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To cite this article: Ebuzer Ayyul *et al* 2020 *Mater. Res. Express* 7 035402

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RECEIVED
26 November 2019

REVISED
27 February 2020

ACCEPTED FOR PUBLICATION
4 March 2020

PUBLISHED
16 March 2020

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Microstructural analysis of sintered pure-titanium and titanium/hydroxyapatite (HA) surgical implant materials under different temperatures and HA doped conditions produced by powder metallurgy

Ebuzer Aygul¹ , Senai Yalcinkaya¹ and Yusuf Sahin²

¹ Marmara University, Faculty of Technology, Mechatronics Engineering, 34722, Istanbul, Turkey

² Near East University, Faculty of Engineering, Mechanical Engineering, 99138, Nicosia, Turkey

E-mail: ebuzer.aygul@marmara.edu.tr

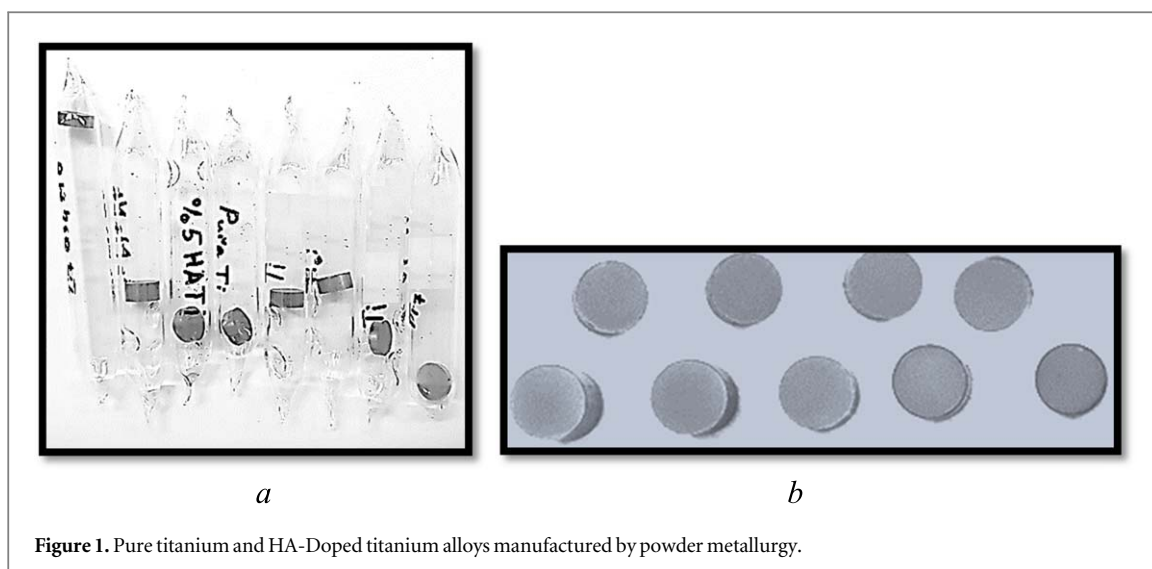
Keywords: titanium, hidroxyapatite, powder metallurgy, microstructure, temperture, hardness, SEM/XRD

Abstract

In this study, pure titanium and hydroxyapatite (HA) doped titanium alloys used as Surgical Implant Materials by weight percentage (wt%) of 5% and 10% were sintered by powder metallurgy method. Total 9 samples of these alloys are produced, three of them are pure titanium's, which are sintered at 900, 1000 and 1150 °C temperatures, respectively, for 4 h. From the rest of 6 samples, 3 samples were added 5 wt% HA and the last 3 samples were produced by doped 10 wt% HA. Titanium alloys produced by admixture with HA are sintered for 4 h at 900, 1000, 1150 °C temperatures, respectively. Titanium and HA powders were milled for 2 h in a ball-milling mixer and then pressed for half an hour at 20 MPa pressure. EDX, SEM, XRD and Vickers hardness tests were carried out for the analysis of the samples. As a result of the analysis, it was observed that different sintering temperatures caused to various Vickers hardness values and micro-structural changes occurred for pure titanium and HA doped titanium alloys. In addition, multiple phase and Ti plus HA structures were detected in XRD diffractometers of the samples at these temperatures. Most importantly, for the first time in our study, P_3Ti_5 phase was revealed with 00-045-0888 > XRD card. Finally, the effects of sintering temperatures and HA-doped amounts on particle sizes and pore sizes of the samples were determined by SEM analysis.

