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Advanced materials for metal implant coatings[♣]

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Metal materials have been used as implants, due to their excellent mechanical properties and corrosion resistance. However, in order to better bind to living bone they need an interfacial inorganic layer. Biological apatite is a bioactive and biocompatible inorganic material, and the main structural component of human bones. However, it has weak mechanical properties and adhesion to metal implant surfaces. Combination of the good mechanical properties of metals with the bioactive properties of apatite has fostered the application of apatite coatings on metal implants. On the other hand, carbon-based materials (diamond-like carbon, detonational nanodiamond, carbon nanotubes, amorphous carbon, etc.) significantly improve the mechanical properties of AP, increase its adhesion, and prevent metal ion release from metal implants. Our goal was to create a new advanced composite material that is to serve as a coating of metal implants. Stainless steel was used for the electrodeposition of the apatite-nanodiamond coatings in simulated body fluid. The results revealed the formation of dense and homogeneous apatite-nanodiamond composite coatings, with better ductility, hardness, cohesion and adhesion to stainless steel, in comparison to pure apatite coatings. We consider that the nanodiamond-reinforced apatite coatings can be considered as advanced materials for the surface modification of metal implants.

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1. Introduction

Biological apatite (AP) is Ca-deficient, non-stoichiometric (ns) and low crystallinity calcium phosphate material. It has a Ca/P ratio lower than 1.67, and is susceptible to ionic substitutions. Biological AP is a highly bioactive and biocompatible inorganic material; however, it has weak mechanical properties and adhesion to surfaces [1].

Carbon-based coatings such as diamond-like carbon, carbon nanotubes and amorphous carbon have shown favourable properties. They improve the mechanical properties of AP coatings, increase their adhesion to metal implants and prevent metal ion release from the metal surfaces [2,3]. Nanosized diamond particles are attracting increasing scientific and technological interest, because of their unique mechanical and tribological properties, including extreme hardness, inertness to chemical attack, and biological compatibility [4,5]. Nanodiamond (ND) particles have also the advantage of extremely high surface areas, surface charges and the existence of surface functional groups [6]. They can be easily synthesized by detonation, and they are promising materials for obtaining mechanically strong composites [6].

Metal materials (Ti, Ti alloys, austenitic stainless steel, Co-Cr alloys) on the other hand, have excellent mechanical strength and corrosion resistance in aggressive media. Thus, various composite materials of AP coated on metals have been developed [7]. A frequently used method for coating metals with AP is the electrodeposition (ED), which allows one to obtain dense AP coatings with good adhesion to the underlying metal, uniformity, controlled thickness and deposition rate, at low temperatures and under ambient conditions [8]. Moreover, ED is suitable for producing desirable composite coatings, which gives the possibility for combining the beneficial properties of any single material used in the composite.

The goal of our study is by incorporating ND particles into the AP, to obtain advanced AP-ND composite coatings with ductility, improved hardness and adhesion in comparison to pure AP.

2. Experimental

Substrates were prepared from austenitic stainless steel (AISI 316L rods, ∅15 mm, ASTM standard F183-92, Grade 2) and subjected to standard metallographic polishing with SiC papers, diamond and alumina suspensions to obtain a mirror-finish surface. Finally, the samples were ultrasonically rinsed in acetone, dried under a stream of pure nitrogen (99.9 %) and stored in a desiccator.

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A potentiostat (Hokuto Denko HA150G) was used for the deposition of the AP-ND composite coatings. The deposition was performed using the stainless steel sample as the cathode, a Pt foil as the anode and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte resembled the ion composition, concentrations and pH of the human blood plasma, and is known as simulated body fluid (SBF) [9]. It was prepared by mixing the reagent grade chemicals NaCl, $NaHCO_3$, KCl, K_2HPO_4-$3H_2O$, $MgCl_2$-$6H_2O$, Na_2SO_4-$10H_2O$, and $CaCl_2$-$2H_2O$ with Milli-Q pure water (18.3 MΩ) and buffered at pH 7.4. As-prepared SBF is named ‘pure SBF’, in the text below. ND particles were synthesized by detonation of trinitrotoluene and hexogen at high pressure and high temperature [10]. Subsequent purification from graphite by applying oxidation with potassium dichromate in sulphuric acid was carried out, and after several washings with HCl and water, the ND powder was dried. The as-obtained ND particles were added to the SBF electrolyte in a concentration of 0.5 g/l and ultrasonically shaken for 20 min. The as-prepared solution is named ‘ND-SBF’ hereafter. Cathodic ED was performed at 37^0C, at a potential of -1.5 V versus SCE for 15, 30 or 60 min. After the deposition, the samples were washed under a flow of Milli-Q pure water and dried in air. Two groups of samples were thus prepared:

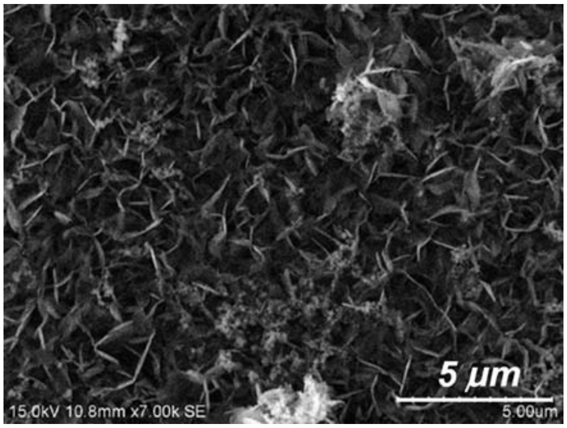

Fig. 1. SEM image of the coating obtained after ED from ND-SBF for 15 min: a *dense and uniform white coating with platelets and randomly distributed white aggregates was observed.*

(i) by ED from ND-SBF (samples named ‘ED-AP-ND’);

(ii) by ED from pure SBF (samples named ‘ED-AP’ and used as controls for the first group);

Prepared coatings were studied by scanning electron microscopy (SEM; Hitachi S-3400 NX), Fourier transform infrared spectroscopy (FTIR; JASCO FTIR-300E, reflection mode), Vickers hardness (HV) tester (HMV-1, Shimadzu, 0.245 N load, 10 s), and a surface and interfacial cutting analysis system (SAICAS; CN-20, constant load mode: $F_{Hor} = F_{Vert} = 0.01$ N, diamond blade).

3. Results and discussion

Cathodic ED for 15, 30 or 60 min from the ND-SBF solution resulted in the formation of dense and uniform white coatings with thin platelets, as observed by SEM (Fig. 1). In addition, white aggregates of platelets were found, randomly distributed within the underlying homogeneous coatings. Fig. 1 depicts the surface of the ED-AP-ND samples after deposition from the ND-SBF solution for 15 min. Increasing the duration of the ED to 30 or 60 min did not change the coating morphology, and the same platelet coating with attached aggregates was detected by SEM. The deposits on the ED-AP control samples, obtained from the pure SBF after 15, 30 or 60 min had the same morphology, which shows that the ND particles do not influence the coating morphology.

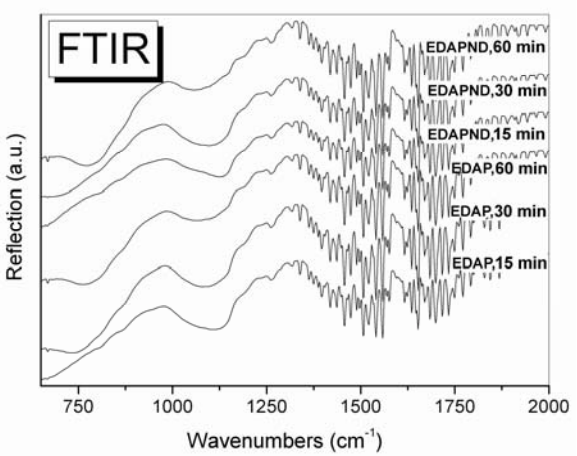

Fig. 2. Non-stoichiometric CO_3 and HPO_4-containing AP was found by FTIR of the coatings obtained by: (i) ED from ND-SBF; (ii) ED from pure SBF.

The coating structures were investigated by FTIR spectroscopy (Fig. 2). A broad peak envelope was observed for all samples at 950-1180 cm^{-1}. A peak fitting procedure revealed that it was an envelope of five underlying peaks, due to ν_3 PO_4^{3-}, ν_1 CO_3^{2-} and HPO_4^{2-} vibrational modes. In addition, absorption due to ν_3 CO_3^{2-} stretching at 1430 and 1620 cm^{-1}, characteristic of partial CO_3 substitution of PO_4 ions in the AP structure, was detected in the spectra. Thus, it was concluded that the coatings deposited from either pure SBF or ND-SBF solutions were ns-, CO_3- and HPO_4-containing low crystalline AP, similar to the bone AP. Both CO_3 and HPO_4 ions are known to induce disorder in the AP structure, thus leading to the formation of Ca-deficient and low crystalline AP [11], which explains the broad peaks in the FTIR spectra in our study.

