Applied Surface Science 437 (2018) 28–40

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Impact of annealing on features of BCP coating on NiTi shape memory alloy: Preparation and physicochemical characterization

Mateusz Dulski[a,b,*], Karolina Dudek[a,b,c], Michał Grelowski[b,d], Jerzy Kubacki[b,d], Justyna Hertlein[e], Marcin Wojtyniak[b,d], Tomasz Goryczka[a,b]

[a] Institute of Material Science, University of Silesia in Katowice, 75 Pulku Piechoty 1a, Chorzow, 41-500, Poland
[b] Silesian Center for Education and Interdisciplinary Research, 75 Pulku Piechoty 1a, Chorzow, 41-500, Poland
[c] Institute of Ceramics and Building Materials, Refractory Materials Division in Gliwice, Toszecka 99, Gliwice, 44-100, Poland
[d] A. Chelkowski Institute of Physics, University of Silesia in Katowice, Uniwersytecka 4, Katowice, 40-007, Poland
[e] Centre of Polymer and Carbon Materials (CMPW) of the Polish Academy of Sciences (PAN) M. Curie-Skłodowskiej 34, Zabrze, 41-819, Poland

ARTICLE INFO

Article history:
Received 18 August 2017
Received in revised form 4 December 2017
Accepted 7 December 2017
Available online 9 December 2017

Keywords:
Hydroxyapatite
Tricalcium phosphate
NiTi shape memory alloy
Surface science
Surface and interfaces
Electrophoretic deposition
Hybrid composite
Annealing
Surface modifiaction

ABSTRACT

A multifunctional composite structure consisting of resorbable tricalcium phosphate with non-resorbable hydroxyapatite and NiTi shape memory alloy (SMA) has been manufactured to develop a biocompatible system for long-term implant applications. The hybrid system has been vacuum sintered to consolidate and form chemical binding between phosphate biomaterials and NiTi SMA. In this context, the impact of sintering on biomaterial's features in relation to initial material has been analyzed using a combination of structural and surface sensitive approaches. Moreover, a partial decomposition of the NiTi parent phase to the equilibrium Ti_2Ni with cubic structure, and non-equilibrium Ti_3Ni_4 with hexagonal structure has been detected. Moreover, a sintering has provided a reconstruction of the orthophosphate surface through the disintegration of calcium phosphate material and increase of hydroxyapatite with smaller particles in volume. The biomaterial surface has become more enriched in calcium in relation to the initial composition, with a simultaneous decline of the roughness parameters due to the gradual consolidation of orthophosphates. Finally, surface modification accompanied with heat treatment has led to an increase of surface Young's modulus as an effect of partial recrystallization of calcium phosphates.

1. Introduction

Calcium phosphate (CaPs) based biomaterials such as non-resorbable hydroxyapatite (HAp: $Ca_{10}(PO_4)_6(OH)_2$), resorbable β-tricalcium phosphate (β-TCP: $Ca_3(PO_4)_2$) and biphasic HAp/β-TCP mixture belong to the most frequently studied synthetic bone grafts [1–10]. Those materials were clinically tested and used in medical applications for over 20 years in various forms: cement, coatings, granules, porous or solid blocks, as well as in the form of numerous composite materials. They are commonly used as a bioactive bone substitute material, especially in orthopedics and dentistry [1,2,11–15]. The CaPs ceramics demonstrate high biocompatibility, bioactivity, and osteoconductivity as well as initiate building a chemical connection between bone tissues and ceramic implants. Moreover, the CaPs ceramics facilitate hard-tissue regeneration and fulfill osseointegration [16–20]. Due to their bioactive properties, these materials are useful in a direct bone bonding, or as scaffolds for tissue engineering [21]. Thanks to their porosity they can be used as drug delivery system [22] or as a carrier of bone growth factors [21,23]. In addition, phosphate ceramics used as a coating material improve the corrosion resistance of the metallic implants and suppress the release of toxic metallic ions into organism [3,4,7,10]. Unfortunately, inherent poor mechanical properties of phosphate ceramics (brittleness, low tensile strength, and poor impact resistance) limit their application, especially in many load-bearing applications [23].

Therefore, it is not advisable to use the mentioned ceramics in a bulk form, but rather as a coating. This is especially important since thin films of phosphate coatings improve bone-to-implant bonding and prevent fibrous capsule formation after implantation. Thus, there are the most likely used in medical applications [24–27]. What is more, the implants coated with orthophosphates layers usually do not form fibrous tissues with bone, but rather a thin, epitaxial bonding layer. It is crucial to understand their physical properties leading the better understanding of the

* Corresponding author at: Institute of Material Science, University of Silesia in Katowice, 75 Pulku Piechoty 1a, Chorzow 41-500, Poland.
E-mail address: mateusz.dulski@smcebi.edu.pl (M. Dulski).

