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Effect of TiO_2 Addition on Some Physical and Mechanical Properties of Crystalline Hydroxyapatite

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*Abstract***.** Glass-ceramics are considered one of the most important types of ceramics that are used in biological applications. This work consists of studying the effect of TiO_2 addition (4 wt%) to the Hydroxyapatite .The samples were prepared by powder technology at pressure of 78 MPa and sintered at different temp. (950,1050, 1150, 1250) ^{0}C. Physical properties were studied (apparent density, porosity, linear shrinkage and mechanical properties (hardness, tensile strength), and X-Ray diffraction was studied. The samples were tested biologically using SBF (stimulated body fluid). The Glass-ceramics used in this work were expected to show a good Biocompatibility and tight chemical bonding with Biological tissue.

1. Introduction

Surgery in the late twentieth century places heavy demands upon sophisticated technology, ranging from functional imaging equipment that assists in diagnosis, to lasers and robotics to improve accuracy and reliability. One of the most important areas in which technological advances have significantly enhanced surgery involves the use of synthetic materials for reconstruction of the body. These materials are generally referred to as (biomaterials) defined as materials intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body [1,2].

Calcium compounds are not renowned for their mechanical properties non for their hardness, but some do have a special characteristic, which is attractive for certain medical uses. This is the chemical and structural similarity between certain calcium compounds and the mineral phase of bones and teeth. In particular, the substance calcium hydroxylapatite very closely resembles this phase and it has been known for some time that this material can be placed in contact with bone and stimulate bone regeneration [3].

Sintered hydroxylapatite (HA) is well known as a biocompatible material and its use for substitute bone grafts has attracted considerable attention in the field of orthopedic surgery, in addition to its experimental or clinical application as a bone substitute,(HA) is expected to display firm contact with the soft tissue [4,5].

Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is chemically similar to bone mineral. In terms of the time in days required to attain optimum bioactivity *in vivo*, (HA) requires (110) days.

Enhancement of the bioactivity of (HA) is generally achieved by increasing the porosity, but the low strength of porous (HA) limits its use to bioactive coating, or to monolithic implants in non-load bearing sites. The manufacture of (HA) characterized by both high strength and high bioactivity, is therefore difficult to achieve in practice. Although reinforcement additives can enhance the toughness of dense(HA) [6].

Hydroxyapatite ceramic is very promising for biomedical applications. The requirements forits ceramics raw powders are excellent powder characteristics and stoichiometric composition. To fulfill the former requirement, a wet process is generally favored, and has been applied for the preparation of active (HA) powders [7,8].

2. Experimental Work

2.1 Preparation of Glass Raw Materials

The preparation of hydroxyapatite is shown in Fig. 1.

2.2 Samples Preparation

Samples were produced by powder technology as shown in Fig. 2.