1. Introduction

Pure titanium (Ti) and its alloys have been used in biomedical applications for a long time because of their good mechanical properties and suitable biocompatibility values [1]. It is mainly used for artificial hip joints, artificial knee joints, bone plates, dental implants and implant devices that replace hard tissues, dental products such as crowns, bridges and toothpaste. Titanium alloys consist of toxic elements that are not dangerous to the body that used in appropriate quantities (Al, V, Mo etc) [2]. However, in long-term use, aggressive body fluid and millions of burdens that it is exposed to cause alloys to be ion release, which creates a very dangerous situation for health. Therefore, alloying titanium with bioactive substances instead of toxic elements may be a more logical solution for health of body [3]. The properties of titanium and its alloys can be improved and made more suitable for use. The best way to achieve this purpose can be fulfilled by using bioactive materials [4]. Although many researchers have chosen the way of alloying titanium to correct this situation, due to the toxic effects and poor denaturation of alloying metals, studies have again focused on using HA into the titanium structure. HA is the best option among bioactive materials because its chemical and crystallographic structure is similar to bone mineral [5]. Efforts to use HA make it impossible to use this material as bone prosthesis due to low mechanical strength [6]. So, combining the best option HA with a biocompatible material that has higher mechanical strength, such as Ti alloy, to form a composite has been more attractive for researchers [7].



Ha/Ti alloys produced are expected to have more flexibility in biocompatibility and more osseointegration property. Osseointegration is the name given to integration between the applied biomaterials and the living tissue without any other tissue, and is used quite often in the biomaterial lexicon [8]. The main factor that increase and regulate osseointegration is biocompatibility. It has also been observed that the production technique of biomaterials also accelerates osseointegration. It is not only the alloy types that change the microstructures and mechanical properties of materials, but also the production methods are known to change the microstructures and mechanical properties [9].

In this study, a method of powder metallurgy was chosen to produce the targeted biomaterials. Powder metallurgy (PM) technology is considered to be a very convenient method for producing the targeted bio metal alloys because of more suitable for mass manufacturing of small, complex and dimensionally sensitive parts [10]. The high melting temperature of the metals intended to be produced and the difficulty of reaching these temperatures, some properties of the material can only be achieved with PM. Powder metallurgy is a very comprehensive material production method covering the stages of the conversion of metal powders of different sizes and shapes into solid, sensitive and high performance parts [11]. During this process, the powders mixed or made into alloyed by preheating are filled into a mold and pressed as required by applying a certain pressure. These raw samples are then pressed by sintering in an atmosphere-controlled oven to provide thermal binding of these metal powders. The microstructure of the material is controlled by the pore structure, particle size and the amount of oxidation. Therefore, the analyses were evaluated according to the criteria mentioned above.

