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Influence of shot peening on corrosion properties of biocompatible magnesium alloy AZ31 coated by dicalcium phosphate dihydrate (DCPD)

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ABSTRACT

Magnesium alloys are promising materials for biomedical applications because of many outstanding properties like biodegradation, bioactivity and their specific density and Young's modulus are closer to bone than the commonly used metallic implant materials. Unfortunately their fatigue properties and low corrosion resistance negatively influenced their application possibilities in the field of biomedicine. These problems could be diminished through appropriate surface treatments. This study evaluates the influence of a surface pre-treatment by shot peening and shot peening + coating on the corrosion properties of magnesium alloy AZ31. The dicalcium phosphate dihydrate coating (DCPD) was electrochemically deposited in a solution containing 0.1 M $Ca(NO_3)_2$, 0.06 M $NH_4H_2PO_4$ and 10 mL/L of H_2O_2. The effect of shot peening on the surface properties of magnesium alloy was evaluated by microhardness and surface roughness measurements. The influence of the shot peening and dicalcium phosphate dihydrate layer on the electrochemical characteristics of AZ31 magnesium alloy was evaluated by potentiodynamic measurements and electrochemical impedance spectroscopy in 0.9% NaCl solution at a temperature of 22 ± 1 °C. The obtained results were analyzed by the Tafel-extrapolation method and equivalent circuit method. The results showed that the application of shot peening process followed by DCPD coating improves the properties of the AZ31 surface from corrosion and mechanical point of view.

1. Introduction

Traditional biomedical metal alloys such as Co–Cr–Mo, stainless steel, and titanium alloys have played an essential role in load-bearing implants for the repair or replacement of diseased or damaged bone [1,2]. However, the elastic modulus of these metal alloys is much higher than that of bone, leading to stress shielding and bone absorption [1]. Compared with the traditional metals alloys, a biodegradable material will not cause permanent physical irritation, avoiding the secondary surgery to remove implants [3,4]. Magnesium alloys as new potential biomaterials have recently inspired the researchers [5], owing to its attractive mechanical properties, such as its special density (1.7–2.0 g/cm^3) and elastic modulus (41–45 GPa), which are most close to those of the human bone (1.8–2.1 g/cm^3, 10–40 GPa) [6–8] thus minimizing stress shielding effect [1,9]. Magnesium and its alloys also exhibit non-toxicity and good biocompatibility [4]. Interestingly, magnesium ions are present in a large amount on the human body and involved in many metabolic reactions and biological mechanisms [10]. This means that magnesium can serve as a metallic biodegradable material in the human body in which magnesium can be gradually dissolved, consumed or absorbed [3,6,11]. The presence of Mg enhances bone cell adhesion and has no inhibitory effect on cell growth [6]. Witte et al. indicated that high magnesium ion concentration even could lead to bone cell activation [12]. The degradable properties of Mg and its alloys are, however, a double-edged sword [13]. Mg is a highly reactive metal and exhibits high corrosion rates when immersed in physiological solutions. Such higher corrosion rates must be controlled and reduced if Mg will be used for orthopedic applications. In this sense, coatings have been suggested as a mean of reducing the corrosion rate. Ideally, corrosion would be decreased to allow the mechanical integrity of the metal to remain intact during bone healing. Applying of coating would also minimize hydrogen production, which has been observed as corrosion by product [14–16]. Hydrogen production is considered as a potentially disadvantageous. Theoretically, it would be then expected that the coating slowly wear away, allowing a controlled degradation of the substrate [13]. The most perspective coatings for implants are calcium phosphates, including hydroxyapatite (HA), octacalcium phosphate (OCP) and brushite (DCPD — dicalcium phosphate dehydrate), because of their excellent biocompatibility, non-toxicity and bioactivity [17,20].

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Table 1
Chemical composition of AZ31 alloy (wt.%).

Component	Al	Zn	Mn	Si	Cu	Ni	Fe	Mg
wt.%	2.96	0.828	0.433	0.004	0.004	0.001	0.002	Balance

Shot peening (SP) is a mechanical surface treatment technique widely considered as simple and comparatively cheap method to enhance the fatigue properties of structural metallic materials made of steel, aluminum, titanium and Mg alloys [18–24]. The improvement in fatigue life after SP stems from a combination of surface work hardening and the introduction of near-surface compressive residual stresses [19–22]. Compressive surface residual stresses help to improve the life of engineering components by retarding fatigue crack initiation and growth [25]. However, the beneficial effect of shot peening can only be achieved by carefully selecting the peening parameters to avoid the strong over-peening effect [24,26]. The effects of SP parameters on the fatigue life of ZK60 Mg alloy has been studied in a previous work [24]. The authors found that applying SP with an optimum parameters leads to a significant improvement in the fatigue life of Mg alloy ZK60`. This improvement was related to the induced compressive residual stresses that which shifted the fatigue crack nucleation site from the surface to subsurface regions. Liu W. C. et al. [27] has reported that shot peening of Mg–10Gd–3Y Mg alloy resulted in different degrees of the enhancement of fatigue performance depending on the applied Almen intensity. SP improves not only the fatigue strength of smooth fatigue samples but also the notched fatigue strength as reported by Zahng P. et al. [28]. The authors stated that the notched fatigue strength of AZ80 increased from 45 to 110 MPa after optimum shot peening, regardless of particular peening media. Optimum SP conditions were obtained at high Almen intensities, implying that surface defects and high roughness induced by heavier SP played a tiny role on the notched fatigue strength of AZ80.

