Densification, Mechanical and Bioactive Properties of Borosilicate Glass/Anatase Nano-Composites

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Abstract: This work included the preparation and *in-vitro* bioactivity studies of glass, rutile, anatase and composite samples with different compositions, using infrared reflection spectroscopy (IR), X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques. The formation of hydroxyl apatite (HAP) layer, which is the only indication of the bioactive properties, was detected on the surfaces of composite samples after their immersion in simulated body fluid (SBF). Characterization of the prepared bioactive composites through their mechanical properties was also studied. Infrared reflection spectra of bioactive glass surface before and after immersion in the simulated body fluid (SBF) confirmed its bioactivity. XRD showed that the prepared composite samples have biological behavior with different rates, i.e. the ability of samples to form HAP layer on their surfaces is higher in case of composites with high glass content. Photo-micrographs of samples surfaces confirmed the above results through the formation of granules HAP layer. Transmission electron microscope photos (TEM) indicated the nano-particles of prepared ceramics. Also, XRD patterns for ceramics after their immersion in SBF showed the bioactivity of anatase through the formation of HAP layer and the bio-inertness of rutile due to the disappearance of latter phase from the XRD pattern. Microhardness measurements showed that composite samples are qualified to be used as bone replacement for highly – load region in the body.

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Key words: Bioactive glass, anatase, rutile, bioactive nano-comosites, SEM, XRD, biological and mechanical behaviors.

1. Introduction

The repair of damaged bone tissue has been widely investigated for centuries. Bone tissue loss caused by severe injury or disease is a critical problem in orthopedic clinics, and involves the issues of bone repairs and substitutes. Autografts, allografts and synthetic grafts are the main approaches to repairing bone defects or replacing lost bones. Although autografting has good compatibility and no immunological response, the limited donor bone supply and the additional trauma involved have limited its application. Severe immunological problems and disease transmission have also limited the application of allografts [(1)]. Synthetic materials for the bone repair and substitute have been studied extensively in recent decades with the development of material sciences. Ceramics, glass, metals, polymers and their composites have all been investigated as bone substitutes [(2,3)]. Besides showing good biocompatibility and bioactivity, any material used for bone repair and substitution should also be matched for mechanical properties [(4)].

Because of the excellent biocompatibility of titania, it has been widely used for orthopaedic replacement. However, because titania is lack of the ability to induce apatite formation, it could only form mechanical attachment with the host tissue [(5)].

Since the discovery of bioglass® by Hench, bioactive glass (BG)(45S5), that contains SiO_2, Na_2O, CaO and P_2O_5 in specific proportions, has been found to gain a strong ability to form biological bonding with host tissue via an appetite layer between the tissue and material, which is formed by a complex mechanism based on ion leaching, controlled dissolution of the glass surface and precipitation of Ca and P from the body fluid [(6)].

But due to the limiting fracture toughness of different bioactive glass types, they do not always have the mechanical properties required in prosthetic devices (i.e. load bearing). For that reason composite materials have been developed, with the aim of combining the properties of bioactive material with the toughness or the tensile strength of a second phase. The production of composite materials has proven to be suitable solutions for improving the mechanical properties of weaker materials. Glass matrix biocomposites were reinforced by introducing many tough phases [(7)] like, Al_2O_3, ZrO_2, and others. The choice or the design of best materials for a specific application plays an important role in the feasibility of

high performance components. Among the most promising materials and already a reality in many applications are advanced whose properties in specific fields are seldom matched.

Recently, insufficient attention was paid to composite with a brittle matrix, but their importance should grow in future. Low- melting glasses hold the highest promise as matrices for composite material (CM) structure. The physicochemical and thermal compatibility of the filler and the matrix is apparently one of the most essential problems which have to be solved in developing practical compositions. Appropriate adhesion between them is needed to provide an adequate strength and optimum load distribution, whose mechanism is determined by the type of CM and method of its production [8]

The aim of the present work is to study the effect of adding nano titania (anatase or rutile) to borosilicate glass on the mechanical properties and bioactivity. Also, these biocomposites were followed in simulated body fluid (SBF) to verify the formation of a bone-like apatite layer on their surfaces by using *in vitro* test, Fourier transmission IR (FT-IR), scanning electron microscope (SEM) and X-ray diffraction (XRD) techniques.

