STRUCTURE AND MORPHOLOGY OF WHITLOCKITE COATING ELECTROPHORETICALLY DEPOSITED ON NiTi SHAPE MEMORY ALLOY

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Introduction

The NiTi shape memory alloys (SMA) with its chemical composition near to that of equiatomic ones are used in a wide range of biomedical fields. Their biomechanical properties make it more suitable for bone fixation than other metallic materials [1]. In order to improve biocompatibility, the surface of NiTi alloys is modified by producing biocompatible layers [2]. It is desirable that the protective layers increase the functionality of the implant surface, for example by enhance the osseointegration. The best bonding of the metal implant surface to bone tissue is achieved by producing calcium phosphate-based coatings (CaPs) such as hydroxyapatite (HAp) or whitlockite ceramic (TCP) [3].

The main aim of presented results was focused on the biocompatibility intensification of NiTi SMA done by its surface modification. The technology of material preparation was concentrated on the passivation of NiTi substrate by autoclaving and following electrophoretic deposition (EPD) of whitlockite ceramic (β-TCP).

Materials and Methods

A NiTi alloy with the following chemical composition of 50.6 at.%. Ni and 49.4 at.%. Ti (Memry GmbH) was used as substrate for layers deposition. Before EPD, the substrate was passivated in autoclave at 134°C for 30 min. The autoclaving resulted in formation of a thin amorphous TiO_2 layer what improves the corrosion resistance and provides a stable connection of deposited ceramic particles to metal substrate [2,4].

The powder of whitlockite (nGimat) consisted of 87.1 ±1.0 wt% β-$Ca_3(PO_4)_2$ and 12.9 ±0.2wt% β-$Ca_2P_2O_7$ was used to prepare a colloidal suspension having a concentration of 0.1wt% the powder in 99.9% ethanol (Avantor). Next, the mixture was put into a magnetic stirrer (30 min) and then transferred to an ultrasonic bath (30 min). The average size of the particles was ca. 550 nm [5]. Afterwards, electrophoretic deposition (EPD) under cathodic condition and room temperature was performed to cover the NiTi substrate by CaPs particles. The constant voltages (from 20 to 80 V) at time periods (from 30 to 120 s) were applied. After deposition, the green form coatings were dried for 24h at ambient temperature. Then, in order to consolidation and increase the adhesion strength of the ceramic coating to the metal substrate samples were heat treated in vacuum furnace at 1000°C for 2h.

Results and Discussion

The outcomes revealed that applied voltage and deposition time have a great impact on the quality of whitlockite coatings electrophoretically deposited on the passivated NiTi substrate. Due to lower voltage and deposition time, the ceramics particles spread on the surface heterogeneously forming larger agglomerates. Increase of the quantity of deposited particles, at the constant voltage with elongation deposition time, in comparison to constant time and increase of voltage was observed. Deposition parameters such as 80V/120s impact on a significant increase in the density and thickness of the coating. The applied heat treatment conditions (1000°C for 2h) resulted in a visible change in the morphology of the coating. The areas between the agglomerates changed from smooth to rough. It may be caused by the intensification of the titanium oxide crystallization from the amorphous oxide layer, previously formed on NiTi substrate during the autoclaving. The presence of crystallized clusters of fine particles, especially close to CaP aggregates, was also stated (FIG. 1).

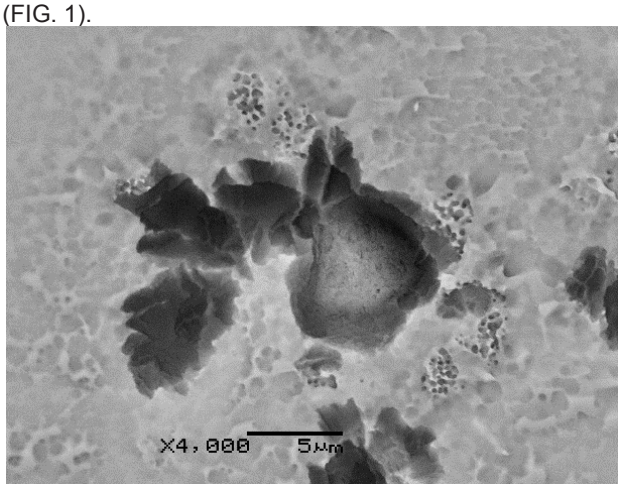

FIG. 1. SEM image of surface observed for the NiTi coated substrate.

Diffraction data (GIXRD) collected for samples after deposition and after sintering process reveled well-defined peaks both of β-TCP (ICDD - PDF 04-008-8714) with rhomboedral structure (R-3c) and trace amount of β-$Ca_2P_2O_7$ phase with tetragonal structure ($P4_1$) (ICDD-PDF 04-009-8733). The crystal structure of coatings materials remain unchanged in comparison to starting material. The presence of diffraction lines from whitlockite decomposition products was not proved. The applied heat treatment (1000°C / 2h in vacuum) resulted in a partial decomposition of NiTi substrate (ICDD - PDF 01-078-4618) to equilibrium phases: Ti_2Ni (ICDD - PDF 04-007-1531) with cubic structure (Fd-3m) and Ni_3Ti with hexagonal structure ($P6_3/mmc$). In addition, the appearance of diffraction lines belonging to non-stoichiometric $TiO_{0,325}$ with hexagonal structure ($P6_3/mmc$) (ICDD - PDF 04-005-4356) and TiO with cubic structure (Fm-3m) (ICDD - PDF 04-016-4319) were be identified.

Conclusions

Application of deposition voltage of 20V for 60s resulted in homogenous covering of passivated NiTi substrate by whitlockite layer. As a result of heat-treatment (1000°C / 2h in vacuum) crystallization of titanium oxides and partial decomposition of NiTi alloy were observed. However, the structure of CaP coating material remains unchanged.

References

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