ELECTROCHEMICAL FORMATION AND CHARACTERIZATION OF CALCIUM HYDROXYAPATITE ON Mg ALLOY

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Introduction

Biodegradable implants are one of the promising areas of Mg and its alloys application. Implant materials must be biocompatible, which is defined as the ability of materials not to cause severe adverse reactions in organisms. Mg is a non-toxic, easily adsorbed element, naturally occurring in the tissues of living organisms and involved in physiological processes. The aim of this work was to electrochemically form calcium hydroxyapatite (CHAp) coatings on AZ31 alloy, identify their composition, structural morphology and corrosive behaviour in balance Hanks' salt solution.

Experimental

Calcium hydroxyapatite (CHAp) coatings were precipitated from electrolytes No. 1 and No. 2, the composition is given in Table 1. 0.5 M NaOH solution was also used for the immersion of precipitated CHAp coatings to form more $Ca_{10}(PO_4)_6(OH)_2$ crystals on 1 mm thick AZ31 alloy sheet (*Alfa Aeser, composition Mg: Al: Zn; 96: 3: 1 wt%*).
CHAp coatings were deposited by galvanostatic and potenciostatic methods. By the galvanostatic method, CHAp coating was formed on the AZ31 alloy in a two-electrode cell. The current density selected for galvanostatic electrode coating was, $-0{,}5\ mA/cm^2$ and $-3\ mA/cm^2$ and the selected coating time was: 30, 60 and 120 min. Coating parameters in electrolytes No. 1 and No. 2 were based on data from the literature [2, 3]. Potentiostatically CHAp coatings were deposited in a standard three-electrode cell at room temperature. Based on the literature and preliminary measurements, constant potential values were chosen: -1.72V and -1.65V and a coating time of 60 min. The structure, morphology and electrochemical studies of the formed CHAp coatings were performed after 24 hours. Electrochemical measurements were performed using a three-electrode cell filled with Hank's balanced salt solution, which has physiological pH and salt concentrations.

Table 1. Electrolyte composition.

Electrolyte composition	
Electrolyte No 1	*Electrolyte No 2*
0,1M $Ca(NO_3)_2 \cdot 4H_2O$	0,05M $Ca(NO_3)_2 \cdot 4H_2O$
0,06M $NH_4H_2PO_4$	0,03M $NH_4H_2PO_4$
0,2M $NaNO_3$	0,1M $NaNO_3$
10ml/l H_2O_2	5ml/l H_2O_2
pH = 4,3	pH = 5,0
T = 20°C	T = 20°C

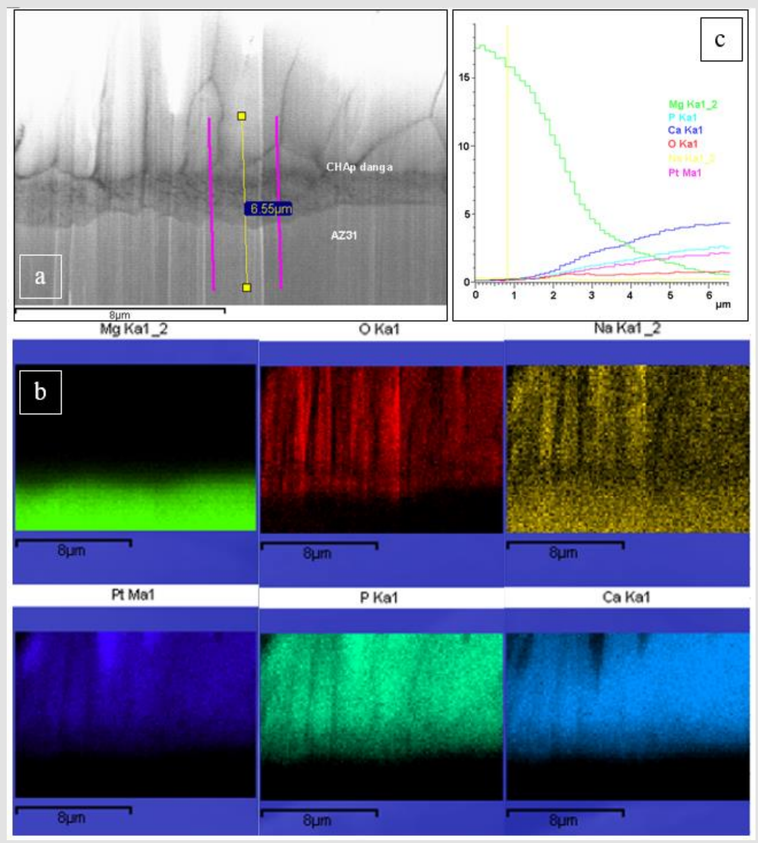

Fig.1. Cross-section of the calcium hydroxyapatite coating: (a) - SEM image, (b) - color map of the elements, (c) - distribution of the elements determined by the EDS method.

