



Effect of Hydroxyapatite on the Properties of Wollastonite Bioceramics

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ABSTRACT

Replacement for worn or injured body parts is the area wherein biomaterials are predominantly used. In the research, we have developed compact of hydroxyapatite-wollastonite for bone implant applications. The effect of crystalline hydroxyapatite amount on the mechanical, physical, and biological properties for the prepared biocomposite material was evaluated. The wollastonite matrix was synthesized by solid state reaction method from its constituent e.g. CaO, which prepared from natural source belong to oyster shells by calcinations at 900°C for 1 hour, and high purity silica foam. The silica foam and calcium oxide powders were mixed in 1:1 molar ratio then sintered at 1300 °C for 2 hours. The prepared wollastonite was mixed with different weight percent's of hydroxyapatite (10, 20, 30, 40, and 50 %). Hydroxyapatite-wollastonite samples were prepared by cold pressing at (200MPa). The compacts prepared from powders of (hydroxyapatite-wollastonite), sintered at 1100°C and 1200°C for 3 hours. The microstructures for the prepared samples are investigated employing XRD and SEM technique. The biological properties of the ceramics samples were examined by immersion of the prepared samples in the stimulated body fluid solution. The interaction of these materials with an SBF produces bonelike apatite layer on their surfaces, which is thicker when the hydroxyapatite is in a higher proportion. The variations in ionic concentrations of Ca and Si demonstrate that the dissolution of the material surfaces with a simultaneous took place during the soaking tests, being slightly faster on 100W, 20H–80W, and 50H–50W, respectively. This could be due to the fact that the dissolution rate of the wollastonite phase was higher than that of the hydroxyapatite phase in SBF solution. The best results are obtained at 1100 °C and 1200°C for samples contained 30%HAP, due to good biological, mechanical, and physical properties compared with the pure HAP, and the prepared wollastonite .The physical properties of prepared samples (porosity, firing shrinkage) were tested. The results showed enhancement in the physical properties of hydroxyapatite/wollastonite sample.

Keywords: *Hydroxyapatite; Wollastonite; Bioactivity; Biocomposite ; Solid State Reaction Method; SBF.*

1. INTRODUCTION

The fundamental requirement of any biomaterial is the ability of the material to perform effectively with an appropriate host response for the desired application i.e. the material and the tissue environment of the body should coexist without having any undesirable/toxic effect (Hench et al., 1993). During the last forty years a applications in biomedicine has big revolution has occurred in the use of ceramics to improve the quality of human life, this revolution was due to the development of specially designed and fabricated ceramics called bioceramics, for repair and reconstruction of diseased, damage or worn out parts of the body. The development of ceramic material applications mostly concentrated in orthopedics and dentistry. Orthopedic bioceramics provide the advantage of chemical similarity to natural skeletal materials. Also the dental applications for ceramics are attractive due to the chemical similarity between engineered ceramics and natural dental materials (Desai et al., 2008). Ceramics like wollastonite, hydroxyapatite (HA), β -tri calcium phosphate are the various bioceramics, have been shown to bond with living bone directly hence they received important attention in the field of biomedical engineering as a significant bone substitute (Anjaneyulu et al., 2013). The characteristic of a bioactive material is the ability to form hydroxyapatite layer on its surface in presence of physiological environment, which provides the bonding interface with the tissues and bone (De Aza et al., 2005). Hydroxyapatite–wollastonite bioceramics manufactured by the sintering technique the samples were densified by sintering at 1200°C for 4 h. The material obtained from