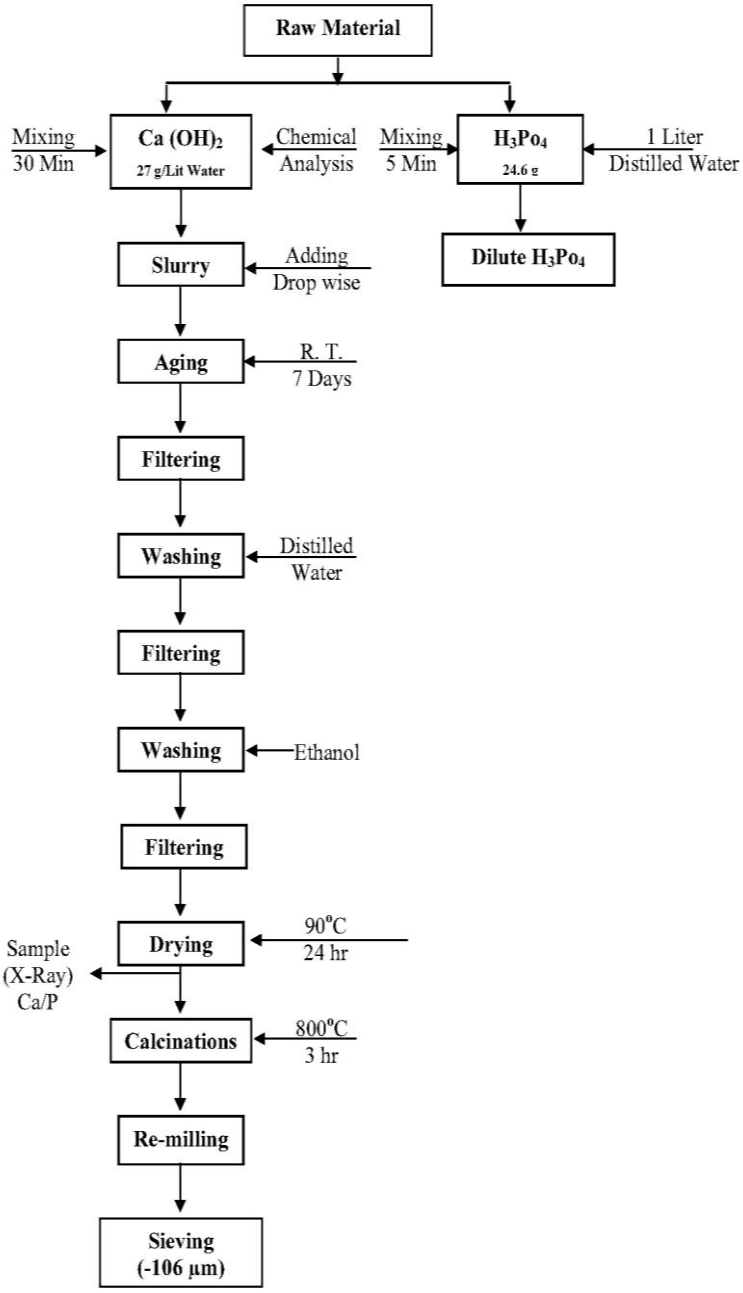

Fig. 1. Flow chart of hydroxyapatite preparation.

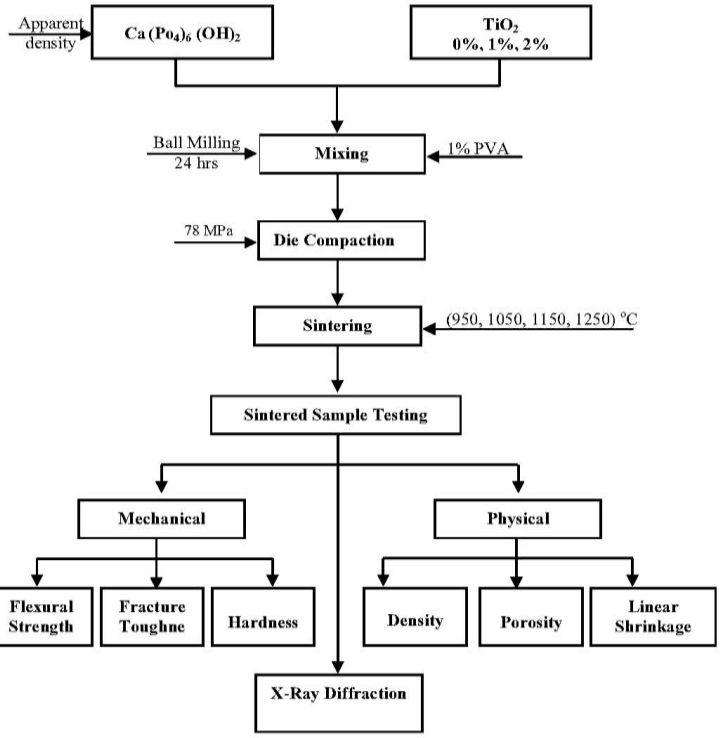

Fig. 2. Flow chart of samples preparation and testing.

