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Corrosion protection by zirconia-based thin films deposited by a sol–gel spin coating method

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Abstract

This paper focuses on the structure and corrosion behavior of 316L stainless steel coated by inorganic ZrO_2, hybrid ZrO_2–PMMA, and combined inorganic–hybrid films. The coatings were deposited by a particulate sol–gel spin-coating route, using carboxymethyl cellulose as a nanoparticle dispersant. The electrochemical evaluations were conducted in a simulated body fluid, via potentiodynamic polarization and impedance spectroscopic experiments. According to the results, the hybrid coating presented a better corrosion protection compared to the inorganic coating, due to a lesser density of structural defects. However, the best corrosion resistance was found for a combined coating which consists of an inorganic bottom layer and a hybrid top layer, due to a desirable compromise of good adhesion and low defect density.

Keywords: A. Sol–gel processes; B. Surfaces; C. Corrosion; D. ZrO_2

1. Introduction

Metals and alloys are the oldest materials used in surgical purposes to make devices for fracture fixation, joint replacement, external splints, braces, traction apparatus, and dental amalgams [1]. Nowadays, the widely used metallic biomaterials include stainless steels, titanium and its alloys, and cobalt–chromium-based alloys, as well as tantalum, niobium, and gold. Stainless steels, typically AISI 316L, are conventionally used in orthopedics, with the main advantages of low cost, good mechanical properties, sufficient corrosion resistance, and easy processing. However, problems have been found with this type of medical-grade stainless steels. The most important problem is the negative effect of metal ions or fretting debris released from the implant due to corrosion and wear [2,3].

In the biomaterials field, as well as the modification of chemical composition, surface modification techniques are used with the principal purpose of an improvement in corrosion resistance, wear resistance, antibacterial property, and tissue compatibility [1,4]. Coating, as one of these methods, not only can increase the corrosion resistance of the implant, but also can improve the implant–tissue interaction. Among various methods used to process coatings, the sol–gel deposition process has advantages, such as high homogeneity, low sintering temperatures, and simplicity of complex shape coating [5,6].

Zirconia (ZrO_2) is one of the most interesting ceramics in biomedical purposes, due to biocompatibility and bioactivity. In the literature, there are a number of studies on the corrosion protection of stainless steels by zirconia-based coatings prepared by polymeric sol–gel processes, especially in acidic electrolytes, via polarization experiments [7–10]. It has been known that ZrO_2 has a high expansion coefficient very close to those of stainless steels, which can reduce the formation of cracks during high-temperature curing processes. ZrO_2 presents also a good chemical stability and high hardness, making it a good protective material [11]. However, to our knowledge, little systematic work has been reported on the corrosion protection of 316L stainless steel in a simulated body fluid by zirconia-based thin films processed by particulate sol–gel methods, rather than polymeric sol–gel processes.

In this paper, three types of coating, inorganic ZrO_2, hybrid ZrO_2–PMMA, and combined inorganic-–hybrid films, were deposited on 316L stainless steel, via a particulate sol–gel spin

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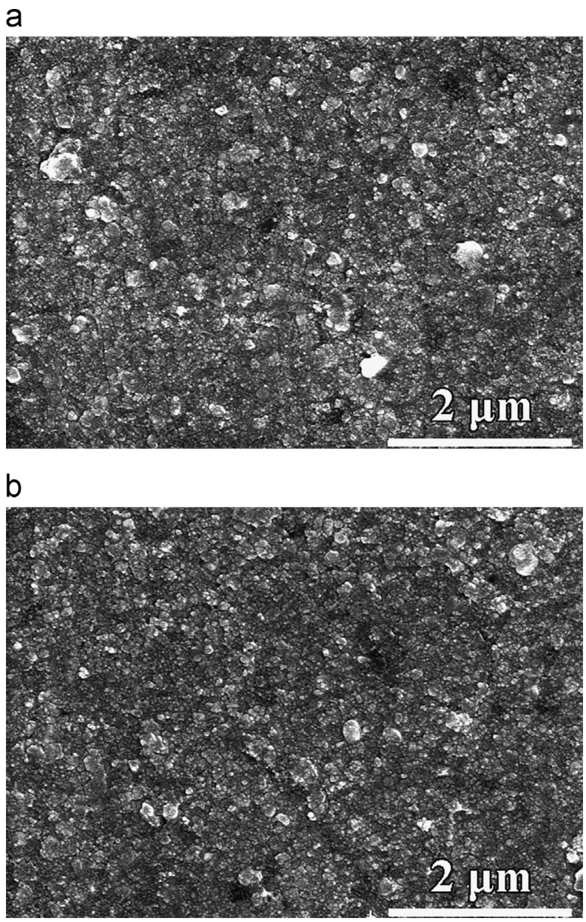

Fig. 1. Morphological SEM micrograph of the inorganic (a) and hybrid (b) coatings.

coating method. After studying the coating structure, the corrosion behavior of the specimens was also evaluated in a simulated body fluid, via potentiodynamic polarization and electrochemical impedance spectroscopic experiments.

