The Effect of ZrO2 and TiO2 Reinforcing Agent on the Microstructure and Mechanical Properties of Hydroxyapatite Nanocomposites

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Various weight fractions (5, 10, 15, 20 and 25 wt.%) Hydroxyapatite (Ca10(PO4)6(OH)2-(HAp)) based composites reinforced by ZrO2 and ZrO2+TiO2 nano particle (20-40 nm) were fabricated using High Energy Ball Milling (HEBM) at 300 rpm for 1h , compacted at 100 bar with a dwell time of 150 s and sintered at 12000 C. X-ray diffraction studies showed that the crystallite and grain size gradually decreased with the increase in ZrO2 and ZrO2+TiO2 content till 20wt%, after which there was a sudden raise in both composites. A dominant ZrO2 phase was observed in X-ray diffraction studies (XRD) and micro structural analysis (Scanning Electron Microscopy-SEM) of sintered samples. Mechanical properties were found to be significantly improved on adding 20wt% of ZrO2 and ZrO2+TiO2 at 12000C. However, the addition of 25wt% of ZrO2 and ZrO2+TiO2 decreased the mechanical properties of HAp. The reduction could be due to the increase in grain size and dominant smaller particles of ZrO2. The improved mechanical properties were correlated with the observed micro structural features.

***Keywords*:** High Energy Ball Milling, ZrO2, TiO2, grain size, Mechanical properties

**1. Introduction**

Excellent biocompatibility and bioactivity has been observed in Hydroxyapatite (Ca10(PO4)6(OH)2-(HAp)) Its structure or chemical composition is found to be similar to human hard tissues such as bone and teeth [1]. HAp, can provide scaffolds for the formation of new bone tissues after implantation in to human body as artificial material. Calcium and phosphorous can be free from the material surface and absorbed by the body to new tissues. It is one of the important aspects with respect to human health in the field of medicine and surgery. Among different categories of biomaterials, bioactive ceramics such as HAp are attractive candidates for body's hard tissues replacement [2-3]. In order to improve the mechanical properties of the HAp, addition of nano particles has created a great interest. Among those, TiO2 and ZrO2 nano particles addition to HAp and forming a composite has been studied extensively [4].Titanium oxide has been extensively employed as biomaterial due to its excellent biocompatibility and superior corrosion resistance, Titanium oxide has been used to improve the bonding strength of the HAp layer and the Ti substrate, as well as the high stability, erosion resistance and corrosion resistance [5]. Pure zirconia has three polymorphs: monoclinic, tetragonal, and cubic phases. Due to the large volume change associated with the tetragonal to monoclinic phase transformation, pure zirconia has no practical applications for engineering components [6]. Zirconia can be stabilized with various additives, among which yttria and cerium are the most useful stabilizers. In particular, yttria-stabilised zirconia (ZrO2) is known to be both hard and tough at room temperature [7]. For the application of bioimplant, Al2O3, ZrO2 and their composite ceramics have been considered as a matrix as well as reinforcement phases due to their excellent oxidation resistance, good biocompatibility and wear resistance [8-10]. Que et. al., [11] reported the major effect on the HAp structure and enhanced HAp properties on addition of titania to HAp. The phase changes in the composites at higher sintering temperatures are observed due to the introduction of secondary phases. Zhangxihua et.al, [12] reported the fabricating high performances of hydroxyapatite matrix ceramic composites with low cost, alumina are introduced in hydroxyapatite. Wei Yu et al., [13] reported the effect of nano-ZrO2on the mechanical properties of reinforced HAp bone cement. Hongbo Guoa et al., [14] investigated first of its kind the fabrication of laminated and functionally graded HAp/Y-TZP composites by means of the Spark Plasma Sintering (SPS). The laminated and functionally graded HAp/Y-TZP(yttria stabilized tetragonal zirconia) composites are designed as a strong Y-TZP core-bioactive HAp layer structure, a non-symmetric Y-TZP layer to HAp later structure or a bioactive HAp core-strong Y-TZPlayer structure. Aminzare et.al.,[15] studied the nano composite by high- energy ball milling in order to obtain highly dense objects with desired mechanical properties. The effects of alumina and titania nano particles on microstructure, phase decomposition and mechanical properties have been investigated. Ahmed et. al., [16] reported the Hydroxyapatite / titania nano composites produced by High Energy Ball Milling (HEBM). The effect of titania addition and sintering temperature and time on the formed phases and their influence on the compressive strength of HAp were investigated. Viswanath and Ravishankar [17] studied the interfacial reactions in hydroxyapatite/alumina nano composite in which alumina reacted completely with hydroxyapatite. Khalil Abdelrazek et. al., [18] studied HAp and HAp–20 vol % 3YSZ composites sintered at different temperatures by High Frequency Induction Heat Sintering (HFIHS). The objective of their study is to synthesize and sinter HAp–3YSZ (yttria stabilized zirconia) powders with high hardness high toughness, fine grain size and homogeneous constituent distribution. Oktar [19] studied the influence of sintering of composite materials, made of hydroxyapatite, derived from bovine bone, with 5 and 10 wt. % of TiO2, on their mechanical properties. The experimental results revealed that the developed microstructure and the phases formed during sintering affect the densification and the mechanical properties of the produced composite materials. Mobasherpour et.al, [20] adopted a precipitation method to synthesize nano crystalline HAp and investigated the effects of ZrO2-Al2O3 on the mechanical properties of nano crystalline HAp powder. Byonget.al, [21] studied Hap-(t-ZrO2)/Al2O3-(m-ZrO2) composite to improve the mechanical properties using the multi-pass extrusion process. . Improved bending and the tensile strength of HAp by using La2O3, ZrO2, and TiO2 as binders has been observed by Shin-Ike et.al, [22]. Their study has clearly showed that doping can increase the bending strength of HAp.

