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Titanium-ceramic nanocomposites fabricated by the mechanical alloying process

K. NIESPODZIANA[1*], K. JURCZYK[2], M. JURCZYK[1]

[1]Poznań University of Technology, Institute of Materials Science and Engineering, pl. Skłodowskiej-Curie 5, 60-965 Poznań, Poland

[2]Poznań University of Medical Sciences, Department of Conservative Dentistry and Periodontology, ul. Bukowska 70, 60-812 Poznań, Poland

Wide use of titanium and its alloys as biomaterials stems from their low elastic moduli, good fatigue strength and better corrosion resistance compared to other metals and alloys used in medicine. However, they have poor tribological properties and a release of titanium alloy elements into surrounding tissues can cause eventual inflammation, failure and removal of an implant. For this reason, there is a great need for creating composite materials using ceramic particles to reinforce titanium which would give the possibility of optimizing mechanical and biological properties. In the present work Ti hydroxyapatite (HA, 3, 10 vol. %) and Ti–SiO_2 (3, 10 vol. %) nanocomposites were fabricated by a combination of mechanical alloying (MA) and sintering processes. Mechanical properties and corrosion resistance of these composites were investigated by the Vicker hardness measurement and *in vitro* studies. The experimental results show that Ti–10 vol. % HA and Ti–10 vol. % SiO_2 nanocomposites have good corrosion resistance ($I_c = 1.1\times10^{-6}$, $E_c = -0.48$; $I_c = 9.23\times10^{-7}$, $E_c = -0.45$, respectively) in comparison with microcrystalline titanium ($I_c = 2.7\times10^{-5}$, $E_c = -0.47$). Vickers' microhardness of the prepared nanocomposites is a few times higher than that of microcrystalline titanium. In conclusion, titanium ceramic nanocomposite is a suitable material for hard tissue replacement from the point of view of both mechanical and corrosion properties.

Key words: *titanium; bioceramics; nanocomposite; mechanical alloying*

1. Introduction

Titanium and titanium alloys are employed widely in biomedical and dental applications because of relatively low moduli of elasticity, low densities, high strength, good biocompatibility and corrosion resistance. Titanium and titanium alloys are generally regarded to have good biocompatibility and high corrosion resistance *in vitro* [1] although accumulation of titanium in tissues adjacent to the implant has been re-

*Corresponding author, e-mail: katarzyna.niespodziana@put.poznan.pl

ported signifying metal release and corrosion *in vivo* [2, 3]. Besides, titanium and titanium alloys have relatively poor tribological properties because of their low hardness [4]. In addition, metal implants may loose and even separate from surrounding tissues during implantation because of their low bonding strength [5–7]. Much better biomaterials for hard tissue replacement implants may be acquired by the preparation of titanium composites. The most commonly used materials are ceramics such as hydroxyapatites, silicas or bioglasses.

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), the basic mineral in natural bones, shows excellent biocompatibility with the bone. Besides, HA is bioactive and able to form strong chemical bonds with natural bone [8, 9]. Silica (SiO_2) is also a bioactive material with high corrosion resistance. Unfortunately, neither hydroxyapatite nor silica can be used for hard tissue replacement implants due to their poor mechanical properties [10].

Therefore, the connection of excellent biocompatibility and bioactivity of ceramics with good mechanical properties of titanium is considered to be a promising approach for fabrication of more perfect hard tissue replacement implants. There are two creative ways to meet this idea: use of ceramics as a coating or as a reinforcing phase in metallic-ceramic composites [11]. In general, the coating techniques became a common method, although they have some drawbacks: the toughness of ceramic is low; during the coating stage interfacial cracks can occur; the metal/ceramic adherence is low and can diminish in time [12]. For this reason, composite materials containing both ceramic and titanium are expected to have broad practical applications due to the fact that each material can compensate for the shortcomings of the other. To date, however, there are only few reports dealing with the microcomposite of ceramics and titanium manufactured by powder metallurgy [13–15].

The aim of this study was to develop new materials composed of Ti and hydroxyapatite or silica for biomedical applications. The Ti–HA (3, 10 vol. %) and Ti–SiO_2 (3, 10 vol. %) composites were prepared by a combination of mechanical alloying and powder metallurgical process. The structure and mechanical and corrosion properties of the composites were investigated.

