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Comparative investigation of antibacterial yet biocompatible Ag-doped multicomponent coatings obtained by pulsed electrospark deposition and its combination with ion implantation

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ABSTRACT

The aim of this work is to obtain antibacterial yet biocompatible coatings using pulsed electrospark deposition (PED). For this purpose new composite electrodes were fabricated from reaction mixtures Ti–C–20%Fe-10%$Ca_3(PO_4)_2$–3.4%Mg–X%Ag with different amount of antibacterial component (X = 0, 0.5, 1.0, 1.5 and 2.0 at % of Ag) using self-propagating high-temperature synthesis method. The electrodes consisted of TiC grains surrounded by $TiFe_2$ and TiFeP intermetallic matrix, CaO and MgO inclusions, and Ag-based phase. The influence of Ag content on the electrode mass transfer kinetics was studied by comparing the total substrate weight gain and electrode mass loss during PED. The structure, elemental composition, and surface roughness of coatings were studied by means of X-ray diffraction, scanning electron microscopy, and optical profilometry. The coatings were characterized in terms of Ag^+ ion release, mechanical and electrochemical properties, as well as biocompatibility. The antibacterial characteristics of Ag-doped PED coatings were compared with those obtained by PED using Ag-free electrode and then implanted with Ag^+ ions. The results indicated that an increase in the Ag content in electrode leads to a decrease in electrode erosion and substrate weight gain, but the efficiency of the PED process increases. Doping with a small amount of Ag ($\leq$ 1 at%) resulted in 100% antibacterial effect against both gram-positive *S. aureus* and gram-negative *E. coli* bacteria. In addition, the dynamics of MC3T3-E1 cell proliferation on the surface of PED coatings with 0.6–0.7 at% of Ag was similar to that in control samples, hereby indicating their biocompatibility. The coating biological characteristics were discussed based on the results of Ag^+ ion release and electrochemical tests.

1. Introduction

Bone and joint degenerative and inflammatory problems affect millions of people worldwide, and the development of antibacterial yet biocompatible surfaces is a challenge that the biological community has been facing for many years, but the “materials of dream” have not been developed yet. Although the bulk properties of metallic materials in healthcare applications have been more or less optimized, the poor interfacial bonding between their surface and the surrounding tissue, as well as the occurrence of implant-related microbial infections remains a serious problem in reconstructive surgery. Surface engineering is an effective tool to impart desirable chemical, biological, and mechanical characteristics to the surface without compromising material bulk properties [1]. For example, changing the chemical composition and surface roughness of metal implants can significantly improve their osteoconductive and osteoinductive characteristics [2–5]. Another important task is imparting antibacterial characteristics to a surface in order to reduce the risk of microbial contamination when integrating the implant into living tissue [6].

Self-propagating high-temperature synthesis (SHS) has become a “hot” and a rapidly developing topic in surface engineering. The most notable progress has been made in the field of SHS-produced targets and electrodes, which are widely used for deposition of various types of coatings [7]. For example, pulsed electrospark deposition (PED) using Co-based and Co-free SHS electrodes was successfully utilized to fabricate thick (up to 30 μm) and relatively rough (average surface

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roughness of more than 6 μm) multicomponent coatings on the surface of metallic implants in a single technological run [8,9]. The obtained PED coatings were multiphase and contained Ag-based inclusions to impart antibacterial characteristics and dissolved P, Ca, and O elements to provide bioactivity [10]. The shortcomings of the resultant PED coatings included a large size of the phase components and a small toxicity due to the presence of relatively coarse (up to 1 μm) Ag-based particles. When Ag-doped multiphase coating is immersed in a biological environment, microgalvanic effects can occur between Ag and more electronegative elements in the surrounding matrix, for example, Ti, Mg or Co, that are detrimental to living cells [11]. Hence, the reduction in size of structural components is critical in order to decrease the galvanic currents and to achieve more homogeneous Ag^+ ion release.

Iron is an important element of the human body, where it mostly binds with proteins. In terms of designing new biomaterials, it is important that Fe is biocompatible [12] and well wet the surface of Ti carbide [13,14]. Fe-doped hydroxyapatite/titanium composites were shown to improve the material bending strength, fracture toughness, and fatigue strength [15]. Iron, similar to Mg, is a base of many biodegradable materials, but unlike the latter, the degradation rate of Fe-based materials is low [12,16].

When choosing the composition of an electrode, it is necessary to ensure the following characteristics: (i) presence of a given amount of various chemical elements to provide the required level of the coating mechanical and biological properties, (ii) pore-free state, (iii) small grain size, (iv) homogeneous distribution of the phase components, and (v) high electrode erosion capacity. Preliminary mechanical activation of the initial reaction mixture permits achieving an even distribution of the components [17,18], whereas the electrode erosion capacity can be enhanced through introduction of plastic binder that contains relatively low-melting metallic or intermetallic phases [8].