In the present study, the application of HEBM technique to produce HAp/ZrO2 and HAp/ ZrO2+TiO2 nano composites and the effect of the addition of ZrO2 and ZrO2+TiO2to HAp on the micro structure and mechanical strength of the composites were investigated. The correlation between the mechanical and micro structural properties was systematically established.

**2. Materials and Methods**

**2.1. Sample Preparation**

Originally, HAp and its composite powders are chosen to have the particle size of 20-40 nm. Various amounts of ZrO2 and ZrO2/TiO2 (0, 5, 10, 15, 20 and 25 wt. %) were mixed with HAp by HEBM with 300 rpm for 1 h. The milled powder was cold compacted at a pressure of 100 bar with a dwell time of 150 s. The compacted powders were fabricated into cylindrical specimen (compression strength, Hardness) of sizes 20 mm diameter and 5 mm height; and rectangle specimen (Flexural Strength and Fracture Toughness) of sizes 40 mm length, 10 mm width, and 3 mm thickness. To consolidate the specimen, sintering was done at 1200 °C for 1 h in an electrical resistance box furnace followed by furnace cooling.

**2.2. Experimental Procedure**

HAp and its composites are characterized by an X-ray diffractometer equipped with Cu-Kα radiation (wave length λ=1.5406 A0). The diffraction test was operated in the range of 6-900 using a step size of 0.010. Using the measured width (β) of their diffraction pattern, the average crystallite size (D) was estimated using Scherer’s formula [16]. Scanning Electron Microscopy (SEM) has been used to investigate the micro structural information. The compositions of the elements Ca, P, O and Zr are determined using Energy Dispersive Analysis of X-rays (EDAX) attached with SEM. The densities of the given composites were measured using Archimedes’ principle. The compressive strength of the nano composite ceramics of size 20 mm (diameter) and 5 mm (height) was evaluated using a universal testing machine. The compression test was carried out under a quasi-static loading range, in which the initial strain rate (ε\*) is set to 0.001 s-1, i.e., the machine crosshead speed (ϑ = ε\*.ho) is 0.005 mm/s. Here, ho is the initial height of the specimen. The sintered specimens are loaded till fracture [16].Knoop hardness measurements of the polished cross-sections of the HAp composites were performed using the Shimadzu HMV-2000 micro hardness tester. A test load of 4.905 N and a holding time of 15 s are used in the measurements according to ASTM E384. The indenter has a width to length ratio of 1:7.11. Its respective face angle for the long edge is 172 degrees and for the short edge is 130 degrees. The indentation depth is approximately (1/30)th of the longer dimension.

