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Full Length Article

Antimicrobial and biocorrosion-resistant MoO_3-SiO_2 nanocomposite coating prepared by double cathode glow discharge technique

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ABSTRACT

In this investigation, a MoO_3-SiO_2 nanocomposite coating was developed on a 316L stainless steel (SS) substrate by double-cathode glow discharge deposition. Chemical valence states, phase composition and microstructure features of the nanocomposite coating were studied using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was found that the nanocomposite coating was composed of a mixture of crystalline MoO_3 and amorphous phases, in which amorphous SiO_2 phase was embedded between the hexagonal-structured MoO_3 grains with an average grain size of ~8.4 nm. Nanoindentation and scratch tests, together with SEM and TEM observation of locally deformed regions, indicated that the nanocomposite coating exhibited high load-bearing capacity due to a combination of high hardness and good adhesion. Contact angle measurements suggested that the nanocomposite coating was more hydrophobic than uncoated 316L SS. The anti-bacterial activity of the MoO_3-SiO_2 nanocomposite coating against two bacterial strains (*E. coli* and *S. aureus*) was determined by the spread plate method. This showed that both bacterial strains exposed to the coating suffered a significant loss of viability. The influences of *sulfate-reducing bacteria* (*SRB*) on the electrochemical behavior of the MoO_3-SiO_2 nanocomposite coating in modified Postgate's C seawater (PCS) medium were investigated through potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The electrochemical tests revealed that the coating had a greater resistance to microbiologically influenced corrosion induced by *SRB* than uncoated 316L SS. This was corroborated by electrochemical testing (potentiodynamic polarization and EIS), in conjunction with SEM observations of the corroded surfaces.

1. Introduction

Microbiologically influenced corrosion (MIC), caused by the metabolic activities of microorganisms, is a grave challenge faced by metallic parts used in marine and soil environments [1–4]. Such a destructive attack accelerates the surface degradation of the material and compromises its structural integrity, often resulting in the premature failure of the components [5]. It was reported that nearly 20% of annual corrosion is associated with microbial activities on the metal surface, leading to the formation of biofilms induced by bacteria colony [6]. Among various types of microorganism that stimulate bio-corrosion of metals, *sulfate-reducing bacteria* (*SRB*), which belongs to a large group of sulfidogenic microorganisms, is commonly regarded as the dominant corrosive species responsible for bacterial corrosion of metals under anaerobic conditions. For instance, it has been estimated that more than 77% of the corrosion damage in the production of oil wells in the United States was induced by *SRB* [7]. In anoxic environments, such as those involving in oilfield water and offshore rigs, the metabolic energy for *SRB* growth results from reducing sulfate compounds to sulfides assisted with characteristic enzyme, accompanied by consuming hydrogen accumulated at the cathode. During the past few decades much research has been devoted to exploring the role of *SRB* in enhanced anaerobic corrosion. To date, several mechanisms have been proposed in an attempt to interpret *SRB*-induced MIC, for example the cathodic depolarisation theory

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[8], formation of iron/iron sulfide galvanic cells [9], and corrosion behavior of metabolic products [10,11].

Due to its combination of good corrosion resistance, desirable mechanical properties and low production cost, 316L austenitic stainless steel (SS) has become one of most popular materials used in a wide variety of engineering applications, such as chemical, petrochemical, marine structures and biomedicine uses, where a high corrosion resistance against aggressive media is required. Nevertheless, the protective oxide film formed naturally on its surface is extremely vulnerable to localized corrosion by chloride ions and *SRB*-induced sulphidation in marine environment [12]. This is because the constitution of the passive film changes from oxides/hydroxides into active compounds, e.g. sulfides due to *SRB* metabolism, promoting corrosion damage of stainless steels. Because the performance of a metal surface is affected by the formation of biofilm over its surface, the application of various antibacterial coatings, that provide a physical barrier preventing aggressive species from attacking the metallic surface or reducing microbe adhesion and growth, is considered to be a cost-effective way to combat MIC attack on the metallic materials [13]. In light of this, the development of an effective antibacterial agent in the coating is essential to maximize its efficacy in service.

