

Surface properties in titanium with hydroxyapatite coating

AGATA DUDEK

Institute of Materials Engineering, Częstochowa University of Technology,
Armii Krajowej 19, 42-200 Częstochowa, Poland

*Corresponding author: dudek@mim.pcz.czest.pl

Due to its wide range of possible applications in current technology, hydroxyapatite, as a biomaterial, has been of great interest to scholars. Improvement in mechanical properties can be achieved by addition of zirconia, partially stabilized by yttrium, into a resistant oxide phase. The present study describes the microstructure and phases which are typical of composite coatings after plasma spraying.

Keywords: hydroxyapatite, zirconia, XRD.

1. Introduction

Due to progressing population ageing, skeleton diseases (*e.g.*, spine diseases) are becoming a common problem in society. Thus, the fact that a great emphasis is on development of bone-replacing materials which allow for filling bone defects resulting from a variety of reasons seems to be understandable.

The attempts to use titanium and its alloys on a wider scale date back to as early as the forties of the past century. Particular popularity in bone surgeries emerged mainly for Ti–6Al–4V and Ti–6Al–4V ELI alloys. These alloys are used, among other things, for joint prostheses, plates, bone screws, dental implants. Main advantages that determine application of titanium alloys include excellent mechanical properties and biocompatibility.

Assessment of perspective opportunities of use of metallic biomaterials for reconstruction of tissue structures, according to numerous researchers, leads to the conclusion that a possibly highest level of improvement in their biotolerance in human body has been reached [1–6]. The methods of improvement in physicochemical properties of metallic implants include production of bioceramic coating on their surface, thanks to which, if the porosity is at adequate level, living tissue overgrows the surface [7, 8].

Examples of bioceramic materials resorbed in tissues include hydroxyapatite materials that contain calcium orthophosphates. Hydroxyapatite materials (HA, HAp), marked with its $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ chemical symbol, is an osteoconductive material and, to a smaller extent, osteoinductive and thus the implants made of this material can be adjacent to the bone. After implantation of the material, osteogenesis occurs and the layer which connects the surface of hydroxyapatite implant with bone tissue appears. The condition for proper osseointegration is close adhesion of an implant to the bone and its mechanical post-surgical stability. HA is a material that is characterized by insignificant level of biodegradation – resorption in human body is within the range of 5 to 15% yearly. The process of integration of the implant with bone takes a year on average.

Hydroxyapatite coatings are applied, among other things, on joint prostheses components, particularly on the heads located on stems. Their application causes 5-time rise in durability as compared to conventional prostheses.

A variety of coating techniques have been explored to develop thin coatings of HA, such as plasma-spray technique, pulsed laser deposition, electrodeposition, sol–gel processing and radio-frequency magnetron sputtering. Many research works concern determination of the most optimal conditions of spraying and their impact on the creation of hydroxyapatite coating [2, 5–12]. During the process of spraying, powder is subject to interaction with high temperatures which exceed HA melting point (1550 °C). Melted portions of particles can crystallize on the base material or create amorphous compounds of calcium phosphate. Rapid cool-down, which typically accompanies plasma spraying, limits the scope of crystallization. Moreover, the problem becomes more difficult due to the possibility of phase transitions which might occur during spraying. HA might be subject to decomposition into the mixture of α -tricalcium phosphate (α -TCP) (it might transfer into β -TCP at 1000 °C or remain as a metastable phase) and tetracalcium phosphate (TTCP) or calcium oxide at temperatures over 1400 °C [1–4].

Mechanical properties of hydroxyapatite materials are determined with their structure, density, porosity, phase composition and crystallinity degree.

The methods of improving mechanical strength and cracking resistance in HA ceramics also include implementation of ZrO_2 , Y_2O_3 or CaO oxides into HA.

Zirconia ZrO_2 , especially for yttria stabilized zirconia (YSZ) having the attributes of high strength and stress-induced phase transformation toughening, has been used to reinforce the hydroxyapatite coatings and to improve the bond strength of the HA coatings [12].