2. Experimental Details

2.1. Preparation of glass and ceramic materials

Glass was prepared from chemically pure grade materials with the composition shown in Table 1. The materials include H_3BO_3 for B_2O_3 and NH_4 (H_2PO_4) for P_2O_5 while Na_2O and CaO were introduced in the form of their respective anhydrous carbonates. SiO_2 was added as pure sand. The weighed batches were melted in a porcelain crucible at 1100°C for 2 hrs. The melt was rotated at intervals of 30 min apart to ensure homogeneity. The homogenized melt was cast into warmed stainless steel molds. The prepared samples were immediately transferred to a muffle furnace regulated at 350°C for annealing and removing thermal stresses. The muffle was switched off after 1 h and left to cool to room temperature.

For ceramic system, preparation of TiO_2 nanoparticles by sol–gel method has been carried out in several steps and it needs to mix two different solutions. These two solutions are called as precursor and hydrolysis solutions. The precursor solution is a mixture solution of tetrabutyl titanate ($(C_4H_9O)_4Ti$, 98.00%) and absolute ethyl alcohol (C_2H_5OH, 99.70%) with a molar ratio of 1:(2–5). The hydrolysis solution is prepared by mixing deionized water and glacial acetic acid (CH_3COOH, 99.50%) with a ratio of 1 :(1.5–2) to control the sol–gel reactions (hydrolysis and condensation). Then the hydrolysis solution was added drop wise to the precursor solution under vigorous stirring at room temperature. In this procedure, pH of solution must be controlled strictly in the range of 3–4. After mixing for several minutes, the stirring rate was reduced in order to minimize coagulation of the titanium oxide particles during the sol–gel reactions. The resulting clear solution was kept undisturbed for 48 hrs to become a transparent pale yellowish sol which was then dried in a desiccator at 60 °C to form a gel. At last, the dried powder gel was calcined at 220–600 °C for 2 hrs in an oven to prepare the pure anatase samples, which is examined by x-ray diffraction (XRD) and transmission electron microscope (TEM).

By raising the calcined temperature up to 700°C, rutile phase was precipitated which can be followed up by XRD.

2.2. Preparation of glass/ceramic composites

Fine glass powders, obtained by grinding the prepared glass blocks, were well mixed with the ceramic material. Five composite batches were designed as 1, 2, 3, 4 and 5; their batch compositions are summarized in Table 1. The mixed batches were uniaxially pressed at 60 MPa in a disc shape of about 1/2 inch in diameter and height. The pressed batches were then fired for 2 hrs in air at 850 °C; less than this temperature, all samples were friable.

2.3. Bioactivity studies

To study the bioactivity, glass, ceramic and composites samples were soaked in 50 ml of Tris-buffered simulated body fluid (SBF) solution, which resembles the human blood plasma, at 37±0.5 °C, for one month. The ion concentrations of SBF are summarized in Table 2. The SBF was prepared by dissolving reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2$ and Na_2SO_4 in 700 ml deionized water. The solution was buffered to pH 7.4 with tris-(hydroxyl methyl)-amino methane taken out after immersion in (SBF), washed with deionized water and finally air dried. Its surface analyses were conducted by Fourier transmission IR (FTIR) using FTIR spectrometer (type Jasco FT/IR-430, Japan) and scanning electron microscope (SEM mode Philips XL30) and x-ray diffraction (XRD) analysis using a Philip Powder Camera (Type CPM 9920/02) with $CuK_\propto$ radiation and Ni filter.

2.4. Properties of glass/ceramic composites

Apparent porosity and bulk density of the sintered samples of glass/ceramic composites were measured by the Archimedes method. Identification of crystalline phases for the obtained composites was carried out by XRD analysis. The microstructure of the sintered composites was observed by scanning electron microscope. Biological characters of the samples were also studied by immersing them in SBF solution.

Hardness was measured using Vickers microhardness indenter (Shimadzu, Type-M, Japan). Polishing was necessary to obtain smooth and flat parallel surfaced samples before indentation testing.

Testing was conducted with a load of 100 g and loading time was 15s. The measurements were carried out under normal atmospheric conditions.

