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COMPOSITES THEORY AND PRACTICE

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ELECTROPHORETIC DEPOSITION OF BIPHASIC CALCIUM PHOSPHATES ON NiTi SHAPE MEMORY ALLOY

The application of NiTi shape memory alloys as long-term implants is dependent on ensuring better biocompatibility of the alloy, which is achieved by modification of the surface by protective coatings or layers. In the present work, the surface of the NiTi alloy was covered by biocompatible composite coatings. First, a thin rutile layer was formed by autoclaving. Passivation was carried out at 134°C for 30min which resulted in forming an amorphous TiO_2 thin film. Next, a biphasic calcium phosphate (BCP) layer was deposited using electrophoresis (EPD). The BCP layer was composed of hydroxyapatite (HAP) and β-tricalcium phosphate (β-TCP). The deposition voltage ranged from 40 to 80 V at a constant time of 60 s. The deposited samples were vacuum-sintered at 800°C for 2 h. Observations of the surface revealed that the obtained coatings are crack-free. Measurements done with X-ray diffraction confirmed that the top layer consisted of β-TCP and HAP.

Keywords: NiTi, electrophoretic deposition (EPD), composite coatings, biphasic calcium phosphates (BCP)

ELEKTROFORETYCZNE OSADZANIE DWUFAZOWEJ CERAMIKI FOSFORANOWO-WAPNIOWEJ NA POWIERZCHNIĘ STOPU NiTi WYKAZUJĄCEGO EFEKT PAMIĘCI KSZTAŁTU

Zastosowanie stopów NiTi w medycynie na długoterminowe implanty uwarunkowane jest zapewnieniem lepszej biokompatybilności, co uzyskuje się poprzez modyfikację powierzchni wyjściowej stopów odpowiednimi biozgodnymi warstwami lub powłokami ochronnymi. W prezentowanej pracy powierzchnia stopu NiTi została zmodyfikowana poprzez wytworzenie warstwy kompozytowej składającej się z rutylu (TiO_2) oraz dwufazowej ceramiki opartej o fosforany wapnia (BCP), złożonej z hydroksyapatytu (HAP) oraz ceramiki whitlockitowej (β-TCP). Warstwa rutylu została wytworzona poprzez pasywację w autoklawie parowym w warunkach stosowanych do sterylizacji narzędzi chirurgicznych (134°C, 30 min). Następnie na spasywowanej powierzchni została wytworzona metodą elektroforezy powłoka składająca się z dwufazowej ceramiki CaPs. Warstwy nałożono, stosując napięcie z zakresu 40÷80 V przy stałym czasie depozycji wynoszącym 60 s. Naniesione warstwy spiekano w piecu próżniowym w temperaturze 800°C przez 2 h. Obserwacje powierzchni przy użyciu skaningowego mikroskopu elektronowego nie wykazały pęknięć na powierzchni warstw. Badania rentgenowskie potwierdziły kompozytowy skład warstwy wierzchniej.

Słowa kluczowe: NiTi, elektroforetyczne osadzanie (EPD), powłoki kompozytowe, BCP

INTRODUCTION

Calcium phosphate (CaP) ceramics (CaP) are promising materials for medical applications. They may be used in various orthopedic and dental applications [1]. The interest in these materials is clear due to their high chemical similarity to the inorganic parts of bones and teeth of mammals. Calcium phosphates are bioactive and conduct bone apposition by direct bone bonding [1-3]. Among the various forms of CaP ceramics, the most attention is gained by non-resorbable hydroxyapatite (HAP), resorbable β-tricalcium phosphate (β-TCP) and biphasic calcium phosphates (BCP) [1-5]. In order to enhance implant biocompatibility, calcium phosphate ceramics are used for surface modification [5, 6].