2. Experimental detail

The pure titanium powder used in this study was obtained from Nanografi (Turkey) company. In the study, 3 pure titanium being 11 mm diameter pellets were pressed in a mold based primarily on 5 gram samples and then sintered for 4 h at 900 °C, 1000 °C and 1150 °C temperature, respectively. They were then produced by doped 5 wt% and 10 wt% concentration to HA titanium alloys. HA added to Ti alloys were mixed and milled in a circular grinder (PASCAL L9FS brand) for 2 h. After grinding, HA-doped Ti alloys are pressed for 30 min at 15 MPa by taking 11 mm diameter pellets into the container. The pressed samples were sintered for 4 h at 900 °C, 1000 °C and 1150 °C values, respectively. The samples produced by PM are given in figure 1(b). Before sintering, the samples were sealed in vacuumed quartz tubes, the open end of quartz tubes was vacuumed with the help of a hose, and then the quartz tube was melted and cut off at the other end with the help of portable hydrogen oxygen welding at an appropriate distance. After this process, residual samples were sintered without need for a prime gas atmosphere. Vacuumed samples in quartz tubes are shown in figure 1(a). This process will be a first-time applied production process for these samples in the literature. For phase analysis of samples produced by PM. X-ray diffraction (XRD) analysis was applied. Measurements carried out using XRD –6100 Shimadzu), XRD scan range was determined as (100–900) and CU X-ray tube target, voltage = 40.0 (kV) and current = 30.0 (mA) fractions were used. Energy dispersive x-ray analysis (EDX) was used to describe the elemental composition of the produced samples. The biggest benefit of EDX is the ease in analysing the microstructure and being able to identify the simultaneous composition. Scanning electron microscopy (SEM) was used for the analysis of the quantities counted in our PM-produced samples, which are compared with regards to particle size, pore diameters and oxide quantity. The surface morphology and EDX of the samples

