BIO-FUNCTIONAL COMPOSITE COATING OF CALCIUM APATITE AND ZnO ON A PRINTED POROUS ORTHOPEDIC IMPLANT

Amanzhol TURLYBEKULY [1], Alexandre POGREBNJAK [2], Sergey PLOTNIKOV [1], Zhasulan SHAYMARDANOV [1], Botagoz SHAYMARDANOVA [1], Nazgul YERDYBAYEVA [1], Syrym ZHANYSSOV [1], Alexandre MIAKININ [1], Ruslan KIMOSSOV [1], Nurgamit QANTAY [3]

[1]*D.Serikbayev East Kazakhstan state technical university, Oskemen, Republic of Kazakhstan,* *aturlybekuly@gmail.com*

[2]*Sumy state university, Sumy, Ukraine,* *alexp@i.ua*

[3]*East Kazakhstan State University named after S. Amanzholov, Kazakhstan,* *nurgan85@mail.ru*

Abstract

To date, a large number of different alloys based on CoCr, Ti, stainless steel, etc. are used in medicine. However, metal implants are bioinert, despite the development of biodegradable magnesium-based alloys. In addition, because of their mechanical properties, only few numbers of alloys have come close to mechanical properties of the cortical part of human bone. These superelastic alloys are usually based on the Ti-Nb-Ta, Ti-Nb-Ta-Zr systems which have a high cost. It is advisable to apply bioactive coatings that would have the best resemblance to human bone in terms of chemical composition, physical properties and biological parameters.

In this paper, the physical and chemical properties of hydroxyapatite (HAP) coatings with the addition of ZnO, obtained by electrochemical deposition in an aqueous solution on a printed porous sample of 316L steel, were studied.

The HAP study was carried out by the methods of analysis as: scanning electron microscopy with the energy dispersive microanalysis system, transmission electron microscopy with EDAX analysis system.

The laser melting of powdered 316L steel was carried out using the Mlab cusing R machine. The SLM process parameters were: laser power 90 W, a frequency 50 kHz, a scanning speed 500 mm/s, a spot size 100 µm, the oxygen content was less than 0.1 %.

A new type of materials for use in medicine was obtained and investigated. The ratio of Ca/P of the obtained coating corresponds to generally the accepted parameters. The structure of HA is characterized by a high degree of crystallinity.

Keywords: 316L printing, hydroxyapatite coatings, Zn doped hydroxyapatite, electrochemical deposition of hydroxyapatite, ceramic coatings on printed

1. INTRODUCTION

Metal implants are inherently bioinert, which reduces the duration of use in the human body. One of the important properties of the implant is the ability to osseointegration. In addition to osseointegration, the necessary properties are biocompatibility, corrosion resistance. The modern direction in medical material science is giving new products osteoconductive and antibacterial properties [1-5].

Giving porosity to metal products leads to a decrease in density with little effect on mechanical properties. Calcium phosphate coated on metal implants provides the necessary porosity for bone ingrowth, while the lower metal substrate carries a load, with complete weight tolerance shortly after surgery. The main requirement for the development of hydroxyapatite (HA) coatings on metal implants is the production of a stoichiometric powder material (i.e., a Ca/P ratio of about 1.67) with preferred chemical and phase properties, a close affinity for bone tissue and ease of deposition on irregular forms. [6]. High-crystalline HA coatings show low dissolution rates in vitro, with less resorption and more direct bone contact in vivo. Amorphous HA undergoes rapid dissolution in a physiological environment. Therefore, HA with a low crystallinity rapidly becomes weak and can contribute to inflammatory responses. Therefore, it is desirable to have a high degree of crystallinity in HA coatings, although the presence of a small amount of amorphous HA is allowed [7]

The addition of zinc ions makes it possible to improve its biological characteristics, since recent studies [3] show its antibacterial properties.

In this paper, we present a new type of medical products using additive technologies and coating a bio-compatible composite material based on calcium apatite supplemented with Zn.

2. MATERIALS AND METHODS OF ANALYSES

The AISI 316L steel substrate was obtained by a selective laser melting process. The prototypes were plates 12 x 10 x 2 mm in size with pores, the pores' size did not exceed ≤800μm.