sintering process would be a bioceramics consisting of apatite and wollastonite phase with much leaser volume of the residual glass phase, it would possess a higher bioactivity than pure HAP, and it would amenable to manufacturing synthetic bones with customized pore architecture(Ahmet Oglu 2005).Hydroxyapatite/wollastonite scaffolds were prepared by polymeric sponge replica method using slurry containing HA: Calcium silicate in the weight ratio of 50:50 and sintered at 1300°C. In-vitro bioactivity and bioresorbability confirmed the feasibility of the developed scaffolds(S. K. Padmanabhan et al. 2012). Synthesizing hydroxyapatite-wollastonite bioceramics by an alternative sol-gel route, using calcium nitrate and ammonium phosphate as precursors of hydroxyapatite, and high purity natural wollastonite was added in ratios of 20, 50 and 80 percent by weight the sintered biocomposite, exhibiting a certain grade of porosity. Although this porosity could have a negative effect on the mechanical properties, it is important for ensuring the efficient integration of these materials with bony tissues (Encinas-Romero et al., 2013). The aim of the present work was to synthesize and characterize hydroxyapatite-wollastonite biocomposite by solid state method using oyster shells powder as a calcium source and silica foam to produce wollastonite , and high-purity commercial hydroxyapatite added in ratios of (10,20, 30, 40, and 50) wt%. Studying the effect of hydroxyapatite amount the bioactive properties of several hydroxyapatite-wollastonite compact.

2. EXPERIMENTAL PROCEDURES

2.1 Preparation of Wollastonite

Calcium oxide prepared in laboratory (calcinations of oyster shells at 900 °C for 1 hours), and silica foam bought from local market, were used to prepare wollastonite. 48.3 wt% of calcium oxide and 51.7 wt% of silica foam these materials were weight out using analytical electric balance. The starting materials were stoichiometric mixed to provide the exact molar ratio of $\text{SiO}_2=\text{CaO}$ equal to one. This mixture was dry mixed using a planetary ball mill with runs at 300 rpm, for 12 hours. The mixture of calcium oxide CaO and silica SiO_2 were heated to 1300 °C for 2 hours to get wollastonite phase.

2.2 Preparation of Hydroxyapatite /Wollastonite Specimens

The constituents powders of hydroxyapatite, and wollastonite weighted to obtain batches of 100 g consist of (10, 20, 30, 40, 50) wt% of HAP. The powders were dry mixed using a planetary ball mill with runs at 300 rpm, for 12 hours. Subsequently the powder mixture was compacted at 200 MPa with adding 2wt% of PVA to serve an aid in the subsequent shaping pressing process. All compacted samples were dried at 100 °C for 24 hours to remove moisture before firing process and sintered at different temperatures of 1100 and 1200 °C for 3 h with an average heating rate of 5 °C/min.

2.3 Biological Experiments

In order to study the biological behavior of the hydroxyapatite-wollastonite biocomposite in vitro biological study was carried out by immersing all samples of different batches in simulated body fluid (SBF) solutions for 21 days. The ions concentration of SBF is given in table (1) equal to those of human blood plasma.

Table (1) Ion concentrations of the simulated body fluid and human blood plasma (Liu et al., 2004).

Ion	Concentration (mol/dm ³)	
	Simulated body fluid (SBF)	Human blood plasma
Na ⁺	142.0	142.0
K ⁺	5.0	5.0
Mg ²⁺	1.5	1.5
Ca ²⁺	2.5	2.5
Cl ⁻	147.8	103.0
HCO ₃ ⁻	4.2	27.0
HPO ₄ ²⁻	1.0	1.0
SO ₄ ²⁻	0.5	0.5

2.4 Characterizations

To determine the changes in phase assemblages in the sintered as well as in vitro dissolved samples, X-ray diffraction (XRD) using x-ray diffractometer (Shimadzo, 6000) at room temperature using Cu α radiation ($\lambda = 1.5405 \text{ \AA}$), and a scanning speed of 5°/min from 20° to 50° of 2θ

(Bragg angle) and 40 kV/30 mA as an applied power to estimate the crystallized phases. Scanning electron microscopy was done to reveal the changes in topographical features and to visualize the extent of dissolution in SBF using the scanning electron microscopy (SEM) (VegaII XMV). All samples were finely polished and then coated with a thin layer of gold by sputtering deposition technique (EMITEC k350 UK), prior to being scanned using SEM instrument to produce images with a magnification of (X5000). Energy dispersive spectroscopic (EDS) pattern was also order to identify to various elements present.

