Arabian Journal of Chemistry (2015) 8, 372–379

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Fabrication and evaluation of porous Ti–HA bio-nanomaterial by leaching process

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Received 20 September 2014; accepted 28 November 2014
Available online 8 December 2014

KEYWORDS

Ti–HA composite;
Biomaterial;
Leaching solution;
PCAS;
Porosity;
Powder metallurgy

Abstract A porous surface of Ti–HA composite was successfully fabricated by pulsed current activated sintering (PCAS), followed by leaching using diluted H_3PO_4. The Ti and HA powders were mixed at different contents of the HA, Ti-5, 10, 30 and 40 wt% HA powders. The mixed powders were pressed in a coated graphite die using pulsed current activated sintering (PCAS) under pressure of 60 MPa at temperature of 1000 °C for 5 min. The sintered Ti–HA specimens were immersed in the eight kinds of leaching solutions at room temperature for 24 h. The leached specimen's surfaces were characterized using XRD, SEM, EDX and Rockwell hardness. The XRD patterns after sintering show that many phases were detected at the sintered specimen surfaces such as; Ti_2O, CaO, $CaTiO_3$, Ti_xP_y in addition to the remaining Ti and HA. Furthermore, the high concentration H_3PO_4 leaching solution is more efficient than the low concentration. Also the produced porous surfaces of Ti–HA materials containing more than 30% HA have a low relative density and hard-

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2014.11.052

ness than the commercial Ti–6Al–4V ELI alloy. In a word, the presence of porous surface coated by HA will promote the nucleation of the biological apatite created with the human tissue and increase the bonding between them. So, the produced porous materials are considered so easy for the muscle cells to permeate after transplanted with high coherence.

1. Introduction

The materials used in medical applications must have suitable mechanical properties, excellent compatibility, good corrosion resistance, and elastic modulus matching with human bone (Ahmed et al., 1995; Langsberg et al., 1992). Metallic biomaterials such as titanium and Ti–6Al–4V alloy have been widely used as permanent implant materials in the replacement of damaged hard tissues. It has been also used in artificial hip joints and teeth due to their excellent corrosion resistance, high strength and biocompatibility (Yumoto et al., 1992; Okazaki et al., 1995). Although Ti–6Al–4V ELI alloys have been registered as standard material for biomedical applications, they still have some problems such as high elastic modulus and poor biocompatibility. (Long and Rack, 1998; Omran et al., 2008; Turkan et al., 2006; Ma et al., 2003). During the use of these alloys, the dissolution of Al and V cause some side effects on the human body, the dissolution of aluminum causes Alzheimer's disease and the V classified as toxic elements causing scaling back the surrounding tissue or cells, it can cause catastrophic damage (Ahmed et al., 1995; Langsberg et al., 1992; Yumoto et al., 1992; Okazaki et al., 1995). To solve these problems, researchers are trying to find alloys that are free of Al and V and have good biocompatibility and superior mechanical properties close to human bones as possible (Long and Rack, 1998). Therefore, good biocompatible biomaterials with low elastic modulus and that are non-toxic are highly required. HA has been widely used as artificial bone substitute due to good biocompatibility and similar composition of human bone (Omran et al., 2008). Many scientists have been working on the fabrication of HA for biomedical applications. Unfortunately, the applications of bulk HA compact are hindered by the low strength of the sintered HA (Turkan et al., 2006). Therefore, mixing HA with Ti or Ti alloys to have good bonding between tissues and HA surface will solve some of these problems. However, there are still some problems such as low bonding strength between HA and Ti due to different thermal expansion coefficient and mechanical properties (Ma et al., 2003). Recently, there are increasing interests in the fabrication and development of porous HA. These porous bioactive ceramics promote bone or tissue ingrowths into the open pores of the implants, thereby allowing a rapid return to the physiologically acceptable state of function (Thian et al., 2001). Porous titanium (Ti)-based materials have recently attracted increasing interest for applications in bone tissue engineering on account of their strength and toughness to other bioceramics or polymers, as well as reasonable biocompatibility (Jakubowicz a et al., 2009). Therefore, good biocompatible materials with low elastic modulus and that are non-toxic need to be developed. The objective of this study was to manufacture a composite of porous Ti and HA and sinter it by pulsed current activated sintering (PCAS). The sintered product surfaces were leached by chemical solvents to remove the boundary discontinuity between the metal substrate and HA and therefore produce small cavities or pores. The treated products have porous surfaces which may increase the effectiveness of coherent bond of the precipitated biological bone. The rough surface is formed to allow the precipitation of bone and increase the cohesion between them.

