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Electrophoretic deposition of bioactive glass nanopowders on magnesium based alloy for biomedical applications

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Abstract

To slow down the initial biodegradation rate of magnesium (Mg) alloy, crystalline nano-sized bioactive glass coating was used to deposit on micro-arc oxidized AZ91 samples via electrophoretic deposition (EPD). Zeta potential and conductivity of the bioactive glass suspension were characterized at various pH values to identify the most stable dispersion conditions. The bone-bonding properties of bioactive glass coated samples were evaluated in terms of apatite-forming ability during the immersion in simulated body fluid (SBF) solution. Results revealed that the ability to form a bioactive glass coating via EPD was influenced by the degree of its crystalline phase composition. Moreover, the potentiodynamic polarization tests recorded significant drops in corrosion current density and corrosion rate of the coated samples which implies a good level of corrosion protective behavior. These preliminary results show that this process will enable the development of Mg implants in the later stage of bone healing.

Keywords: Magnesium; Biodegradable implants; Bioactive glass; Electrophoretic deposition

1. Introduction

Orthopedic bone implants involve the use of some types of materials to augment the function of a damaged portion of the hard tissue or to replace either a portion of the bone tissue [1]. All the conventional metallic materials like cobalt based alloys should be capable of withstanding biological environment and remain inert in the human body to function accurately within prolonged periods. It is known that elevated levels of particular metals in the bloodstream originated from permanent implants can lead to various problems, including metal sensitivity, genotoxicity and carcinogenesis [2]. Furthermore, they can limit somatic growth in children [3]. Recently, intensive research has been undertaken to develop a new generation of biodegradable/bioabsorbable Mg based implants to be applied in regeneration of critical injury sites of the skeletal system and bone remodeling [4]. The main purpose of these prosthetic implant materials is to replace a part or improve a function of the body in a manner that will be safe, reliable, and physiologically acceptable [1]. Any time a foreign material is placed into the human body, the way that material reacts within the body is the main criterion. As known, implant materials must be designed to minimize the serious side effects associated with introducing a foreign material to the body. Although these materials appear to be efficacious in terms of biocompatibility, osteoconductivity and mechanical properties, the major processing challenge is controlling their high degradation rate in body environment. It is therefore, crucial to fulfill a technique that strikes a suitable balance between the corrosion rate of the implant and the tissue healing rate [5]. One of the main apparent solutions to tackle this problem rests with performing surface modification techniques, such as electrodeposition [6,7] and electrophoretic deposition [8] of various types of bioceramics, micro-arc oxidation [9,10] and polymer coatings [11,12]. Among these coating methods, it has been proven that micro-arc oxidation (MAO) treatment is one of the most promising alternatives for Mg based medical

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implants, stents and wires. MAO is based on the plasma-electrolytic oxidation, which produces a porous microstructure owing to the intense sparking discharges and evolution of gas bubble on the sample surface [13]. This oxide layer helps to reduce the level of degradation products during post-implantation [14].

Bioactive glass has been known for its excellent biocompatibility/bioactivity and a range of successful applications from tissue replacement to emphasize on osteogenesis stimulation. They play an increasingly important role in bone tissue engineering applications from middle-ear to dental defects due to their excellent osteoconductivity and surface bioactivity [15]. Furthermore, it was observed that ionic dissolution products from bioactive glass enhance angiogenesis in new tissue formation, antibacterial activity, enzyme activity, and differentiation of mesenchymal stem cells [16–18]. Studies have shown that nanostructured ceramic biomaterials exhibit enhanced absorbability and higher bioactivity than the micron-sized bioceramics. In addition, demineralization reactions can be restrained when particle size dimension falls into certain critical nanoscale levels [19]. Therefore, nanostructured bioactive glass coatings mimic the mineralized components of natural bone and provide better integration of metallic surfaces with host bone tissue after implantation [20,21]. The interest in electrophoretic deposition (EPD) has received a great deal of attention in the area of bioactive surface modification, specifically in nanostructured bioactive coatings and biomedical devices [22]. The EPD process is based on electrophoresis mechanism that exploits the movement of charged particles in suspension in the presence of an appropriate external electric field. This technique involves low temperature and allows controlling the thickness of the ceramic functionally graded coatings on complex shaped substrates [23,24].