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction (XRD)

Figure(1) shows the XRD patterns for synthetic wollastonite which is heat treated at 1300 °C for 2 h scanned in diffraction angle (2θ) from 20° to 60°. It will be interested to notice that the presence of α -CaSiO₃ (as a predominate phase). The other phases which accompanying the major phase (α -wollastonite) were Ca₂SiO₄ (larnite), and SiO₂ (cristobalite). Figures (2) and (3) show the XRD patterns for compact samples of (10% HAP-90% W), (30% HAP-70% W), and (50% HAP-50% W) which are heat treated at 1100 °C and 1200 °C for 3 h, scanned in diffraction angle (2θ) from 10° to 60°. It will be interested to notice that HAP, α -CaSiO₃, β -CaSiO₃, and β -TCP are considered the major phases attending in diffraction patterns of the compact samples. The increasing sintering temperature from 1100 °C to 1200 °C will cause growth of stable α -TCP at the expense of unstable β -TCP.

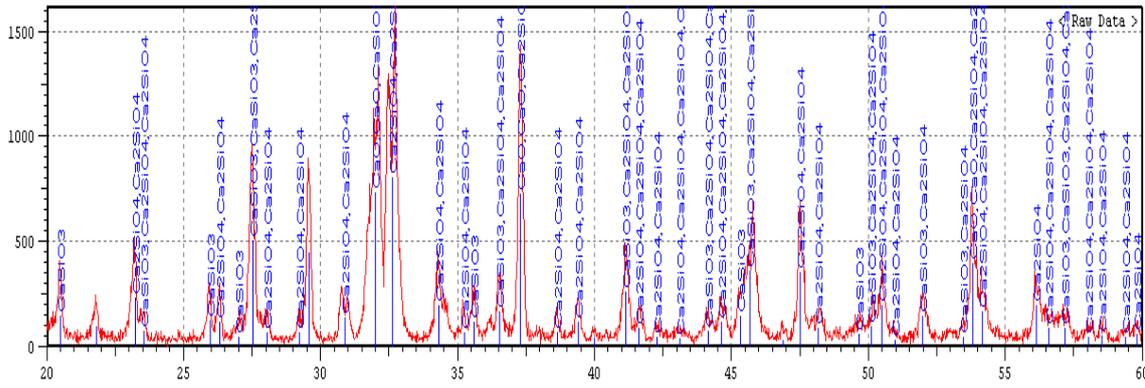


Figure1 XRD analysis of (CaO+SiO₂) mixture sintered at 1300°C.

