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TITANIUM-SILICA NANOCOMPOSITES: PREPARATION AND CHARACTERIZATION

OTRZYMYWANIE I WŁASNOŚCI NANOMATERIAŁÓW KONPOZYTOWYCH TYPU TYTAN-KRZEMIONKA

In this investigation Ti-SiO_2 (3, 10 vol%) nanocomposites were produced by the combination of mechanical alloying (MA) and powder metallurgical process. The resulting microstructures were characterized using X-ray diffraction, scanning electron microscope with energy dispersive X-ray spectrometry and transmission electron microscopy. The properties of the nanocomposites were investigated by mechanical, corrosion and biocompatibility studies. The experimental results show, that Ti-SiO_2 nanocomposites have good corrosion resistance and biocompatibility in comparison with microcrystalline titanium. Vickers' microhardness of Ti-10 vol% SiO2 nanocomposites is 650 HV0.2 (pure Ti metal – 225 HV0.2). In conclusion, titanium – ceramics nanocomposite are suitable for hard tissue replacement from the point of view of both mechanical and corrosion properties.

Keywords: nanocomposites, titanium, silica, mechanical alloying

Celem niniejszej pracy było wytworzenie nanokompozytowych biomateriałów typu Ti-SiO_2 (3, 10% wag.) metodą mechanicznej syntezy i metalurgii proszków. Mikrostruktura wytworzonych kompozytów była badana przy użyciu dyfrakcji promieni rentgenowskich, skaningowego mikroskopu elektronowego z mikroanalizatorem rentgenowskim i transmisyjnego mikroskopu elektronowego. Zbadano również własności mechaniczne, odporność korozyjną i biokompatybilność otrzymanych kompozytów. Z przeprowadzonych badań wynika, że nanokompozyty typu Ti-SiO_2 posiadają lepsze własności mechaniczne (mikrotwardość Vickersa dla Ti-10% SiO2 wynosi 650 HV0.2 a dla tytanu 225 HV0.2), wyższą odporność korozyjną i biozgodność w porównaniu do mikrokrystalicznego tytanu. Z tego względu, nanokompozyty tytanowo – ceramiczne mogą stać się perspektywicznymi biomateriałami do zastosowań na implanty medyczne.

1. Introduction

Over the past years, nanoscale materials, also called nanomaterials have attracted enormous amounts of interest among researchers. Nanomaterials, are commonly defined as those materials with very small grains with at least one dimention in the range of 1-100 nm [1]. Nanomaterials can be metals, ceramics, polymers and composite materials which demonstrate novel properties compared to conventional (polycrystalline) materials due to their nanoscale features [2]. Moreover, researchers have exhibited an increased interest in exploring numerous biomedical applications of nanomaterials and nanocomposites [2, 3-5]. Till now it has been shown, that implants made from metallic, carbon or oxide bionanomaterials improved considerably the prosthesis ultimate strenght and their biocompatibility.

Ti and Ti-based alloys are preferred materials in the production of implants in both medical and dental applications. Ti and its alloys possess favorable properties, such as relatively low Young modulus, low density, high strength. Apart from that, titanium and titanium alloys are generally regarded to have good biocompatibility and high corrosion resistance, although there are reports [6,7] that show the accumulation of titanium in tissues adjacent to the implant, signifying metal release and corrosion in vivo. Titanium materials are bioinert biomaterial and cannot directly bond to the bone [8]. In addition, metal implants may loose and even separate from surrounding tissues during implantation [9-11]. Titanium and titanium based alloys have relatively poor tribological properties because of their low hardness [8]. One of the methods that allows the change of biological properties of Ti alloys is the modification of its chemical composition. Selected elements, including zirconium and niobium, have been incorporated into titanium alloys

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to replace toxic elements such as vanadium [12]. The other way is to produce a composite, which will exhibit the favorable mechanical properties of titanium and excellent biocompatibility and bioactivity of ceramics. The most commonly ceramics, used in medicine are hydroxyapatite, silica or bioglass. Silica (SiO_2) is bioactive material with high corrosion resistance and the ability to form strong chemical bonds with natural bone. However, the SiO_2 cannot be used for load bearing applications, due to their poor mechanical properties regarding to natural bone. The ceramic coating on the titanium, improves the surface bioactivity, but often flakes off as a result of poor ceramic/metal interface bonding, which may cause the surgery to fail [13,14]. For this reason, composite materials containing titanium and ceramic as a reinforced phase are expected to have broad practical applications.