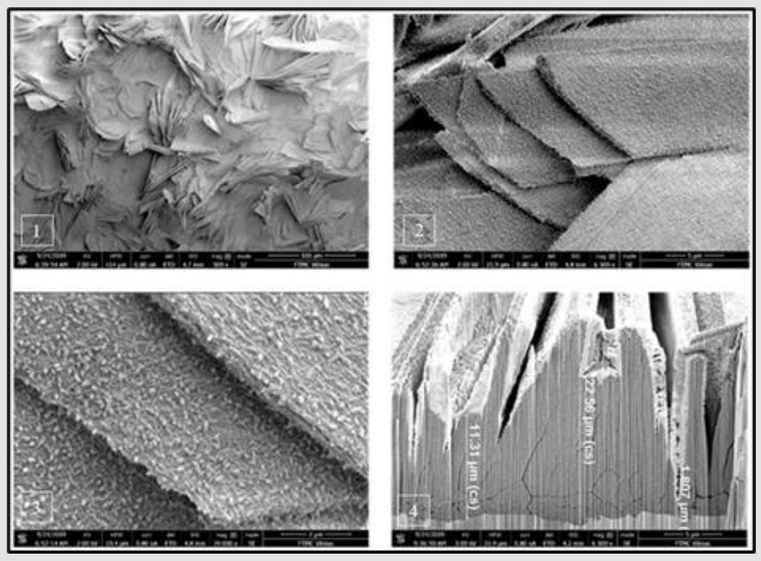

Fig.2. SEM images of surface (1-3) and cross-section (4) of CHAp coating deposited by galvanostatic method (i_k=0.5 mA·cm-2, 60 min) at different magnifications: 1 - 500x, 2, 4 - 6500x, 3 - 20000x.

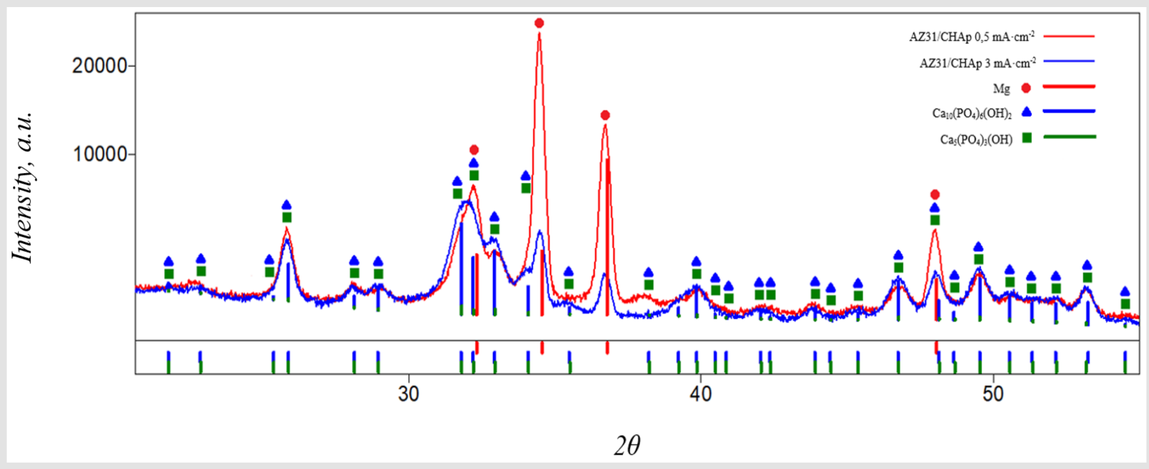

Fig.3. RSD diffractogram of calcium hydroxyapatite on AZ31 alloy.

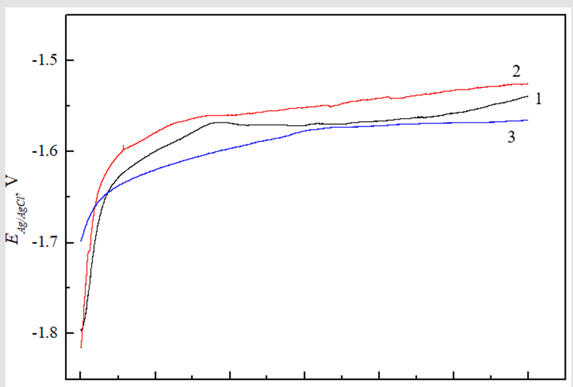

Fig.4. E_{ocp} variation of AZ31/CHAp electrodes in Hank's solution. CHAp coating deposition current density i_k=0.5 mA·cm-2, deposition time: 1- 30 min; 2 - 60 min; 3 - 120 min