2. Experimental

The starting materials used were titanium (< 45 μm), hydroxyapatite and silica (< 68 μm) powders. The raw powders with various Ti/HA and Ti/SiO_2 mixing ratios were first blended by mechanical alloying processes under argon atmosphere using an SPEX 8000 Mixer Mill. The vial was loaded and unloaded in a Labmaster 130 glove box in high purity argon atmosphere. The mixture of Ti–HA (3, 10 vol. %) and Ti –SiO_2 (3, 10 vol. %) powders were ball milled for 44 and 20 h, respectively. Then the milled powders were compacted at 1300 MPa and heat treated at 1150 °C in a gas atmosphere composed of 95% Ar and 5% H_2 under the pressure of 0.15 MPa holding for 2 h.

X-ray diffraction (XRD) was employed to study the effect of mechanical alloying and of any subsequent heat treatment on the phases present in the samples. Typical crystallite sizes were estimated from the half-width of lines using the Scherrer equation. A scanning electron microscope (SEM) with energy dispersive spectrometry (EDS) was used to study the microstructure and chemical composition of the produced samples. The effect of various amounts of HA or SiO_2 on mechanical properties of titanium composites was assessed by density measurements (Archimedes method) and Vickers' microhardness tester on polished surface under the load of 200 g.

The corrosion resistance in 0.1 M H_2SO_4 aqueous solution was measured using *in vitro* potentiodynamic corrosion tests. Saturate calomel electrode was used as the reference electrode and graphite as the counter electrode. The polarization curves were obtained for each specimen and corrosion potentials and corrosion current densities were determined by the Taffel extrapolation methods.

3. Results and discussion

MA process on Ti–HA (3, 10 vol. %) and Ti–SiO_2 (3, 10 vol. %) composites has been studied by X-ray diffraction. For example, Fig. 1a shows the XRD pattern of the starting titanium and hydroxyapaptite powders. During MA process, the originally sharp diffraction lines of starting materials gradually become broader and their intensities decreased with the milling time. The amorphous phase forms directly from the starting mixture of the compounds (Ti, HA) without formation of other phases (Fig. 1b). Formation of the nanocomposites was achieved by annealing of the amorphous material in high purity gas atmosphere composed of 95% Ar and 5% H_2 at 1150 ºC for 2 h.

XRD analysis of Ti–3 vol. % HA showed the presence of α-Ti (hexagonal-type structure with cell parameters a = 2.768 Å, c = 4.497 Å) and HA phases (Fig. 1c). When hydroxyapatite is added to titanium, the lattice constants of Ti decrease, as manifested by a shift of the diffraction peaks of the (100), (002) and (101) crystal planes of titanium towards larger angles in comparison with pure titanium.

XRD analysis of Ti–3 vol. % SiO_2 showed the presence of α-Ti (hexagonal-type structure with the cell parameters a = 2.972 Å, c = 4.774 Å). The formation of crystalline SiO_2 phase was not observed (Fig. 1d).

Table 1 shows the average crystallite size of titanium-silica and titanium-hydroxyapatite composites estimated from XRD experiment.

The results of the EDS analysis and a scanning electron micrograph of the surface of Ti–3 vol. % HA and Ti–3 vol. % SiO_2 nanocomposites mechanically alloyed and heat treated at 1150 °C for 2 h are shown in Fig. 2. EDS analysis shows that the Ti –3 vol. % SiO_2 nanocomposite consists of titanium matrix with silica or silicon particles (Fig. 2a). A similar microstructure can be observed in Ti–10 vol. % SiO_2 nanocomposite.

