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ORIGINAL RESEARCH

Improvement of corrosion performance of 316L stainless steel via PVTMS/henna thin film

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Abstract Metallic materials are the most used materials as orthopedic or dental implants due to their excellent mechanical properties. However they are not able to create a natural bonding with the mineralized bone and occasionally suffer localized corrosion. This work describes the electrochemical behavior of a hybrid sol–gel thin film with the addition of green inhibitor. These films enhance the ability of the implant to make a union with the existing bone and improve its resistance to aggressive environment. An ethanol solution of the polymerized vinyltrimethoxysilane (PVTMS) was mixed with an aqueous solution of henna extract (*Lawsonia inermis*) and refluxed to give homogeneous sols. Nanostructure hybrid PVTMS/henna thin films were deposited on the stainless steel 316L by spin-coating. The morphology, composition and adhesion of hybrid sol–gel coatings have been examined by SEM, EDX and pull-off test, respectively. Addition of high additive concentrations (0.1%) did not disorganize the sol–gel network. Direct pull-off test recorded a mean coating-substrate bonding strength larger than 20.6 MPa for the hybrid sol–gel coating. The effect of henna extract, with various added concentrations from 0.012% to 0.1%, on the anticorrosion properties of sol–gel films have been characterized by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization tests in simulated body fluid (SBF) solution and has been compared to the bare metal. Henna extract additions (0.05%) have significantly increased the corrosion protection of the sol–gel thin film to higher than 90%. The *in vitro* bioactivity of prepared films indicates that hydroxyapatite nuclei can form and grow on the surface of the doped sol–gel thin films. The present study shows that due to their excellent anticorrosion

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properties, bioactivity and bonding strength to substrate, doped sol–gel thin films are practical hybrid films in biomedical applications.

1. Introduction

Glasses and ceramics are generally bioactive but they cannot bear stresses in service, on the other hand metals and alloys have a high mechanical strength, while they cannot bond to live tissues spontaneously. Titanium, cobalt alloys and 316L stainless steel have been wildly used for orthopedic surgical. Stainless steels are extensively used in industrial fields due to their high corrosion resistance, good mechanical properties and cheapness comparing to other metals. Despite the alloying elements, stainless steel has still the tendency to corrode in an aggressive environment, i.e., medium containing Cl^-. Therefore, it is important to further improve their corrosion resistance in these mediums [1,2]. Amongst the wide variety of corrosion protection techniques, corrosion inhibitors are considered to be very effective in preventing corrosion of metals and coatings. Organic–inorganic hybrid coatings prepared by the sol–gel process are considered as promising candidates for environmentally compliant surface protection. They represent a new class of covalently bonded materials, combining the excellent mechanical properties of the ceramic component with the flexibility, transparency and adhesion of organic substances. For corrosion protection purposes, polysiloxane-based hybrid materials are of particular interest due to their dense structure of siloxane nodes cross-linked with polymeric groups. The coatings not only ensure the adhesion between metal substrate and organic coatings but they also provide a thin, but efficient, barrier against oxygen diffusion to the metal interface [3,4]. Recently, silane coatings have attracted the attention of the nanotechnology industry because they provide a highly uniform, robust and reliable coating with lateral resolution on the nanometer scale [5–7]. Vinylalkoxysilanes are one of the potential starting materials for preparation of the hybrid, because they consist of vinyl and silan-functional alkoxy groups which are capable to form carbon–carbon and siloxane chains by polyaddition and hydrolytic polycondensation, respectively [8,9].

Although the originally developed sol–gel derived pure inorganic or hybrid organic–inorganic coating formulations have been introduced as promising treatments for long-term protection of various metals against atmospheric corrosion, their corrosion protection performance is limited when integrity of the coating is compromised. To improve corrosion protection properties of the coating when it is mechanically damaged, the incorporation of active corrosion inhibitors into the coating is needed. Organic corrosion inhibitors are promising candidates, as they appear to be compatible with hybrid coating material that can be loaded with inhibitors by adding the inhibitor into application solution prior to cross linking and film formation. Some authors have incorporated organic inhibitors with the purpose of obtaining a self-healing effect in organic–inorganic hybrid coatings [10–13]. The inhibitors incorporated in the film should migrate and precipitate producing a passivating effect where a defect was originated. The known hazardous effects of most synthetic organic inhibitors and the need to develop cheap, nontoxic and eco-friendly processes have now urged researchers to focus on the use of natural products. Natural organic compounds such as henna extract, are well-known corrosion inhibitors, they are biodegradable and do not contain heavy metals or other toxic compounds and are abundant in nature [14–16].

The objective of this work was the development of new hybrid coating designed to produce an effective barrier as well as an appropriate support for passivating agents. In the present study, hybrid organic–inorganic sols were developed from polymerization and hydrolytic polycondensation of vinyltrimethoxysilane (VTMS) and henna extract as a green inhibitor. The 316L stainless steel was chosen as a substrate due to its extensive use in many technological applications, consumer products and specifically in biomedical applications [17,18]. The research on application of coatings that reduce the release of the potentially toxic ions from stainless steel 316L to the human body and increase the corrosion resistance as well as bioactivity would be necessary. The structural features of the hybrid films with addition of henna extract were studied by SEM, EDX and UV–visible. The corrosion protection efficiency of the coatings on steel was studied in SBF using potentiodynamic polarization curves and electrochemical impedance spectroscopy.

2. Experimental methods

Hybrid thin film coatings were obtained from sols prepared through polymerization, hydrolysis and polycondensation of vinyltrimethoxysilane (VTMS, Merck) as precursor. The henna was incorporated as an aqueous solution of henna extract, (Gol Darou—Iran). VTMS was polymerized to 20-mers (PVTMS) with tertiary butyl peroxide as an initiator with refluxing for 2 h at 150 °C in flowing nitrogen [19,20]. An ethanol solution of PVTMS was mixed with an aqueous solution of henna extract, calcium acetate, and refluxed for 2 h at 120 °C. The molar ratio PVTMS/EtOH/H_2O/Ca:1/8/9/0.05 and a concentration of 2 vol% of polymers were used in sols.

Coatings were deposited by spin coating on stainless steel (AISI 316L) samples. The composition of the stainless steel 316L in wt% was listed as follows: 0.0356%C, 0.624%Si, 1.49%Mn, 0.0284%P, 0.005%S, 16.6%Cr, 1.99%Mo, 9.17%Ni, 0.0226%Al, 0.101%Co, 0.147%Cu, 0.002%Nb, 0.021%Ti, 0.079%V, 0.02%W and balanced Fe. AISI 316L samples (12 mm diameter and 4 mm thickness), steel specimens were mechanically ground with emery paper up to 1500 grit and then were polished with 0.3 μm alumina powder to approach mirror-like surface, then degreased, hand washed with distilled water, and rinsed in ethanol, being maintained in ethanol up to coating procedure. The coatings were obtained at room temperature using a spin rate of 4000 rpm, dried at room temperature for 24 h and heat treated for 72 h at 60 °C in electric furnace. One layer coating was prepared on AISI 316L.