The aim of the present work was to study the structure, mechanical, corrosion properties and biocompatibility of Ti-SiO_2 (3, 10 vol%) nanocomposites, prepared by mechanical alloying and powder metallurgical process.

2. Experimental

The titanium-silica nanocomposite materials with different content of silica were prepared by mechanical alloying and powder metallurgical process. The row powders were first blended by mechanical alloying process, under argon atmosphere using a SPEX 8000 Mixer Mill. The vial was loaded and unloaded in Labmaster 130 glove box in high purity argon atmosphere. The mixture of Ti-SiO_2 (3, 10 vol%) powders were first ball milled for 20 hours and then compacted at 1300 MPa. Finally, green compacts were heat treated at 1150 °C in for 2 h under a gas atmosphere composed of 95% Ar and 5% H_2 to form ordered phases.

The titanium-silica powders were examined, at the various stages during milling, prior to annealing and after annealing, by means of X-ray diffraction (XRD), with Co $K_{\alpha 1}$ radiation, and high resolution transmission electron microscopy (TEM). The TEM images and selected area electron diffraction (SAED) patterns were recorded with a Philips CM 20 Super Twin microscope, which provides a 0.24 nm resolution at acceleration voltage of 200 kV. The crystallite sizes were estimated from the half-width of lines using the Scherrer equation. Scanning electron microscope (SEM) with energy dispersive X-ray spectrometer (EDS) was used to study the microstructure and the chemical composition of the prepared nanocomposites.

The effect of the different content of SiO_2 powders on mechanical properties of titanium was assessed by density and Vickers' microhardness measurements. The density was determined by Archimedes method using distilled water. The Vickers' microhardness of the bulk samples was measured using microhardness tester on polished surfaces under a load of 200 g. The 10 indentations was made on each sample and the mean calculated.

The corrosion resistance was measured using in vitro potentiodynamic corrosion test. The counter electrode consisted of two graphite rods and standard calomel electrode was used as the reference electrode. Corrosion test was performed in Ringer's solution (9.0 g/l NaCl, 0.42 g/l KCl, 0.48 g/l $CaCl_2$ and 0.2 g/l $NaHCO_3$) which was maintained at a temperature of 37 ±1°C. The surface area exposed to the electrolyte was 0.5 cm^2. Corrosion potentials (E_C) and corrosion current densities (I_C) were determined by Tafel extrapolation methods. The corrosion rate, C_R (rate of metal dissolution), in millimeters per year, was estimated with the following equation:

$$C_R = \frac{I_C \cdot EW}{F \cdot \rho} \qquad (1)$$

were I_C is a corrosion current density ($\mu A/cm^2$), EW is an equivalent weight of the corroding species in grams (g), ρ is the density of the corroding species (g/cm^3) and F is the Faraday constant.

The cytotoxicity tests were performed in dynamic conditions [15]. The discs rotated in extracting medium with SiO_2 balls at 37 °C for 14 days, and the collected extracting medium was added into CC-2538 culture to examine its inhibitive effect on cell growth. Relative viability of the cells (RVC) was calculated by the following equation:

$$\mathrm{RVC}(\%) = [(a - b)/(c - b)] \times 100, \qquad (2)$$

where a was the absorbance of the sample well, b was the absorbance of the blank well, and c was the absorbance of the control well at 595 nm.

The quantification of metallic elements in each extract of studied samples was performed by inductively coupled plasma optical emission spectrometry (ICP-OES); (Thermo Jarrell Ash, USA). Quantification was performed for five elements such as Ca, Cr, Ni, P and Ti under the optimum condition for each element.

3. Results and discussion

X-ray diffraction was employed to study the effect of mechanical alloying on Ti-SiO_2 composites. Fig. 1a, b shows the XRD patters of the starting titanium and amorphous silica powders. During MA process the intensity of diffraction line of titanium decreases with milling time and after 20 h of milling has transformed completely to an amorphous phase, without formation of any other phases (Fig. 1c). But differentiation between a "truly" amorphous, extremely fine grained or a material in which very small crystals are embedded in an amorphous matrix in so produced materials it was not possible on the basis of diffraction basis. Formation of the bulk nanocomposites were achieved by annealing of the amorphous materials in high purity gas atmosphere composed of 95% Ar and 5% H_2 at 1150°C for 2 h (Fig. 1d). XRD analysis of Ti-10 vol% SiO_2 showed the presence of -Ti type structure with cell parameters a = 2.972 Å, c = 4.774 Å. The formation of crystalline SiO_2 phase was not observed. According to the Scherrer method of XRD profiles, the average size of heat treated Ti-SiO_2 nanocomposites is about 40-50 nm.