The laser melting of the powder was carried out using the Mlab cusing R machine manufactured by Concept Laser (Germany). The SLM process parameters were: a fiber laser power 90 W, a frequency 50 kHz, a scanning speed 500 mm/s, a spot size 100 μm. The process was carried out in a nitrogen atmosphere. The oxygen content (in accordance with the integrated sensors) at all stages was less than 0.1 %.

The coating deposition process was carried out as follows: the substrate was attached to a copper electrode and dipped into a solution containing $CaCl_2$ (99 % purity) and NaH_2PO_4 (99 % purity), with a molar ratio of Ca/P = 1.67 and concentrations of 10 mmol/L and 6 mmol/L, respectively. The solution was heated by a chemical reactor with a thermo-shirt. The temperature of the coolant was 90 °C, the temperature of the solution was 86.4 °C. The deposition time is 1 hour at pH 6.5. To maintain a uniform temperature distribution throughout the bulk of the stock solution, uniform mixing was used. The substrates were previously cleaned, including: 15 minutes ultrasonic treatments in acetone, 96 % ethanol and triple washing in distilled water. The addition of Zn was carried out by electrochemical method, at a voltage of 5 V, the distance between the electrodes was 12 cm. After coating deposition, the sample was annealed in a muffle furnace at 400 °C for 1 hour.

The samples were analyzed by scanning electron microscopy (SEM) using the JSM-6390LV microscope with the energy dispersive microanalysis system INCA Energy Penta FET X3. The functional groups were studied on an IR Fourier spectrometer FTIR-801 Simex, measuring range 500 - 4000 cm^{-1} with a resolution of 1 cm^{-1}. The phase composition was investigated by XRD (Panalytical Xpert Pro), K-Alpha - 1.54060 Cu.

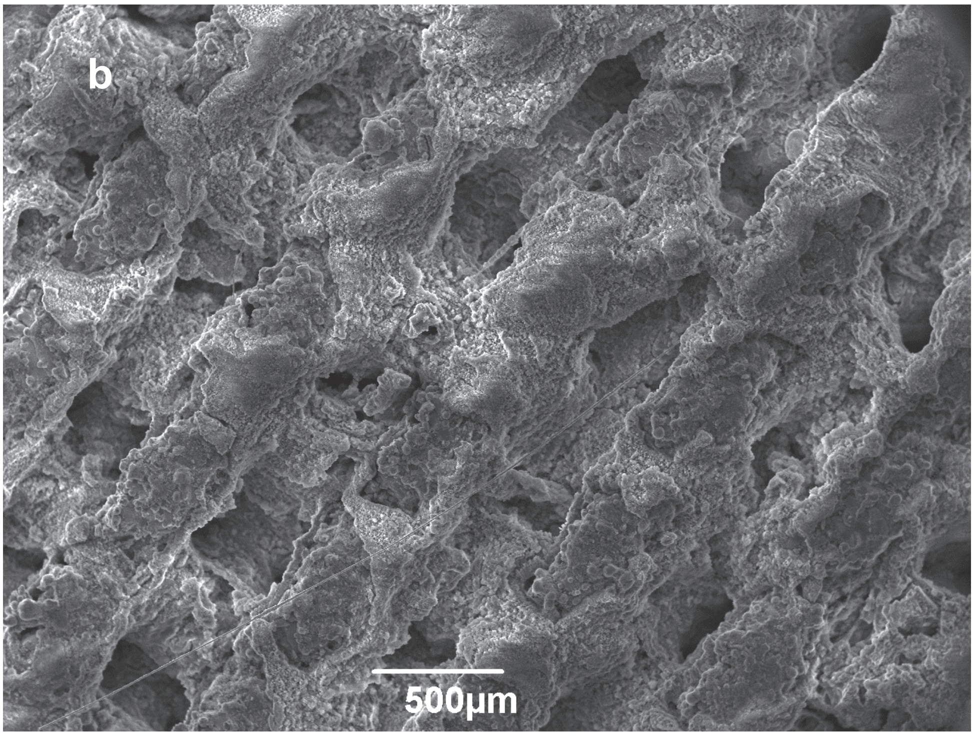
3. RESULTS AND DISCUSSION

The microstructure of the sample surface is shown in **Figure 1** at different magnifications. It is noticeable that the HA penetrated into the depths of metal cells and formed a complex architecture with pores ≤450 μm. At higher magnification, it becomes apparent that the deposited coating is highly crystalline HA, with a particle size of ≤10 μm. Non covered areas were not found. This indicates a well-chosen deposition regime.