2. Experimental methods

Ti and HA powders with 30 μm and 35 nm particle size respectively have been used in this study. HA powders with different concentrations were mixed with Ti to get the following compositions: Ti-5, 10, 30 and 40 wt% HA powder. The powders were uniformly mixed in cylindrical polyethylene bottle using a zircona ball with ball-to-powder ratio of 6:1 using horizontal mixing machine (Mechanical mixer, ABB ACS100), with 150 rpm and 24 h mixing time. The mixed powders were hot pressed in a coated graphite die using pulsed current activated sintering (PCAS) provided with vacuum chamber 13.3×10^{-2} Pa. The pressing was done under a pressure of 60 MPa at temperature of 1000 °C for 5 min as shown in Fig. 1, then the specimens were cooled to room temperature. The heating and shrinkage curves were plotted using (pyrometer) LVDT (Linear variable differential transformer) conducted at the surface of graphite die.

Phase analysis was observed using XRD (Cu Kα) at a rate of 4°/min measured in the range of 2Θ 20–80 degree. The density of sintered Ti–HA was measured by Archimedes principle. The sintered specimens Ti–HA were leached by eight kinds of the leaching solutions having different concentration as shown in Table 1.

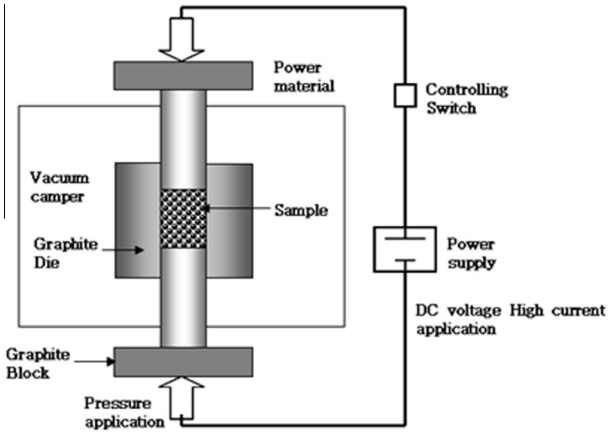


Figure 1 Schematic diagram of apparatus for PCAS.

Table 1 Leaching with several kinds of leaching solutions.

No.	Composition
1	H_3PO_4 40% + 60%H_2O
2	H_3PO_4 20% + 80%H_2O
3	H_3PO_4 40% + 60%Methanol
4	H_3PO_4 20% + 80%Methanol
5	H_3PO_4 40% + 36% acetic acid + 24%H_2O
6	H_3PO_4 20% + 48% acetic acid + 32%H_2O
7	60% acetic acid + 40%H_2O
8	10% acetic acid + 90%H_2O

Four kinds of the sintered Ti–HA specimens were immersed in the eight kinds of leaching solutions at room temperature for 24 h. The surfaces of the leached specimens were washed several times by distilled water and draying in a vacuum furnace at 110 °C. The porosity of the specimens and microstructure of the polished surface for the dried specimens after and before leaching was examined using SEM (JSM-6400) coupled with EDX. The image analysis was done using Leica Qwin analyzer, Germany. The hardness of the specimens before and after leaching was measured by Rockwell Hardness (HRF) under the load 60 Kgf and compared to the hardness of Ti–6Al–4V ELI alloy.

3. Results and discussion

3.1. The characteristics of the sample before and after sintering

Fig. 2 shows the elemental analysis of Ti–40% HA using EDX-mapping. From this Figure, it can be seen that, the mixture consists of Ti particles surrounded by fine particles of HA (cotton like) Fig. 2(a). It can be also observed that the distribution of the P, Ca and Ti elements through the matrix from EDX-mapping shown in Fig. 2(b)–(d). The HA constituents, P and Ca, are dispersed at all matrixes, but the Ti element has limited propagation. This is due to the size of Ti 30 μm and HA 35 nm which were mixed together for 24 h, the shape of HA powders changed from sphere to cotton like shape. All the Ti particles were coated with HA powders because of the high surface area (Khor et al., 2003). Fig. 3 shows the elemental analysis of Ti–40% HA using EDX-mapping after sintering and leaching.

Fig. 4 shows the XRD patterns for Ti–HA mixture before sintering at different HA contents 5%, 10%, 30% and 40% HA. From this Figure, the phase change was not observed, but the intensities of HA peaks increased with increasing the contents of HA in the mixture.

Fig. 5 shows the variation of temperatures and shrinkage displacement with heating time during PCAS of the Ti–5%, 10%, 30% and 40% HA. It can be seen that, the shrinkage displacement is increased with increasing the temperature and time up to the maximum shrinkage at the temperature reached 918 °C. There is no noticeable change in shrinkage displacement with increasing of temperature. This means that the densities of the samples reached the maximum at this particular sintering temperature, indicating that the sintering is completed (Kumar et al., 2002). The sintering temperature was kept constant at 1000 °C for 5 min to guarantee high densification.

