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Fabrication and physico-mechanical properties of thin magnetron sputter deposited silver-containing hydroxyapatite films

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ABSTRACT

As a measure of the prevention of implant associated infections, a number of strategies have been recently applied. Silver-containing materials possessing antibacterial activity as expected might have wide applications in orthopedics and dentistry. The present work focuses on the physico-chemical characterization of silver-containing hydroxyapatite (Ag-HA) coating obtained by radio frequency (RF) magnetron sputtering. Mechanochemically synthesized Ag-HA powder ($Ca_{10-x}Ag_x(PO_4)_6(OH)_{2-x}$, $x = 1.5$) was used as a precursor for sputtering target preparation. Morphology, composition, crystallinity, physico-mechanical features (Young's modulus and nanohardness) of the deposited Ag-HA coatings were investigated. The sputtering of the nanostructured multicomponent target at the applied process conditions allowed to deposit crystalline Ag-HA coating which was confirmed by XRD and FTIR data. The SEM results revealed the formation of the coating with the grain morphology and columnar cross-section structure. The EDX analysis confirmed that Ag-HA coating contained Ca, P, O and Ag with the Ca/P ratio of 1.6 ± 0.1. The evolution of the mechanical properties allowed to conclude that addition of silver to HA film caused increase of the coating nanohardness and elastic modulus compared with those of pure HA thin films deposited under the same deposition conditions.

1. Introduction

Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and silver are the materials being currently intensively studied by the researchers due to their potential applications in the field of biomaterials. HA possessing chemical and structural similarity to bone tissue has been used commercially as a coating on metallic implants for decades [1–4]. The advantages of using HA as a bio implant coating are attributed to its capability to connect structurally and functionally with human bone and increase biocompatibility and osteoinductivity of medical devices [5,6]. Silver has been known for ages for its antibacterial properties [7,8]. Over an extended period of time studies have shown that silver provides advantageous biochemical inertness and display broad spectrum of antibacterial activity [9–11]. As a measure to achieve the dual aims of bacterial inhibition and enhancement of osteoblast functions of implant materials silver-containing HA (Ag-HA) composite coatings are of special interest for researchers. Successful results have been shown recently for silver-incorporated HA coatings developed by plasma electrolytic oxidation process on Ti_6Al_4V substrates [12]. The authors demonstrated that the developed coatings possess a strong antibacterial ability against the *Porphyromonas gingivalis* bacteria strain and good biocompatibility. Significant antibacterial properties and considerable biocompatibility as well as low toxicity of the Ag-HA thin films electrochemically deposited on TiO_2 nanotubes was shown in the study [13]. Similar results have been reported for silver-containing HA coating synthesized via sol–gel method [14], plasma-spraying [15] and ion-beam assisted deposition [16,17]. The coating was evaluated to be effective against *Escherichia coli* and *Staphylococcus aureus*. It is reported that 3 wt% of silver in the HA coating can be favorable to attain the antibacterial effect without cytotoxity [17]. So, silver-doped HA seems to be very promising as a bone graft substitution material.

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Among the diverse variety of the methods exploited for the preparation of thin films, RF magnetron sputtering is considered to be particularly useful for the deposition of calcium phosphate-based (CaP) coatings [5]. The advantage of this method is the possibility to ensure tunable coating properties, in particular to control the coating structure (amorphous or crystalline) and the Ca/P ratio by changing the deposition conditions [5,18]. RF magnetron sputtering allows to produce HA coating doped with additional elements by using co-deposition of multiple target materials or by sputtering multicomponent target of a mixed composition [19–22]. For instance, Chen et al. previously reported the properties of Ag-HA coatings co-sputtered using Ag and HA targets [22]. Ozeki et al. characterized the features of Sr-substituted HA coatings deposited using the target containing Sr [21]. In this study Ag-HA coating deposited via RF magnetron sputtering using as a target of silver-containing HA is reported. The objective of the study was to reveal the effect of silver on the properties of the deposited coating. The composition, phase structure, microstructure and morphology as well as the mechanical features of the Ag-HA sputter deposited coating are presented and discussed.

2. Materials and methods

The target of 220 mm diameter and thickness of 9 mm was used for RF magnetron sputter Ag-HA coating deposition. It was prepared using mechanochemically synthesized HA precursor-powder doped with silver. The starting compounds for silver-loaded HA synthesis were dicalcium phosphate anhydrate, $CaHPO_4$, calcium oxide, CaO, and silver nitrate, $AgNO_3$. Ag-HA powder ($Ca_{10-x}Ag_x(PO_4)_6(OH)_{2-x}$, $x = 1.5$) was prepared in a planetary ball mill in three steel drums having a volume of 1800 mL for 12 min at room temperature followed by subsequent annealing in air at 950 °C for 1 h [23]. The mechanochemical synthesis was carried out at the Institute of Solid State Chemistry and Mechanochemistry SB RAS (Novosibirsk, Russia) according to the following reaction:

$$6CaHPO_4 + 2.5CaO + 1.5AgNO_3 \rightarrow Ca_{8.5}Ag_{1.5}(PO_4)_6(OH)_{0.5} + 2H_2O + 1.5HNO_3. \quad (1)$$

