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A new double-layer sol–gel coating to improve the corrosion resistance of medical-grade stainless steel in a simulated body fluid

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Abstract

One of the effective ways to overcome some of the drawbacks of oxide coatings for corrosion protection of metal surfaces is the incorporation of an organic component into the inorganic network, although, commonly, film adhesion is disadvantageously affected. In this

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work, for the first time, by exploiting both inorganic and organic-inorganic coatings, a new double-layer thin film, which comprises $ZrTiO_4$ as the bottom layer and $ZrTiO_4$ -PMMA as the top layer, was deposited on a medical-grade stainless steel substrate via a sol-gel spin coating method. According to potentiodynamic polarization experiments in a simulated body fluid, the substrate coated with this film exhibited superior corrosion resistance, compared with the same steel coated with purely inorganic $ZrTiO_4$ and hybrid $ZrTiO_4$ -PMMA films. The superior corrosion resistance of the newly developed coating was found to be due to simultaneously the good adhesion of the lower, inorganic film and the low defect density of the upper, hybrid film.

Keywords: Sol-gel preparation; Corrosion; Electron microscopy; Adhesion

1. Introduction

Coating is one of the most efficient surface modification approaches to improving the corrosion resistance of metallic substrates. Among the various methods used to prepare coatings, the sol-gel deposition process has many advantages, such as high homogeneity, low sintering temperature, and simplicity of coating complex shapes [1,2]. Generally, sol-gel derived coatings are classified into two categories: inorganic oxide coatings and organic-inorganic hybrid coatings. The latter has been developed to overcome the drawbacks of the former, especially brittleness and the need for high temperature treatment (sintering) after deposition, by introducing an organic component into the inorganic network [3].

According to the literature, organic-inorganic hybrid coatings improve corrosion resistance more effectively than do inorganic coatings [3]; however, the adhesion of inorganic coatings to metallic substrates is better than that of organic-inorganic coatings [4].

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In a rather similar situation, Fedrizzi et al. [5] found that the anti-corrosion performance of polyester organic coatings on low-carbon steel is improved, due to the pretreatment of the substrate by applying an inorganic zirconia coating, which enhances the film's adhesion to the substrate. However, to our knowledge, a combination of sol-gel derived inorganic and organic-inorganic hybrid coatings has not been studied to exploit the advantageous characteristics of both types of coating.

In the current study, a new double-layer, sol-gel coating, comprising inorganic $ZrTiO_4$ as the lower layer and hybrid $ZrTiO_4$ -PMMA as the upper layer, on a medical-grade stainless steel was developed. Afterward, the corrosion protection by this coating was compared with the protective properties of the purely inorganic $ZrTiO_4$ and hybrid $ZrTiO_4$ -PMMA coatings, by considering the adhesion and failure mechanism of the films.

2. Experimental

In this work, two kinds of sols were used: inorganic and hybrid. The inorganic sol was synthesized by a sol-gel process starting from $ZrCl_4$ (Alfa Aesar, 99.5 %) and $TiCl_4$ (Alfa Aesar, 99.99 %), followed by the addition of deionized water and carboxymethyl cellulose (CMC, sodium salt, Alfa Aesar) as a dispersant, as detailed in Refs. [6-8]. To prepare the hybrid sol ($ZrTiO_4$ -10 vol.% PMMA), the proper amount of polymethyl methacrylate (PMMA, Alfa Aesar, average molecular weight: 550 gr/mol) was dissolved in acetone and added to the inorganic sol.

Three types of two-layer sol-gel coatings were deposited on a medical-grade stainless steel substrate: 1) inorganic $ZrTiO_4$, 2) hybrid $ZrTiO_4$ -PMMA, and 3) inorganic-hybrid $ZrTiO_4$ -($ZrTiO_4$ -PMMA). The inorganic and hybrid layers were sintered at 700 °C and 150

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°C for 1 h, respectively. To prepare the inorganic-hybrid coating, an inorganic ZrTiO₄ film was deposited and sintered at 700 °C as the lower layer; and then a hybrid ZrTiO₄-PMMA film was deposited and sintered at 150 °C as the upper layer. The film surfaces were investigated using a field emission scanning electron microscope (SEM, Hitachi S-4800). The film adhesion to the substrate was also evaluated by the adhesive tape test, in accordance with ASTM D 3359.