2. Materials

The samples with 25 mm diameter and 5 mm thickness were cut from Ti–6Al–4V ELI titanium alloy. The surfaces of titanium pills were then subject to sandblast

cleaning and plasma spraying. To create coatings, two types of powder were used: HA with mean particle size of 50 μm , characterized by high level of purity ($\text{Pb} = 0.8$ ppm, $\text{As} < 1.0$ ppm, $\text{Cd}, \text{Hg} < 0.1$ ppm) and the ratio of $\text{Ca/P} = 1.67$ as well as zirconium oxide ZrO_2 modified with 8% (wt.) Y_2O_3 (YSZ – yttria stabilized zirconia) with mean particle size of 80 μm . Both powders showed regular, spherical grain shape.

Plasmatron with internal arc, fed with direct current was used for spraying. The parameters of the process of spraying were as follows: $U = 45\text{--}60$ V, current intensity $I = 350\text{--}550$ A, gas flow rate: argon – 3 m^3/h , H_2 – 0.5 m^3/h , distance of the nozzle from the sample surface: 15–35 cm.

As a result of spraying, the HA coatings and HA coatings with different addition of ZrO_2 phase were obtained according to the following proportions:

- 100% HA,
- 80% HA + 20% YSZ,
- 60% HA + 40% YSZ
- 50% HA + 50% YSZ.

3. Methodology

Microstructure testing of the powders and the coatings obtained were carried out using Joel 5400 scanning microscope.

Phase composition testing of the powders used were conducted by means of Raman spectroscopy. To achieve this, a Raman spectrometer (EZRaman-L Enwave Optronics, Irvine, CA, U.S.A.) was used; inducing laser wavelength: 785 nm, laser power: 50 mW. The main goal of the spectroscopy testing was to compare the results with the results of X-ray tests.

In order to determine phase composition in the samples obtained, Seifert XRD 3003 X-ray diffractogram with Co lamp with wavelength $\lambda_{\text{K}\alpha} = 0.17902$ nm was employed. The measurements were taken with consideration of the following diffractometer parameters: voltage: 40 kV, current intensity 30 mA, measurement step 0.2° , impulse count time 10 s.

The profile of element distribution was tested by means of emission GDOS GD Profiler HR optical spectrometer with discharge lamp with a 4 mm cathode.

4. Results and analysis

The microstructures obtained of the sprayed ceramic coatings are presented in Fig. 1. Raman spectra for the used ceramic powders are presented in Fig. 2. Figure 3 presents diffractograms of the coatings under investigation. Distribution of percentage content of elements as a function of the distance from the surface for each coating is presented in Fig. 4.

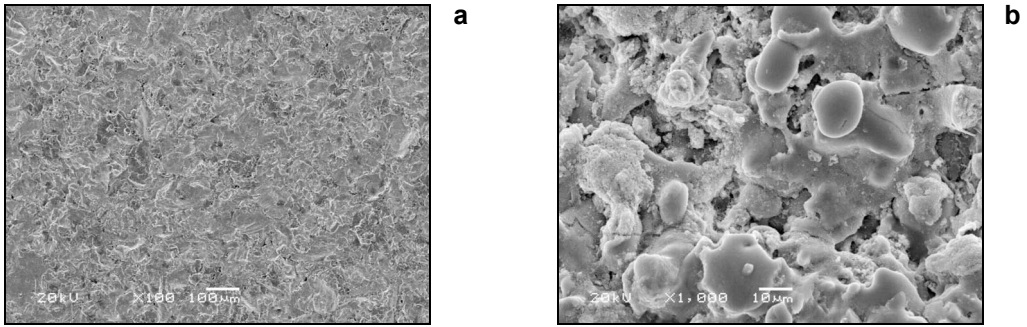


Fig. 1. HA coating microstructure, mag. 100× (a) and 1000× (b).