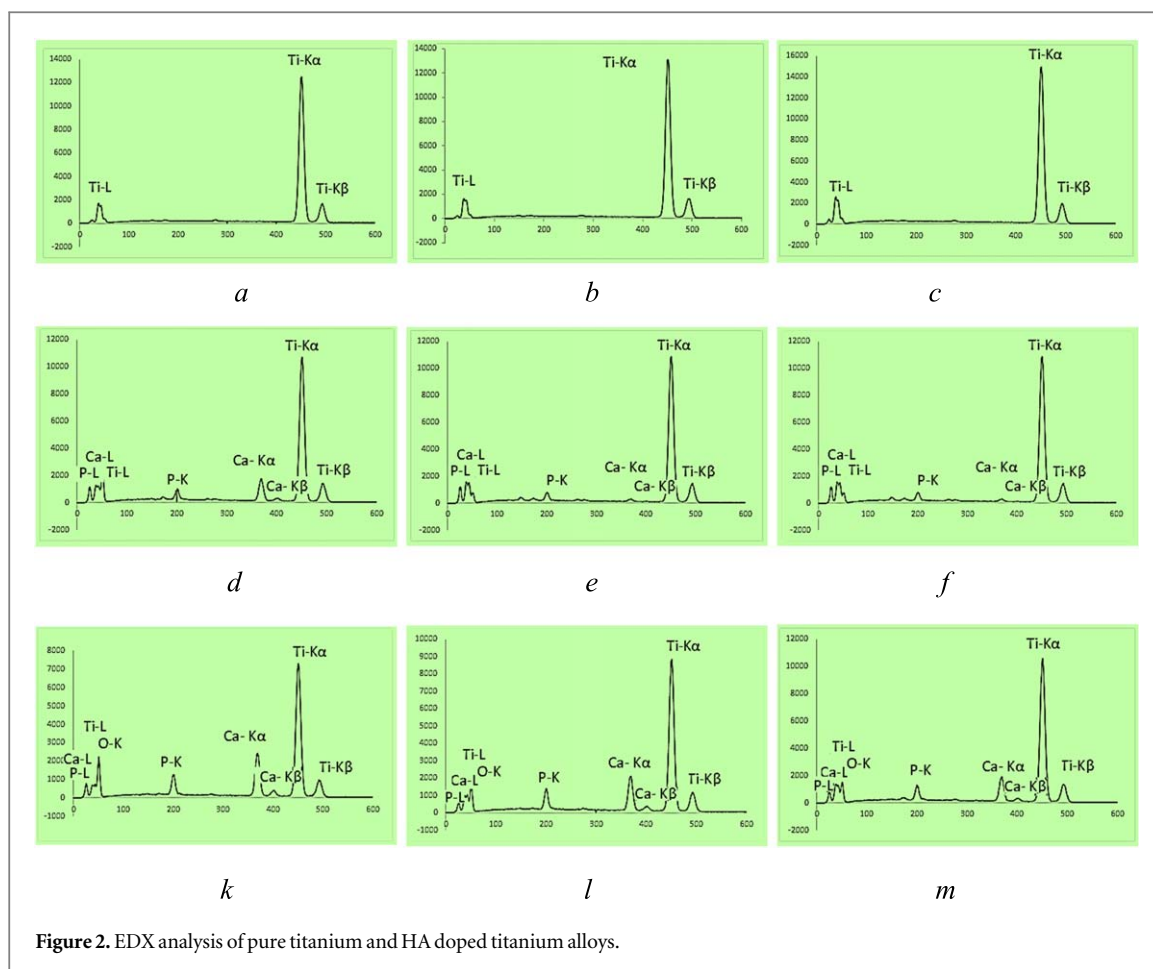


Figure 2. EDX analysis of pure titanium and HA doped titanium alloys.

were observed using a field emission scanning electron microscope (FEI XL30 Sirion). For hardness measurements, the Vickers hardness notch machine (Micro Hardness Tester FM-310e) was used to obtain hardness values of the surface of samples. Hardness values were taken under 10 s standby time and 100 gr load. Hardness values were taken from 5 different points on the surface of each sample and the average value of 5 Vickers was accepted as the final hardness value.

3. Results and discussion

3.1. SEM and EDX analysis

Figures 2(a)–(c) indicate EDX analysis of pure titanium and HA doped titanium alloys. These samples were sintered at 900 °C, 1000 °C and 1150 °C, respectively for 4 h. Figures 2(d)–(f) also shows the 5 wt% HA doped titanium sintered at 900 °C, 1000 °C and 1150 °C for 4 h, respectively. In the case of figures 2(k)–(m), 10 wt% content of HA doped titanium were produced and sintered at 900 °C, 1000 °C and 1150 °C, respectively for 4 h.

Analysis of EDX has shown the presence of high amounts of Ti. In pure titanium samples, peaks formed from Ti-K α , Ti-K β , Ti-L shells at all temperatures. No other L and Ca-L respectively. Peaks for Ca and P elements from the HA formula [Ca₅(PO₄)₃(OH)] are evident. This situation is more evident with the increase of peak density in titanium alloys with 10 wt% HA doped. In addition, some oxide peak O-K is observed in 10 wt% HA-doped alloy. Microstructural property is the most important factor in PM production methods. Microstructural properties are analysed based on their oxygen content, porosity and particle size. Therefore, figure 3 shows a SEM image of particle size and pore. SEM images of the samples seen in these figures were taken from 5 μ m, 10 μ m and 20 μ m for increasing temperature. The particle sizes of pure titanium produced at 900 °C were measured as 10–20 μ m. The measured pore sizes are around 4–7 μ m. The particle sizes of pure titanium produced at 1000 °C were measured at about 8–12 μ m. The measured pore sizes are about 3.5–5.5 μ m sizes. The particle sizes of pure titanium produced at 1150 °C were unwanted elemental peak is present. The peaks formed in 5 wt% HA-doped titanium alloys are Ti-K α , Ti-k β , Ti-L, Ca-k β , Ca-k β , P-K, P-measured at (8–11) μ m The measured pore sizes are about 3–6 μ m size. The particle sizes of 5 wt% HA-doped titanium alloy produced at 900 °C were measured at around 10–20 μ m. The measured pore sizes are approximately 6–8 μ m. The particle sizes of 5 wt% HA-doped titanium alloy produced at 1000 °C were measured as 9–15 μ m. The measured pore