The electrochemical corrosion behavior of the coated samples was studied in the simulated body fluid (SBF) proposed by Kokubo and Takadama [9], using a Gamry PC3/300 Potentiostat/Galvanostat/ZRA. A platinum wire and saturated calomel electrode (SCE) were used as the auxiliary and reference electrodes, respectively. After 6 h of immersion in the SBF, potentiodynamic polarization curves were obtained at a scan rate of 1 mVs⁻¹ from -0.1 V vs. the open circuit potential (*ocp*) to the transpassive potential. The sample surfaces after the polarization tests were observed by SEM to determine the failure mechanism of the films.

3. Results and discussion

The SEM micrograph of the two-layer coatings (Figs. 1a, 1b, and 1c) shows the development of relatively dense, smooth, high-coverage, uniform, and crack-free coatings. The surface of the inorganic coating is composed of particles/clusters of 30 nm to 250 nm in size with an average value of 80 nm, where the outermost layer of the coating consists of nanoparticles of about 20 nm in size [7]. However, the surface of the hybrid and inorganic-hybrid coatings is covered with relatively mono-sized nanoparticles of 20 nm (Fig. 1d). This difference of the surface feature is due to the higher firing temperature used for the preparation of the inorganic coating.

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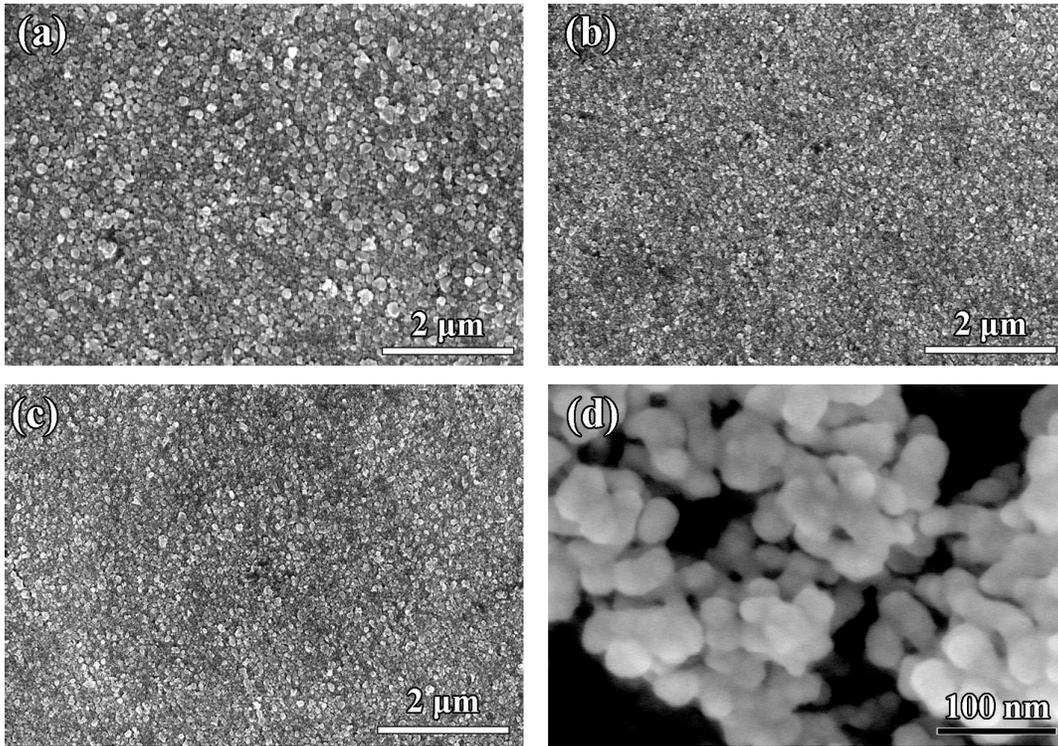


Fig. 1. Low-magnification SEM micrograph of the inorganic (a), hybrid (b), and inorganic–hybrid (c) coatings. High-magnification SEM micrograph of the hybrid coating (d).