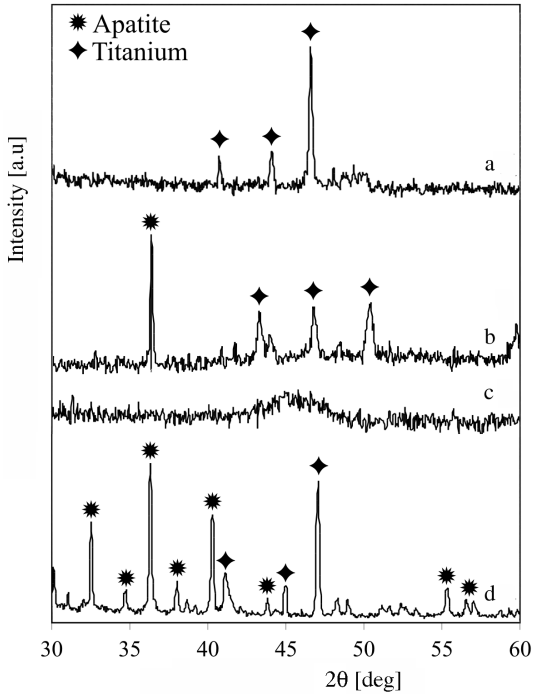


Fig. 1. XDR spectra of Ti–3 vol. % HA and Ti–3 vol. % SiO_2 nanocomposites: a) Ti, HA powders – 0 h MA, b) Ti–3 vol. % HA – 44 h MA, c) Ti–3 vol. % HA after annealing, d) Ti–3 vol. % SiO_2 after MA and annealing

Table 1. Characteristics of Ti–HA and Ti–SiO_2 nanocomposites and titanium

Nanocomposite	d [nm]	$HV_{0.2}$	ρ [g/cm^3]
Ti–3 vol. % HA	25	480	3.51
Ti–10 vol % HA	40	1500	4.03
Ti–3 vol. % SiO_2	40	550	4.26
Ti–10 vol. % SiO_2	50	670	4.48
Ti	–	250	4.51

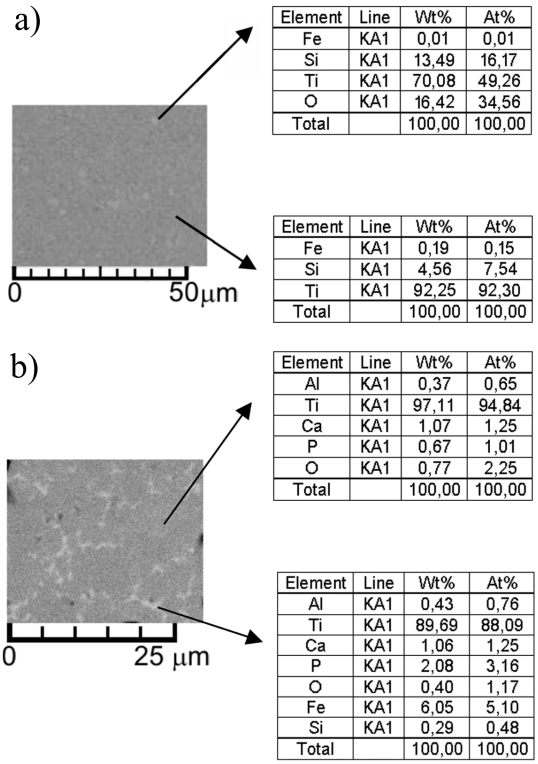
The EDS results indicate that a predominant phase in Ti–HA composites is titanium with some amount of apatites with various Ca/P ratios. The Ti–3 vol. % HA nanocomposite consisted of titanium matrix with apatites (Fig. 2b) with the Ca/P ratios 1.6 and 0.51 which were close to the values characteristic of hydroxyapatite and $Ca(PO_3)_2$, respectively. Ti–10 vol. % HA nanocomposite consisted of titanium matrix with calcium and titanium matrix with apatite, in which Ca/P ratio was 1.07, the value similar to the Ca/P ratio in $Ca_2P_2O_7$ (not shown). The existence of a second phase is a common feature of HA-based composites because the presence of titanium can degrade the structural stability of HA crystal and promote dehydration and decomposi-

tion of HA phase [15–17]. Besides, extreme heating conditions can produce secondary HA phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TTCP) and calcium oxide (CaO). This is the result of cooling from a high temperature which can be postulated in the following reactions [18]:

$$Ca_{10}(PO_4)_6(OH)_2(HA)(s) \rightarrow 2Ca_3(PO_4)_2(TCP)(s) + Ca_4P_2O_9(TTCP)(s) + H_2O(g)$$

$$Ca_4P_2O_9(TTCP)(s) \rightarrow Ca_3(PO_4)_2(TCP)(s) + CaO(s)$$

These secondary HA phases can influence the final properties of Ti–HA nanocomposites as well. The presence of some amount of iron atoms in the nanocomposite Ti–HA could be explained by Fe impurities trapped in the MA powders from erosion of the milling media [19].