Fig. 6 shows SEM micrographs of the sintered Ti–5% and 40% HA composites after PCAS for 5 min, at 1000 °C. The comparison between the sintered samples with low HA content (Ti-5) and high HA content (40% HA) proved that the amount

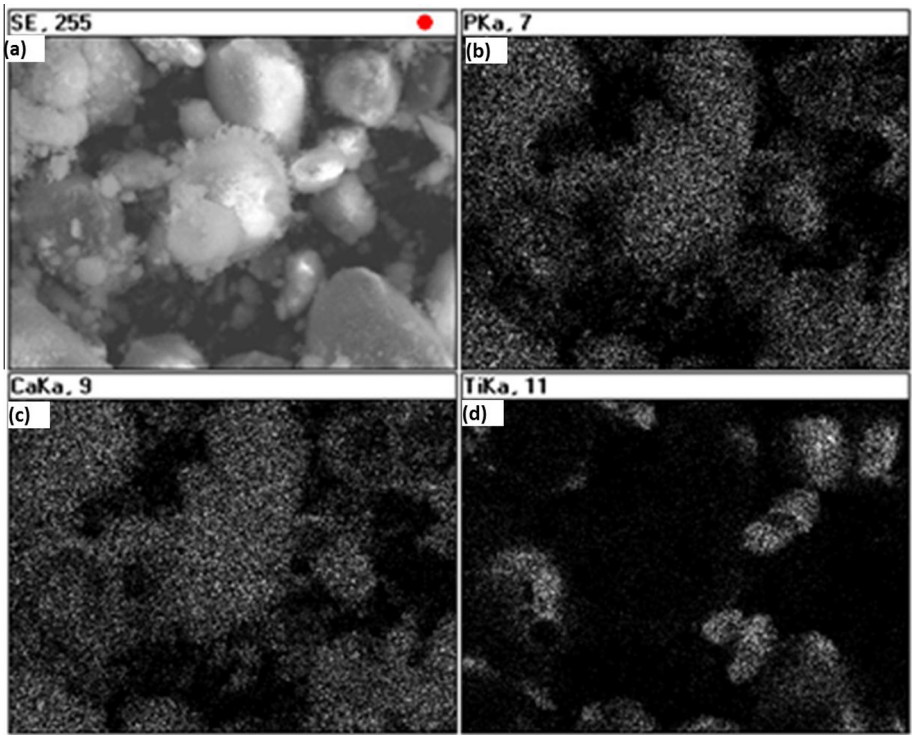


Figure 2 Elemental analysis of the Ti–40 wt% HA powder using X-ray mapping; (a) SEM image, (b) P composition, (c) Ca composition and (d) Ti composition.

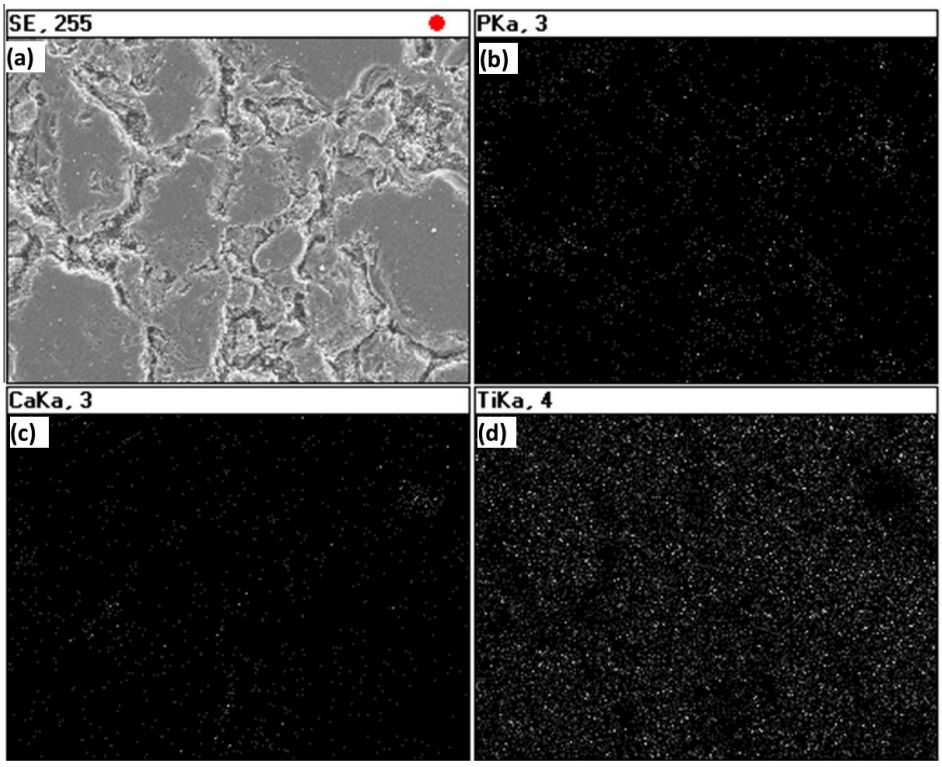


Figure 3 Elemental analysis of the Ti–40 wt% HA powder using X-ray mapping after sintering and leaching; (a) SEM image, (b) P composition, (c) Ca composition and (d) Ti composition.

