Surface & Coatings Technology 340 (2018) 177–189

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

# Needle-less electrospinning employed for calcium and magnesium phosphate coatings on titanium substrates

M. Streckova[a,*], T. Sopcak[a], R. Stulajterova[a], M. Giretova[a], L. Medvecky[a], A. Kovalcikova[a], K. Balazsi[b]

[a] Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04 0 01 Kosice, Slovak Republic
[b] Institute of Technical Physics and Materials Sciences, Center for Energy Research, Hungarian Academy of Sciences, Konkoly Thege Miklós str. 29-33, 1121 Budapest, Hungary

ARTICLE INFO

*Keywords:*
Electrospinning
Fibers
Titanium substrate Ti6Al4V
Coating
Sol-gel method
In vitro tests

ABSTRACT

The needle-less electrospinning method was employed for a preparation of calcium phosphate (CP) and magnesium calcium phosphate (MgCP) fibers as biocompatible coatings on Ti substrate. The polyvinylalcohol, triethyl phosphite, calcium and magnesium nitrates were used for a preparation of spun solutions and subsequent precursor fiber formation. The citric acid of 10 wt% was added to the spun solution in order to increase conductivity as well as a convenient complexing agent. A possible mechanism of complexation process of triethyl phosphite with calcium and magnesium nitrates with citric acid is presented. The optimization of calcination temperatures was defined according to the results obtained from TG/DSC analysis. The XRD analysis confirmed the formation of hydroxyapatite and Mg-whitlockite phases at both used temperatures 600 and 800 °C. The final morphology and thickness of prepared CP and MgCP fibrous coatings was designed by a suitable choice of the used sols, spinning time and calcination temperature. The SEM/FIB observations revealed that the average thickness of the CP coating was around 1 μm, which is almost two times thinner than the MgCP coating with the approximate width 2 μm. The in vitro cytotoxicity tests of the substrate surfaces revealed that the osteoblastic MC3T3-E1 cells have a good proliferation activity when cultured on the 600 °C calcined substrates covered by smooth and uniform fibrous nets. A strong cytotoxic cell response was observed in the samples treated at 800 °C, where the fibrous coatings were disrupted by the newly formed sharp rutile ($TiO_2$) micro-crystals. Such surface topography acts against the initial adhesion and proliferation of osteoblast like cells.

## 1. Introduction

There are many metallic alloys, which are currently used as implant materials in clinical practice [1]. Among them titanium and its alloys hold a predominant place in orthopedic and dental applications because of their good biocompatibility, resistance to corrosion and mechanical strength [2]. In spite of these advantages the main drawback of titanium alloys relates to the motion at the implant – bone interface as a result of inadequate material osseointegration with the host tissue [3]. The solution to this problem lies in creating a coating on implant surface with biological active layer, which can significantly improve the fixation properties and prevent implant failure [4]. Calcium phosphate (CP) bioceramics as a basic mineral part of connective tissue has been extensively used in various field of biomedical applications thanks to good bioactivity, osseointegration and osteoconductive properties [5]. Despite of excellent biological properties, the CPs are known as materials with low mechanical strength and toughness, which allow their use only as filling materials or coatings. The CP-based coatings, mainly in the most stable - hydroxyapatite (HAP) form, were deposited onto the metallic surface in order to maintain the high mechanical strength of implants in combination with notable biological properties of CP layers. The recently used deposition techniques include, for example, thermal plasma spraying [6], radio-frequency magnetron sputtering [7], dip coating [8], electrophoretic deposition [9], etc. The main disadvantage of high temperature deposition methods (e.g. plasma spraying) lies in a degradation of HAP phase during the heat treatment as well as controlling the thickness of deposited layers [10]. Nowadays, low-temperature electrohydrodynamic techniques like for instance electrospinning and electrospraying have received much attention in many different industrial areas due to capability of developing fibers or particles at micron, submicron or nanoscale range [11]. The basic principle of electrospinning is based on generating free charges on the surface of polymer solution by a high voltage potential, which overcomes the solution's surface tension and produces a charged jet of

* Corresponding author.
*E-mail address:* mstreckova@imr.saske.sk (M. Streckova).

https://doi.org/10.1016/j.surfcoat.2018.02.063
Received 13 December 2017; Received in revised form 25 January 2018; Accepted 18 February 2018
Available online 20 February 2018
0257-8972/ 

**Table 1**
Notation of the samples before and after the thermal treatment process. The composition of the solutions adjusted for spinning process according to ionic conductivity and applied voltage.