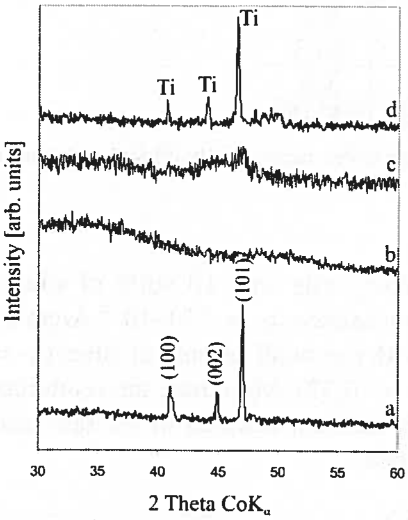


Fig. 1. XRD spectra of Ti and SiO_2 (10 vol%) powders mechanically alloyed for different times: (a) Ti – 0 h, (b) SiO_2 – 0 h, (c) 20 h, (d) after annealing at 1150 °C for 2 h

TEM results shows that the powder milled for 20 h was mostly amorphous (Fig. 2a). SAED pattern (Fig. 2d) contains broad rings at position expected for Ti with hexagonal structure. Fig. 2b shows the high resolution image of grain containing nano-particles of titanium with visible lattice planes. The interplanar distance was 0.234 and 0.224 nm, which corresponds to the (002) and (101) crystallographic planes of titanium, respectively. Apart from grains with nano Ti particles, the milled powders contained small amount of Ti crystals (Fig. 2c). which was confirmed by SAED measurement (Fig. 2e). The same structure was observed for Ti-3 vol% SiO_2 composite. The lack of any sharp reflections in the XRD pattern (Fig. 1c) suggests that the amount of the crystalline phase is very low and/or it forms during in TEM observation. During TEM studies, it has been found that the amorphous powders was unstable upon exposure to electron beam and underwent some crystallization.

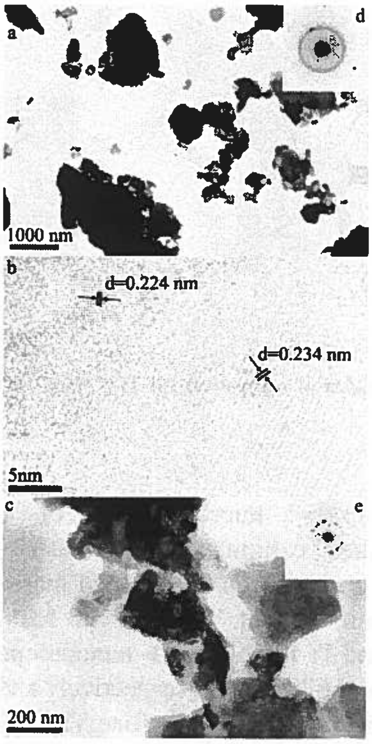
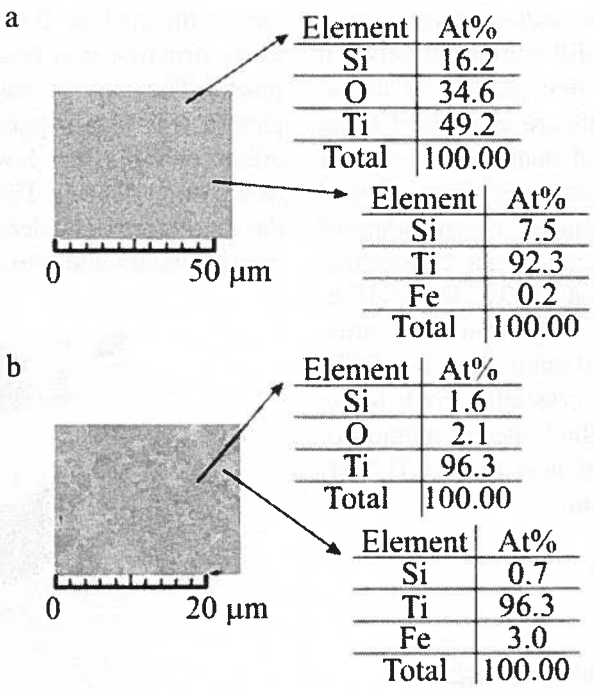