Table (1): Chemical and batch compositions of glass and glass/ceramic composites

Chemical composition of glass		Sample No.	Batch composition (wt.%)	
Oxides	wt.%		Glass content	Ceramic content (anatase)
SiO_2	10	1	50	50
B_2O_3	30	2	70	30
CaO	30	3	90	10
Na_2O	25	4	40	60
P_2O_5	5	5	20	80

Table (2): Reagents for preparation the simulated body fluid (SBF)

Order	Reagent	Amounts in grams
1	NaCl	7.996
2	$NaHCO_3$	0.550
3	KCl	0.224
4	$K_2HPO_4.3H_2O$	0.228
5	$MgCl_2.6H_2O$	0.305
6	1M HCl	40 ml
7	$CaCl_2$	0.278
8	Na_2SO_4	0.071
9	$(CH_2OH)_3CNH_2$	6.057

3. Results and Discussion

3.1. Characterization of prepared ceramics

Figures 1 and 2 exhibit the XRD analysis and TEM of the prepared ceramics used in this work.

XRD of the as-prepared calcined ceramic shows Sharp XRD peaks corresponding to anatase phase (Fig.1). Therefore, well-crystallized ceramic powder has been obtained. Anatase phase was precipitated at 600°C. Above this temperature, rutile phase is appeared (Fig.2). Also, TEM photomicrographs of prepared ceramics reveal very fine ceramic particles with a size of several nano-meters.

3.2. Biological behavior of glass and ceramic

A significant characteristic of bioactive glasses is their ability to bond with living bone both *in vitro* and *in vivo* through the formation of a HAP layer on their surfaces [9] as shown in Fig. 3(b), many nanoparticles of HAp formed on the surface of samples after incubation for 30 days in SBF which can be recognized clearly by comparing both SEM photos before (Fig. 3a) and after glass immersion in SBF solution.

XRD analyses results for the bioglass before and after soaking in SBF are shown in Fig.4. The pattern of borosilicate glass showed that it is in an amorphous state which is indicative of the internal disorder and glassy nature of this material. There are obvious changes in the structure of the glass after immersion for 30 days in SBF. New peaks were emerged which corresponded to the reflections of HAP according to the standard JCPDS card (72-1243). The appearance of that phase indicates the bioactive characteristics of borosilicate glass.

Figure 5 exhibits the FTIR spectra of glass sample before and after its immersion in SBF solution. As shown in Fig. 5a, the typical bands associated with Si–O–Si bonds appeared at 810 and 1049 cm^{-1} [10]. The band at 1417 cm^{-1} corresponds to B–O symmetric stretching vibrations from the $[BO_3^{-3}]$ units [11]. The appearance of a band from $[BO_3^{-3}]$ illustrates that $[BO_3^{-3}]$ partially replaces $[SiO_4^{-4}]$ sites in the glass structure. Broad bands at 3483 and 1636 cm^{-1} are attributed to the stretching and bending vibrational modes of O–H in water molecules and Si–OH stretching of surface silanols[12], respectively. After immersion in SBF (Fig. 5b), the concentrations of Ca and P increased significantly, and were accompanied by a decrease in the concentration of Si, which signified the extended development of HAP. That HAP crystals formed on the surface of the borosilicate glass after incubation in SBF was further confirmed by performing FTIR spectroscopy, as shown in Fig. 3b, obvious bands from P–O appeared at 574, 607, and 1033 cm^{-1} indicating the growth of a HAP layer on the surface of the borosilicate glass. In addition, a band consistent with carbonate appeared at 877 cm^{-1}, suggesting the formation of carbonate-HAP, which is of similar composition to bone mineral [12].

Fig. 6a presents XRD pattern of anatase after one month soaking in SBF at 37°C.; the other phase which precipitated after immersion in solution is halite, syn.-NaCl. The precipitation of the halite phase could be attributed to the bioactive behavior of anatase [13]. In-vitro bioactivity of anatase has been attributed to chemisorbed hydroxyl (OH) groups, hydroperoxide (OOH) groups, and negative charges of the hydrated titania gels [14], which is confirmed by Wang *et al.*[15], who prepared titania gel by soaking Ti into hydrogen peroxide (H_2O_2) solutions containing $TaCl_5$. They found that a subsequent heat treatment transformed the amorphous titania to anatase, which improved the bioactivity remarkably, despite of the possible decrease in Ti–OH groups that played key roles on the apatite deposition process. This was interpreted by (a) the crystallographic lattice match between the anatase and the deposited apatite; and (b) the elimination of superoxide ions, which are suspected to disturb apatite nucleation, from the gel layer [15]. The former explanation agreed with Mao *et al.* [16] who also stressed the roles of the crystal lattice match between anatase and apatite. On soaking in SBF, Uchida *et al.* [17] also found that the apatite formation was much more pronounced on the heating induced anatase gels than on the amorphous or heating induced rutile gels.