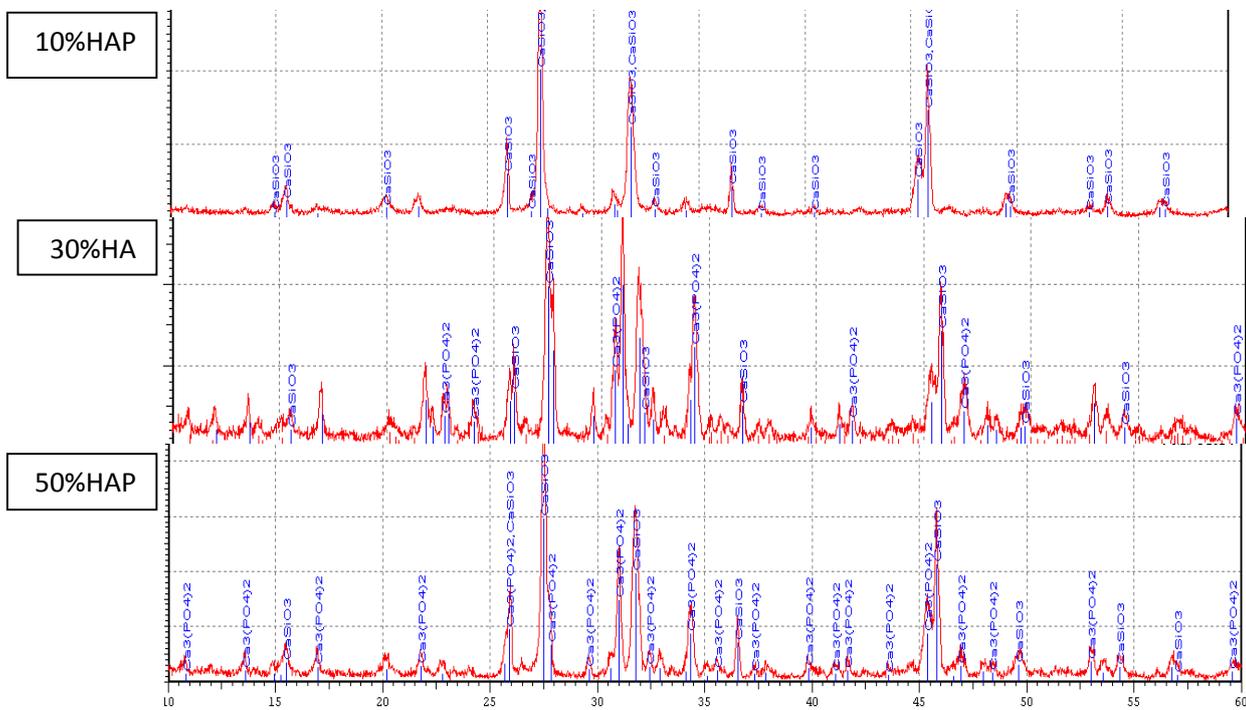


Figure (2) XRD analysis of (HAP+W) batches sintered at 1100°C.

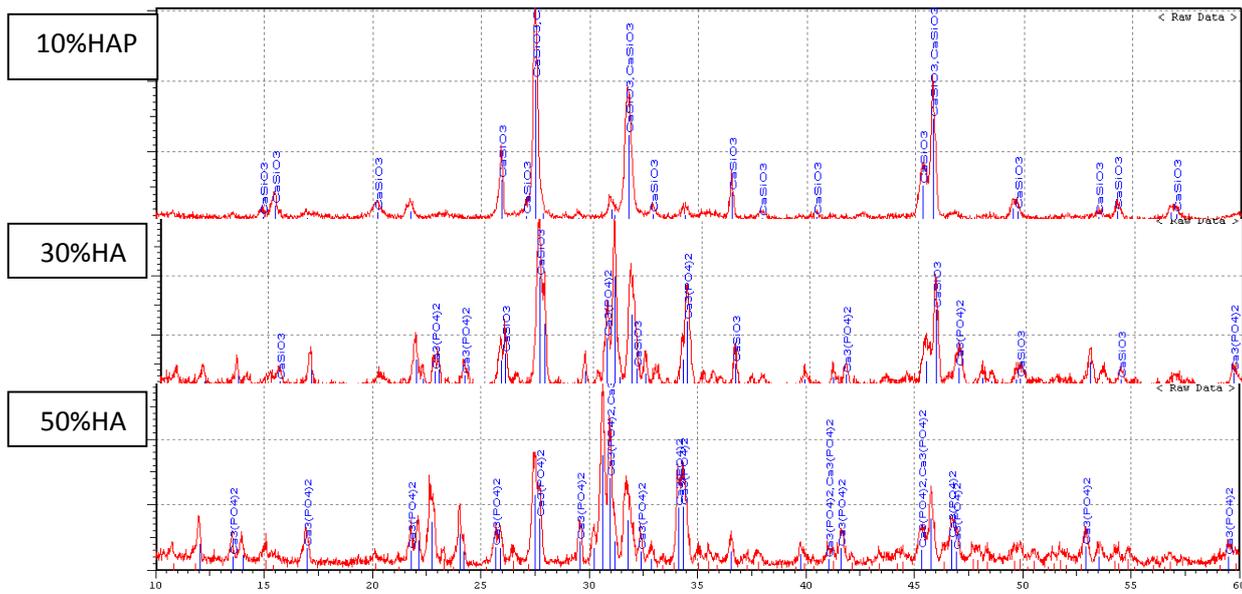
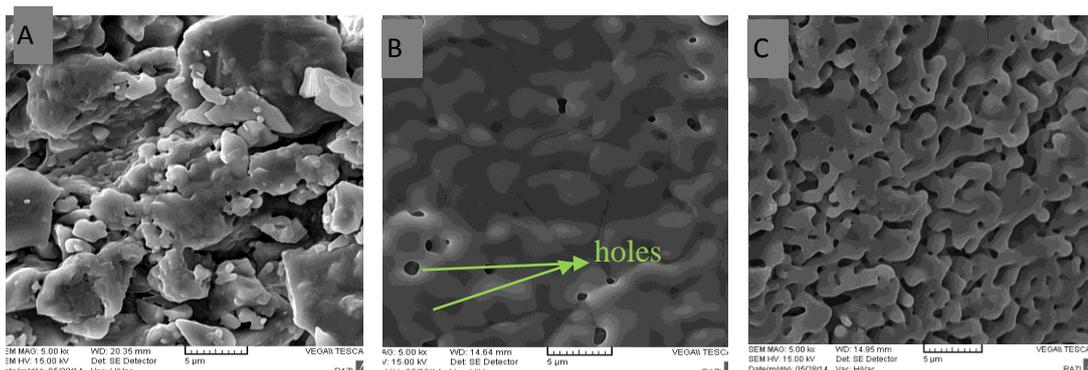