An investigation of the elemental composition using EDAX showed that Zn is present in the composition of HA at a concentration of 10.35 % by weight. The Ca/P ratio is 1.99, which is close to the stoichiometric HA, and indicates good biocompatibility.

Table 1 chemical composition of the coating, in % by weight.

O	Al	P	Ca	Zn	Ca/P
45.23	0.23	14.78	29.41	10.35	1.99



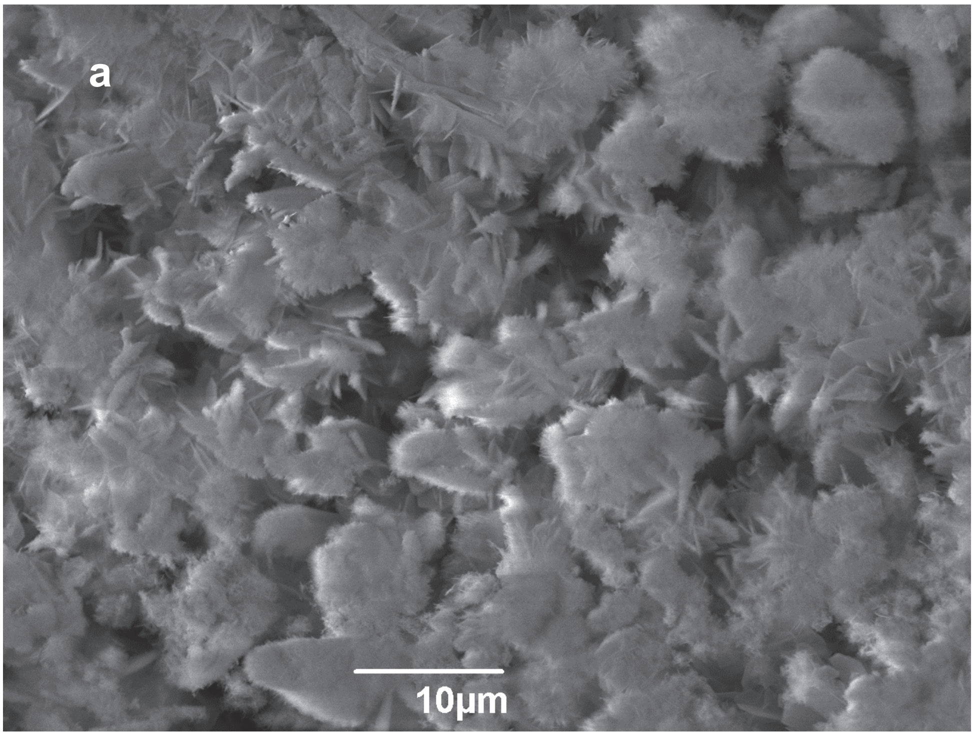


Figure1 Microstructure of printed AISI 316L sample with Zn doped HA coating

A study of the phase composition showed that the main peaks of the X-ray picture correspond to the HA with a hexagonal structure (JCPDS 01-084-1998) and to the iron, main component of the AISI 316L steel, **Figure 2**. Parameters of HA cell: a- 9.4172 A, b - 9.4172 A, c - 6.8799 A. The structure of ZnO microcrystals is also hexagonal, cell parameters: a- 3.2420 A, b - 3.2420 A, c - 5.1760 A.

