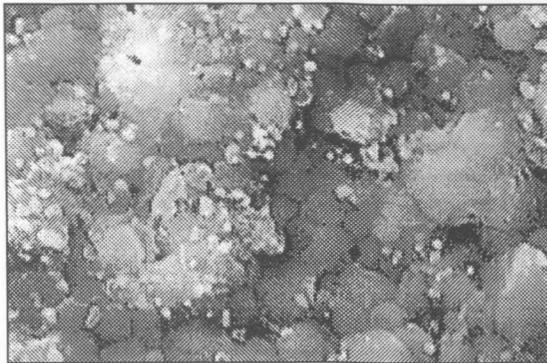


Fig. 4. SEM micrographs of HA containing 50 wt% Y-TZP revealing the presence of remnant supercool glassy phase remaining on the surface after sintering. The rounded pores in (a) indicated that a liquid phase was involved during sintering. The white phase is zirconia.

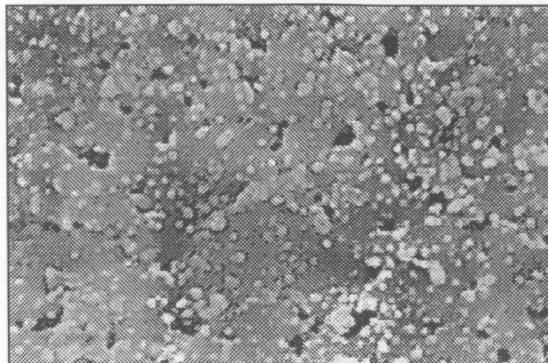
Therefore, based on the XRD and SEM analysis, it is suggested that at the sintering temperature of 1600°C and for composite containing 50 wt% Y-TZP, the β -TCP and CaZrO_2 phase could have been taken into solid solution with the zirconia-rich glassy phase. This would then provide an explanation for the absence of these phases on cooling to room temperature. However, more work have to be carried out to elucidate this phenomenon.

Microstructural Evolution

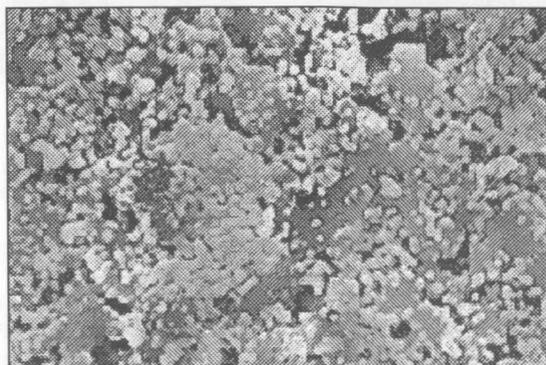
The microstructural evolution of composites sintered at 1250°C, 1400°C and 1600°C are presented in Figures 5, 6 and 7 respectively.



(a) 10 wt% Y-TZP - HA : 1250°C



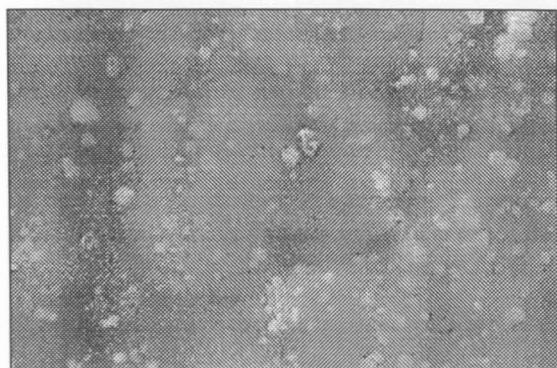
(b) 20 wt% Y-TZP - HA : 1250°C



(c) 50 wt% Y-TZP - HA : 1250°C

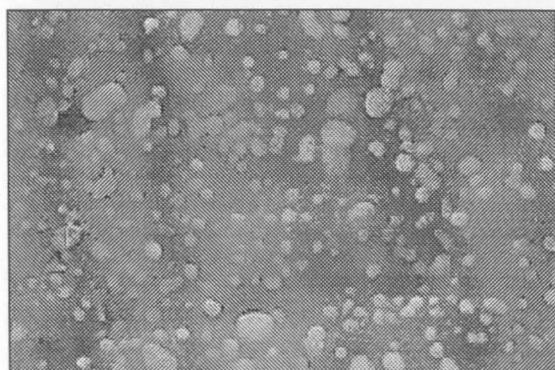
Fig. 5. SEM micrograph of composites sintered at 1250°C.

In general, analysis of the microstructure of the composites revealed a homogeneous dispersion of zirconia particles in the HA matrix (e.g. Figure 6b) and a regular HA grain distribution as illustrated in Figure 5a. No abnormal grain growth of HA was observed.