Fig. 6b exhibits XRD pattern for rutile before and after soaking in SBF, the pattern confirms the above discussion. There is no change in precipitated

phase before and after immersion which means that the prepared rutile is inactive. For that reason, the synthesized composites in that work were composed of anatase and glass with different compositions.

3.3. Densification properties

Table 3 summarizes the change of bulk density and apparent porosity of the prepared composites sintered at 850°C for 2 hrs. It was noticed that, by increasing the glass content in the composite, the porosity decreases.

In glass/ceramic systems, sintering takes place by viscous flow of the glass phase. Liquid phase sintering mechanisms are classified by three stages: glass redistribution, solid-particle rearrangement and viscous flow of liquid-phase glass [(18)]. The desired characteristics of glass/ceramic composites are achieved by sintering to possible densification at lower temperature.

There are two factors affecting the bulk density and apparent porosity of glass/ceramic composites. They are: the glass content in the composite material and / or the sintering temperature which should be higher than the softening point of the borosilicate glass [(19)], which is 815°C [(20)]. Thus, when these composite samples are treated at higher temperatures, the borosilicate is much more softened and viscous flow occurred much easily; therefore, the glass/ceramics composites are better densified. Consequently, the closed pores increase.

3.4. Biological behavior of composite samples

Precipitated phases in borosilicate glass and its corresponding composites, during sintering at elevated temperature, have an important effect on the biological properties of the final materials. Fig.7 shows XRD patterns of the five composite samples sintered at 850°C. Considerable changes are observed; these phase transformations indicate a high chemical interaction between calcium oxide of the glass and titanium nano- particles. The change of phases is presented in all samples, the reaction products of the chemical interaction are identified as tetragonal calcium titanate (main phase), which has been studied for bioactivity purposes [(3)].

Due to melting of glass at high temperature, the molten glass could not stay on the surface of the composite due to the gravity and the capillary forces from anatase matrix. Thus, the surface of the composite became depleted in SiO_2 and the molten glass trapped inside the composite would later become solidified during cooling [(21)].

From Fig. 7(1), it is noticed that rutile phase was appeared, because of the anatase-rutile phase transformation at high temperature[(22)] , and the other precipitated phases, Provoskite ($CaTiO_3$) and calcium titanium oxide silicate ($Ca(Ti(SiO_4))$), are due to solid state reaction between glass and ceramic.

By lowering ceramic content in composite samples (2&3), rutile and provoskite phases are decreased. But by further increasing the ceramic content (samples 4&5), all phases are precipitated again.

Composite samples were immersed in SBF for 30 days in order to assess bioactivity. Fig. 8 shows XRD patterns of all samples after this period of immersion in SBF. Hydroxyapatite (HA) is formed on all composite samples. This result indicates the bioactivity of prepared composites. In samples with lower glass content, the intensity of precipitated apatite phase decreases, but its interference with other phases leads to high and sharp appearance of the peaks in XRD pattern.

The above results are confirmed by figures 9&10 which exhibit the photomicrographs of composites before and after soaking in SBF for one month.

Figure 9 shows SEM photos of the five composites before immersion. From this figure, one can notice the high crystallization of samples 1, 4 & 5 due to high percent of ceramic contents in those composites, but samples 2& 3 are poorly crystallized due to lower ceramic contents.

Figure 10 illustrates the effect of 30 days immersion in SBF on composite samples, it is clear that the apatite phase, with its round shape, is precipitated on the surface of all composites which gives them the bioactivity nature. The intensity of the apatite phase differs according to the samples composition, i.e. by increasing glass content; apatite phase is well-crystallized due to the high bioactivity characters of borosilicate glass related to the ceramic. Also, the other phases are clearly precipitated according to the composition of composite samples.

3.5. Hardness

Hardness of studied composites is exhibited in Fig. 11. It appears that the hardness increases by increasing bulk density and decreasing porosity; this may be attributed to glass content in composites, once the glass passed its softening point (more than 800 °C), the hardness increased abruptly due to the much increased densification of the samples[(21)].

Table (3): Apparent porosity & Bulk density of sintered glass/ceramic samples.