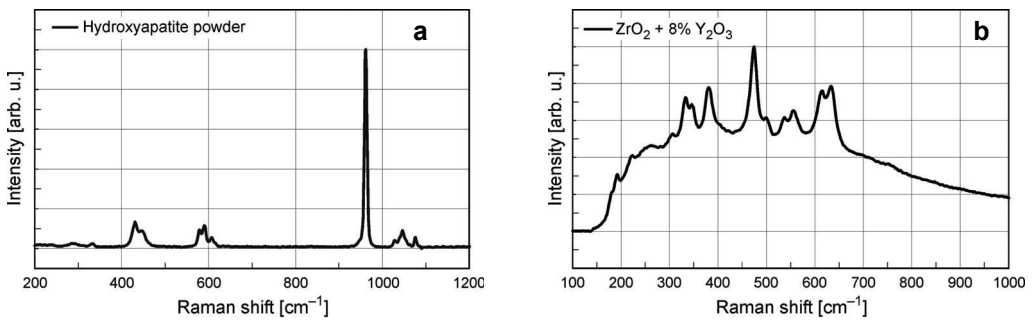


Fig. 2. Raman spectrum for hydroxyapatite powder (a) and $\text{ZrO}_2 + 8 \text{ wt.} \% \text{ Y}_2\text{O}_3$ powder (b).

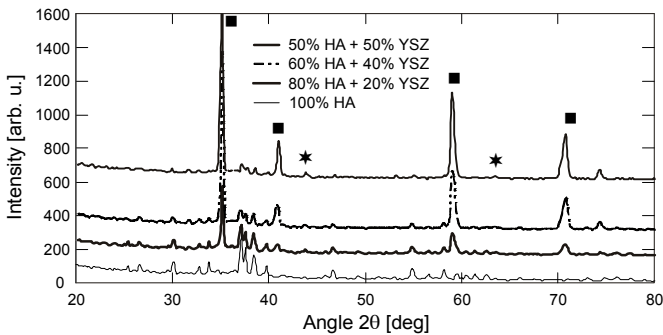


Fig. 3. X-ray diffractograms of the coatings investigated, ■ – ZrO_2 tetragonal, ★ – CaO, peaks without markings – HA.

The analysis of microstructures revealed structures typical of sprayed coatings, *i.e.*, laminarity, porosity and presence of non-melted or partially-melted particles of the powder (Fig. 1).

The comparison of the results of X-ray tests and Raman spectroscopy allowed for assessment of the internal structure in the coatings used for investigations. It has been