2.3 Physical Testing

2.3.1 Apparent Density for Powder

Apparent density for powder is carried out by using the formula [9,10]:

$$\rho_{app} = (W_2 - W_1) / V_p \quad (2.1)$$

Where:

w_1 = weight of empty cup
w_2 = weight of cup full with powder
V_p = volume of powder
ρ_{app} = apparent density for powder

2.3.2 Bulk Density of Sintered Samples

They were determined by the archimeds method, using the following equation[9,10]:

$$\text{Bulk density} = (WD / Wa - Wb) \times D \quad (2.2)$$

Where:
Wa = weight of test piece soaked and suspended in air.
Wb = weight of test piece soaked and suspended in distilled water.
WD = weight of test piece.

The sintered samples are soaked in distilled water for (24) h before measuring or boiled in water for (1) h.

2.3.3 Porosity

The apparent porosity, true porosity, and sealed porosity can be calculated depending on the data obtained by Archmides method for densities measurements, as in the following equations[9,10]:

$$\text{Apparent porosity\%} = \{1-(\text{bulkdensity}/\text{apparent solid density})\} \times 100 \quad (2.3)$$

$$\text{True porosity\%} = \{1-(\text{bulkdensity}/\text{true density})\} \times 100 \quad (2.4)$$

$$\text{Sealed porosity} = \text{bulk density}\{(1/\text{apparent solid density})-(1/\text{true density})\} \times 100 \quad (2.5)$$

2.3.4 Linear Shrinkage% (L.Sh%)

L.Sh was measured by using a micrometer to determine the change in dimensions of sintered samples, as in the following equation[9,10]:

$$L.Sh\% = (D_2-D_1/D_1) \times 100 \quad (2.6)$$

Where:
D_2 = the diameter before firing
D_1 = the diameter after firing

2.3.5 Chemical Analysis

Chemical analysis were carried out using X-ray spectrometer to find the composition of calcium hydroxide as shown in Table 1.

Table 1. Chemical analysis for the composition of calcium hydroxide.

Component	$Ca(OH)_2$	$CaCo_3$	Antele	Cl	So4	Pb	Fe	MitAmmonium oxalate/as salt
Wt%	Min.96%	Max.3%	Max.0.1%	0.005%	0.4%	0.005%	0.05%	Max.2.5%

2.4 Mechanical Evaluation of Sintered Samples

2.4.1 Hardness

Rockwell hardness was carried in a digital device, read a direct measurement of hardness which often could transit to Vickers hardness.

Conic indenter is used on scale of (10N) with applied load of (10kg) as in the following equation[11]:

$$HV=1.8544\ p/dav^2 \quad (2.7)$$

Where:
Hv: Vickers hardness (kg/ mm^2)
P: applied load (kg)
d_{av} : average diameter of the indentation geometry (mm)

2.4.2 Fracture Toughness

It was carried out by using Vickers indentation method, where K_{IC} is calculated by measuring the top and cross crack types around Vickers indentation. After inspection of crack under optical microscope, it is seen that the crack coincides with radial median pattern that present by ponton and Rawling.

Based on this result, the following equation[12] is used to calculate the fracture toughness of our fabrication glass-ceramic:

$$K_{IC} =0.079(p/a3/ 2)\log(4.5 \times a/ c) \text{ for } 0.6<ca<4.5 \quad (2.8)$$

Where:
a= half-diagonal of Vickers indent (mm)
c= Radius of the surface crack (mm)= a+L
where L is the length of the crack

2.4.3 Diameter Compression Test

In a diameter-compression test a disk specimen is loaded in compression edgewise along a diameter. The loading generated a biaxial stress state in the specimen with a compressive principle stress in the direction of loading and a transverse tensile stress. These stresses are nearly constant for a significant fraction of the test specimen near the center of the disk. Their magnitudes are given by the relations [13]:

$$\sigma = 2P/ \Pi Dt \quad (2.9)$$

Where:- P= load
D= diameter of specimen
t= thickness of specimen

3. Results and Discussion

3.1 X- Ray Diffraction Observations

X- ray diffraction patterns were used to indicate the major phase of sample. $Ca_2P_2O_7$ phase was observed clearly at almost X- ray patterns of this work as shown in Fig. 3 which intimate with biological texture.