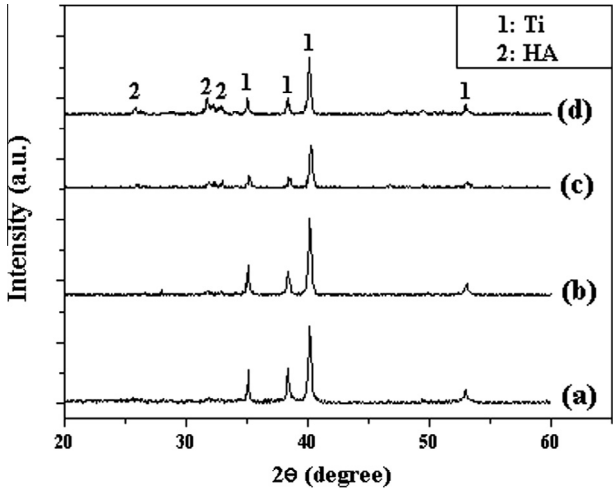


Figure 4 XRD results of the Ti-5%, 10%, 30% and 40% HA mixed powders: (a) Ti–5% HA, (b) Ti–10% HA, (c) Ti–30% HA and (d) Ti–40% HA.

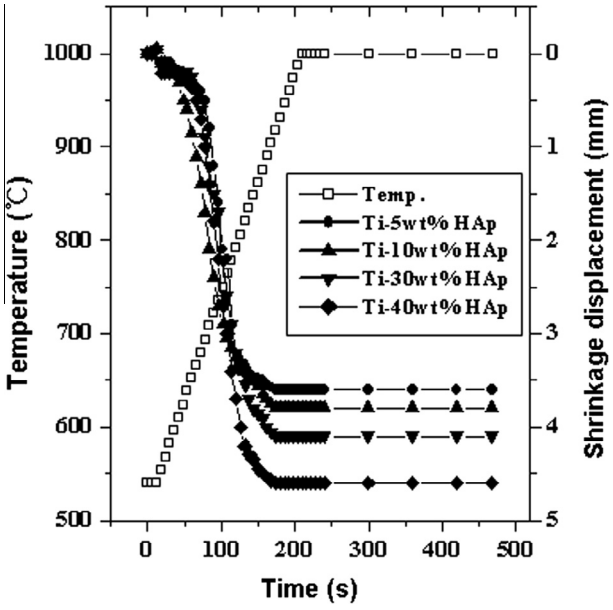


Figure 5 Variation of temperatures and shrinkage displacement with heating time during PCAS of the Ti-5%, 10%, 30% and 40% HA composites.

of pores increased with increasing HA content. Moreover, the pores were located at the grain boundary between Ti particles and HA particles Fig. 6(a) and (b). The pores in the high HA contents are connected with larger amount, causing rough surfaces.

Fig. 7 shows the XRD patterns of the sintered Ti–HA composites at different HA contents 5%, 10%, 30% and 40% HA. From this Figure, we can observe that, new phases are formed at the sintering process. The detected phases were Ti_2O, CaO, $CaTiO_3$, Ti_xP_y which formed along the sintering process at 1000 °C for 5 min as a result of a chemical reaction between part of Ti with HA according to the following equation (Ning and Zhou, 2004):

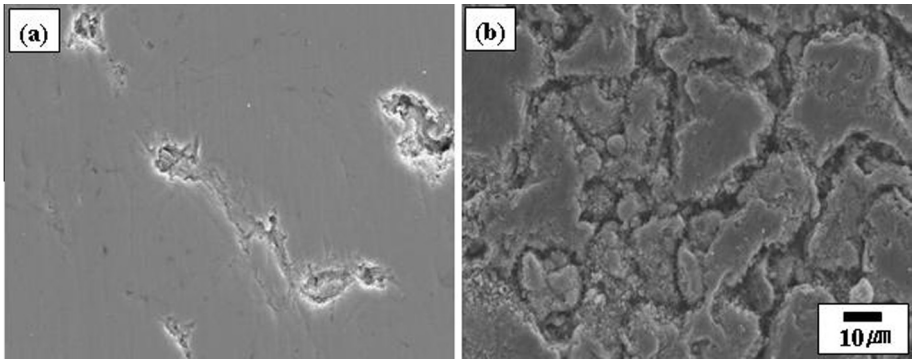


Figure 6 SEM micrographs of the Ti–HA composite after PCAS for 5 min, at 1000 °C; (a) Ti–5% HA and (b) Ti–40% HA.