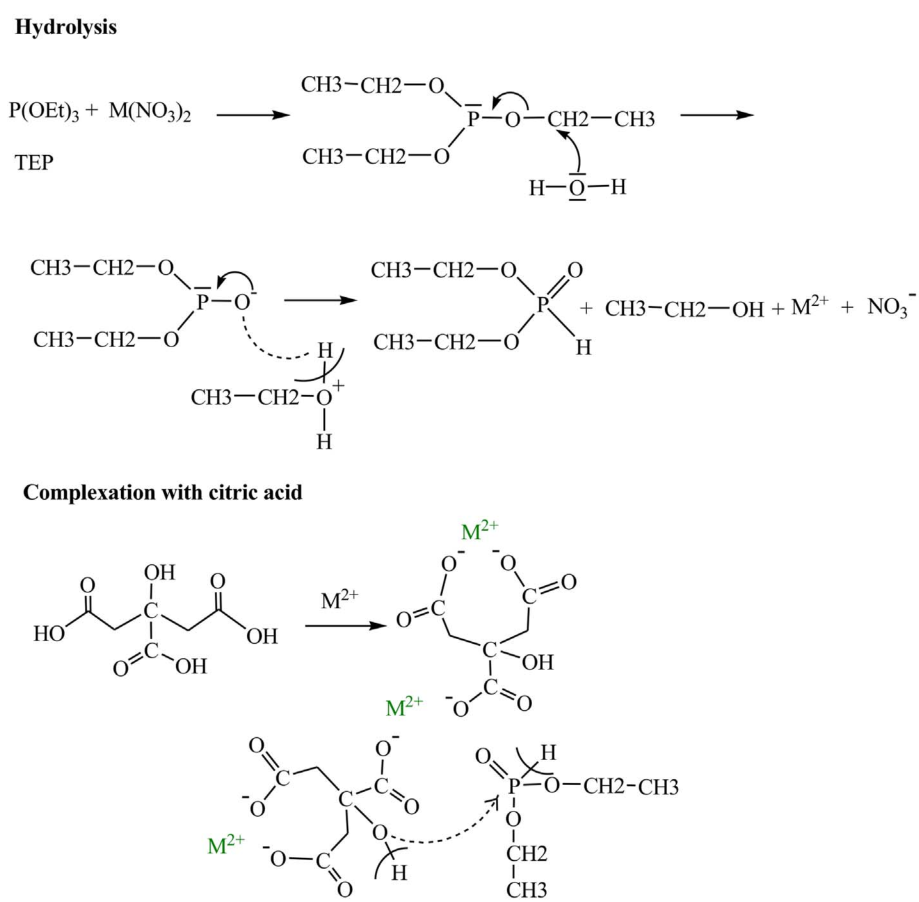
| Precursor solutions | Sample | Ionic conductivity (mS) | Applied voltage (kV) | Final spinning |
|---|---|---|---|---|
| solCP | – | 75 | – | Not spinable |
| solCP/CA | – | 66 | – | Not spinable |
| PVA/solCP | – | 58 | 75 | Slightly spinable |
| PVA/solCP/CA | CP | 65 | 70 | Spinning |
| PVA/solMgCP/CA | MgCP | 84 | 70 | Spinning |

conical shape usually gathered on grounded collector [12]. In a typical setting one or more needles (spinnerets) are generally used to drawn the fibers from solutions or melt. However, the production rate of the simple spinneret is very low, which implies strong limitations for mass production [13]. On the other hand, the needle-less (NLE) or free liquid surface electrospinning can generate numerous jets from the solution surface what enhances the production rate even one or two orders of magnitude in comparison with the conventional method [13,14].

Although the electrospinning is considered as a powerful fiber producing technique, only a few previous studies dealt with the use of this method for the deposition HAP fibers on Ti surfaces. Iafisco et al. [15] has coated Ti alloy by the nanostructured collagen-apatite fibers by combining electrospinning and biomimetic mineralization. Their results showed that the obtained mineralized scaffolds are quite similar to natural bone extracellular matrix from the morphological, structural, and compositional point of view. Santhosh and Balasivanandha Prabu [16] electrospun coated Ti-6Al-4V alloy with nanoHAP – polysulfone. It was demonstrated that the coating containing nanoHAP particles promoted growth of apatite crystals upon immersion in simulated body fluids (SBF) and did not show corrosion over prolonged soaking of 14 days.

Recently, growing interest has been devoted to a production of Mg containing biomaterials such as biocements [17], scaffolds [18] and coatings on metallic substrates [19–21] due to the beneficial biological effect of Mg emerging as a naturally occurring element in human body, especially in bones [22]. The Mg containing calcium phosphates (MgCP), such as Mg substituted hydroxyapatite (Mg-HAP), has been shown as an attractive component to improve the biocompatibility of HAP coatings. For instance, Zhao et al. [20] electrochemically deposited pure HAP and Mg-HAP coatings on the surface of pure titanium discs. They showed that the Mg-HAP coated surfaces promoted osteogenic differentiation of preosteoblasts in vitro and improved implant osseointegration during the early stages of bone healing as compared with the pure HAP coated surfaces. The CP biomimetic coatings doped with $Mg^{2+}$, $Sr^{2+}$ and $Mn^{2+}$ were also recently developed in order to improve the biological performance of Ti implants [21]. The results of the in-vitro test showed that the Mg and Sr doped apatite coatings exhibit a higher adhesion and proliferation of osteoblastic cells with respect to pure Ti or the thin layer of amorphous phosphate coating obtained in the presence of Mn.

The present work is focused on a design of the bioceramic CP and MgCP coatings via needle-less electrospinning method. The CP and MgCP coatings were prepared by the sol-gel method from solutions containing calcium/magnesium nitrates and triethyl phosphite with the Ca/P and Ca + Mg/P ratios set to 5:3. The citric acid was used as a complexing agent as well as for the necessary higher conductivity of the prepared sols. The complexation mechanism of precursor sols was suggested. The coatings were deposited on commercially Ti–6Al–4V




**Scheme 1.** The complexation process of triethyl phosphite with metal cations $M^{2+}$ (calcium or magnesium) and citric acid.