PROPERTIES OF RF-MAGNETRON SPUTTER DEPOSITED SILVER-DOPED HYDROXYAPATITE-BASED COATINGS

E.S. Melnikov, A.A. Ivanova, M.A. Surmeneva
Scientific Supervisor: Associate Professor, Ph.D. R.A. Surmenev
Tomsk Polytechnic University, Russia, Tomsk, Lenin str., 30, 634050
E-mail: melnikov.evgeniy92@mail.ru

ИССЛЕДОВАНИЕ СВОЙСТВ ТОНКИХ СЕРЕБРОСОДЕРЖАЩИХ ПЛЕНОК НА ОСНОВЕ ГИДРОКСИАПАТИТА

Е.С. Мельников, А.А. Иванова, М.А. Сурменева
Научный руководитель: Р.А. Сурменев, к.ф.-м.н., доцент каф. ТиЭФ
Национальный исследовательский Томский политехнический университет,
Россия, г. Томск, пр. Ленина, 30, 634050
E-mail: melnikov.evgeniy92@mail.ru

Аннотация: *В настоящей работе приведены результаты исследования покрытий на основе серебросодержащего гидроксиапатита (Ag-ГА). Покрытия напыляли методом ВЧ-магнетронного распыления многокомпонентной мишени. Порошок Ag-ГА для производства мишени был изготовлен методом механохимического синтеза. В результате проведенного исследования сделаны выводы о том, что ВЧ-магнетронное распыление многокомпонентной мишени позволило создать Ag-ГА покрытия с высокой степенью кристалличности, что подтверждают методы ИК-спектроскопии и рентгеновской дифракции. Результаты сканирующей электронной микроскопии показали образование покрытия с островковой морфологией и столбчатой структурой в поперечном сечении. Наличие Ca, P, O и Ag в покрытии Ag-HA было подтверждено анализом рентгено-дисперсионным анализом. Отношение Ca / P сформированных покрытий составило 1,6.*

Surface modification is an important and predominant way to obtain a biofunction in metals for biomedical application. In this study, the biocompatible antibacterial coatings on the basis of Ag-doped hydroxyapatite (Ag-HA) prepared by radio frequency (RF) -magnetron sputtering were examined. It is known that HA is capable to connect structurally and functionally with human bone and increase biocompatibility and osteoinductivity of medical devices [1]. Silver has been known from ancient times for its antibacterial properties [2]. Silver was reported to possess broad spectrum of antibacterial activity [3]. As a material ensuring both bacterial inhibition and enhancement of osteoblast functions of implant materials Ag-HA composite coatings are of special interest of researchers worldwide. RF-magnetron sputtering is considered to be particularly useful for the deposition of coatings on the basis of calcium phosphates. The advantage of this method is the possibility to deposit coatings with variable properties, in particular to control the coating structure (amorphous or crystalline) and the Ca/P ratio by changing the deposition conditions [4]. Additionally, RF-magnetron sputtering is a rather simple method to produce HA coating doped with additional elements [5].

In this study, a target for sputtering was prepared from mechanochemically synthesized HA precursor-powder incorporated with silver ($Ca_{10-x}Ag_x(PO_4)_6(OH)_{2-x}$, x=1.5). The coating deposition was performed in a vacuum chamber equipped with a RF-generator (13.56 MHz, COMDEL). The investigation of the biocomposite surface properties, microstructure and coating's composition was carried out by SEM, EDX, XRD, FTIR spectroscopy and spectroscopic ellipsometry.

Fig.1. shows X-ray patterns of the Ag-HA precursor-powder after annealing and Ag-HA coating. Two phases corresponding to crystalline HA and metallic silver were resolved on the XRD pattern of the powder. The lattice parameters and crystallite sizes of the HA and silver phases resolved on the XRD pattern of the annealed powder were calculated to be: lattice parameters for HA- a=b=9.423Å , c=6,822Å , V=529.2 $Å^3$ and crystallite size = 89 nm; for Ag- a=b=4.089Å , c=4.089Å , V=68.38 $Å^3$ and crystallite size = 63 nm. So, the applied target preparation approach allowed producing nanostructured source material with two phases: HA and metallic silver.