3.1.1 Effect of Temperature on Phases

Effect of temperature on densification and crystallization of sintered glass-ceramic have been studied at range of temperature (950-1250)°C, X-ray diffraction analysis had revealed the presence of $Ca_2P_2O_7$ phase as the major phase at many reflections. The amount of $Ca_2P_2O_7$ was the same at different temperatures.

3.2 Physical Properties Observation

3.2.1 Apparent Density

Figure 4 shows the effect of the amount of TiO_2 on the apparent density, from this figure we observed that the apparent density increases with increasing TiO_2 amount because of filling the spaces between particles of hydroxyapatite.

3.2.2 Bulk Density

Figure 5 shows the effect of sintering temperature and amount of TiO_2 on the bulk density which increased with increasing temperature because of densification process and with increasing TiO_2 amount due to filling the spaces between particles.

3.2.3 L.Sh%

Figure 6 shows the effect of temperature and amount of TiO_2 on L.Sh% which decrease with increasing temperature due to vibration of the binder and decreasing the spaces between particles.

3.2.4 Porosity

Porosity had been increased with increasing temperature due to grain growth but decreased with the addition of TiO_2 because of mixing of different particle size of particles. As shown in Fig. 7.

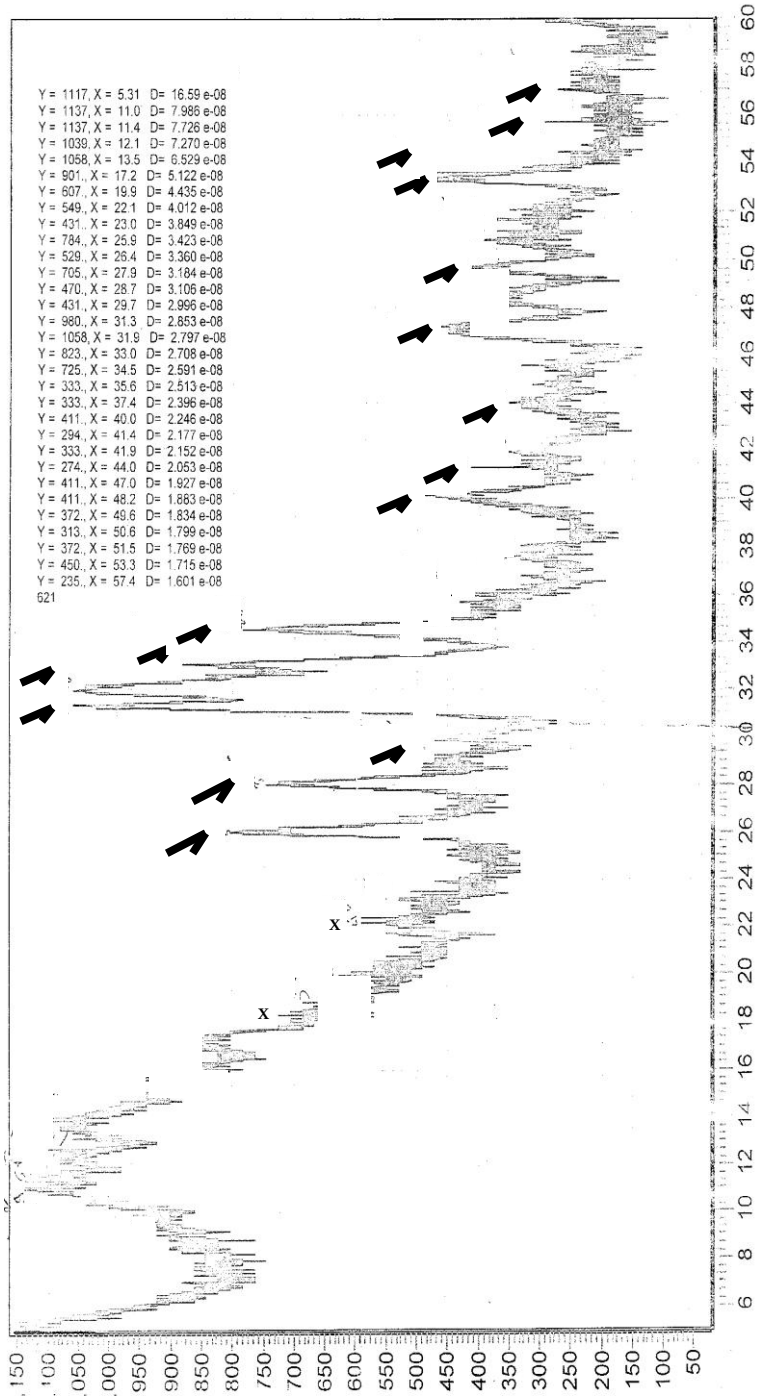

Fig. 3. X- ray pattern for the prepared Hydroxyapatite powder.
√ Hydroxyapatite X : $Ca_2P_2O_7$

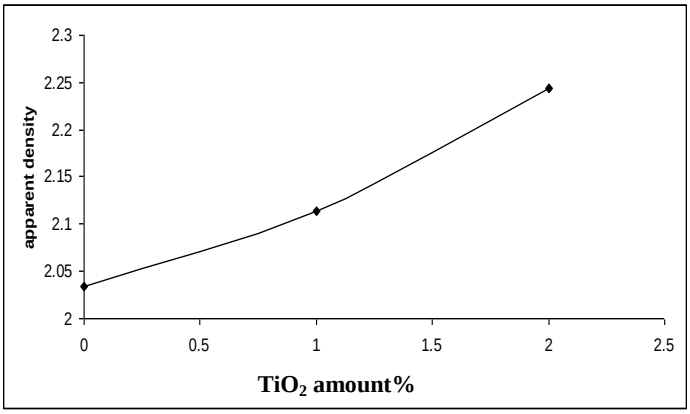

Fig. 4. Showing the effect of amount of TiO_2on the apparent density.

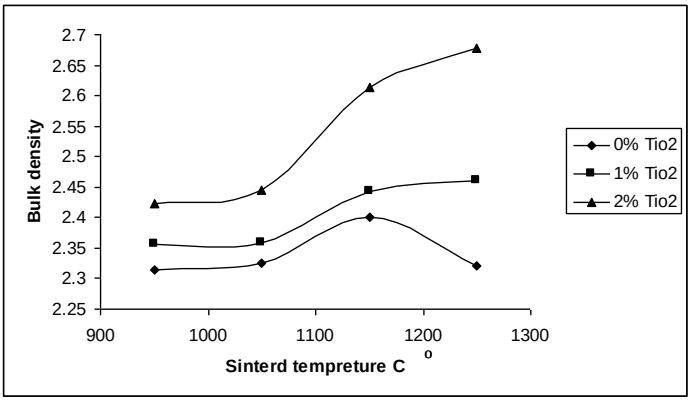

Fig. 5. Showing the effect of sintering temperature and amount of TiO_2on the bulk density.