As the application of Mg based materials has been restricted in bone repairs, therefore, in the current work we successfully prepared a bioactive glass coating on the samples. The corrosion resistance and bioactivity of the samples was observed and the difficulties in the EPD process were investigated.

2. Materials and methods

2.1. Bioactive glass synthesis

The bioactive glass was prepared with the nominal composition of (mol%) 46.1% SiO_2–51.3% CaO–2.6% P_2O_5 by hydrolysis and polycondensation reactions of chemicals using reagent-grade tetraethyl orthosilicate (TEOS, Merck), triethyl phosphate (TEP, Merck), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$, Merck), ethanol (Et(OH), Merck), hydrochloric acid (HCl, Merck) and deionized distilled water. The process is provided in Table 1. In brief, the initial procedure involved mixing particular amounts of TEOS, Et(OH), HCl and deionized distilled water. The appropriate volume of 2 molar (M) HCl was injected drop-wise to the solution as a catalyst of the hydrolysis process. Boonstra et al. [25] found that hydrolysis and condensation time is inversely proportional to the HCl concentration. Subsequently, TEP was added to the solution and stirred for at least 30 min until the solution became clear. The molar ratio of (TEOS + TEP): (H_2O + HCl):Et(OH) was 1:10:15. After the addition of reagents, the solution was stirred for 2 h at room temperature. Then, the gelatin solution was aged at 60 °C within 48 h and dried at 120 °C for 48 h, according to a procedure reported by Mortazavi et al. [26]. Calcination was carried out by heating the powder up to 520 and 1000 °C (30 min, heating rate 10 °C/min) in order to produce amorphous and highly crystallized bioactive glass. The powder was ground by planetary milling (PM 100, Retsch, Germany) and was rinsed three times with ethanol and double distilled water in a centrifuge (EBA20,Hettich, Germany) at 6000 rpm each for 5 min to remove any impurities [27]. Finally, the powder was dried in an oven at 80 °C for 5 h.

2.2. Sample preparation and coating procedure

The biomedical grade AZ91 Mg based alloy samples (20 mm × 10 mm × 2 mm) were mechanically polished up to 600 grit with SiC paper, and finally ultrasonically rinsed (WUC-D10H, Wisd Laboratory Equipments, Germany) for 30 min in turn with acetone and water.

The MAO process was operated in an aqueous saline solution containing NaOH (100 g/l), Na_2SiO_3 (100 g/l), KOH (20 g/l) using a DC power supply (IPC-SL20200J, Iran). The workpiece was operated as an anode and a stainless steel plate as a cathode. To obtain oxide coatings with proper microstructure, roughness, biological performance and corrosion resistance properties, MAO was conducted at a constant applied voltage 30 V cm^{-1} for 30 min until an oxide layer with a thickness of 20 μm was formed, according to the aforementioned preceding paper [28].

Bioactive glass suspensions with a concentration of 50 g/l in methanol (CH_3OH, Merck) were prepared at various pH values. Our preliminary research showed that methanol is one of the most suitable solvents for bioceramic suspensions [28]. Zeta potential and conductivity measurements were performed as a function of pH using a zeta-sizer (ZEN3600, Malvern, England). Nitric acid (HNO_3, Merck) and sodium hydroxide (NaOH, Merck) were used to adjust the pH value of the suspension for the acidic and alkaline ranges, respectively.

Table 1
Recipe for the sol–gel derived bioactive glass material.

Chemical					
TEOS (ml)	TEP (ml)	Et(OH) (ml)	H_2O (ml)	HCl [2M] (ml)	$Ca(NO_3)_2 \cdot 4H_2O$ (g)
16.4	1.4	70.0	14.0	2.4	19.4