The Knoop hardness ‘H’ is expressed using (Equation 1) [14]

*H=14229 \* (L/d2) (1)*

Where ‘L’ refers to the load (unit: Newton), and ‘d’ refers to the longer diagonal of the indentation (unit: mm).

The Young’s modulus (Equation 2) across the graded composites was calculated using the following equation [14]:

*(B1/A1) = (B/A) - α (E/ H) (2)*

Where B1/A1 refers to the indent diagonal ratio obtained after elastic recovery or indentation, and B/A refers to the ratio of the Knoop indenter dimensions. The term ‘α’ refers to a constant having a value of 0.45.

The Flexural Strength of the nano composite was evaluated using the three-point bending test. The sintered specimens (40 mm length, 10 mm width and 3 mm thickness) were first prepared and polished to remove surface flaws and then placed on a three-point bending testing set up. The load (frame cross head speed of 0.05 mm/min) was applied from the top at middle point of the bar.

Using the indentation technique, the Fracture Toughness Kc (Eq: 3) was estimated, and the values were determined by using the below equation [18]:

*Kc=ξ (E/H) 2/5\*P/ (d\*l1/2) (3)*

Where ‘Kc’ refers to the Fracture Toughness, ‘E’ is the Young’s Modulus, and ‘H’ is Hardness (GPa). ‘P’ refers to the applied load (N), ‘ξ’ refers to the constant that depends on the geometry of the indenter (ξ=0.0089), ‘l’ is the crack length (mm), and ‘d’ is the half length of the indents.

**3. Results and Discussion**

**3.1. Microscopic Analysis**

The morphologies of HAp and its composites are carried out by a Scanning Electron Microscopy (SEM). HAp is cross link with each other during the growth process, which provides a conducive condition for the adhesion and growth of biological tissues. Fig. 1 shows XRD patterns of HAp and standard HAp (PdF card no74-0566). The observed diffraction pattern of HAp is in good agreement with the standard HAp pattern and no reflections from impurities can be observed. When pure HAp is pressed, and sintered at 1200oC, only peaks corresponding to HAp are detected, as shown in Fig. 2. ZrO2 powder is added and sintered under the same condition; stronger peaks are detected along with zirconium and HAp. The ZrO2 content of 5, 10, 15, 20 and 25 wt. % is chosen to investigate the contribution of ZrO2 in enhancing the properties of sintered composites. After compacting and sintering, the composition of the specimens sintered at 12000C is analyzed by means of their XRD patterns which are shown in Fig.2. The x-ray diffractograms of HAp and composites (ZrO2+TiO2) recorded are shown in Fig. 3. The observed reflections were matched with the parent phase (HAp-marked with “#”) and its composites (TiO2 (marked with “$”) + ZrO2 (marked with “@”)). No additional reflections are detected from impurities.

The observed increase in intensities of diffraction patterns with increasing ZrO2+TiO2 content is attributed to ZrO2+TiO2 structural stability. On addition of ZrO2+TiO2, it is observed that ZrO2 has shown a dominant phase over TiO2 which can be seen from the identified phases in Fig. 3. The crystallite sizes of all the diffraction patterns are calculated by using Scherer’s formula. HAp, in all of its applications is largely determined by its morphology, composition and crystal size distribution. Thus, to control the mechanical properties of HAp, the influence of synthesis conditions on such characteristics as particles morphology and size distribution, as well as morphology are highly recommended.