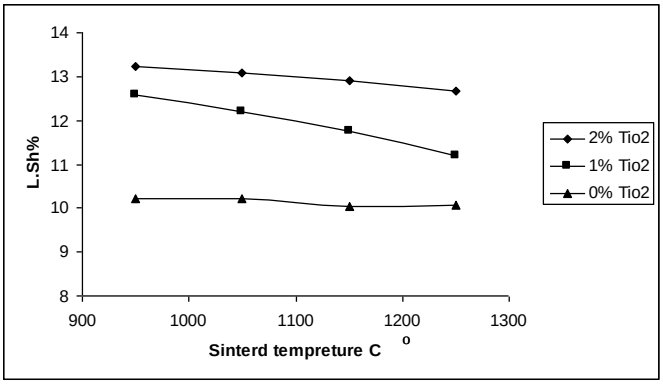

Fig. 6. Showing the effect of temperature and amount of TiO_2on L.Sh%.

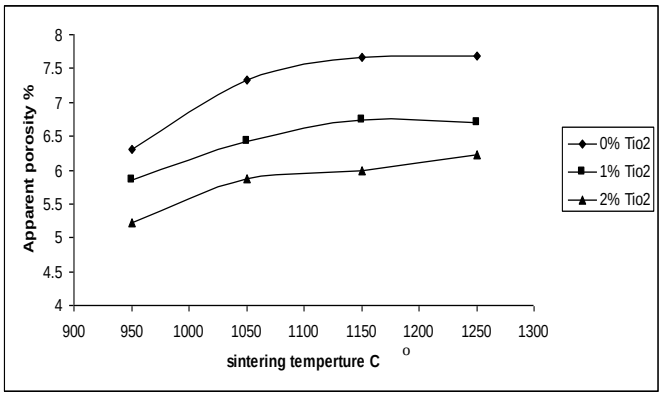

Fig. 7. Showing the effect of temperature and amount of TiO_2 on apparent porosity% .

3.3 Mechanical Properties

3.3.1 Hardness

Hardness measurements released an increasing of hardness with increasing temperature due to crystallization process, but it decreases later because of grain growth. TiO_2 amount effect positively on the hardness value as shows in Fig. 8.

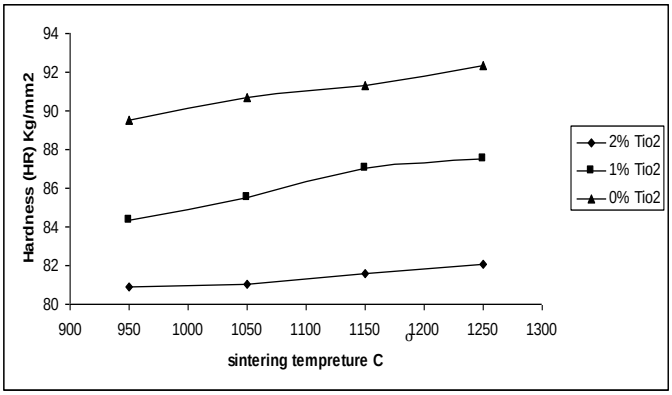

Fig. 8. Showing the effect of temperature and amount of TiO_2 on hardness.

3.3.2 Fracture Toughness

Figure 9 shows the effect of sintering temperature on fracture toughness at different amounts of TiO_2, from this figure we can note that fracture toughness values arriased with increasing temperature due to densification process caused by crystallization and the formation of

$Ca_2P_2O_7$ phase, TiO_2 addition caused an enhanced in fracture toughness because of crystallization process, fracture toughness decreased at 1250 C^o because of grain growth.

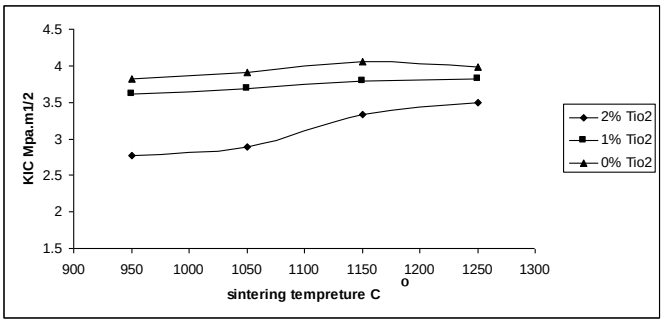

Fig. 9. Showing the effect of temperature and amount of TiO_2 on KIC.

