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Influence of annealing temperature on the structural and anti-corrosion characteristics of sol–gel derived, spin-coated thin films

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Abstract

Recently, an aqueous particulate sol–gel process using metallic chloride precursors was introduced to synthesize zirconium titanate. In this paper, the effect of annealing temperature on the structural and corrosion protection characteristics of spin-coated thin films obtained from this sol–gel system was investigated. Based on scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and spectroscopic reflectometry studies, it was found that the flatness and thickness of the thin films were decreased by increasing the annealing temperature. Also, the corrosion protection of stainless steel AISI 316L provided by the prepared coatings, as analyzed by electrochemical potentiodynamic polarization experiments in a simulated body fluid, was improved in this order: 500 °C-annealed sample < 900 °C-annealed sample < 700 °C-annealed sample, attributed to a compromise between the defect density and the adhesion of the films to the substrate.

Keywords: A. Sol–gel processes; C. Corrosion; E. Biomedical applications

1. Introduction

Zirconium titanate, with the orthorhombic α-PbO_2 type structure, is one of the most promising ceramics for electronic, optical, catalytic, chemical, and biomedical applications [1–3]. One of the successful methods to produce powders of this material is the sol–gel approach, where the synthesized amorphous structures crystallize at temperatures considerably lower than those obtained by other routes [4–6]. High homogeneity (because of atomic-scale mixing), low sintering temperatures (owing to nano-sized particles), and coating simplicity of complex shapes are the typical advantages of this method.

Sol–gel synthesis can be performed by hydrolysis and condensation of inorganic salts or alkoxides. The procedures starting from the former precursors are categorized as the particulate sol–gel processes, in which nanoparticles are directly synthesized and then dispersed in the medium. Recently, a successful particulate sol–gel method using metallic chloride precursors was introduced to synthesize zirconium titanate [7]. The typical advantage of this method is the opportunity of using relatively low-cost chlorides, rather than expensive alkoxide precursors. In the literature, the structural and surface characteristics of monolayer and multilayer coatings obtained from the aforementioned nanoparticles uniformly-dispersed in an aqueous solution using carboxymethyl cellulose, after heat-treating at 700 °C, have been reported [8–11]. Moreover, the corrosion behavior and biocompatibility of stainless steels coated with the abovementioned coating, in the forms of pure oxide and hybrid, have been investigated [12,13].

This work evaluates the influence of annealing temperature (500, 700, and 900 °C) on the structural and corrosion protection

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properties of zirconium titanate nanoparticles and thin films prepared by the above-mentioned sol–gel process.

2. Experimental work

2.1. Coating preparation and characterization

An equal-molar solution of $ZrCl_4$ (Alfa Aesar, 99.5%) and $TiCl_4$ (Alfa Aesar, 99.99%) was prepared in deionized water, which led to a pH value of almost 1. Then, by the dropwise addition of a NaOH solution, the pH of the solution was increased to 7. The obtained hydrogels were rinsed several times with deionized water to remove chloride ion. After adding 2 wt% carboxymethyl cellulose (CMC, sodium salt, Alfa Aesar) as a dispersing agent [8], films were spin-coated on surface-prepared stainless steel AISI 316L substrates at 3000 rpm. The obtained films were then annealed at 500, 700, and 900 °C for 1 h.

To evaluate the variation of the powder particles constituting the films, the powder samples heat-treated with the same thermal cycles were studied by a transmission electron microscope (TEM, JEOL JEM-2100, 200 kV). The film surfaces were then studied by a field emission scanning electron microscope (SEM, Hitachi S-4800) and Veeco Multimode atomic force microscope (AFM, Bruker AXS). The film thickness was also measured by a NanoSpec 3000 system (Nanometrics, CA, USA).