Composite No.	Apparent porosity	Bulk density
1	15.52	2.18
2	8.87	2.22
3	3.38	2.31
4	29.14	2.11
5	51.15	1.89

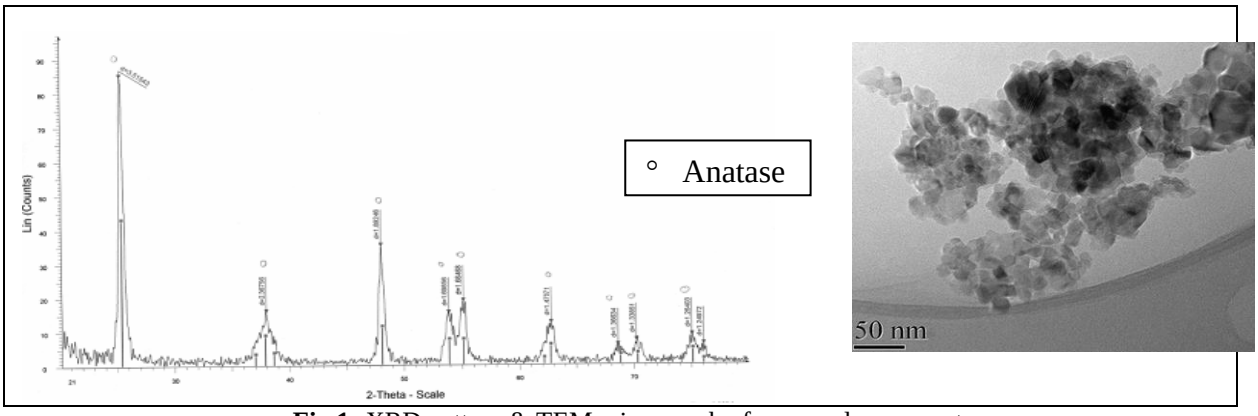

Fig.1: XRD pattern & TEM micrograph of prepared nano-anatase

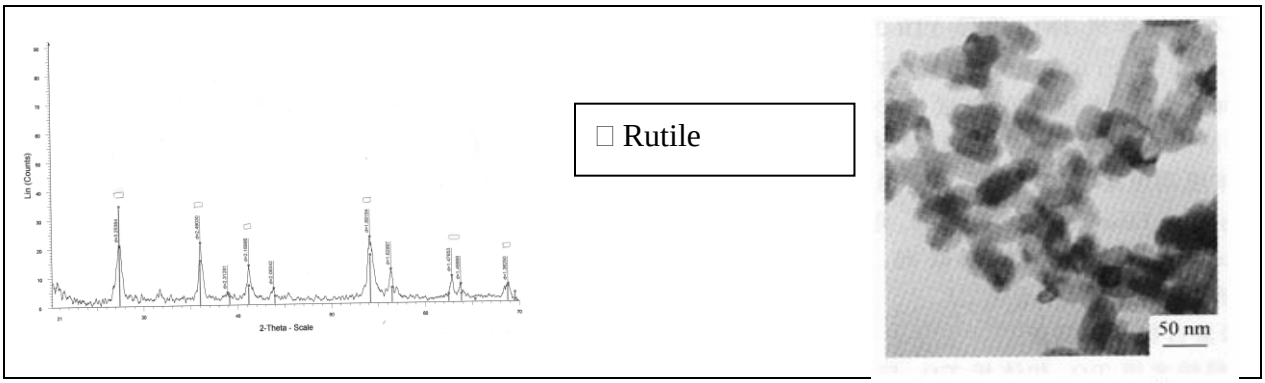

Fig.2: XRD pattern & TEM micrograph of prepared nano-rutile

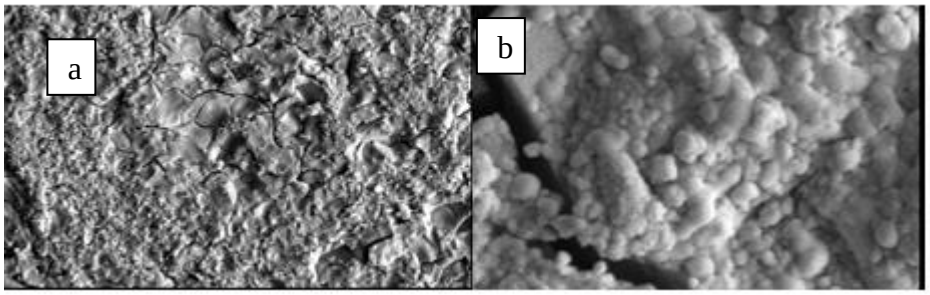

Fig. 3: SEM photograph of borosilicate glass before (a) and after 30 days immersion in SBF (b)