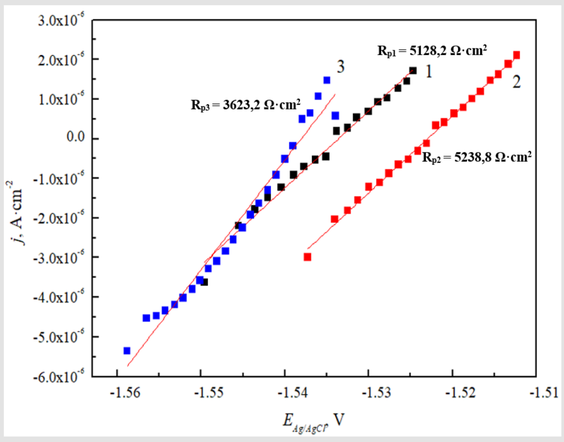

Fig.5. The voltammetric dependence of AZ31/CHAp electrodes in the range E_{ocp} ± 15 mV. CHAp coating deposition current density i_k=0.5mA·cm-2, deposition time: 1-30 min; 2 - 60 min; 3 - 120 min

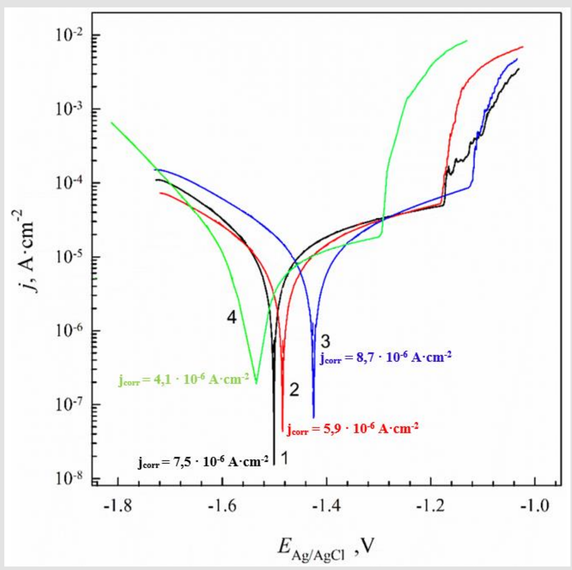

Fig.6. Tafel plots of AZ31/CHAp electrodes in Hank's solution. CHAp coating deposition current density i_k=-0.5 mA·cm-2, deposition time: 1- 30 min; 2 - 60 min; 3 - 120 min

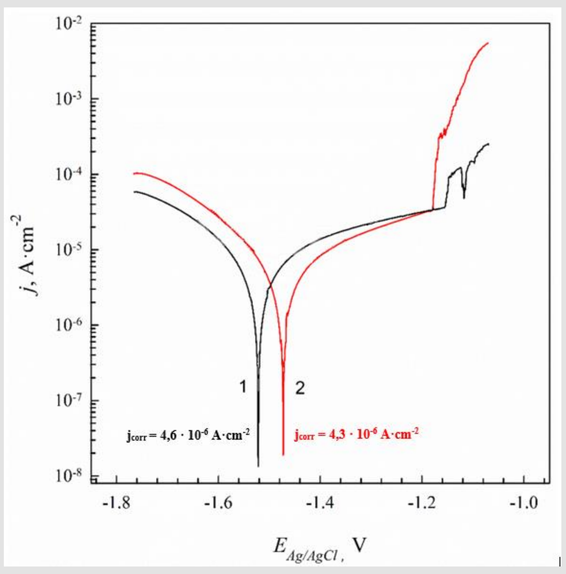

Fig.7. Tafel plots of AZ31/CHAp electrodes in Hank's solution. Deposition potentials of CHAp coating 1 - 1.65 V, 2 - 1.72 V. Deposition time 60 min.

Conclusions

- The structure, morphology and chemical composition of CHAp coatings were evaluated by RSD and SEM-EDS methods. The main components of the coating were found to be hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ - ~41% and calcium hydroxylapatite $Ca_5(PO_4)_3(OH)$ - ~59%. CHAp coatings are dendritic in morphology, coarse-grained, highly porous, uneven, with large variations in coating thickness.
- Coating was found to increase AZ31 resistance to pitting corrosion. CHAp coatings with the best parameters were formed by galvanostatic method with deposition current of $-0{,}5\ mA/cm^2$. As can be seen from Tafel dependences in Figure 6, the open circuit potential of the galvanostatically coated AZ31/CHAp electrodes shifted to a range of more positive values compared to the uncoated AZ31 electrode (curve 4). The largest positive shift of ~0.1V was found for the CHAp coating, with deposition time of 120 min (thickness for reference 13.8µm).
- The analysis of the corrosion behaviour and parameters of the electrodes showed that the protective capacity of the formed CHAp coatings is not high and it can be substantially increased only by forming a coating of CHAp of uniform thickness on the surface of AZ31 and reducing the size of CHAp crystals deposited.

References

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