2.2. Electrochemical corrosion characterization

The corrosion behavior of the coated samples was investigated in the simulated body fluid [14] with the pH value of 7.4. To do so, a platinum wire and saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. Anodic potentiodynamic polarization curves were obtained at a scan rate of $1\ \mathrm{m\ V\ s^{-1}}$ from -0.1 V vs. *ocp* to the transpassive potential. The specimen surfaces that failed

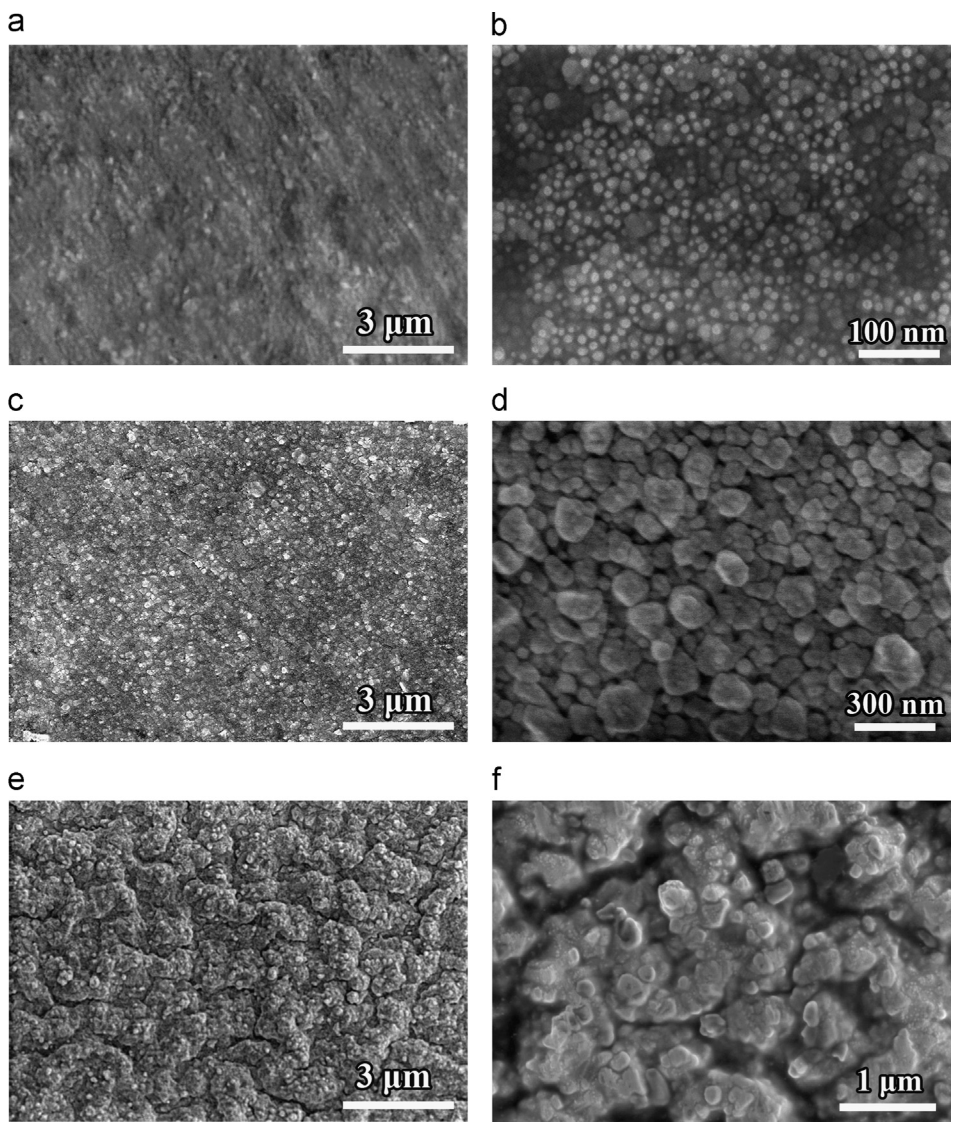

Fig. 1. SEM micrographs of the films annealed at 500 °C (a and b), 700 °C (c and d), and 900 °C (e and f) in two magnifications.