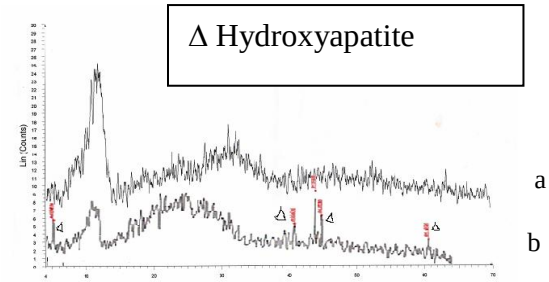

Fig. 4: XRD pattern of glass before (a) and after immersion in SBF (b)

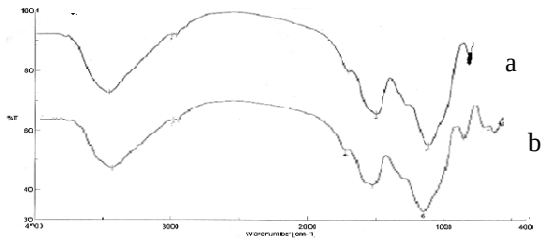

Fig. 5: FTIR spectra of glass before (a) and afte immersion in SBF for 30 days (b)

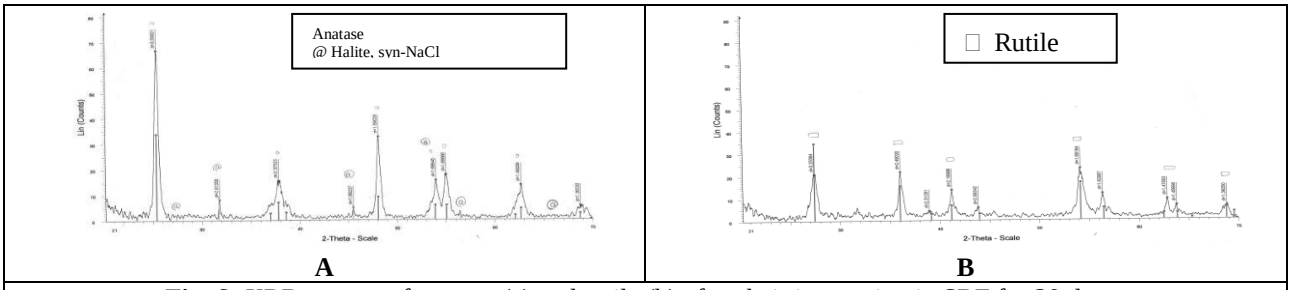

Fig. 6: XRD pattern of anatase (a) and rutile (b) after their immersion in SBF for 30 days.