2. Materials and methods

316L austenitic stainless steel discs were ground by emery papers, polished by alumina powders, and ultrasonically cleaned in acetone, ethanol, and distilled water. Three types of sol–gel derived coatings were deposited on the substrate: inorganic ZrO_2, hybrid ZrO_2–PMMA, and a combination of the inorganic and hybrid coatings. To process the inorganic coating, $ZrCl_4$ (Alfa Aesar, 99.5%) was first dissolved in deionized water. Then, by the dropwise addition of a NaOH solution, the pH of the solution was increased to 7 (hydrogel). To remove chloride ions, the hydrogel was repeatedly rinsed with deionized water. Afterwards, 75 mL of deionized water and 2 wt% carboxymethyl cellulose (CMC, sodium salt, Alfa Aesar) as a dispersing agent were added to the product. To prepare the hybrid $ZrO_2$10 vol% PMMA coating, appropriate amount of polymethyl methacrylate (PMMA, Alfa Aesar) dissolved in acetone was added to the prepared sol. The sols were separately spin-coated on the substrate at a

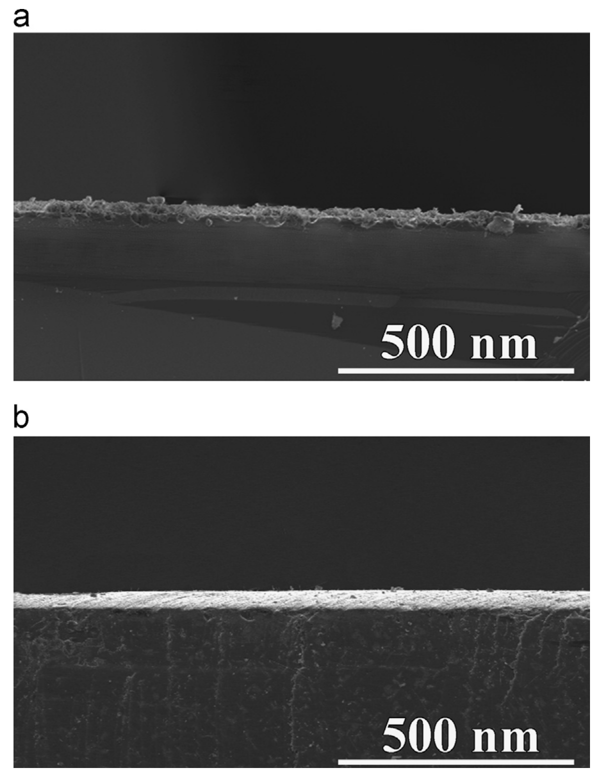

Fig. 2. Cross sectional SEM micrograph of the inorganic (a) and hybrid (b) coatings.

speed of 3000 rpm. Finally, the inorganic and hybrid coatings were sintered at 900 °C and 150 °C for 1 h, respectively. The combined coating also consisted of an inorganic bottom layer and a hybrid top layer, and was electrochemically compared with the double-layer inorganic and hybrid coatings.

The sample surfaces were studied using a scanning electron microscope (SEM, Leica Cambridge) and atomic force microscope (AFM, Bruker AXS). The film adhesion to the substrate was also evaluated by the adhesive tape test, in accordance with ASTM D 3359. The electrochemical corrosion behavior was investigated in the simulated body fluid (SBF) [12] at a pH value of 7.4. A platinum wire and saturated calomel electrode (SCE) were employed as the auxiliary and reference electrodes, respectively. The samples were firstly immersed in SBF for 1 h to obtain a steady-state open circuit potential (*ocp*). Subsequently, anodic potentiodynamic polarization curves were obtained at a scan rate of 1 mV s^{-1} from −0.1 V vs. *ocp* to the transpassive potential. Electrochemical impedance spectroscopic measurements were also performed over 10 frequency decades from 5 kHz to 10 mHz with an excitation potential amplitude of 10 mV at the *ocp*.

3. Results and discussion

Fig. 1 depicts a top-view SEM micrograph of the coatings modified with the CMC addition, showing high-coverage, uniform, and crack-free coatings. The desirable characteristics of the films are attributed to the presence of CMC in the sol [13–15]. The cross-sectional SEM image of the coated samples