In accordance with the SEM micrograph of the inorganic–hybrid coating after the tape test (Fig. 2a), the adhesion of this coating, similar to the inorganic one, is rated as 5B (i.e. a desirable adhesion), where the edge of the cuts is completely smooth and none of the squares of the lattice is detached. The formation of a covalent bond between the bottom layer and the substrate, assisted by the high-temperature sintering process, is responsible for the good adhesion [4]. Nonetheless, the adhesion of the hybrid coating is rated as 4B, since small flakes of the coating, albeit less than 5 % of the area, are detached at intersections (Fig. 2b). This is because of the low-temperature sintering process employed for the preparation of the

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hybrid coating, in which few covalent bonds are likely to be formed between the coating and substrate.

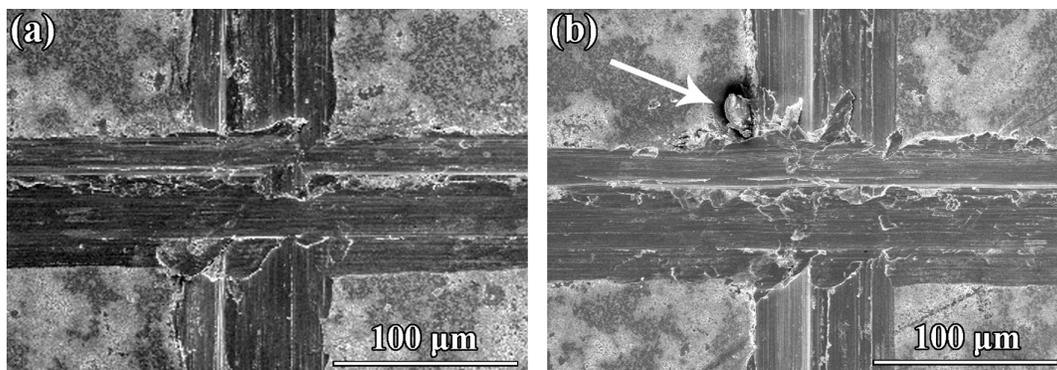


Fig. 2. SEM micrograph of the inorganic-hybrid (a) and hybrid (b) coatings after the adhesive tape test. The arrow in b signifies a detached flake of the hybrid film.

Fig. 3a presents the potentiodynamic polarization curve of the samples, suggesting that the corrosion protection of the substrate by the coatings, in terms of corrosion potential, corrosion current density, passivity, and passive potential range, increases in the order: inorganic < hybrid < inorganic-hybrid. Generally, sol-gel coated samples corrode through physical defects (holes) in the coating, allowing the electrolyte access to the metal surface [10]. Essentially, particulate sol-gel derived thin films contain nanosized porosities, since they are prepared by relatively low temperature sintering of nanoparticles. In the presence of PMMA, during sintering of the films, PMMA, as the low-melting point component, fills the porosity in the inorganic network, thereby making a denser barrier against electrochemical reactions, as reported elsewhere [4,11-13]. Therefore, the inferior corrosion resistance of the sample coated with the purely inorganic film is due to the absence of PMMA and the highly

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porous nature of the coating, which allows electrolyte access to the metal surface.

Nevertheless, it was found that the inorganic-hybrid coating exhibits the best corrosion protection, although the hybrid coating has two PMMA-containing layers and thereby probably a lower level of defects. To realize the origin of the improved corrosion protection by the inorganic-hybrid film, the samples were studied by SEM after the polarization test.