Then to prepare a target for sputtering the powder was uniaxially pressed at the room temperature and sintered in air at 900 °C for 12 h. The coating deposition was performed in a vacuum set up equipped with a RF-generator (13.56 MHz, COMDEL). The distance between the magnetron and substrate holder was fixed at 40 mm. Pure Ti (grade 4) Plates 1 mm thick and silicon were used as substrates (10 mm × 10 mm). The Ag-HA coating was deposited at an RF-power level of 500 W in argon atmosphere at a grounded substrate holder.

The thickness of the deposited films was measured by spectroscopic ellipsometry using ELLIPS-1891 SAG setup. The structure and phase composition of Ag-HA coating and precursor powder were investigated via X-ray powder diffractometry (XRD; Bruker D8 Advance diffractometer; CuKα-radiation; $\alpha = 1.5406$ Å; 40 kV; 40 mA). To calculate an average crystallite size and lattice parameters, Rietveld refinement (using the Le Bail method) with the program package TOPAS 4.2 from Bruker was performed. For each Rietveld refinement, the instrumental correction as determined with a LaB6 standard powder sample from NIST (National Institute of Standards and Technology) as the standard reference material (SRM 660b). Silver (#04-0783), HA (#09-0432) and titanium (#44-1294) patterns from the ICDD database were used as references. Infrared spectroscopy (IR; Bruker Vertex 70; 400–4000 cm^{-1}; resolution 4 cm^{-1}; averaging of 20 scans) was used to determine the nature of the functional groups present in the material. The surface morphology and composition of the coatings were examined by scanning electron microscopy (ESEM Quanta 400 FEG, FEI, equipped with energy-dispersive X-ray analysis; Genesis 4000, S-UTW-Si(Li) detector; operated in high vacuum, 10^{-5} Pa).

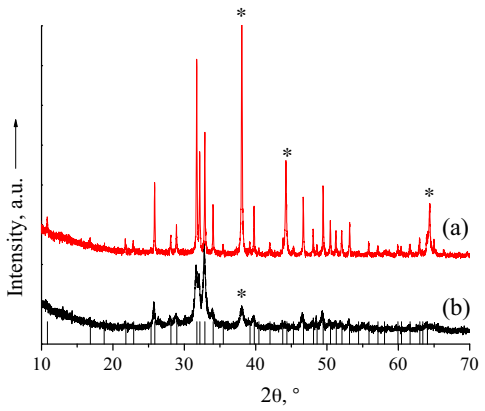

Fig. 1. X-ray diffractograms of the Ag-containing HA powder-precursor before (a) and after (b) annealing. Marked peaks correspond to the peak positions of silver (*), vertical lines show the positions of HA.

Nanoindentation tests [24] were performed using a Nanotriboindenter TI-950 (Hysitron Inc., USA) equipped with a Berkovich tip. The hardness (H) and the reduced modulus (E) of the coatings were obtained from the indentation curves according to Oliver and Pharr method [25]. Load–displacement curves with the load ranging from 100 μN to 500 μN were obtained in order to determine penetration depth (h), elastic modulus (E) and hardness (H) of the composites as a function of the applied load. The following loading-unloading sequence was performed at each peak load: the loading to maximum load for 5 s, hold segment for 2 s to minimize the creep effect, complete unloading for 5 s. Repeated indentations were performed then the values of H and E were calculated as an average of 10 indentations.

3. Results and discussions

Fig. 1 shows X-ray diffractograms of the Ag-HA precursor-powder before and after annealing. Two phases corresponding to the crystalline HA and metallic silver were resolved. The XRD analysis revealed that the crystallinity of the powder increased after annealing. The lattice parameters and crystallite sizes of the HA and silver phases obtained for the annealed powder are given in Table 1. The lattice parameters of the HA were calculated to be smaller compared with those of standard HA (ICDD database #09-432 card number). The slight variation of the unit cell parameters could be due to the strain arose in the material during sintering or partial incorporation of silver atoms into HA structure. Due to the fact that the target preparation was at a lower sintering temperature we assume that the target had the same phase composition as the annealed Ag-HA powder. Thus, target preparation procedure allows us to obtain nanostructured precursor material with two crystalline phases: HA and metallic silver.

Table 1
Lattice parameters of the silver-containing HA powder-precursor after annealing.

		Lattice parameters			Crystallite size (nm)
		$a = b$ (Å)	c (Å)	V (Å^3)	
HA	Estimated	9.423	6.882	611.07	89
	ICDD (09-432)	9.418	6.884	610.6	–
Ag	Estimated	4.089	–	68.37	63
	ICDD (04-0783)	4.086	–	68.22	–

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