Figure (3) XRD analysis of (HAP+W) batches sintered at 1200°C.

3.2 SEM Micrographs of Compact Samples.

EM micrographs of compact samples with magnification x 500 sintered at 1200°C have been presented in (Figure 4). It can be observed from the figure that the microstructure of the sample composed of completely wollastonite is heterogeneous of irregular compacted grains of wollastonite phase (image A). Whereas the microstructure of the compact samples become homogeneous and smooth at increasing the hydroxyapatite content in the compact sample (image B). It is also observed that the grain size be more similar and the porosity is predominately inter granular, where the porosity

of the sample is located at grain boundaries and many of the very small pores disappear through diffusion kinetics. Images C and D show the scanning electron micrographs of wollastonite with percentage by weight of 30 and 50 hydroxyapatite. These images well developed necks were formed between dissimilar grains with uniform distribution of connected porosity. Finally image (E) shows small particle size round.



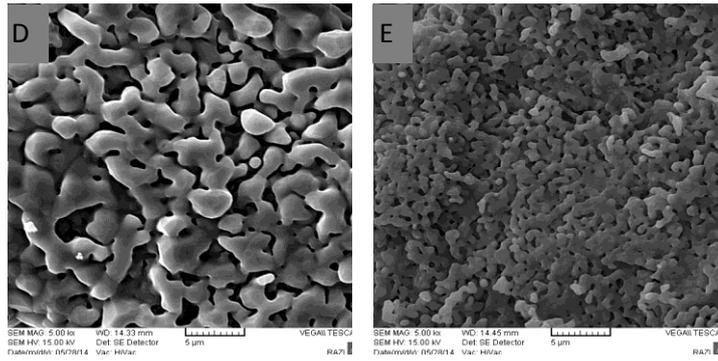


Figure 4 SEM micrographs of A (100%) W, B (10% HAP), C (30% HAP), D (50% HAP), E (100% HAP) sintered at 1200°C.

3.3 SEM micrographs of compact samples after immersion in SBF.

Figure (5) shows microstructure of bioceramics sample (20 wt% HAP+80 wt% W) sintered at 1200°C for 3 hours immersed in SBF for 21 days. It was noted from image (A) there is a layer deposited on the surface of the sample and some crystals clustered grew in different dimensions with interconnected pores. These clusters are mainly composed of hydroxyapatite mineral. Image (B) shows EDS spectra of the sample surface immersed in SBF which appear the presence of P, Si, Ca, and O peaks. The high intensity of Ca peak than the last batch due to thick layer formed when the compact reacts with surrounding SBF solution.

means that the bioceramics reacts with the surrounding SBF solution. Figure (6) shows microstructure of biocomposite sample (40 wt% HAP+60 wt % W) sintered at 1200°C for 3 hours immersed in SBF for 21 days. It was noted from image (A) the same morphology of the last batch. The layer deposited on the surface of the sample denser with small pores due to thick layer covered the surface. Image (B) shows EDS spectra of the sample surface immersed in SBF which appear the presence of P, Si, Ca, and O peaks. The high intensity of Ca peak than the last batch due to thick layer formed when the compact reacts with surrounding SBF solution.