This work has aimed at obtaining antibacterial yet biocompatible coatings using the PED method. For this purpose, new Fe-based composite electrodes with different amounts of an antibacterial component (Ag) have been fabricated using the SHS method. The antibacterial characteristics of the resultant Ag-doped PED coatings have been compared with those obtained through PED using an Ag-free electrode and by further Ag^+ ion implantation. The coating biocompatibility and bactericidal effect against gram-positive *Staphylococcus aureus* (*S. aureus)* and gram-negative *Escherichia coli* (*E. coli)* bacteria have been discussed on the grounds of the Ag^+ ion release and electrochemical test results.

2. Materials and methods

2.1. SHS electrodes

In order to obtain the PED coatings on Ti substrates, we utilized electrodes obtained from Ti–C–20%Fe–10%$Ca_3(PO_4)_2$–3.4%Mg–X%Ag reaction mixtures, where X is the Ag content equal to 0, 0.5, 1.0, 1.5 and 2.0 at% (Table 1), using SHS compaction technology as described elsewhere [8,19]. The Ti/C ratio was chosen to synthesize non-stoichiometric $TiC_{0.5}$ carbide. The following powders were used for the preparation of the reaction mixtures: titanium (~ 10–60 μm, 99.0% purity), technical carbon black (~ 0.2–0.5 μm, 99.9% purity), iron (~ 30–70 μm, 98.9% purity), silver (~ 5–30 μm, 99.0% purity), magnesium (~ 50–100 μm, 99.0% purity) and β-modification tricalcium phosphate (~ 5–30 μm, 97.5% purity). To achieve uniform distribution of components, the initial reaction mixtures were prepared in a high-speed centrifugal planetary mill (Aktivator-2S) in an argon atmosphere using the following technological parameters: drum working volume of 250 cm^3, drum rotational speed of 700 rpm, mixing time of 5 min, a ratio of the ball mass to the charge mixture mass equal to 15:1. Electrodes, 4 × 4 × 40 mm^3 in size, were cut from the central parts of the synthesized billets. The electrodes were marked depending on the Ag charging parameter value X (at%).

2.2. Deposition of coatings

Grade-4 titanium plates, 15 × 15 × 3 mm^3 in size, were used as substrate material. The PED was performed in an argon atmosphere using an Alier-Metal 303 unit. The voltage, energy, current, duration and frequency of the pulses was kept constant at 20 V, 0.06 J, 70 A, 25 μs, and 640 Hz, respectively. The mass transfer kinetics was studied gravimetrically with a KERN-770 balance with accuracy 10^{-4} g. The mass transfer coefficient (Ct) was calculated as a ratio of the substrate weight gain to the electrode weight loss within 5 min of the PED. Before biological tests, After deposition the samples were cleaned using a slot-type ion source. The accelerating voltage, average energy of the argon ions, density of ion current on the substrate, and treatment time were set at 3000 V, 1500 V, 2 mA/cm^2, and 20 min, respectively. Under these conditions, the depth of Ti etching was about 100 nm. A PED coating obtained using an Ag-free X0 electrode with Ag introduced through ion implantation was used as a reference sample. The ion implantation was performed using a Brown-type MEVVA1 ion source operated at an accelerating voltage of 25–30 kV and an average current of 10 mA. The treatment time and radiation dose were 20 min and 2 × 10^{17} ions/cm^2, respectively. Hereinafter the PED coatings will be identified with the electrode type: X0, X0.5, X1, and X2; and the PED coating with Ag introduced through ion implantation will be designated as X0-II.

Measurement of electrode heat capacity C_p was carried out by differential scanning calorimetry using a DSC 404 C Pegasus instrument (Netzsch). Thermal diffusivity a was determined by laser burst method in a LFA 457 instrument (Netzsch) using the Cape-Lehmann model. Thermal conductivity λ was calculated by the equation: $\lambda = aC_pd$. The electrode density d was measured by the hydrostatic weighing method. Specific electric resistance ρ was determined by a two-probe method.

2.3. Microstructure and phase composition

The electrode and coating phase compositions were studied by means of X-ray diffraction (XRD) using monochromatic CuKα radiation at a Bruker D8 diffractometer. The XRD patterns were recorded through step-by-step scanning in the range of 10–110° 2θ with a step of 0.1° at an exposure of 6 s per point. The obtained spectra were identified using the JCPDS card catalog. The sample microstructures were studied at a Hitachi S-3400N scanning electron microscope equipped with a NORAN energy-dispersive X-ray spectroscopy (EDS) module. The coating's surface roughness parameters were measured through optical profilometry at a WYKO NT1100 optical profiler.

Table 1
Compositions of the reaction mixtures.

X	Electrode	Ti (wt%)	C (wt%)	$Ca_3(PO_4)_2$ (wt%)	Fe (wt%)	Mg (wt%)	Ag (wt%)	Ag (at%)
0	X0	59.2	7.4	10.0	20.0	3.4	–	–
0.5	X0.5	58.0	7.3	10.0	20.0	3.4	1.3	0.5
1	X1	56.9	7.2	10.0	20.0	3.4	2.5	1.0
2	X2	54.9	6.8	10.0	20.0	3.4	4.9	2.0

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