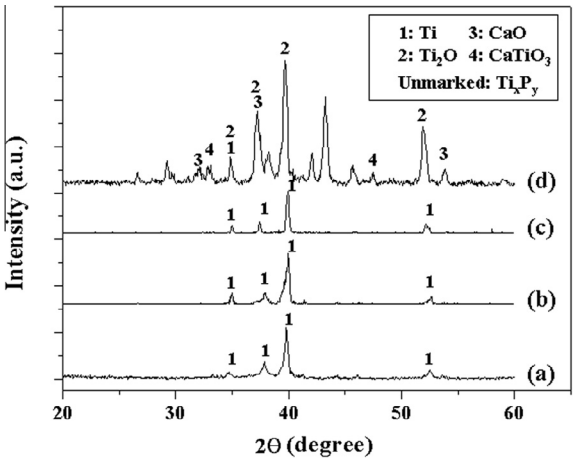


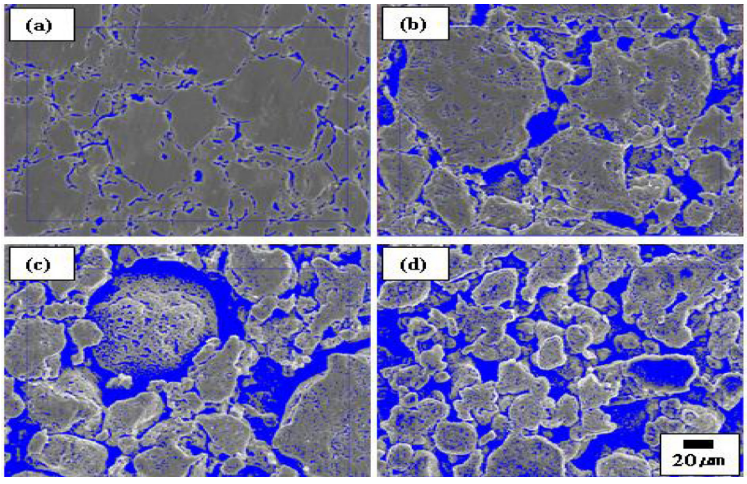
Figure 7 The XRD patterns of the sintered Ti–HA composites; (a) Ti–5 wt% HA, (b) Ti–10 wt% HA, (c) Ti–30 wt% HA, and (d) Ti–40 wt% HA.

$$\mathrm{Ti} + \mathrm{Ca_{10}(PO_4)_6(OH)_2} \rightarrow \mathrm{Ti_2O} + 3\mathrm{CaO} + 7\mathrm{CaTiO_3} + \mathrm{Ti_xP_y} + \mathrm{H_2O} \uparrow \quad (1)$$

The effect of the formed CaO, Ti_2O and $CaTiO_3$ on the biocompatibility of the produced Ti–HA composites has been investigated by many researchers. It was found that the formed CaO and Ti_2O on the surface of the Ti–HA material give the composites similar properties of bones. This promotes the nucleation of the biological apatite created with the human tissue, increasing the bonding between them, and increasing the biocompatibility (Woo et al., 2009, 2010). On the other hand, the biocompatibility of the formed $CaTiO_3$ is still unclear (Sun et al., 2006).

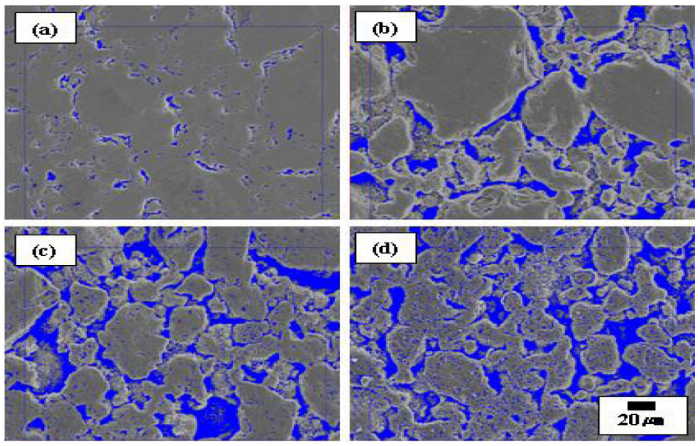
3.2. The characteristics of the sample after leaching