Fig. 2. TEM micrographs of the milled Ti-10 vol% SiO_2 sample for 20 h: (a) typical amorphous parts, (b) grain with nano-particles of titanium, (c) crystalline grain. Panels (d) and (e) show corresponding SAED patterns

The results of EDS analysis and scanning electron micrograph of the surface of sintered Ti-SiO_2 nanocomposites are shown in Fig. 3. EDS results indicate that the predominant phase in Ti-SiO_2 composites is titanium with content of silica or silicon particles (Fig. 3a, b). The presence of some amount of iron atoms in the sintered nanocomposites, could be explained by Fe impurities trapped in the MA powders from erosion of the milling media [16].



a

Element	At%
Si	16.2
O	34.6
Ti	49.2
Total	100.00

Element	At%
Si	7.5
Ti	92.3
Fe	0.2
Total	100.00

b

Element	At%
Si	1.6
O	2.1
Ti	96.3
Total	100.00

Element	At%
Si	0.7
Ti	96.3
Fe	3.0
Total	100.00

Fig. 3. EDS spectra of surface of: (a) Ti-3 vol% SiO_2, (b) Ti-10 vol% SiO_2 nanocomposites mechanically alloyed and heat treated at 1150 °C for 2 h

The Vickers' microhardness of the sintered nanocomposites exhibits various distribution corresponding to composition change and increased with the rise of ceramic content. The Vickers' hardness for Ti-3 vol% SiO_2 and Ti-10 vol% SiO_2 nanocomposites reaches 550 HV0.2 and 670 HV0.2, respectively and is two times higher that of pure microcrystalline Ti (225 HV0.2); see Fig. 4.

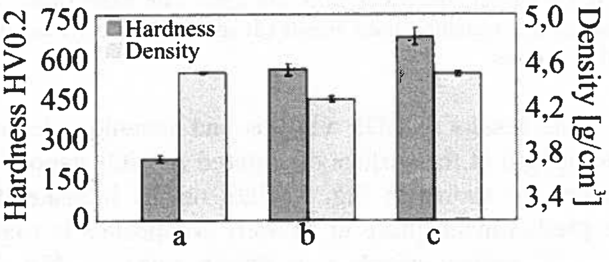


Fig. 4. Vickers' microhardness of studied materials; (a) Ti, (b) Ti-3 vol% SiO_2, (c) Ti-10 vol% SiO_2

The polarization curves of Ti-SiO_2 nanocomposites are reported in Fig. 5. Table 1 show the polarization data obtained for sintered composites and microcrystalline titanium, including corrosion potential (E_C), corrosion current density (I_C) and corrosion rate (C_R) values. According to Table 1 and Fig. 5, it is possible to observe that ceramic doped to titanium had a positive effect on corrosion resistance of Ti. The corrosion test results indicated that the microcrystalline titanium possesses lower corrosion resistance and thus higher corrosion current density ($I_C = 1.31 \circ 10^{-5}$ A/cm²) in Ringer's solutions. Titanium composite with 10 vol% of silica have better corrosion resistance ($I_C = 3.74 \cdot 10^{-8}$ A/cm², E_C = -0.44) than that with the small amount of silica ($I_C = 1.91 \circ 10^{-6}$ A/cm², E_C = -0.37). Moreover, the reinforcement of ceramic with titanium resulted in the decreased of the Ti corrosion rate.

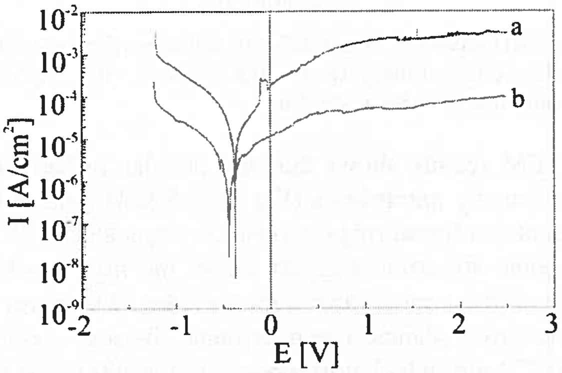


Fig. 5. Potentiodynamic polarization curves of: (a) Ti-3 vol% SiO_2, (b) Ti-10 vol% SiO_2 composites in Ringer's solution

TABLE 1

Mean values of corrosion current density, corrosion potential and corrosion rate of studied Ti-HA and Ti-SiO_2 nanocomposites