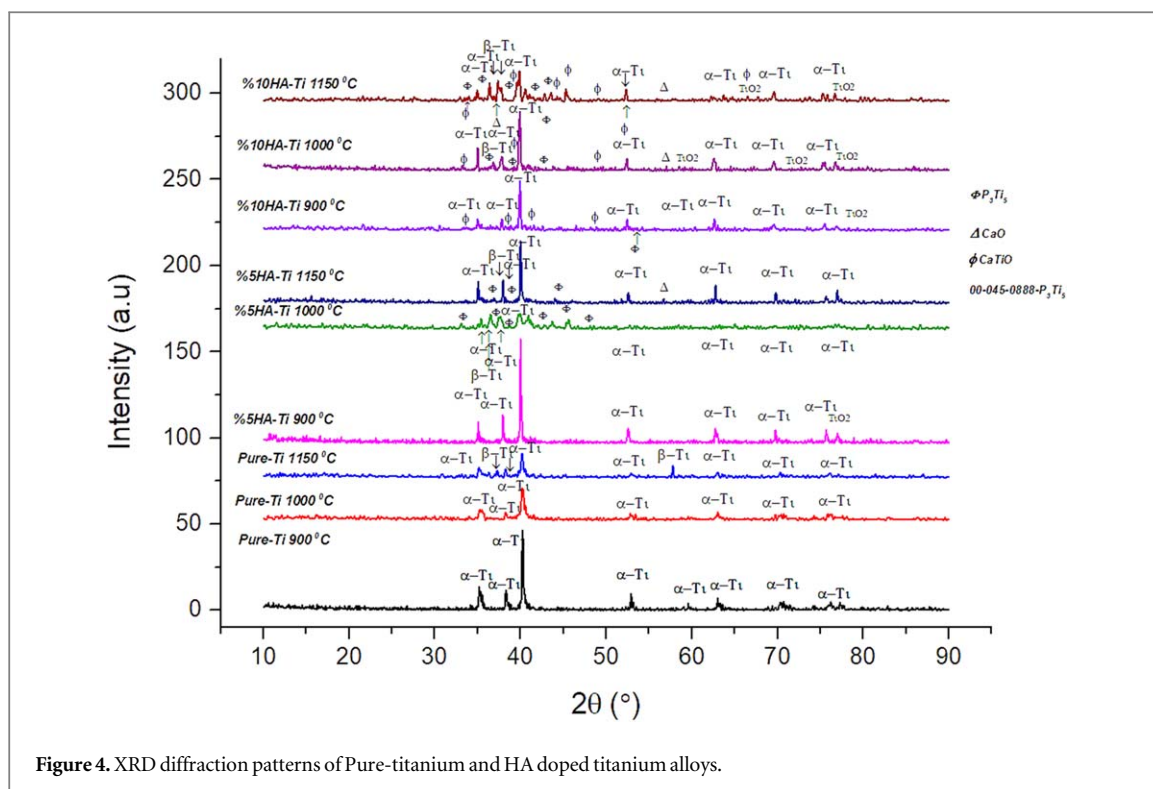


Figure 4. XRD diffraction patterns of Pure-titanium and HA doped titanium alloys.

to be 00,044,1294 > Ti for each 3 samples. By increasing the sintering temperature, it is seen that α -Ti (h.c.p) structure try to transform into β -Ti (b.c.c) structure. Finally, the sample produced at 1150 °C has a β -Ti phase at 37.20 angle. This unexpected phase also appears to repeat in 5 wt% and 10. % HA-doped titanium alloys. The stable state of this repeating state provides an important detail for us that the temperature of 1150 °C is proper important temperature of α -phase (h.c.p) to pass into β -(b.c.c) phase. The 00-045-0888- P_3Ti_5 structure seen in our study for the first time in HA-doped titanium alloys, was revealed at 1000 °C temperature. CaO, $CaTiO_3$, TiO_2 and P_3Ti_5 structures from HA contribution are more common at about 1000 °C and 1150 °C temperatures, respectively. The Bragg angles (2θ) and atomic interplane distance (d) for the pure titanium and HA-titanium samples produced are given in table 1.