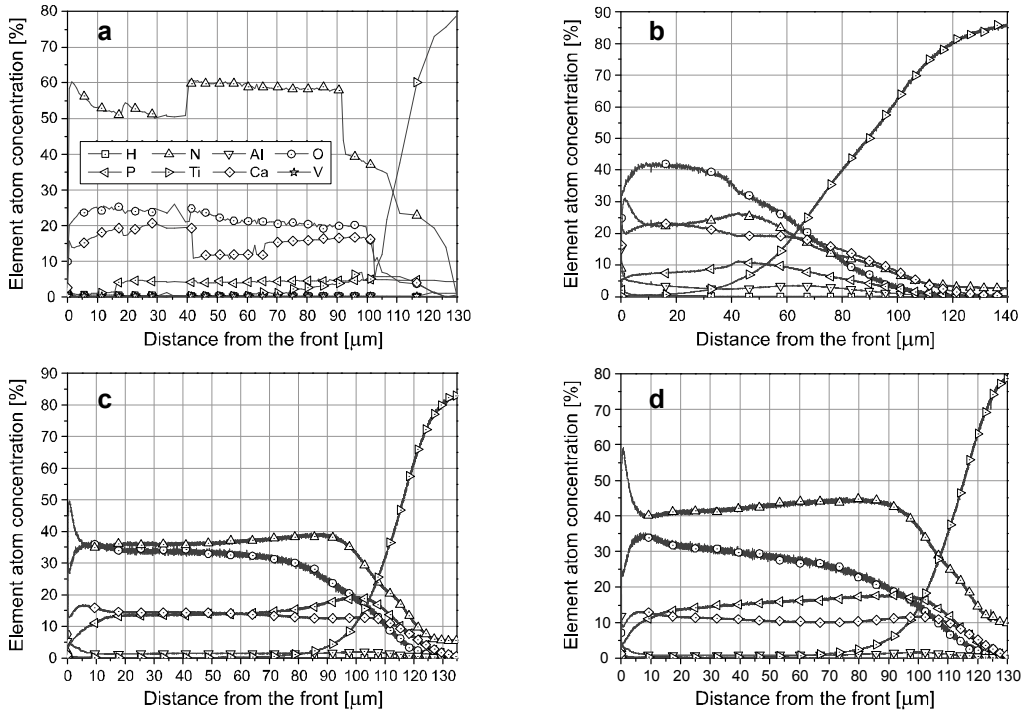


Fig. 4. Chemical composition of 100% (a), 80% (b), 60% (c) and 50% (d) HA coating as a function of the distance from the surface.

assumed that HA powder comprised 100% crystalline phase with hexagonal structure with the following cell unit parameters: $a = b = 9.418$ nm, $c = 6.884$ nm and spatial group of $P63/m$ (Fig. 2a).

The obtained Raman spectrum displays the following bands from phosphate phase PO_4 : 1042 , 1028 $\text{cm}^{-1} - \nu_3$, 959 $\text{cm}^{-1} - \nu_1$, 604 , 590 , 577 $\text{cm}^{-1} - \nu_4$, 443 , 432 $\text{cm}^{-1} - \nu_2$.

ZrO_2 powder revealed tetragonal (Raman band – 148 , 223 , 414 cm^{-1}) and monoclinic (bands 181 , 192 cm^{-1}) phases in its content (Fig. 2b). In the case of the X-ray method, peaks from tetragonal and monoclinic phase overlap, thus making their analysis difficult.

X-ray quantity analysis revealed that the amount of crystalline phase in the coating obtained from 100% powder of HA is at the level of *ca.* 85%. X-ray structural analysis (Fig. 3) revealed the presence of the following phases: HA, small content of CaO and amorphous phase. In consideration of the presence of CaO, one can conclude that HA decomposition occurred and, in consequence, the presence of TCP and TTCP phases cannot be entirely excluded (the amount below the X-ray method detection threshold).

The analysis of HA + YSZ coatings reveals that addition of zirconium phase insignificantly reduces the amount of amorphous phase after the process of spraying

(the amount of crystalline phase rises to *ca.* 90%) – Fig. 3. In the coatings with addition of zirconium phase the presence of HA, CaO and tetragonal modification of ZrO₂ was observed (which proves polymorphous transition of this oxide).

The analysis of chemical composition by means of glow discharge optical spectroscopy (GDOS) method as a function of the distance from the surface revealed that the coatings based on hydroxyapatite show the thickness of *ca.* 120 μm. The presence of nitrogen in the coating might be a result of the method of spraying used. In consideration of complex physicochemical processes, one should also consider the possibility of air being shut in the pores and the adsorption of its components. However, the fact that the presence of nitrogen is the consequence of insufficient vacuum level during the investigation cannot be excluded either.

The rise in addition of zirconium phase to the composition of the coatings manifests itself in the increase of zirconium and oxygen content, which can be observed from the curves obtained (Fig. 4). Moreover, the results of tests also suggest the presence of an interfacial zone between titanium surface and the sprayed coating. Distribution of elements (such as Ti, Ca, P) in the interfacial layer shows that it contains components that come both from HA coating and from Ti–6Al–4V base material. The zone thickness, according to GDOS tests, amounts to *ca.* 10 μm.

5. Conclusions

As a result of plasma spraying, a 120 μm thick hydroxyapatite coating was obtained with different addition of the modified zirconium oxide. The microstructure of the coatings obtained revealed the structure characteristic of this method of deposition.

Considering a variety of treatments described in references aiming to obtain a particular amount of crystalline phases in plasma-sprayed hydroxyapatite coatings, the result obtained in this work (*ca.* 90% of crystalline phase) seems to be high.

X-ray structural analysis confirmed high thermal stability of the hydroxyapatite powder used. The presence of YSZ phase in the composites under investigation did not show considerable effect on decomposition of HA phase.

Raman spectroscopy allowed us to obtain more unambiguous, as compared to X-ray structural analysis results, information on the polymorphous modifications that occur in the materials investigated.

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