Four kinds of the sintered Ti–HA specimens with different compositions, as shown in the Table in Fig. 8, were etched using the eight kinds of leaching solutions as indicated in Table 1 at room temperature for 24 h. The porosities of the etched samples were examined using SEM and image analysis. The results of the samples surfaces show high porosity coming from the single leaching solutions. Then the etchants 1 and 2 were selected to be used in this work. Fig. 8 shows the percentage of porous area in the Ti–HA surface at different HA contents 5%, 10%, 30% and 40% HA after leaching by 40% H_3PO_4 + 60% H_2O for 24hr. From this figure it can be seen



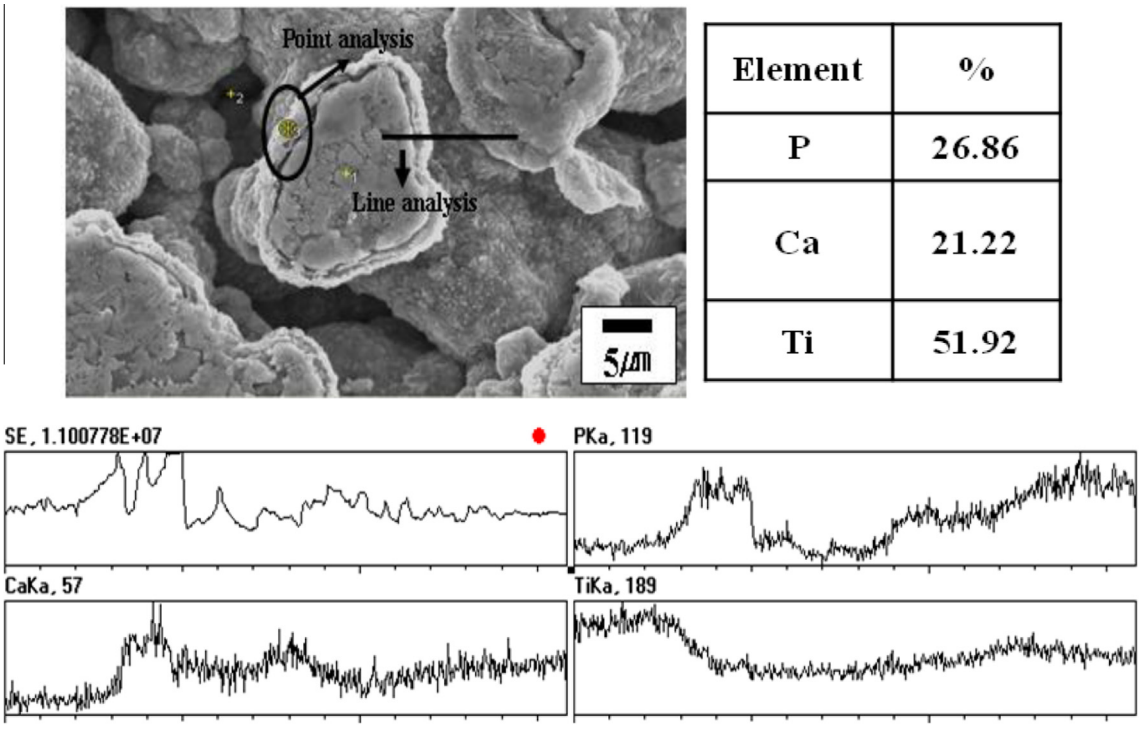
Composition	Porosity (%)
(a) Ti-5%HA	4.64
(b) Ti-10%HA	15.57
(c) Ti-30%HA	25.31
(d) Ti-40%HA	28.61

Figure 8 Area percent of pore of the Ti–HA composite after leaching by 40% H_3PO_4 + 60%H_2O for 24 h: (a) Ti–5HA (b) Ti–10HA (c) Ti–30HA (d) Ti–40HA.



Composition	Porosity (%)
(a) Ti-5%HA	2.36
(b) Ti-10%HA	10.61
(c) Ti-30%HA	20.83
(d) Ti-40%HA	23.84

Figure 9 Area percent of pore of Ti–HA composite after leaching by 20% H_3PO_4 + 80% H_2O for 24 h : (a) Ti–5HA, (b) Ti–10HA, (c) Ti–30HA, and (d) Ti–40HA.



Element	%
P	26.86
Ca	21.22
Ti	51.92

Figure 10 Elemental point & line analysis of the Ti–40% HA after leaching by 40% H_3PO_4 + 60%H_2O for 24 h.

that the percentage of porous area at the treated surfaces (blue color) is increased with increasing of HA contents, due to the increasing of HA coated Ti particles. The leaching solution (H_3PO_4) resulted in dissolution of the HA precipitate at the Ti grain boundary, leaving some pores or cavities at the treated surface. The percentage of porosity was 4.64 from total area in the treated surface contain 5% HA and increased up to 29% porosity from total area in the treated surface contain 40% HA as indicated in Fig. 8.