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| **Fig. 1.** XRD pattern of HAp sample and standard HAp | **Fig. 2.** XRD patterns of HAP/ZrO2 composites after sintering | **Fig. 3.** XRD patterns of HAP/ZrO2+TiO2 composites after sintering |

The micro structure analysis of HAp and its composites after sintering has been carried out by SEM. The analysis is performed both on sintered HAp and on the composites with ZrO2. In Fig 4. HAp can be observed in the basic matrix with traces of melting. The composites with ZrO2 contents (5, 10, 15, 20 and 25 wt. %) exhibits a unique growth of rounded particle which issmall in size. The ZrO2 smaller particles are found to distribute in the matrix can be seen in Figs 4 (a)-(f). With increase in ZrO2 content, the amount of ZrO2 particles smaller in size also increases which in turn altered the micro structural properties of the composites, Fig. 4. The changes in the micro structural properties also affected the mechanical properties of the composites.

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| **Fig. 4.** SEM images of (a) HAp and HAp/ZrO2 composites (b) 5 wt.% (c) 10 wt.% (d) 15 wt.% (e) 20 wt.% and (f) 25 wt.%. | **Fig. 5.** SEM images of (a) HAp and HAp/(TiO2+ZrO2 composites (b)5 wt. (c)10 wt.%(d) 15 wt.% (e) 20 wt. % (f) 25 wt.%. |

In Fig. 5**.** HAp can be observed in the basic matrix with traces of melting. As stated earlier, the composites with ZrO2+TiO2 contents also (5, 10, 15, 20and 25 wt.%) exhibit a unique growth of rounded particle which is small in size. The ZrO2+TiO2 smaller particles are found to be distributed in the matrix, Fig.5. (a)- (f). With increase in ZrO2+TiO2 content, the amount of rounded particles smaller in size also increased which in turn altered the micro structural properties of the composites. Xigeng Miao et. al., [4] reported similar kind of microstructural features like protruding crystals. The protruding crystals were identified to be ZrTiO4 compound, which was confirmed by the X-ray and EDX analysis. Fig. 6 a-b shows EDAX analysis of HAp/ZrO2 composite. The presence Ca, P and Zr can be seen from the figure.

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| **Fig. 6.** EDAX composition of (A) pure HAp and (B) HAp/20wt.% ZrO2and (C) HAp/10 wt.% ZrO2+TiO2 (D) HAp/15 wt.% ZrO2+TiO2 | **Fig. 7.** Grain size of the composites (ASTM line method) (a) HAp+20wt. %ZrO2 (b) HAp+25wt. %ZrO2 and (c) HAp/10 wt.% ZrO2+TiO2 (d) HAp/15 wt.% ZrO2+TiO2 |

Fig. 6 c-d shows the EDX analysis of HAp/ZrO2+TiO2 composite. The protruding crystals reveals Zr and Ti intensities in which background grains exhibited strong Zr intensity but weak Ti intensity, Fig. 6 c-d. The XRD result shows the formation of the ZrTiO4 phase matched well with the SEM micrographs that showed the appearance of the protruding crystals. The above observations are in tune with the results obtained by Xigeng Miao et. al., [4] .Fig.7.shows the grain size of the composites estimated from the ASTM Line Method [25] is observed that decrease gradually till 20 wt. % beyond which a sudden increase has been observed with 25 wt % of reinforcement.

**3.2. Mechanical Properties**

Based on the structural and morphological analysis, an attempt has been made to understand the formation mechanism of the composites ZrO2, and ZrO2+TiO2. The measured density of HAp/ ZrO2 and HAp/ ZrO2+TiO2 composites are shown in Fig. 8. Each sample mentioned represents the dense sample with the similar set of composition. Calculated densities of HAp / ZrO2 and HAp / TiO2+ZrO2 (5, 10, 15, 20, 25 wt. %) samples sintered at 1200oC for 1 h are in close agreement with theoretical density. This can be attributed to the increase in the smaller particles of ZrO2 phase with increase in ZrO2 content as shown in Fig. 4.the same trend can be observed with the HAp/TiO2+ZrO2 nano composite. The density has shown a linear increase with ZrO2 as well as withZrO2+TiO2content till 20 wt. %, after which it showed a decreasing trend. This confirms that the maximum density can be achieved for both the composites, i.e. 20 wt. %. This can be attributed to the background grains with strong Zr intensity but weak Ti intensity [4] of HAp nano compositions can be observed in the Fig.5.