NiTi shape memory alloys (SMA), nearly equiatomic in their chemical composition, reveal outstanding properties such as one-way-, two-way-shape memory and a superelasticity effect as well as good biocompatibility. Based on these features, NiTi alloys are the most common SMA in medicine [7-9]. Nevertheless, the applications of the NiTi shape memory alloy as long-term implants, can be limited by the possibility of toxic nickel ion migration into the organism due to corrosion. In order to improve its corrosion resistance, the surface of NiTi alloys have been modified by the formation of layers / coatings [10-12]. The surface of NiTi has been covered with titanium oxides [13], nitrides [14], polymers [15], bioglasses [16], CaP coverings [17,18] and composites [12, 19, 20].

Most deposition processes require elevated temperatures. In the case of the NiTi alloy, high tempera-

ture treatment can lead to decomposition of the B2 phase to equilibrium ones, such as Ni_3Ti and/or $NiTi_2$, thereby affecting the shape memory and superelasticity effects. Electrophoretic deposition (EPD) is one of the techniques applied for surface modification, which can be carried out at ambient temperature. Moreover, the great advantage of EPD is its simplicity, repeatability and relatively low cost of deposition [21-23].

In the present work, the surface of the NiTi alloy was covered by multi-layers. First, the alloy was passivated by autoclaving [17, 24] and the electrophoretic deposition processes of biphasic calcium phosphates (BCP) was carried out. The paper presents the results obtained from studies done on the morphology and structure of the obtained composite layer.

MATERIALS AND METHOD

The NiTi alloy with the chemical composition 50.6 at.% Ni and 49.4 at.% Ti (Memory) was used as the substrate for layer deposition. In order to obtain the β-phase of the NiTi alloy at room temperature, the samples were submitted to heat treatment according to the procedure in [17]. Next, they were polished and then passivated in an autoclave at 134°C for 30 min. The passivation resulted in forming a thin amorphous titanium oxide layer on the surface of the NiTi alloy [17, 24].

The colloidal suspension of BCP, for electrophoretic deposition, was prepared using the following powders: β-TCP (Sigma Aldrich) and hydroxyapatite (Sigma Aldrich). The 0.1 g of powders mixed in a wt. ratio of 1:1 was added to 100 ml of 99.8% ethanol (POCh). In order to obtain a well-dispersed suspension, it was put in a magnetic stirrer and in an ultrasonic bath.

The BCP coatings were deposited by the electrophoresis technique (EPD). Cataphoretic deposition was carried out using a power supply (Apelex PS 608) at constant voltages of 40, 60 or 80 V for 60 s at ambient temperature. Then the samples were vacuum-sintered at 800°C for 2 h.

The structure of the materials was studied with use of a X-ray diffractometer X'PertPro with monochromatized Cu Kα radiation. The coated NiTi alloy was studied by means the grazing incidence X-ray diffraction technique (GIXRD). The GIXRD patterns were measured at constant incidence angles of 0.2, 0.3, 0.5 or 1.0° at room temperature. The surface morphology of the coated samples was observed using a JEOL JSM-6480 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The NiTi alloy in the β-phase at room temperature was used as the substrate. For the electophoretic deposition, the colloidal suspension of β-TCP and HAP powders was prepared. SEM observations revealed that the TCP particles are significantly larger than the HAP particles (Fig. 1a, 1b). Both materials have a wide range of grain size.