The aim of this study is to improve corrosion properties of biodegradable AZ31 magnesium alloy by using shot peening technique followed by the electro-deposition of calcium phosphate coating.

2. Experimental procedures

AZ31 magnesium alloy with chemical composition listed in Table 1 was used in this investigation. The material was prepared by a continual casting followed by a homogenous aging at 420 °C for 16 h. Electro-deposition of DCPD was carried out at a temperature of 20 ± 2 °C for 60 min in a solution of 0.1 M $Ca(NO_3)_2.4H_2O$ + 0.06 M NH_4HPO_4. Before the electro-deposition, the samples surface was firstly grinded using a P1000 emery paper. The samples were connected as cathode at controlled potential of −1.8 V vs. saturated calomel reference electrode (SCE). Platinum electrode served as an anode. The evaluation of the deposition process was described in a previous study [18]. Part of samples was shot peened. The shot-peened samples were then coated by DCPD. SP was carried out on a grinded surface to 100% coverage using a shot-peening machine of OSK company and ceramic shots Z850 (Ø 850 μm) at Almen intensities of 0.262 mmN, 0.140 mmN and 0.042 mmN. Almen intensity is determined as the saturation value of the arc height measured on so-called Almen strips peened for progressively longer exposure times on one side of the strips. This Almen value is the most important process parameter that characterizes the intensity of the shot-peening treatment [29].

Shot-peened samples were ultrasonic cleaned in ethanol in order to remove contaminants from the shot-peening process and rests of ceramic medium. Microhardness-depth profiles after SP measured on cross section samples applying HV 0.025 hardness testing. Surface roughness after various surface conditions expressed in arithmetic average (R_a) and maximum roughness (R_{max}) was measured by a Perthometer profilometer S8P supplied by the company Perthen Mahr. The surface morphology of the dicalcium phosphate dihydrate (DCPD) coating electrodeposited on grinded and SP-surfaces was observed by scanning electron microscopy (SEM). The corrosion resistance of surface layers was evaluated by electrochemical impedance spectroscopy (EIS) in 0.9% NaCl solution at 22 ± 2 °C. The electrochemical tests were carried out using a classical three electrode cells with platinum as counter electrode, saturated calomel electrode SCE (+0.242 V vs. SHE) as reference electrode and the sample as working electrode. EIS scan frequency ranged from 100 kHz to 100 mHz, and the perturbation amplitude was 10 mV.

3. Results and discussion

The tested material had an average grain size of 220 μm (Fig. 1) and the microstructure revealed polyedric grains of the solid solution of aluminium, zinc and other alloying elements. The microhardness measurements performed after shot peening at various Almen intensities are presented in Fig. 2. As can be seen, the near surface regions after shot peening were plastically deformed that led to significant increased of microhardness of the AZ31. The surface hardness of the bulk material markedly increased from 55 to 86, 83 and 101 HV0.025 after SP using Almen intensities of 0.042, 0.140 and 0.260 mmN, respectively. The significant effect of shot peening on microhardness was observed up to 0.10 mm of depth at 0.042 mmN, 0.15 mm at 0.140 mmN and 0.20 mm at 0.260 mmN.

The surface morphologies of DCPD coating formed by electro-deposition after various surface conditions are shown in Fig. 3. The micrographs reveal that the coating covered the entire surface of the

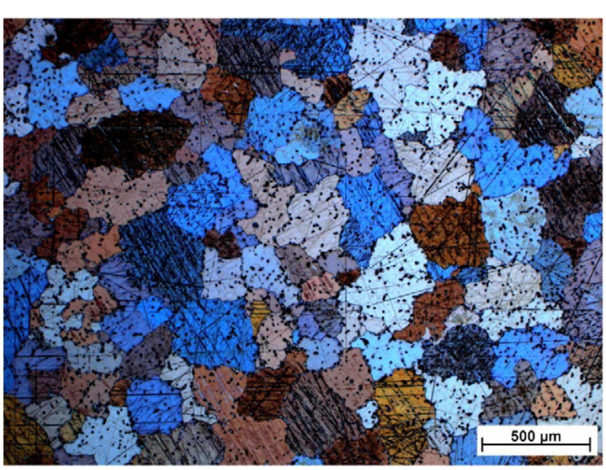

Fig. 1. Microstructure of AZ31 Magnesium alloy.

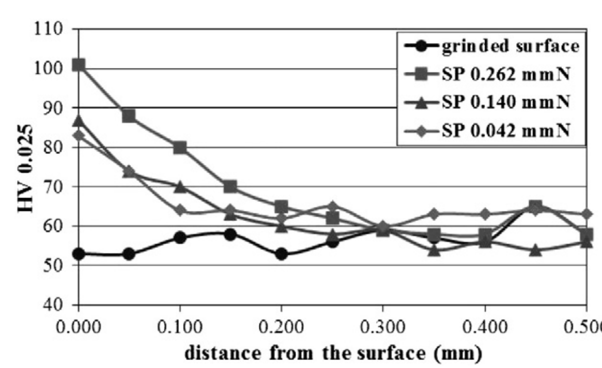

Fig. 2. Microhardness measurements after SP.