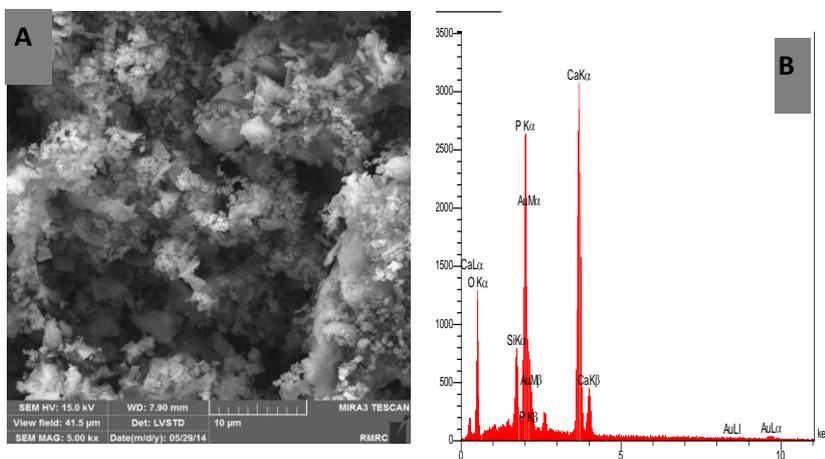


Figure 5 SEM images of bioceramics (20% HAP+80% W) sintered at 1200 °C, (A sample after 21 days of immersion in 1SBF, B EDS profile taken from the surface after immersion)

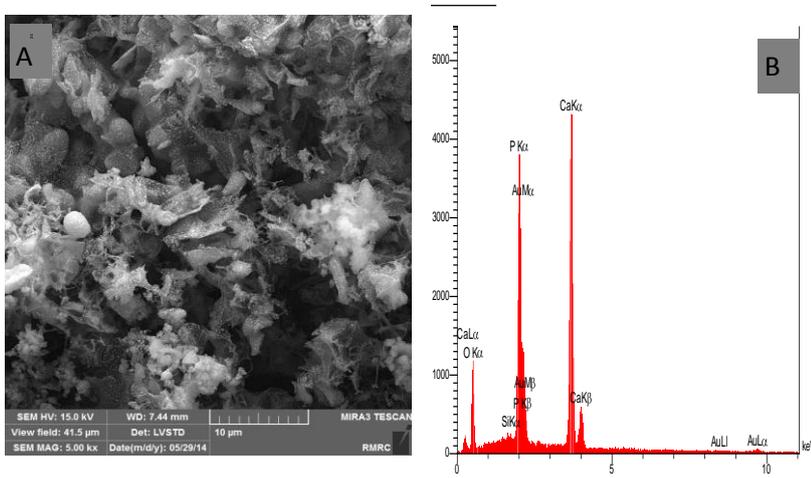


Figure 6 SEM images of biocomposite (40% HAP+60% W) sintered at 1200 °C, (A sample after 21 days of immersion in 1SBF, B EDS profile taken from the surface after immersion).

3.4 EDX Analysis of the Samples Surface

EDX analysis was used to identify apatite formation on the compact surface after 21 days. Figure (7) shows the concentration of Si, Ca, P on the compact samples surface over 21 soaking days in the SBF solution. It is evident that the increasing of hydroxyapatite content in the bioceramics sample will cause increment in calcium and phosphate content. It will be interesting to know that the dissolution of hydroxyapatite crystals and high release of Ca^{2+} , PO_4^{3-} . Concentration of calcium and phosphorus increase in the surrounding fluids and this supersaturation induces reprecipitation of apatite crystals at the compact surface. It is evident that the increasing of hydroxyapatite content in the bioceramics sample will cause decrement in Si concentration on the compact surface because of the release of soluble silica to the solution.