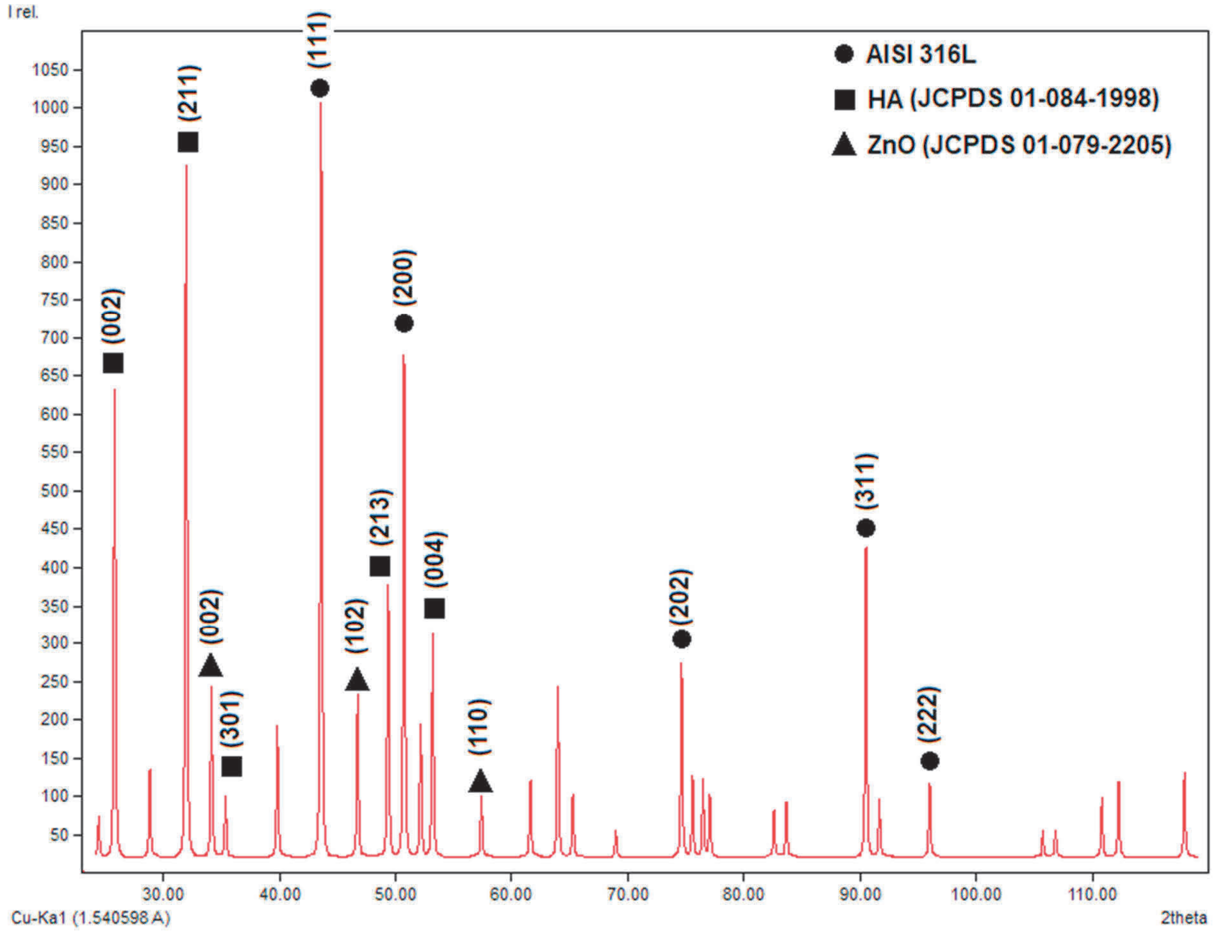


Figure 2 XRD pattern of printed sample AISI 316L with coating of HA/Zn

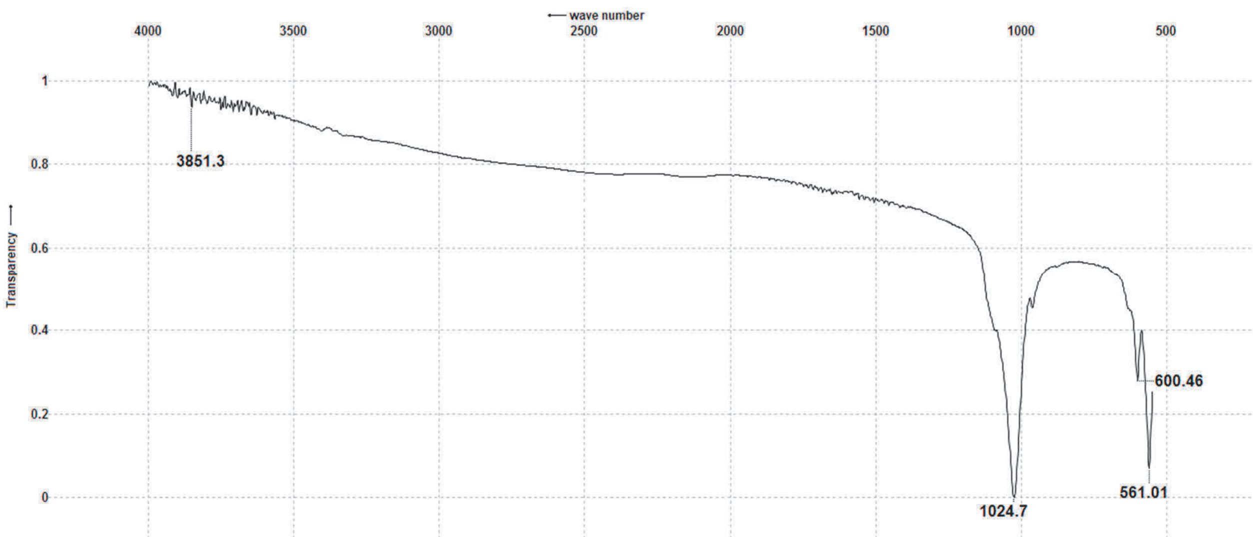


Figure 3 IR spectrum of HA/Zn coating

Thus, in the spectrum of HA/Zn, characteristic vibrations are present: vibration bands in the region of 562 and 602 cm^{-1} (v4 bending mode) belong to the O-P-O groups. The band with a peak at 1024.7 cm^{-1} refers to asymmetric stretching (v3) P-O vibrations. The OH group is weakly expressed, which is explained by the high annealing temperature, **Figure 3**.

CONCLUSION

A new type of materials for use in medicine was obtained and investigated. This work is one of the first works aimed to obtaining new types of orthopedic implants with an artificial trabecular structure similar to the cortical bone. The ratio of Ca/P of the obtained coating corresponds to generally the accepted parameters. The structure of HA is characterized by a high degree of crystallinity. Further in vitro and in vivo researches are needed.

ACKNOWLEDGEMENTS

The present work was carried out with the financial support of the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan for the targeted financing program "Targeted scientific and technical program of the D. Serikbayev East Kazakhstan State Technical University, focused on the development of new types of products for production at the leading industrial enterprises of the East Kazakhstan region" for 2017-2019 years.

REFERENCES