As indicated in Fig. 3b, the failure mechanism of the hybrid coating after the polarization test is described as debonding and delamination. Indeed, the penetration of the electrolyte through film's defects and hence the evolution of the electrochemical processes under the film promote blistering and delamination of the coating, as pointed out previously for other coatings [14]. On the other hand, based on SEM observations, no characteristic delamination was observed for the inorganic-hybrid coating (Fig. 3c). This results from the different adhesive strength of these coatings, as revealed above in Fig. 2. Thus, it is realized that the better adhesion of the inorganic-hybrid coating to the substrate is responsible for the higher corrosion resistance of the specimen coated with this film, compared with the hybrid coating.

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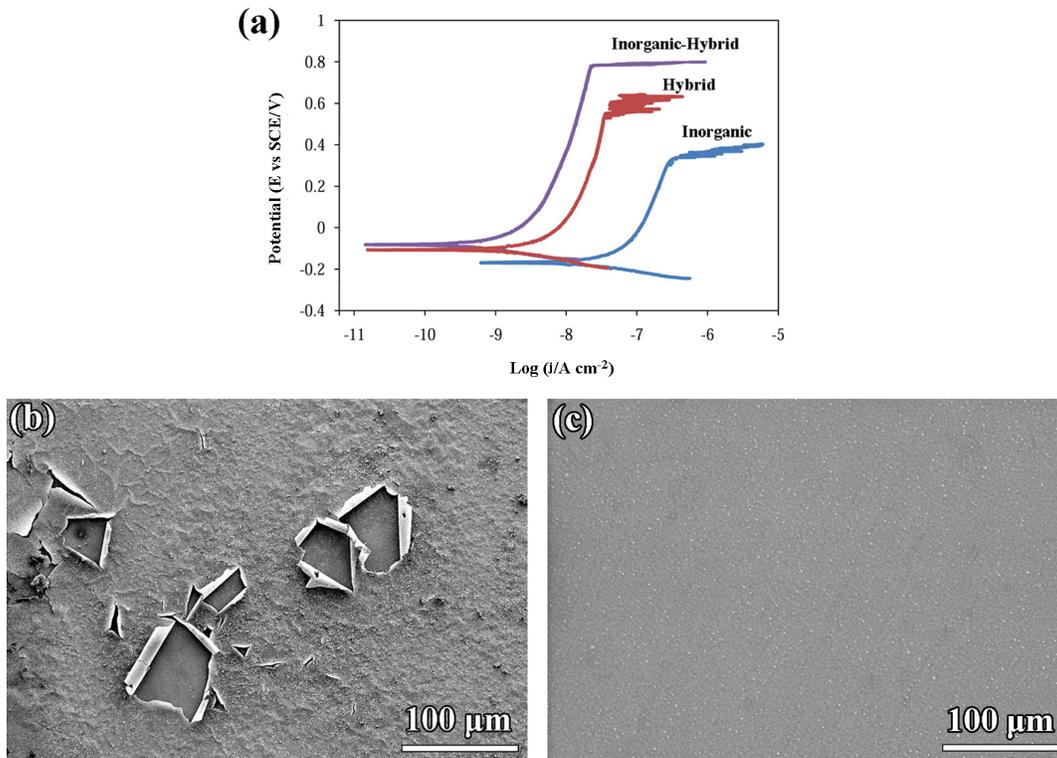


Fig. 3. Potentiodynamic polarization curves of the samples coated with the sol-gel coatings (a); and SEM micrograph of the hybrid (b) and inorganic-hybrid (c) coatings after the polarization test.

4. Conclusions

In this work, a double-layer coating, comprising ZrTiO₄ as the bottom layer and ZrTiO₄-PMMA as the top layer, was prepared by the sol-gel deposition method. According to potentiodynamic polarization experiments, this coating offers a better corrosion protection of the stainless steel substrate, compared to the purely inorganic ZrTiO₄ and hybrid ZrTiO₄-PMMA coatings. The reason is that the bottom inorganic layer provides better adhesion to the substrate and the organic component of the upper layer fills the physical defects in the film,

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thereby rendering the upper layer to be a denser, less porous barrier for blocking the electrochemical processes that otherwise would occur on the metal substrate.

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