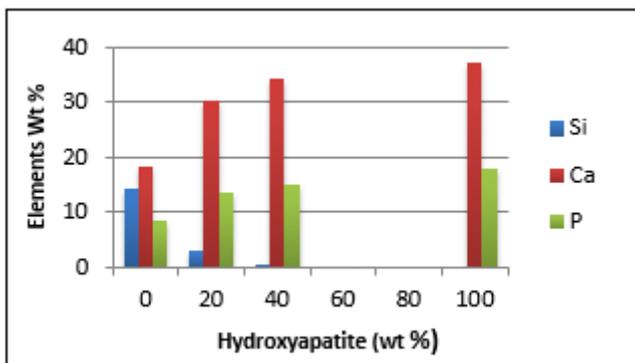


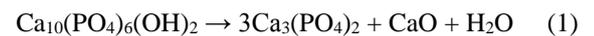
Figure 7 Variations of elemental concentration (Wt %) on the bioceramics sample surface at different weight percent of hydroxyapatite in the SBF solution.

4. PHYSICAL CHARACTERIZATIONS

4.1 Apparent Porosity

Figure (8) shows the relation between the bioceramics samples with different weight percent of hydroxyapatite and porosity. It is evident that the increasing of hydroxyapatite content in the bioceramics sample will cause increment in porosity value of the sample. In the contrast, the increasing

in sintering temperature will reduce the porosity values. It will be interesting to know that the HA decomposes into β -TCP/ α -TCP and CaO as the sintering temperature is increased as shown in fig (4-3). The reaction is proposed as follows (MONMATURAPOJ et al., 2010)



The presence of these phases in the bioceramics sample will grow the porosity value. Also large amount of water lost by decomposition of HAP created many pores.

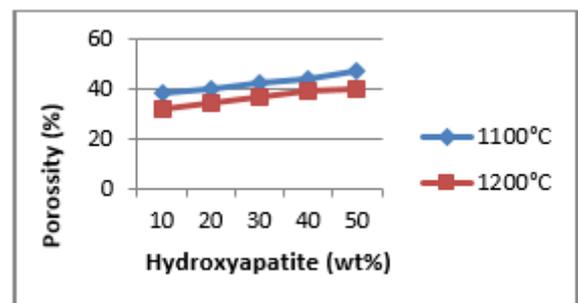


Fig (8) Variation of apparent porosity of HAP/W bioceramics with HAP percentage.

4.2 Firing Shrinkage

Figure (9) shows the relation between the samples with different weight percent of hydroxyapatite and firing shrinkage. The increasing of hydroxyapatite content in the bioceramics sample will cause increment in firing shrinkage value of the sample. In the contrast, the increasing in sintering temperature will increase the firing shrinkage values. It will be interesting to know that the decomposition of HAP and formation of CaO according to the reaction (1) which has high firing shrinkage causes holes inside the grains as shown in fig (4B).

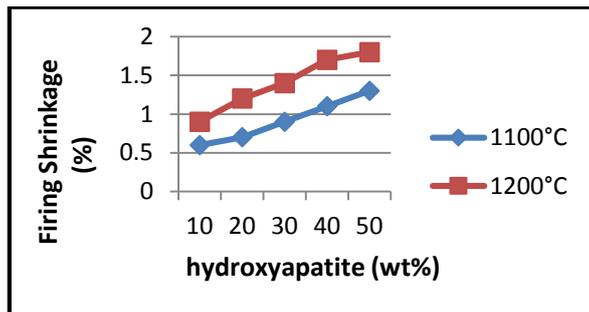


Fig (9) Variation of firing shrinkage of HAP/W bioceramics with HAP percentage.

5. CONCLUSIONS

Compacts of hydroxyapatite–wollastonite were synthesized by solid state reaction method at temperature range of 1100-1200 °C using oyster shells powder as a calcium source and silica foam to produce wollastonite, and high-purity commercial hydroxyapatite added in ratios of (10, 20, 30, 40, and 50) wt%. Microstructure of biocomposite of hydroxyapatite-wollastonite, showed efficient interaction of both phases in the biocomposite samples without any amounts of unreacted phases. Biocomposite of (HAP/W) showed good biological behavior in vitro test, by immersion in (SBF), and forming dense apatite layer covered the sample surface when the bioceramics reacts with the surrounding SBF solution which is thicker when the hydroxyapatite is in a higher proportion.

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