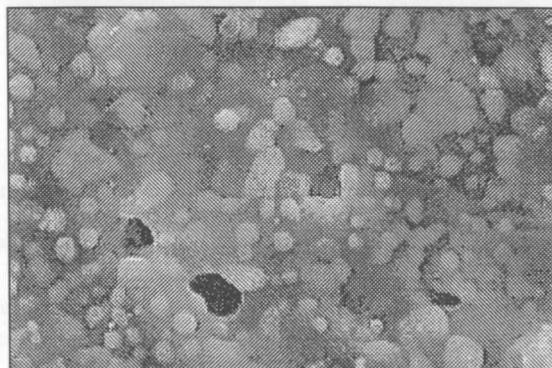
(a) 10 wt% Y-TZP - HA : 1400°C

3.3 μm



(b) 20 wt% Y-TZP - HA : 1400°C

3.3 μm

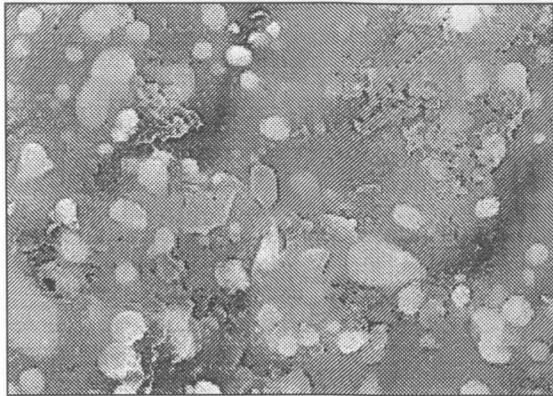


(c) 50 wt% Y-TZP - HA : 1400°C

2.5 μm

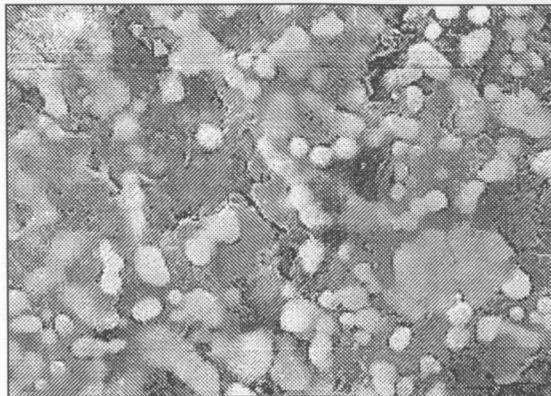
Fig. 6. SEM micrograph of composites sintered at 1400°C.

There are evidenced to indicate that the zirconia particles accumulate mainly at the matrix grain boundaries. Also, no significant reaction can be seen between zirconia and HA when sintered at 1250°C. However, above 10 wt% Y-TZP additions and > 1250°C the reaction was significant.



(a) 20 wt% Y-TZP - HA : 1600°C

2.5 μm



(b) 50 wt% Y-TZP - HA : 1600°C

3.3 μm

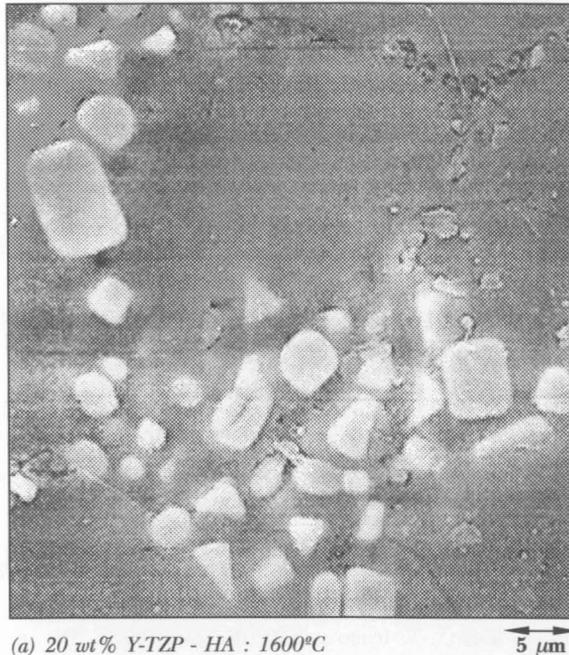
Fig. 7. SEM micrograph of composites sintered at 1400°C.

One of the reasons to explain the low bulk density measured for the composites (see Table 3) can be in part attributed to the significant amount of porosity remaining after sintering as illustrated in Figures 5-7. In general, it was found that the porosity increases with increasing zirconia content and more pronounced at lower sintering temperatures. Similar observations were also reported by Chang *et al.* (1997).

It can also be noted from the SEM micrographs that the zirconia particle size increases with increasing temperature and is not so dependent on the Y-TZP content. Most of the particles are of a few microns, but occasionally very large zirconia particles (as large as 6 μm) and isolated cluster of ZrO₂ particles were observed, as typically shown in Figure 8. At this stage, it is not clear whether they were introduced by agglomeration during powder processing. More work has to be done to clarify these phenomena

CONCLUSIONS

HA-YTZP composites were prepared using commercially available HA and YTZP powders. The sintering behaviour of the composites was investigated using X-ray diffraction and scanning electron microscopy. Composites could not be sintered to high density by pressureless sintering at 1250°C - 1600°C in air. XRD analysis revealed that the HA started to decompose at 1250°C to form TCP. Reaction between Ca and ZrO_2 occurred in the composites containing up to 20 wt% YTZP. Observation by XRD and SEM technique shows that the additions of zirconia adversely affect HA phase stability and resulted in low bulk density.



(a) 20 wt% Y-TZP - HA : 1600°C

5 μ m

Fig. 8. Microstructure of the HA-10 wt% Y-TZP composite sintered at 1600°C showing the presence of isolated cluster of zirconia particles in the HA matrix.

ACKNOWLEDGEMENT

This work was supported under the IRPA grant No. 09-01-01-0014. The authors gratefully acknowledge the support provided by SIRIM Berhad, in particular, Dr. Mustaza Hj. Ahmadun of AMREC and Ms. Wan Zaharah of Ceramics Technology Centre for their interest and continuing support in this work. Thanks are also due to Ms. Zalena Saem for preparing the samples & her assistance during SEM examination, and Miss Renee Marcia for proof reading this manuscript.

NOTATION

ZrO_2	Zirconia
HA	Hydroxypatite

Y-TZP	Ytria-Tetragonal Zirconia Polycrystal
α -TCP	α -Tricalcium Phosphate
β -TCP	β -Tricalcium Phosphate
CaO	Calcium Oxide
CaZrO ₂	Calcium-Zirconia

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