Khalil Abdelrazek et. al., [18] has made similar observation for HAp and HAp-20 vol % 3YSZ composites, where sinrteing has been carried out at different temperatures by HFIHS.The density of the specimens is the function of sintering temperature, consequently reaching maximum at 10000C for HAp and 11000C for 20 vol % 3YSZ.ZrO2 and ZrO2+TiO2 nano particles influenced the mechanical properties of HAp remarkably. The effect of reinforcement on hardness of HAp has been studied as a function of density and grain size. The hardness values are plotted against wt.% of HAp composites as shown in Fig.9.

The hardness of the HAp and ZrO2 composites are found to increase from 5.56 to 7.86 GPa, respectively with ZrO2 content. Among the composites of HAp and ZrO2 (5, 10, 15, 20 and 25 wt. %), highest hardness of 7.86 GPa, is observed for the 20 wt. % ZrO2 content. It can be further observed that at 25 wt. % of ZrO2 content, a sudden increase in grain size, which resulted in the decrease in density and hardness. This is attributed to the amount of HAp grain growth that might be prohibited as the amount of ZrO2 content goes beyond 20 wt. %.A similar trend has been observed for HAp/TiO2+ZrO2 nano composite,The hardness of the composites HAp / ZrO2+TiO2 increased from 5.56-14.01 GPa, respectively, with ZrO2+TiO2 content. Among the composites the highest hardness of 14.01 GPa was observed for the 20 wt. % compositeZrO2+TiO2 content. The knoop's hardness value observed was in good agreement with the work conducted by Hongbo Guo et al. [14] (7.5GPa at 20wt% of Y-TZP).The hardness values found to exhibit a gradual increase till 20 wt. % beyond which a sudden decrease has been observed for 25 wt. %. Salman et.,al.[24] have studied HAp (BHA-bovine derived HAp and EHA-tooth human enamel HAp) and Ti composites (Ti-doping was 5 and 10 wt.%) sintering at different temperatures. Micro hardness (69.7 HV and 93.43HV) and young’s modulus (7GPa and 39 GPa) for BHA-Ti composites at 12000C. Micro hardness (97.90 HV and 74.70 HV) and young’s modulus (22 GPa and 29.2 GPa) for EHA-Ti composites at 12000C.

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| **Fig. 8.** Variation of density in HAp/ZrO2 and HAp/ZrO2+TiO2 composites | **Fig. 9.** Variation of hardness in HAp/ZrO2 and HAp/ZrO2+TiO2 composites |

Fig. 10. Shows Young’s modulus of HAp /ZrO2 and HAP/ZrO2+TiO2 composites in sintered condition. Young’s modulus of the composites HAp and ZrO2 are found to be in the range of 89.09 to 188.14 GPa.Where as,for HAP/ZrO2+TiO2 composites Young’s modulus of the HAp composites were found to be in the range 89.09 to 328.08 GPa. Young’s modulus of HAp composites in sintered samples increases with increasing ZrO2 and ZrO2+TiO2content. For both the composites, the Young’s modulus reaches a maximum at 20 wt. %, reinforcement content followed by a slight decrease at 25wt. % composite. As explained earlier, with increase in reinforcement content, grain size decreases and density increases as a result hardness improved. The improvement in young’s modulus can be speculated to the solitary effect of the ceramic as additives and hence more dense composites [23]. Wenxiu Que et.,al.[23] observed the hardness and young’s modulus of the Pure HAp samples and the HAp/TiO2 (10% mol) composites as a function of the sintering temperature. The highest hardness and young’s modulus, which are 2.81GPa and 45.33GPa respectively, are obtained at the sintering temperature of 11000C.

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| **Fig. 10.** Variation of Young’s modulus in HAp/ZrO2 and HAp/ZrO2+TiO2 composites | **Fig. 11.** Variation of Fracture toughness in HAp/ZrO2 and HAp/ZrO2+TiO2 composites |

Fig.11 shows the relationship between Fracture toughness of HAp/ZrO2 and HAp/ZrO2+TiO2 composites in sintered samples. Fracture toughness of HAp/ZrO2 composite material are found to be in the range of 0.742 MPa.m1/2 to 2.08 MPa.m1/2.Whereas for HAp / ZrO2+TiO2 components were found to be in the range 0.742 to 3.73 MPa.m1/2, for maximum fracture toughness occurs at 20wt. % of composite material. These two HAp composites consequently reach a maximum at 20 wt. %, followed by a slightly decrease at 25 wt. % composite. Apparently, these results are in good agreement with results of Hardness, Young’s modulus and Fracture toughness which can be understood the evolution of the density and grain size.