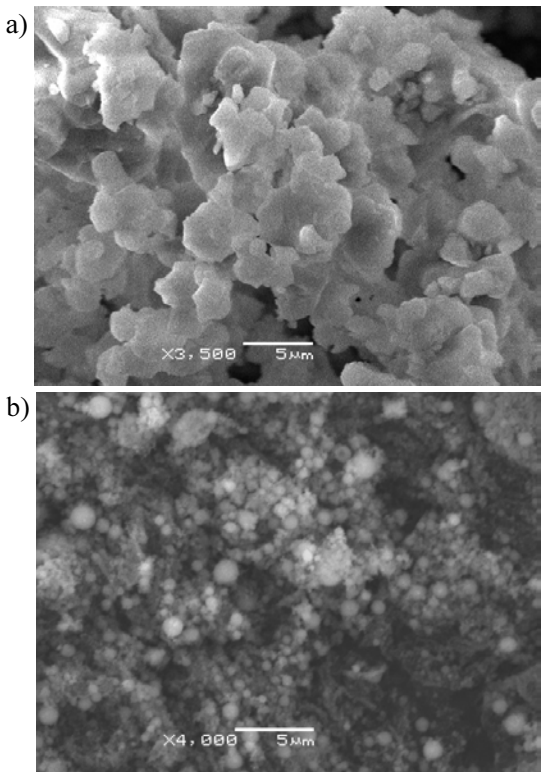

Fig. 1. SEM images observed for β-TCP (a) HAP powder (b)

Rys. 1. Obrazy mikroskopowe obserwowane dla proszku β-TCP (a) i hydroksyapatytu (b)

Figures 2 a-c present the SEM images observed for the surface of the BCP coatings deposited under various deposition voltage. It was found that the applied voltage significantly influences the morphology of the coatings. An increase in voltage caused deposition of a greater amount of ceramics particles. It is clearly visible for the large size of the β-TCP particles. The SEM observations revealed that the applied deposition conditions result in relatively homogenous distribution of the β-TCP particles located between the smaller hydroxyapatite grains. The measured X-ray diffraction patterns revealed the presence of peaks belonging to the HAP, β-TCP and the β-phase of NiTi. No additional diffraction lines were identified.

In the subsequent step, the deposited coatings were vacuum-sintered at the temperature of 800°C for 2 h. The surface of the coatings was observed with use of SEM in order to verify the possibility of cracks creation as well as assess changes in the microstructure due to the sintering process. Figure 5a shows an example SEM image of the microstructure observed for a sample deposited at 80 V/60 s. Based on this, it was proved that the applied sintering conditions resulted in densification and forming crack-free coatings. From the X-ray diffraction, it was found that sintering does not cause decomposition of the HAP or β-TCP. Diffraction peaks

of both phases were identified (Fig. 5b). However, the sintering temperature and lower cooling of the deposited sample leads to decomposition of the B2 parent phase. Diffraction lines, with relatively low intensity, were found of the equilibrium phases: Ti_2Ni (PDF-2, card no 72-0442) and Ni_3Ti (PDF-2, card no 51-1169).