Another leaching solution (No. 2) contains 20% H_3PO4 + 80%H_2O was used to leach the four kinds of Ti–HA composite 5%, 10%, 30% and 40% HA as shown in Fig. 9. The percentage of porous area at the treated surfaces is increased with increasing HA contents. The percentage of porosity at the surface ranged from 2.36% to about 24% at the treated surface of samples containing 5% to 40% HA respectively as indicated in Fig. 9. As a comparison, it can be seen that, the high concentration leaching solution 1 which contains 40% H_3PO_4 is more efficient, because HA is more soluble in the high concentration of H_3PO_4 (Jakubowicz a et al., 2009). The difference of thermal expansion coefficient (Ti is 8.35×10^{-6}/°C, and HA is 16.9×10^{-6}/°C) and mechanical properties between Ti and HA reduces the bonding strength between them and help to dissolve the HA with the presence of leaching solution.

Fig. 10 shows the elemental point and line analysis by using SEM, EDX of the Ti–40% HA after leaching in solution No. 1 for 24 h. The elemental analysis at the grain boundary indi-

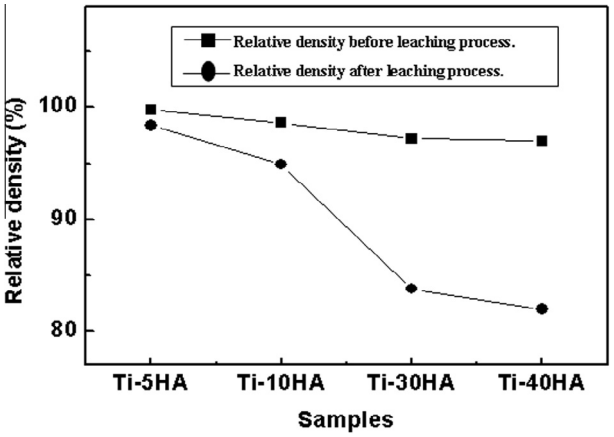


Figure 11 The relative density of specimens before & after leaching process by 40% H_3PO_4 + 60% H_2O for 24 h.

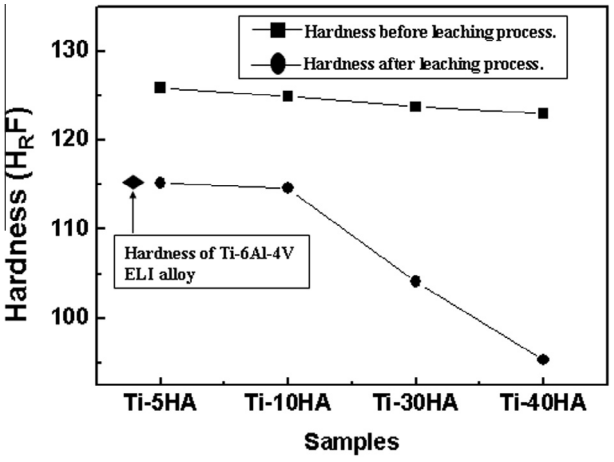


Figure 12 The hardness of specimens before & after leaching process by 40% H_3PO_4 + 60% H_2O for 24 h.

cates that, Ti to HA be about 50–50. This means that, HA is concentrated at the grain boundary, also the elemental analysis at this point as shown in this Figure proved that, the ratio Ca to P was about 7:9 whish was not confirmed with the chemical analysis of HA when the Ca:P ratio is about 20:9. The line analysis was done along two grains and the grain boundary, as shown in Fig. 10, is supported the point analysis. The Ti is concentrated at the end of the line (at the bulk of the particle) but the Ca and P are increased at the grain boundaries and all elements Ti, Ca and P are decreased in the middle of the line (at the pores).

It can be concluded that at the sintering process, the reaction (1) has occurred forming Ti_2O, CaO, $CaTiO_3$, Ti_xP_y at the surface in addition to the remaining Ti and HA. When the sintered samples were immersed in leaching solution, the HA are dissolved in the leaching solution, which leads to change in the leaching solution color from clear to violet, and H_2O is decrease the concentration of the leaching solution. This explains that is why the high concentration leaching solution is more efficient than the low concentration.

3.3. Hardness and densities of the samples before and after leaching

The relative density and hardness of the specimens before and after leaching in solution 1 for 24 h are shown in Figs. 11 and 12, respectively. Relative density and hardness was decreased gradually, because the appearance of cracks in the HA and Ti due to the difference of thermal expansion coefficient as mentioned before. After leaching as shown in Fig. 11, the relative density is decreased at the same specimen, because HA was eluted from the surface causing increase in the pore width. Also it can be observed that the relative density decreased sharply with increasing HA content due to increasing the porosity.