Flexural strength data measured using three-point bending test revealed that HAp and HAp/ZrO2 composite possessed flexural strength range of 50 to126.1 MPa. Similarly Flexural strength data revealed that HAp/ZrO2+TiO2 composites possessed flexural strength range of 50 to 236.8 MPa, respectively the maximum flexural strength is observed at 20 wt. % of composite after which it shows a decreasing trend as shown in Fig. 12.Generaly,sintered samples with higher density improved mechanical properties such as flexural strength, compression strength and hardness.

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| **Fig. 12.** Variation of Flexural strength in HAp/ZrO2 and HAp/ZrO2/TiO2 composites | **Fig. 13.** Variation of compression strength in HAp/ZrO2 and HAp/ZrO2/TiO2 composites |

Fig.13. shows that compressive strengths of HAp / ZrO2 and HAp / ZrO2+TiO2 with various Wt. %. HAp after sintering exhibited the minimum compressive strength of 54.72 MPa and maximum compressive strength of 211.4 MPa is achieved for 20 wt. % of ZrO2.Similarly the same trend has been observed with the HAp / ZrO2+TiO2having a maximum compressive strength of 230.67 MPa was achieved for 20 wt. %, after which it shows a decreasing trend as shown in Fig. 13. It can be attributed to the increase in the dispersion of reinforcement particles in the matrix phase as observed from the micro structural features, fig.4 and 5. Salman et.,al.[24] have studied HAp (BHA-bovine derived HAp and EHA-tooth human enamel HAp) and Ti composites (Ti-doping was 5 and 10 wt.%) sintering at different temperatures. Compression strength (44.6MPa and 48.83MPa) for BHA-Ti composites at 12000C. Compression strength (43.30MPa and 39.96 MPa) for EHA-Ti composites at 12000C.

**4. Conclusions**

The HAp/ZrO2 and HAp/ ZrO2+TiO2 composites are successfully prepared using HEBM. It is observed that the improved mechanical properties are obtained for 20 wt. % composite. This could be due to the increase in density, decrease in grain size and increase in hardness. With further increase in reinforced content, say 25 wt. % of composite the density and mechanical properties were found to degrade. This may be due to increase in dominant smaller particles of ZrO2 in the matrix phase and sudden increase of grain size for content greater than 20 wt. %. This in turn altered the microstructure of the HAp-ZrO2 composites.

The following major observations can be drawn from the present investigation:

* All the composites of HAp and ZrO2 possess hardness values of are 5.56 to 7.86 GPa, and the hardness values of HAp/ ZrO2+TiO2 composites in the range of 5.56-14.01 GPa.
* The Young’s modulus of the sintered HAp/ZrO2 composites varied from 89.09 GPa to 188.14 GPa , The Young’s modulus of the sintered HAp/ ZrO2+TiO2 composites varied from 89.09-328.08 GPa which are high compared to the pure HAp.
* The composites of HAp and ZrO2 fracture toughness is found to be in the range of 0.742 to 2.08MPa.m1/2 and HAp/ ZrO2+TiO2 composites fracture toughness was found to be in the range of 0.742-3.73 MPa.m1/2 Comparing the hardness, Young’s modulus and toughness observed for pure HAp, the composites of HAp/ZrO2 and HAp/ ZrO2+TiO2 with 20wt. % of composites are found to yield better.
* The flexural strength of HAp/ZrO2 composites increased from 50 to 126.1 MPa whereas the flexural strength of HAp/ ZrO2+TiO2 composites was found to increase from 50 to 236.8 MPa.
* The compression strengthof HAp/ZrO2 composites for 20wt. % addition is 211.4MPa significantly higher than pure HAp, whereas the compression strengthof the 20 wt.% HAp/ ZrO2+TiO2 composites is 230.67MPa which higher than pure HAp and HAp/ZrO2.
* Enhanced mechanical properties have been obtained with the addition of (ZrO2+TiO2) to HAp composites. The obtained properties are proved to be better than HAp/ZrO2composites. The investigated bio composite materials can be used for implant applications