3.3. Micro hardness

Hardness is defined as a resistance in which one material prevents penetration of another material. It has also been described as a resistance to drawing, friction, cutting, and plastic deformation. Hardness property can indicate the wear resistance and ductility of a sample. Vickers hardness is a determined technique for measuring metal hardness. The Vickers hardness measurement is the least destructive test of the samples among material experiments. Similar properties have been reported between the Vickers hardness and mechanical properties of the materials. For the hardness measurements, the Vickers hardness notch machine (Micro Hardness Tester FM-310e) is used to obtain hardness values of the surface of the samples. Hardness values were taken under 10 s standby time and 100 gr load. Hardness values were taken from 5 different points on the surface of each sample and the average value of 5 Vickers measurements was accepted as the final hardness value.

According to Vickers measurement results as shown in figure 5, HV values for pure titanium were found to be about 263 $kgf\ mm^{-2}$ for the sample produced at around 900 °C, 382 $kgf\ mm^{-2}$ for the sample measured at about 1000 °C, and 528 $kgf\ mm^{-2}$ for the sample measured at about 1150 °C. HV values measured for 5 wt% HA doped titanium alloy were found to be 221 $kgf\ mm^{-2}$ for the sample produced at about 900 °C, 310 $kgf\ mm^{-2}$ for sample measured at about 1000 °C, and 425 $kgf\ mm^{-2}$ for the sample measured at 1150 °C, respectively. The measured HV values for 10 wt% HA doped titanium alloy were found to be 80 $kgf\ mm^{-2}$ for the sample produced at about 900 °C, 173 $kgf\ mm^{-2}$ for the sample measured at 1000 °C and 426 $kgf\ mm^{-2}$ for the sample measured at 1150 °C, respectively. Accordingly, both pure and HA-doped titanium alloys have been shown to increase the value of micro-hardness with temperature. In alloying titanium metal with HA as the amount of HA increases, the micro-hardness value of the alloy decreases. The highest Vickers hardness belongs to pure titanium, but sintered at 1150 °C while the lowest value belongs to 10 wt% HA doped titanium alloy produced at about 900 °C.

Table 1. Distance atomic layer and Bragg angle (2θ).

Pure-Ti 900 °C		Pure-Ti 1000 °C		Pure-Ti 1150 °C		%5HA-Ti 900 °C		%5HA-Ti 1000 °C		%5HA-Ti 1150 °C		%10HATi 900 °C		%10HA-Ti 1000 °C		%10HA-Ti 1150 °C	
2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$	2θ	$d \text{ \AA}$
35,13	2,53	35,22	2,53	35,15	2,55	35,07	2,54	33,18	2,26	35,06	2,54	21,38	4,17	33,21	2,55	35,18	2,23
38,27	2,25	38,26	2,34	37,28	2,54	37,94	2,36	35,50	2,55	37,96	2,53	34,73	2,49	35,01	2,36	36,59	2,36
40,23	2,22	40,28	2,23	38,24	2,34	52,54	1,73	36,60	2,36	40,00	2,36	37,55	2,37	36,78	2,25	37,57	2,27
52,88	1,75	52,87	1,73	40,18	2,24	62,73	1,47	37,68	2,25	52,54	1,73	39,67	2,25	37,83	2,26	40,03	2,25
59,54	1,54	63,02	1,47	52,84	1,72	69,74	1,32	40,07	2,24	62,76	1,47	52,18	1,74	39,92	2,25	43,01	2,27
62,94	1,47	70,41	1,33	57,78	1,56	75,68	1,25	41,07	2,22	69,78	1,23	62,37	1,26	52,42	1,73	43,71	1,91