https://doi.org/10.1016/j.apsusc.2017.12.056
0169-4332/

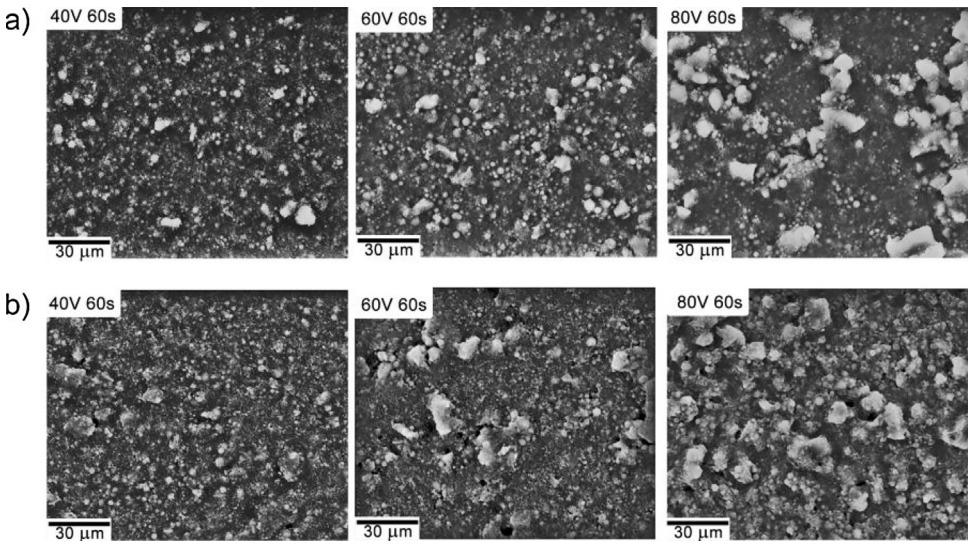

Fig. 1. SEM images of BCP observed before a) and after b) sintering at 800 °C for 2h.

relationship between structure and function [28–30]. Thus, the surface-sensitive analytical tools such as X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Atomic Force Microscopy (AFM) will be implemented.

Another issue that has to be addressed is the choice of the substrate (or the implant material if it comes to medical application). The NiTi shape memory alloys (SMA) was chosen, due to its good mechanical properties, biocompatibility and unique features such as one-way-, two-way-shape memory, and superelasticity effects belong to one of the most common materials used in medicine [31–36]. SME is closely related to reversible martensitic transformation occurring between the B2 parent phase (with cubic structure) and the B19' martensite (with monoclinic structure) [1–4,7,8,10]. The martensitic transformation (B2 → B19') is induced by reducing the temperature, whereas the reverse martensitic transformation (B19' → B2) occurs due to heating. However, the possibility of nickel ion releasing into surrounding tissues limits their use as materials for long-term implants. In this way, the main key to the development of new type of coatings is their surface modification by the formation of bioactive, calcium phosphate coatings [37–46]. In this context, the coating for the NiTi alloy cannot be too thick and/or rigid, since that could limit or completely block the shape memory effect. Furthermore, most of the typical methods for coating formation require usage of elevated temperature, what in the case of NiTi alloys may lead to the decomposition of parent phase (B2) and significantly reduce a shape memory and superelasticity effects.

Summarizing, the selection of suitable methods for coating formation, material consolidation, deposition parameters, and type of materials is crucial to develop innovative implant material for long-term performance.

In recent years, the electrophoretic deposition (EPD) has become a very popular technique, especially for the formation of hybrid composite layers on substrates with irregular shape, chemical composition and morphology [47–51]. The EPD is relatively noninvasive and does not affect material decomposition, giving the opportunity to prepare layers of varying thickness (from nm to μm) formed of different inorganic materials (metallic nanoparticles, ceramics, carbon nanotubes) [47–49,52–55]. By controlling deposition parameters one can obtain layers with a variable ceramic mass, thickness, and surface topography (i.e. porosity/roughness). However, EPD coatings suffer from low mechanical stability or poor adhesion. Thus, the final ceramic product of electrophoretic deposition process has to be a subject of a subsequent heat treatment to improve coating/substrate chemical contact and to densify deposited material. However, the temperature applied during the sintering might have an impact on the CaP materials, such as the composition, phase, or thermal stability [47].

This paper is focused on the preparation and characterization of multifunctional hybrid composites produced of BCP/TiO_2/NiTi. The NiTi surface alloy was functionalized by biocompatible amorphous titanium oxide with a combination of hydroxyapatite (HAp), and tricalcium phosphate (β-TCP). The impact of the various physical and chemical conditions on the formation and functional properties of hybrid composites were thoroughly investigated. The microstructure was analyzed by scanning electron microscopy (SEM) while structural and chemical features using X-ray diffractometry (GIXRD), auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Atomic force microscopy (AFM) was applied to follow the impact of heat treatment on surface topography, particle distribution, surface roughness and mechanical features. Finally, the wetting ability of the initial composite was compared with the sintered material.

2. Experimental

XRD X'PertPro with monochromatized Cu *Kα* radiation (λ = 1.54 Å) was used to analyze structural features of the composite materials. The quantitative phase analyzes and lattice parameters were refined by Rietveld method with HighScore Plus 4.6 software.

The surface morphology was analyzed using SEM from JEOL JSM-6480 equipped with energy dispersive spectrometer (EDS).

The electronic structure was measured using the PHI 5700/660 Physical Electronics XPS combined with AES. XPS spectra were obtained from 3 to 4 nm depth by using monochromatized Al *Kα* radiation (1486.6 eV) and surface chemical composition was estimated with a precision of 1.0 at.%. All photoelectron spectra were calibrated against the peaks of Au $4f_{7/2}$ at 83.98 eV, Ag $3d_{5/2}$ at 368.27 eV and Cu $2p_{3/2}$ at 932.67 eV of binding energy. The flood gun was constantly used to compensate the charge build-up. The survey spectra were obtained at pass energy 187.5 eV. The photoemission spectra of the Ca 2p, P 2p, O 1s and C 1s core levels were recorded at 23.5 eV pass energy and calibrated to the position of the C 1s peak at 285.0 eV. The fitting procedure were applied to the analysis of the shape of core levels according to method used to in Multipak software with a percentage share of 60% Gaussian