**References**

1. S. Pushpakanth, B. Sriinivasan, B. Sreehar and T. P. Sastry, Materials Chemistry and Physics. 107, 492 (2008).
2. Z. Xihua, L. Changxia, L. Musen, B. Yunqiaiang and S. Junlong, Ceramics International. 35, 1969 (2008).
3. X. Mian , Y. Hu , J. Liu and X. Huang, Materials Science and Engineering C. 27, 257 (2007).
4. Xigeng Miao, DanSun, Pui Woon Hoo, Jiani Liu and Yanming Chea, Ceramic International. 30, 1041 (2004).
5. B. Faratash, H.Liao, J. Li, N. Fouda, L. Hermansson, J. Mater. Sci. Mater. Med. 6 (8), 451 (1995).
6. L. Fu, K.A. Khor and J.P. Lim, J. Am. Ceram. Soc. 85 (4), 800 (2002).
7. C. Wen, W. Xu, W. Hu, and P. Hodgson, Acta Biomaterialia. 3, 403 (2007).
8. B. T. Lee, S. K. Sarkar, A. K. Gain, S. J. Yim and H.Y. Song, Materials Science and Engineering A. 432, 317 (2006).
9. A. K. Gain and B. T. Lee, Materials Science and Engineering A. 419, 269 (2006).
10. B. T. Lee, D. H. Jang, I. C. Kang, C. W. Lee, Journal of The American Ceramic Society. 88, 2874 (2005).
11. W. Que, K. A. Khor, J. L. Xu, and L. G. Yu, Journal of the European Ceramic Society. 28, 3083 (2008).
12. Zhang Xihua, Liu Changxia, Li Musen, Bai Yunqiang and Sun Junlong, Ceramics International. 35, 1969 (2009).
13. Wei Yu, Xixin Wang, Jianling Zhao, Qingguo Tang, Mingli Wang and Xuewen Ning, Ceramics International. 41, 10600 (2015).
14. Hongbo Guoa, Khiam Aik Khorb, Yin Chiang Boeya and Xigeng Miaoa, Bio Materials. 24, 667 (2003).
15. M. Aminzare, A. Eskandari, M.H. Baroonian, A. Berenov and Z. Razavi, Ceramics International. 39, 2197 (2013).
16. Ahmed E. Hannora and Sabbah. Ataya, Journal of Alloys and Compounds. 658, 222 (2016).
17. B. Viswanath and N. Ravishankar, Scripta Materialia. 55, 863 (2006).
18. Khalil Abdelrazek Khalil ,Sug Won Kim and Hak Yong Kim, Journal of Material Science and Engineering A. 456, 368 (2007).
19. F.N. Oktar, Materials Letters. 60, 2207, (2006).
20. I. Mobasherpour, M. Solati Hashjin , S. S. Razavi Toosi and R. Darvishi kamachali, Ceramics International. 25, 1569 (2009).
21. Byong –Taek lee, Chi-Woo Lee and Min-Ho-Yeon Song, Composites Materials Science and Engineering A. 458, 11 (2007).
22. M. Shinke, J. Tsutsui, A. Tanaka, S. Murayama and A. Fujita, Journal Osaka Odontol. Soc. 52, 854 (1989).
23. Wenxiu que, K. A. Khor, J. L. Xu and L. G. Yu, Journal of European Ceramic Society. 28, 3083 (2008).
24. S. Salman, O. Gunduz, S.Yilmaz, M. L. Ovecoglu, Robert L. Snyder, F. N. Oktar and S.Agathapoulos, Ceramic International. 35, 2965 (2009).
25. Standard Test Methods for Determining Average Grain size Designation:E112-96 (ASTM International).