In Fig. 12, the hardness was decreased as well after leaching at the same composition, because many porosities were introduced. Furthermore, the hardness is decreased sharply with increasing HA due to the increasing of porosities. For a comparison, the hardness of Ti-5, 10 HA were similar to Ti–6Al–4V ELI alloy, while the hardness of, Ti-30, 40 HA was lower than the commercial Ti–6Al–4V ELI alloy. It can be observed that, the leached specimen containing more than 30% HA have a low relative density and hardness than the commercial Ti–6Al–4V ELI alloy. In addition to increasing of porous surface coated by HA and CaO lead to promote the nucleation of the biological apatite created with the human tissue increasing the bonding between them, and increasing the biocompatibility. It is expected that, in case of using porous Ti–HA composite as implant in the human body, the tissues will be deposited inside the pores, therefore the biocompatibility of these materials and the coherence of biological materials in human body will be probably increased.

4. Conclusion

In the present study, the porous Ti–HA composite was successfully fabricated by Pulse current activated sintering (PCAS) and leaching process. The main results were concluded as following. During the sintering process using PCAS, the Ti_2O, CaO, $CaTiO_3$, Ti_xP_y phases are formed at the surface of specimen as observed from XRD pattern after sintering in addition to the Ti and HA. When the samples are immersed in the leaching solutions, the CaO reacts with leaching solution, the HA are dissolved in the leaching solution making some pores in the surface. The high concentration leaching solution 40% H_3PO_4 + 60%H_2O is more efficient than the low concentration 20% H_3PO4 + 80%H_2O, because the reaction occurs between leaching solution and CaO to obtain HA and H_2O, leading to reduction in the concentration of solution used for leaching. The increasing of the porosity at the surface of Ti–HA composite which is coated by some of HA and CaO may lead to help the nucleation of the biological apatite created with the human tissue and increasing the bonding between them. The leached specimen containing more than 30% HA have a low relative density and hardness than the commercial Ti–6Al–4V ELI alloy and increasing the biocompatibility. It is expected that, in case of using porous Ti–HA composite as implant in the human body, the tissues are deposited inside the pores, therefore the biocompatibility of these materials and the coherence of biological materials in human body may increase.

Acknowledgement

The authors would like to extend their sincere appreciation to the Deanship of Scientific Research at king Saud University for funding this Research Group No. (RG 1435-001).

References

Ahmed, T., Long, M., Silvestri, J., Ruiz, C., Rack, H.J., 1995. Titanium 95 Sci. Technol. 2, 1760.
Langsberg, J.P., McDonald, B., Watt, F., 1992. Nature (London) 360, 65.
Yumoto, S., Ohashi, H., Nagai, H., Kakimi, S., Ogawa, Y., Iwata, Y., Ishii, K., 1992. Inter. J. PIXE 4, 493.
Okazaki, Y., Ohota, M., Ito, Y., Tateishi, T., 1995. J. Jpn. Inst. Met. 59, 229.
Long, Marc, Rack, H.J., 1998. Biomater 19, 1921.
Omran, A.M., Woo, K.D., Kim, D.K., Kim, S.W., Moon, M.S., Barakat, N.A., Zhang, D.L., 2008. Met. Mater. Int. 14, 321.
Turkan, Ugur, Ozturk, Orhan, Eroglu, Ahmet E., 2006. Surf. Coat. Technol. 200, 5020.
Ma, J., Ling, C.H., Kong, L.B., Wang, C., 2003. J. Mater. Sci. Mater. Med. 14, 797.
Thian, E.S., Khor, K.A., Loh, N.H., Tor, S.B., 2001. Biomaterials 22, 1225.
Jakubowicz a, J., Jurczyk, K., Niespodziana, K., Jurczyk, M., 2009. Electrochem. Commun. 11, 461.
Khor, K.A., Gu, Y.W., Quek, C.H., Cheang, P., 2003. Surf. Coat. Technol. 168, 195.
Kumar, R.R., Yang, Q.Z., Troczynski, T., Tseng, W.J.J., 2002. Biomater 23, 1679.
Woo, K.D., Kang, D.S., Kwon, E.P., Moon, M.S., Shon, I.J., Liu, Z., 2009. J. Kor. Inst. Met. Mater. 47, 8.
Woo, K.D., Kim, B.R., Kwon, E.P., Kang, D.S., Shon, I.J., 2010. Cer. Int. 36, 1.
Ning, C.Q., Zhou, Yu, 2004. Biomater 25, 3379.
Sun, Ruixue, Li, Musen, Yupeng, Lu, An, Xianghai, 2006. Mater. Sci. Eng. 26, 28.