Table 1 lists the thickness and calculated mechanical parameters by SAICAS data: shear (τ) and peel (P) strengths, related to the coating cohesion and coating-substrate adhesion, respectively. The thicknesses of the

ED-AP-ND60 coatings (935 nm) were slightly lower than those of the ED-AP60 coatings (1033 nm). However, more importantly, both the τ and P strengths increased as the ND particles were incorporated in the AP coatings (ED-AP-ND60 samples). As discussed at the beginning of the paper, ND particles are a promising material for obtaining mechanically strong composites. Thus, it was considered that the cohesion of the electrodeposited composite coatings and their adhesion to the steel substrates was enhanced, due to the presence of the ND particles as a second phase, which was one of the goals of this study.

High hardness is a guarantee for good wear resistance, which is crucial for the AP implant coatings. According to the HV results (Table 2) deposition of the composite coatings for 15 min from the ND-SBF did not increase the AP hardness (HV310 versus HV335 for the ED-HA coatings). However, the composites obtained after 30 or 60 min (HV394 and HV454, respectively) showed higher HV values than the ED-HA coatings deposited for the same time from the pure SBF (HV355 and HV374, respectively). Thus, despite the low initial concentration of the ND particles in the ND-SBF electrolyte, and the sedimentation of the bigger ND particles with the ED time, the AP hardness was improved with the higher content of the ND particles, and the difference was most significant after 60 min of ED from the ND-SBF electrolyte.

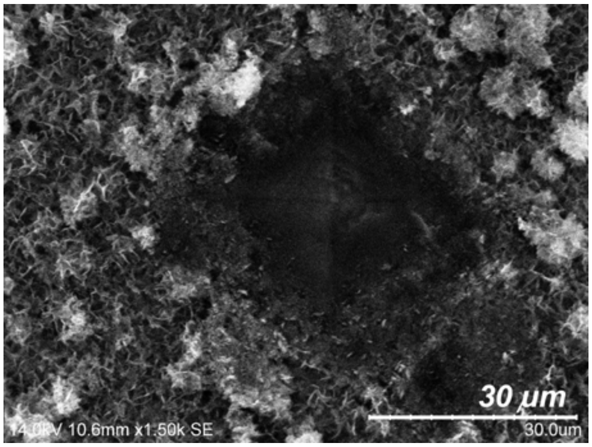

Fig. 3. Qualitative data obtained by a SEM image of the imprint left by the diamond blade revealed no cracks in the ED-AP-ND coatings, which testified to the good ductility of the composite coatings and the lack of residual stress.

The ED in this work was performed at low temperatures, in order to simulate the body environment and to avoid thermal stress at the metal-coating interface, which could lead to cracks in the coating and phase transformations. Low temperatures during ED are known to yield enhanced binding strength between the substrate and the coating, as confirmed in our experiment by the SAICAS data. In addition, the growth of thin homogeneous coatings, as in this experiment (maximum thickness of about 1 μm), is advantageous against coating delamination and crack formation, as usually observed with thick (tens of micrometers) AP coatings. In our study, SEM images of the ED coatings obtained in both ND-SBF and pure SBF showed that cracks were totally absent. An image of the imprint left by the diamond blade (Fig. 3) revealed no cracks extending from the imprint corners for the ED-AP-ND coatings, which testified to the good ductility and the lack of residual stress in the composites. No delamination of the coatings was observed, even at testing with the highest available load (980 mN).

Table 1. Shear (τ) and peel (P) strength data, showing an increase after the ND incorporation.

Sample	τ [MPa]	P [N/m]	d [nm]
EDAP60	20.3	33.5	1033
EDAPND60	44.4	51.0	935

Table 2. Vickers hardness results for the coatings obtained by: (i) ED from the ND-SBF and (ii) ED from pure SBF showed higher hardness of the ED-AP-ND samples

EDAP ND15	EDAP ND30	EDAP ND60	EDAP 15	EDAP 30	EDAP 60
310.0	394.0	453.8	335.0	355.0	373.7

4. Conclusions

Dense and homogeneous ns-apatite-nanodiamond composite coatings, containing CO_3 and HPO_4 groups, were prepared by potentiostatic mode electrodeposition on austenitic stainless steel. This work showed that the as-obtained composite coatings were ductile and had better hardness and adhesion, in comparison to pure apatite coatings. No residual stress and cracks were observed in the composites, whose shear and peel strengths were also higher than those of pure apatite. Thus, the nanodiamond-reinforced apatite coatings can be considered as an attractive surface modification for medical device metal materials.

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