[1] BHOWMICK, A. Development of porous and antimicrobial CTS-PEG-HAP-ZnO nano-composites for bone tissue engineering. *RSC Advances* [online]. 2015. Vol. 5, iss.120, pp.99385-99393 [viewed 2018-02-25]. Available from: DOI: 10.1039/c5ra16755h.

[2] KANHED, S. Microporous Hydroxyapatite Ceramic Composites as Tissue Engineering Scaffolds: An Experimental and Computational Study. *Advanced Engineering Materials* [online]. 2018. Vol.0, iss. 0, pp. 1438-1656[viewed 2018-02-25]. Available from: DOI:10.1002/adem.201701062.

[3] SAXENA, V. Effect of Zn/ZnO integration with hydroxyapatite: A review. *Materials Technology*[online]. 2017. Vol. 33, iss. 2, pp. 79-92[viewed 2018-01-25]. Available from: DOI:10.1080/10667857.2017.1377972.

[4] ITO, A. and OTSUKA, M. Zinc-containing tricalcium phosphate and related materials for promoting bone formation. *Current Applied Physics*[online]. 2005. Vol. 5, iss. 5, pp. 402-406 [viewed 2018-02-21]. Available from: DOI:10.1016/j.cap.2004.10.006.

[5] POGREBNJAK, A. and KRIVETS, A. Surface properties, technology of fabrication and prospects of application of medical implants from porous titanium obtained by powder metallurgy. In 2016 *International Conference on Nanomaterials: Application & Properties (NAP).*Zatoka: IEEE, 2016, pp. 02NABM08-1-02NABM08-3, doi:10.1109/nap.2016.7757292.

[6] ELIAZ, N. Electrochemical and electrophoretic deposition of hydroxyapatite for orthopaedic applications. *Surface Engineering*[online]. 2005. Vol. 21, iss. 3, pp. 238-242 [viewed 2018-02-15]. Available from: DOI: 10.1179/174329405X50091.

[7] CHOUDHURY, P. Hydroxyapatite (HA) coatings for biomaterials. In: THOMAS J., P., eds. *Nanomedicine.* Woodhead Publishing, 2012, pp. 84 - 127.