In comparison with powder XRD pattern of the developed Ag-HA coating contain only peaks corresponding to HA. No peaks of silver were observed. Meanwhile, the increase of the lattice parameters was detected compering with the bulk HA (a = 9.502 Å, c = 6,903 Å and unit cell volume, v = 539.7 $Å^3$). It was already reported that structure of HA was quite flexible and could incorporate various metallic ions (Ag, Mg, Sr, Pb etc.) [6]. In the presence of these elements, the lattice parameter of HA was estimated to be changed.

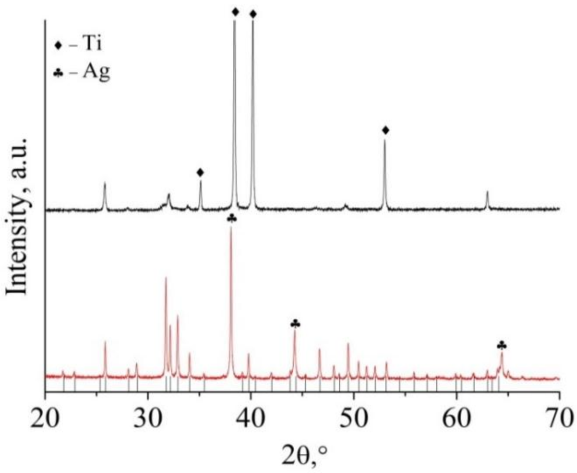

Fig.1. XRD patterns of the silver-containing HA powder-precursor after annealing (bottom) and deposited coating (top). Marked peaks correspond to the peak positions of metallic silver (♣) and titanium (♦), vertical lines show the positions of the HA patterns (ICDD).

The thickness of the deposited Ag-HA coatings is estimated by means of ellipsometry to be of 500±30 nm. The typical morphology and cross-section microstructure of the obtained thin films was studied by SEM. The average grain size was calculated by using SEM images to be of 132±30 nm. The coating cross-section possesses columnar structure which is well known for magnetron sputter deposition [7]. FTIR data obtained from the Ag-HA sintered powder-precursor and Ag-HA magnetron sputter deposited coating are depicted in Fig. 2. All the data revealed the presence of absorption bands at 1028 and 598-566 cm^{-1}, typical for stretching and bending vibrations of P-O-groups in HA . The broad asymmetric bands in the range of 3431 to 3010 cm^{-1} indicate the presence of adsorbed water molecules on the HA surface [8].

The absorption bands assigned to B-type CO_3^{2-} vibration are observed in the region of 1411-1450 cm^{-1}. It is noticed that the stretching and libration mode of O-H band appeared at 3571 and 634 cm^{-1}, respectively are observed in both cases and the O-H vibration peak is getting reduced for Ag-HA coating, compared to the initial

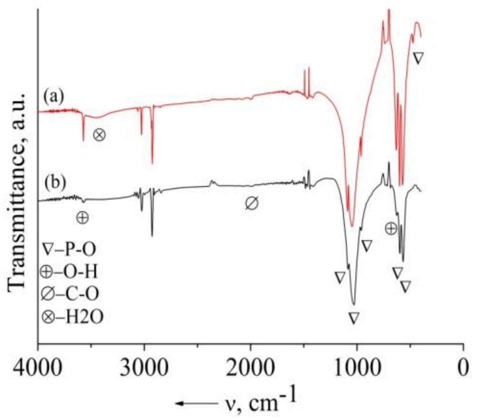

Fig.2. FTIR spectra of the sintered Ag-HA powder-precursor (a) and Ag-HA coating deposited on KBr (b)

precursor material. A number of researchers have reported on the investigation of HA loaded with additional elements and claimed that the reduction of O-H peak may be caused by substitution of Ca ions in the HA structure.

RF-magnetron sputtering of the nanostructured Ag-HA multicomponent source at applied process conditions allowed to deposit Ag-HA coating with high crystallinity, equiaxed morphology and columnar cross-section structure. According to the data obtained from XRD and FTIR measurements, it can be assumed that Ag ions substitution in HA lattice takes place during coating deposition by means of RF-magnetron sputtering.

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