3.3.3 Tensile Strength

Effect of sintering temperature and amount of TiO_2 shown in Fig. 10, this fig. explain that fracture strength increased with increasing temperature because of formation of $Ca_2P_2O_7$ phase due to crystallization process which encouraged by the addition of TiO_2.

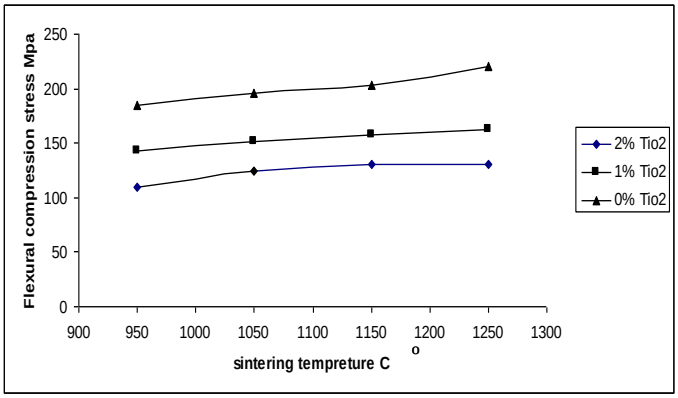

Fig. 10. Showing the effect of temperature and amount of TiO_2 on flexural compression stress.

4. Conclusions and Recommendations

4.1 Conclusions

A study of crystallized glass-ceramic from bulk glass reveals that optimum physical and mechanical properties were as following:

a. Maximum bulk density at (2% TiO_2, 1250 ^{0}C).

b. Minimum porosity at (2% TiO_2 , 950 ^{0}C).

c. Maximum apparent density at (2% TiO_2).

d. Maximum L.Sh% at (2% TiO_2 , 1250 ^{0}C).

e. Minimum bulk density at (2% TiO_2 , 1250 ^{0}C).

f. Maximum fracture toughness at (2% TiO_2 , 1150 ^{0}C).

g. Maximum flexural strength at (2% TiO_2 , 1250 ^{0}C).

4.2 Recommendations

Suggestions that may be recommended for future studies are:

a. Studying the effect of immersion in SBF fluid and measuring the potential for specimens.

b. Studying the effect of crystallization temperature and time of crystallization on glass powder compact at (3-10%) TiO_2.

c. Studying fatigue limit of the prepared glass-ceramics from glass powder compact, which is an important property for implantation in hip joints.

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دراسة تأثير إضافة التيتانيا على بعض الخواص الفيزيائية والميكانيكية للهايدروكسي أباتايت المتبلور

وليد عاصم حنا*، و جنان ستار خشان، و هيثم رزوقي صالح

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المستخلص. يعتبر السيراميك الزجاجي واحدًا من أهم أنواع السيراميك المستخدمة في التطبيقات البيولوجية. هذا البحث يدرس تأثير إضافة 5٪ TiO_2 إلى الهيدروكسي أباتيت. أعدت النماذج بواسطة تكنولوجيا المساحيق بضغط 78 ميجا باسكال، و لبدت في درجات حرارية مختلفة هي(950، و1050، و1150، و1250) م°. وتمت دراسة الخصائص الفيزيائية (الكثافة الظاهرية، والمسامية، والانكماش الخطي) والخواص الميكانيكية (صلادة، ومقاومة الشد)، وتمت دراسة حيود الأشعة السينية. وجرى اختبار العينات بيولوجيا باستخدام SBF (السائل المحفز لنمو خلايا الجسم)، والسيراميك الزجاجي المستخدم في هذا البحث كان من المتوقع أن يظهر النشاط الحيوي، والروابط الكيميائية مع الأنسجة الحية.