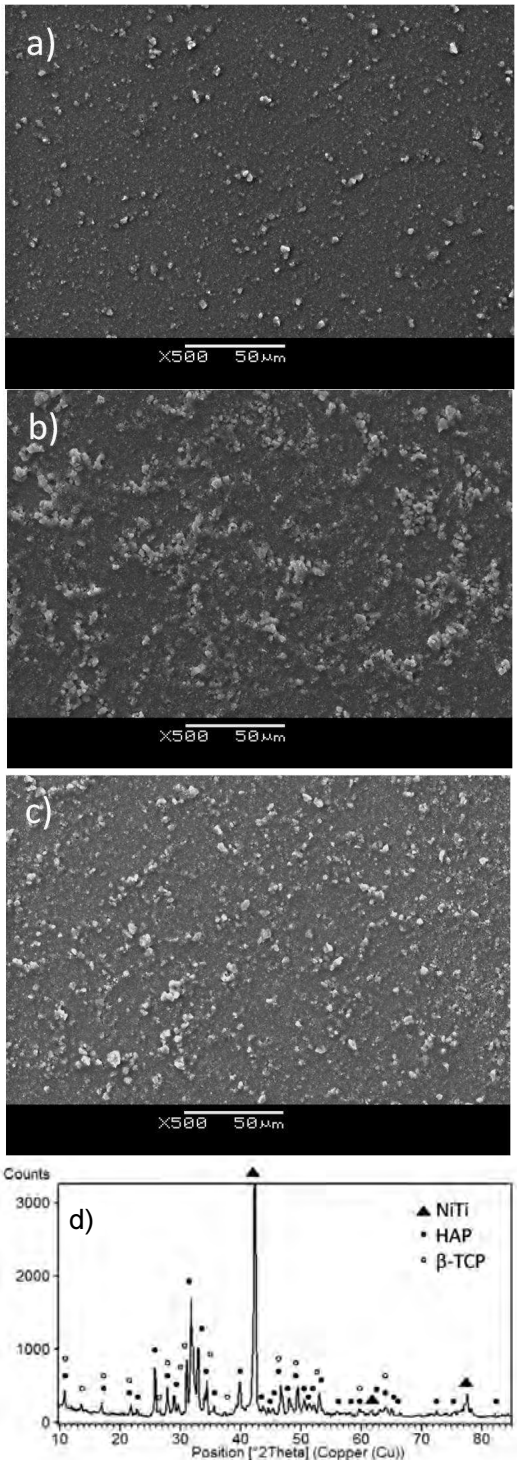

Fig. 4. SEM images observed for BCP coatings deposited at: 40 V/60 s (a), 60 V/60 s (b), 80 V/60 s (c) and GIXD patterns measured at incidence angle of 0.3° for coating deposited at 80 V for 60 s (d)

Rys. 4. Obrazy mikroskopowe powierzchni obserwowane dla powłok BCP wytworzonych przy następujących parametrach osadzania: 40 V/60 s (a), 60 V/60 s (b) i 80 V/60 s (a) oraz dyfraktogram zmierzony pod stałym kątem padania wiązki pierwotnej 0.3° dla powłoki wytworzonej przy napięciu 80 V i czasie depozycji 60 s (d)

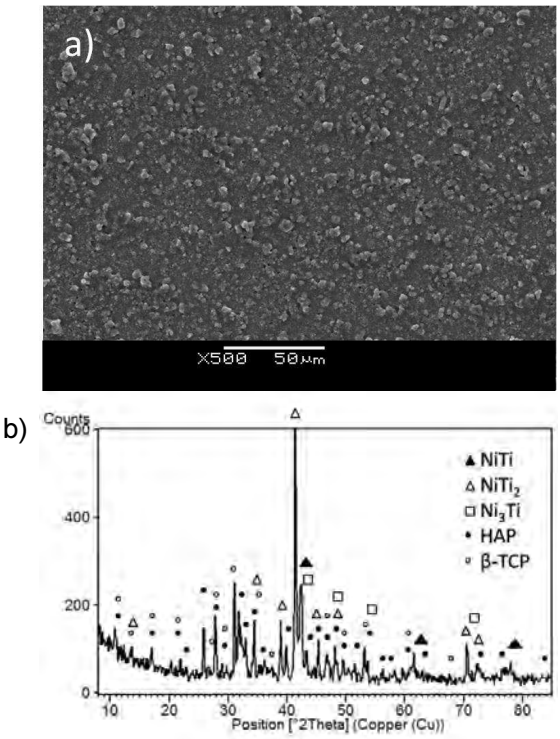

Fig. 5. SEM image (a) and GIXD patterns measured at incidence angle of 0.3° (b) for BCP coatings deposited at 80 V/60 s and sintered at 800°C/2 h

Rys. 5. Obraz mikroskopowy (a) oraz dyfraktogram zmierzony pod stałym kątem padania wiązki pierwotnej 0.3° (b) dla powłoki BCP wytworzonej przy napięciu 80 V i czasie depozycji 60 s oraz spieczonej w 800°C w czasie 2 h

SUMMARY

The SEM and XRD study confirmed the possibility of electrophoretic deposition of biphasic calcium phosphates (BCP) on the passivated surface of the NiTi shape memory alloy. The morphology of the BCP coating can be controlled by the deposition voltage used during the EPD process. Applying a lower deposition voltage (40 V) caused the formation of a layer consisting mainly of HAP particles. Increasing its value led to an increase in TCP participation in the coating. The sintering conditions (800°C/2 h) led to obtaining crack-free coatings and did not decompose the β-TCP or HAP.

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