Element	Line	Wt%	At%
Fe	KA1	0,01	0,01
Si	KA1	13,49	16,17
Ti	KA1	70,08	49,26
O	KA1	16,42	34,56
Total		100,00	100,00

Element	Line	Wt%	At%
Fe	KA1	0,19	0,15
Si	KA1	4,56	7,54
Ti	KA1	92,25	92,30
Total		100,00	100,00

Element	Line	Wt%	At%
Al	KA1	0,37	0,65
Ti	KA1	97,11	94,84
Ca	KA1	1,07	1,25
P	KA1	0,67	1,01
O	KA1	0,77	2,25
Total		100,00	100,00

Element	Line	Wt%	At%
Al	KA1	0,43	0,76
Ti	KA1	89,69	88,09
Ca	KA1	1,06	1,25
P	KA1	2,08	3,16
O	KA1	0,40	1,17
Fe	KA1	6,05	5,10
Si	KA1	0,29	0,48
Total		100,00	100,00

Fig. 2. EDS spectra of surfaces: a) Ti–3 vol. % SiO_2, b) Ti–3 vol. % HA nanocomposites produced by mechanical alloying followed by annealing

Properties of fabricated nanocomposites depend on the processing parameters. A detailed description of the influence of mechanical alloying and annealing times on mechanical properties of Ti –10 vol. % HA nanocomposite was given elsewhere [20, 21]. Differences in the phase contents of titanium-ceramic nanocomposites also

lead to changes of their properties. As shown in Fig. 3, Vickers' microhardness of bulk samples prepared by mechanical alloying depends on the composite constitution. Vickers' hardness of bulk samples prepared by mechanical alloying is higher than that of a pure microcrystalline Ti metal (250 $HV_{0.2}$) and strongly increases for Ti–10 vol. % HA nanocomposite (1500 $HV_{0.2}$) being three times higher than that of Ti–3 vol. % HA material (480 $HV_{0.2}$). Vickers' hardnesses of Ti–3 vol. % SiO_2 and Ti–10 vol. % SiO_2 composites are 550 $HV_{0.2}$ and 670 $HV_{0.2}$, respectively.

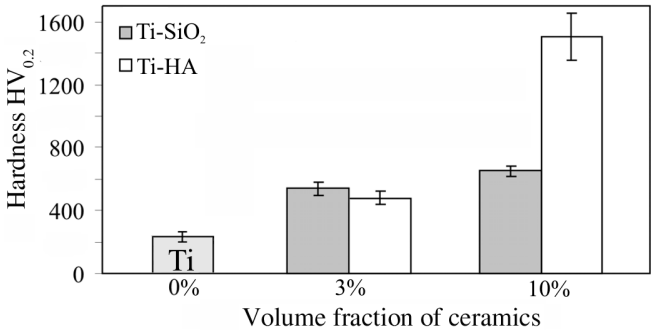


Fig. 3. The influence of volume fraction of HA or SiO_2 on Vickers' hardness in titanium-ceramic nanocomposites

Relative densities of the Ti–HA composites are higher than 85% of the theoretical density of Ti and are lower than that of Ti–SiO_2 composites (90% of theoretical density) (Table 1). The composites with lower volume fractions of ceramics have low densities, which indicates that they are more porous.