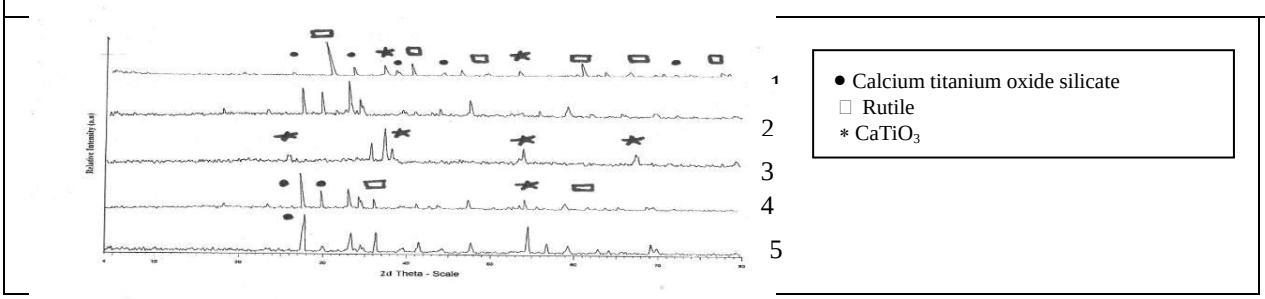

Fig.7: XRD patterns of composite samples before immersion in SBF

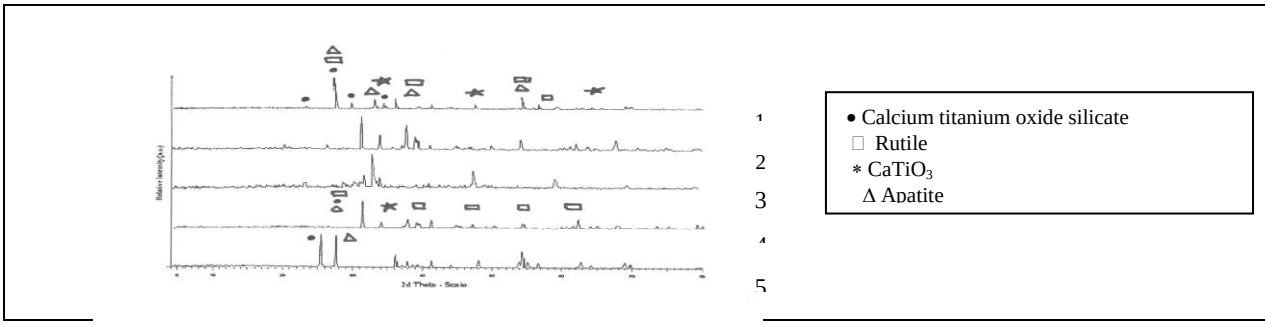

Fig.8: XRD patterns of composite samples after immersion in SBF for 30 days

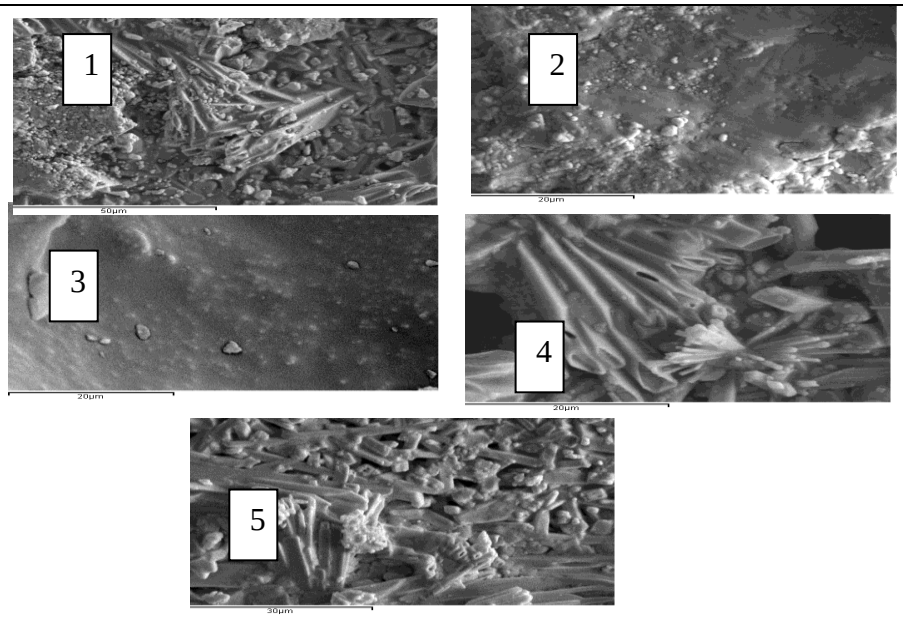

Fig. 9: SEM photographs of composites before immersion in SBF

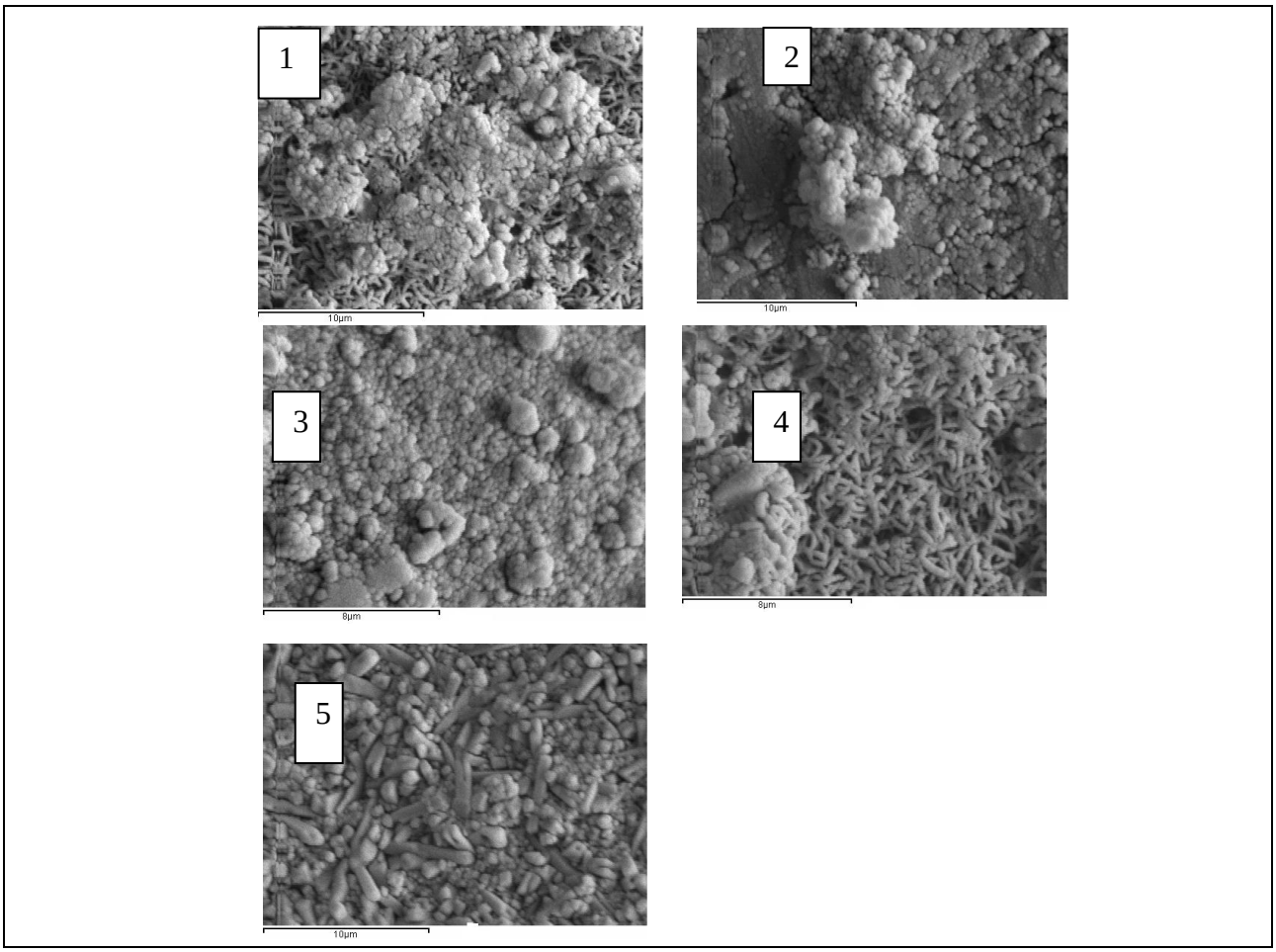

Fig.10: SEM photographs of composites after immersion in SBF for 30 days

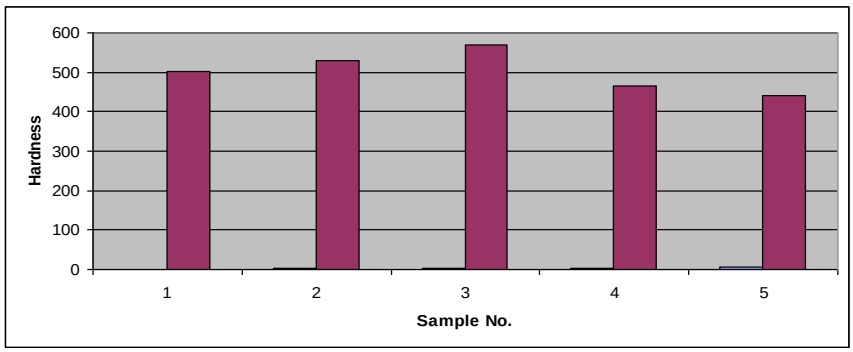

Fig. 11: Hardness of prepared composite samples sintered at 850°C

Conclusion

Materials with high bioactive properties, and low sintering temperature, were studied for application of implantation in human body. A glass/ceramic composite is one of the most effective materials for that purpose; the effect of ceramic-containing nano-Anatase addition into borosilicate glass on the densification, bioactivity and mechanical properties of composite material was studied. In glass/ceramic composites, the bioactivity is increased by increasing glass content due its higher biological properties over the ceramic. Hardness of prepared material increases by increasing the densification. The studied properties of the prepared glass/ceramic nano-composites are affected by the formed phases.

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