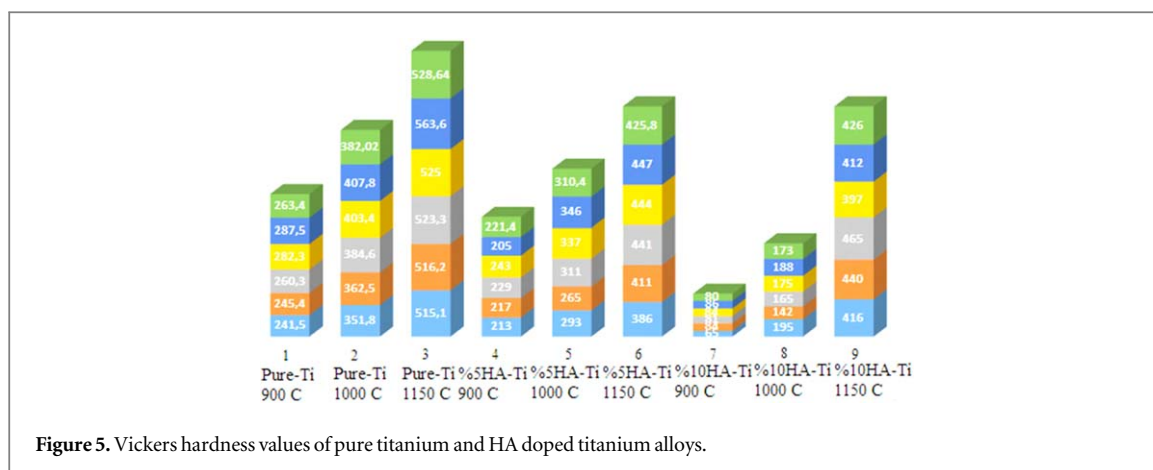


Figure 5. Vickers hardness values of pure titanium and HA doped titanium alloys.

3.4. Findings

Alloying of pure titanium with various elements in order to improve the mechanical properties of titanium alloys and tissue adaptation times in surgical implant applications is continuing rapidly. However, the toxic properties of the alloyed elements pose serious risks to the patient with the release of ions of metals in the aggressive body fluid, so it is very important to select the alloying elements from nontoxic substances such as artificial bone dust (HA). It is predicted that the amount of HA used as the additive in this study will be a reference for researchers examining the microstructural change on titanium implant. The findings of this study are summarized below. In EDX analysis of samples, there are peaks of all elements in the alloy available. There are no other peaks of unwanted elements in the structure of the alloys. 10 wt% HA doped titanium alloys with increased peak density is more evident. In addition, some oxide peak O-K is observed in 10 wt% HA-doped alloy. In pure titanium and HA-doped titanium alloys, it is observed that the particle sizes and pore structures of the alloys are reduced by increasing the sintering temperatures. In addition, it is observed that with the increase of sintering temperature, disfigured pore geometries gain a spherical structure. Positive effects of spherical pore structures against corrosion are known. The surface morphology of pure-titanium and HA-doped titanium alloys produced at about 1150 °C is more stable and uniform than samples produced at other temperatures. XRD diffractometers did not experience a phase shift between all peaks. For the first time in this study, 00-045-0888- P_3Ti_5 structure appeared in titanium alloys with sintered HA doped at 1000 °C for 4 h. The stable state of this repeating state provides an important detail us that the temperature of 1150 °C is proper important temperature of α -phase (h.c.p) to pass into β - (b.c.c) phase. A new β -phase peak has been observed in both pure titanium and HA-doped titanium alloys among the peaks that determine the characteristics of the alloy at this temperature. This is an evidence that this peak is β -phase peak of titanium. When we look at the Vickers hardness values of the alloys, the highest value belongs to pure titanium produced at 1150 °C and the lowest value belongs to titanium alloy produced at 900 °C with 10 wt% HA doped one. It is observed that increased the sintering temperature for both pure titanium and HA-doped titanium alloys increased the Vickers hardness of the alloy. The amount of admixture was reduced by the hardness value of Vickers.

4. Conclusions

The most important results obtained from this study are summarized as follows.

1. Pure titanium and HA doped titanium alloys produced by powder metallurgy method have shown a homogenous microstructure.
2. Increasing the sintering temperature leads to changing the microstructure of the alloy.
3. For the first time in this study, 00-045-0888- P_3Ti_5 phase was identified.
4. Increasing the sintering temperature causes the increase of Vickers hardness for both pure titanium and HA doped titanium.

Acknowledgments

This study was supported by the Marmara University Scientific Research Projects Commission with project number FEN-C-DRP-120917-0544.

ORCID iDs

Ebuzer Aygul  <https://orcid.org/0000-0003-0930-3975>

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