Table 2. Mean values of corrosion current densities and corrosion potentials of Ti–HA and Ti–SiO_2 nanocomposites and titanium

Composite	I_c [A/cm^2]	E_c [V]
Ti–3 vol. % HA	7.2×10^{-5}	–0.36
Ti–10 vol % HA	1.1×10^{-6}	–0.48
Ti–3 vol. % SiO_2	3.59×10^{-5}	–0.42
Ti–10 vol. % SiO_2	9.23×10^{-7}	–0.45
Ti	1.49×10^{-5}	–0.47

The corrosion current densities and corrosion potentials of various specimens were determined from the potentiodynamic polarization curves by the Tafel extrapolation method and summarized in Table 2. For example, the potentiodynamic polarization curves of the nanocrystalline Ti–10 vol. % HA and Ti–10 vol. % SiO_2 composites in 0.1 M H_2SO_4 water solution are shown in Fig. 4. For the sake of comparison, the results obtained for microcrystalline titanium are also shown. The polarization curves

(Fig. 4b, c) of Ti–10 vol. % HA and Ti–10 vol. % SiO_2 composites were wider in the passive range in comparison with microcrystalline titanium (curve *a*).

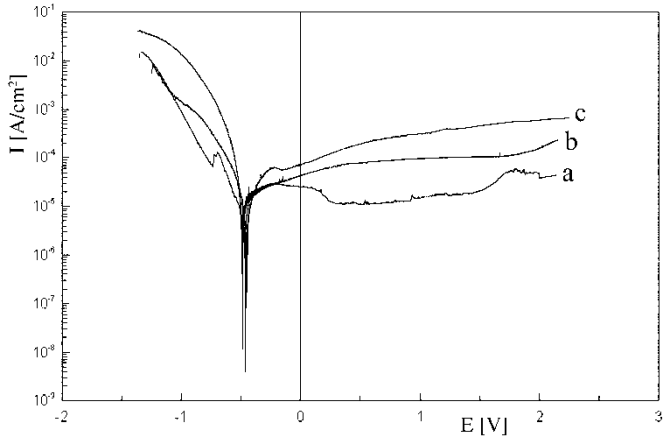


Fig. 4. Potentiodynamic polarization curves of: a) Ti, b) Ti–10 vol. % HA composites, c) Ti–10 vol. % SiO_2 in 0.1 M H_2SO_4 distilled water solution

According to Table 2, the corrosion resistance increases with the rise of ceramics contents. The corrosion resistance of the Ti–10 vol. % SiO_2 composite (I_c= 9,23×10^{-7} A/cm^2, E_c= –0.45 V) was better than Ti–3 vol. % SiO_2 composite (I_c= 3,59×10^{-5} A/cm^2, E_c= –0.42 V). The Ti–10 vol. % HA nanocomposite possesses higher corrosion resistance and thus higher corrosion current densities (I_c= 1.1×10^{-6} A/cm^2) than microcrystalline titanium (I_c= 1.49×10^{-5} A/cm^2) unlike Ti–3 vol. % HA composite (I_c= 7.2×10^{-5} A/cm^2). The Ti–3 vol. % HA nanocomposite executed worse corrosion properties in comparison with other composites and titanium because of its different chemical composition and low density, which indicates that it has a highly porous structure and could easier corrode in a corrosive environment. It is also seen that titanium composites with silica have better corrosion resistances than those with hydroxyapatite. Therefore, an addition of ceramics caused significant changes of corrosion behaviour of titanium.

4. Conclusions

It can be concluded that the titanium-ceramic nanocomposites were successfully fabricated from Ti, HA and SiO_2 powders by mechanical alloying and powder metallurgical process. As the EDS analysis has shown, the Ti–HA and Ti–SiO_2 nanocomposites consist mainly of titanium rich matrix with various apatites and calcium or silica and silicon particles, respectively. The results show an improvement of the properties due to the nanoscale structures in consolidated materials. Vickers' hardness changed upon density changes increasingd with the increase of ceramic content, especially in

Ti–10 vol. % HA composite. Besides, titanium-hydroxyapatite composite with 10 vol. % of HA possesses higher corrosion resistance than microcrystalline titanium. The corrosion resistance of the Ti–10 vol. % SiO_2 nanocomposite is also better than that of pure titanium. The results of electrochemical studies show that titanium-ceramic composite with 3 vol. % of ceramic has lower corrosion resistance than microcrystalline titanium. As discussed above, Ti–10 vol. % HA or SiO_2 nanocomposite is suitable for heavy load-bearing hard tissue replacement from the point of view of both mechanical and corrosion properties.

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