Sample	I_C[A/cm²]	E_C[V]	$CR_{[mm/y]}$
Ti-3 vol% SiO_2	$1.91 \circ 10^{-6}$	-0.37	0,000055
Ti-10 vol% SiO_2	$3.74 \circ 10^{-8}$	-0.44	0,000001
Ti (microcrystalline)	$1.31 \circ 10^{-5}$	-0.36	0,000363

Future application of Ti-SiO_2 nanocomposites focused also our attention on the biocompatibility of synthesized bulk materials. Cytotoxicity tests of the extracts of studied materials under wear conditions are shown in Fig. 6. The relative viability of the cells (RVC) decreases when fraction increases. It is important to note that the RVC of nanoscale Ti-10 vol% SiO_2 is higher in comparison with microcrystalline titanium. The wear and fretting accelerates the corrosion of the studied samples in a biological environment such as cell culture medium.

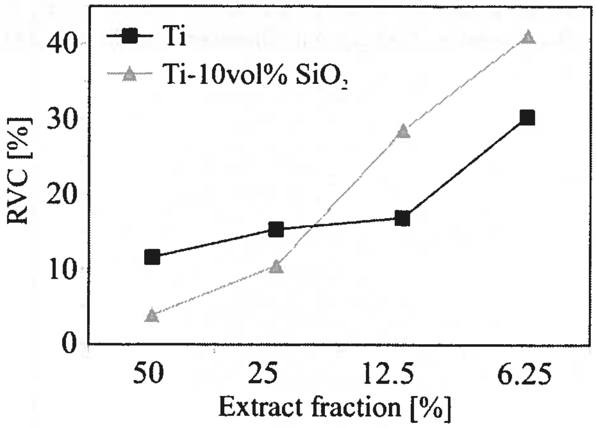


Fig. 6. Cytotoxicity tests of the extracts of Ti-10 vol% SiO_2 and microcrystalline titanium in dynamic conditions (see text for details)

The quantification of metallic elements in each extract of studied samples was performed for five elements such as Ca, Cr, Ni, P and Ti under the optimum condition for each element and the results are shown in Table 2. In the extract of microcrystalline Ti and nanocomposite Ti-10 vol% SiO_2, nickel was detected at the concentration of 0.19±0.03 mg/l and 0.31±0.04 mg/l, respectively. It is important to note, that the preferential release of Ni was also reported on Ti-6Al-4V as impurity at the concentration less than 0.01 wt% [15]. Additionally, in extracts of Ti and Ti-10 vol% SiO_2 chromium was detected at the concentration of 4.4±0.7, and 4.0±0.5 mg/l, respectively. Chromium is one of the essential elements for human, so slight amount of this element may contribute to cell proliferation, resulting in higher cell growth [4, 17]. In all studied extracts of Ti and Ti-10 vol% SiO_2 calcium was present at the concentration of 64±8 and 78±10 mg/l, respectively. The existence of Ca could promote the formation of apatite. On the other hand, titanium element was not detected. These results indicate that Ti-SiO_2 nanocomposites have superior cytocompatibility compared to the conventional microcrystalline Ti. Based on the above results Ti-ceramic nanocomposites have a high possibility for the application in biomedical field.

TABLE 2
Quantification of metallic elements in the extracts (<DL – concentration below detection level)

element	Sample	
	microcrystalline Ti [mg/l]	Ti-10 vol% SiO_2 [mg/l]
Ca	64±8	78±10
Cr	4.4±0.7	4.0±0.5
Ni	0.19±0.03	0.31±0.04
P	0	0
Ti	<DL	<DL

4. Conclusion

In this work, the structure, mechanical and corrosion properties of titanium-silica nanocomposites synthesized by mechanical alloying and powder metallurgical processes were studied. Different phase constitutions have significant influence on the mechanical and corrosion properties of sintered materials. The Ti-SiO_2 nanocomposites mainly consist of silica and silicon particles reinforced with titanium matrix. Ti-3 vol% SiO_2 and Ti-10 vol% SiO_2 nanocomposites posses better mechanical properties than microcrystalline titanium. Besides, the value of the corrosion current density, corrosion potential and corrosion rate determined for titanium-ceramic composite suggest that silica doped to titanium has a beneficial effect on corrosion behavior of Ti. The cytotoxicity tests showed that Ti-ceramic nanocomposites have superior cytocompatibility compared to conventional titanium.

For this reason, they are promising biomaterials for use as heavy load-bearing tissue replacement implants.

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