The most commonly employed inorganic antimicrobials include metals (such as Ag, Zn, and Cu) and metal oxides (such as ZnO, CuO, and MgO). Percival [14] investigated the effect of pure molybdenum metal on the formation of biofilms. This was done through assessing biofilm viability and performing total cell counts by exposing the metal for 5 weeks in flowing water. It was found that compared with 304 stainless steel, the adhesion rate and biofilm development of bacteria were significantly reduced in the presence of the pure molybdenum in potable water. However, it is worth noting that metallic ions released from metal agents could bring many disadvantages, such as cytotoxicity on mammalian cells through adversely altering the intracellular functions. In addition, the antimicrobial activity of metals is often time-limited, resulting from a rapid release rate of metal ions [15], which limits their commercial applications in the biomedical engineering.

Because of their high stability and non-toxic nature, metal oxides have gained much attention in quest of efficient antibacterial additives to meet the fast-growing demand [16,17]. As an important class of transition metal oxide, MoO_3 has found applications in a wide range of areas, including optics, electrochemistry, electronics and sensors [18]. Molybdenum is an essential trace element in mammals and dietary molybdenum deficiency leads to increased incidence of esophageal cancer [19]. Several in vitro cytotoxicity tests have shown that MoO_3 exhibits better biocompatibility than silver nanoparticles [20]. Recent studies have also shown that MoO_3 nanoplates exhibit good antibacterial activity against various bacterial species [21]. Krishnamoorthy et al. [22] found that the antibacterial mechanism deriving from MoO_3 results from the interaction between the MoO_3 and bacteria, leading to the disruption of the bacterial cell wall and, thus, rapid cell death. Hence, MoO_3 has enormous potential as an antibacterial coating for prevention of health care associated with infections in hospitals.

Our initial attempt to synthesize MoO_3 coatings was carried out by two processes enabled by the double glow discharge plasma technique: (1) surface plasma oxidizing of a pre-deposited Mo coating and (2) reactive sputter deposition using a pure Mo target conducted in a flowing Ar + O_2 gas mixture. However, the resultant coatings were of low quality with a high density of defects, i.e., a small holes and cracks and poor bonding between the coating and the substrate. This is because the molybdenum oxides are not oxidation protective and easily sublimate. Suzuki et al. [23] found that siliconized molybdenum, using a molten salt, proved to be effective for avoiding pest oxidation that occurs in pure molybdenum at low temperatures. Moreover, SiO_2 nanoparticles often used as supporting materials, act as hosts for the immobilization of metal antibacterial agents, such as Ag [24] and Cu [25].

In this study, novel MoO_3-SiO_2 nanocomposite coating was fabricated onto 316L SS substrates by double-cathode glow discharge technique. The microstructure of the coating was characterized by X-ray photoelectron spectroscope (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The hardness, contact damage resistance and adhesion strength of coatings/substrate interface were evaluated by nano-indentation and scratching tests. The hydrophobicity of the coating was assessed by contact angle measurement using the sessile drop method. Different bacterial strains, including *Streptococcus aureus*, *Escherichia coli* and *SRB*, were used to examine the antibacterial activity of the coating. Moreover, various electrochemical analysis techniques were employed to investigate and ascertain the influence of *SRB* on the electrochemical behavior of the coating in modified Postgate's C seawater (PCS) medium. The results show that the newly developed MoO_3-SiO_2 nanocomposite coating has great potential for antibacterial applications involving harsh environment.

2. Experimental details

2.1. Preparation of MoO_3-SiO_2 nanocomposite coating

Disc shaped specimens, 30 mm × 3 mm, were used as the substrates. These were cut from a 316L stainless steel rod (solution-annealed and quenched). The nominal chemical composition of this steel in wt.% is: C, 0.029; Mn, 0.97; S, 0.003; P, 0.028; Si, 0.69; Cr, 16.28; Ni, 10.16; N, 0.015; Mo, 2.16; V, 0.11 and the balance, Fe. Samples were ground using a series of SiC emery papers and, then, polished with a 1 μm diamond paste to obtain a mirror surface finish. Subsequently, the substrates were ultrasonically cleaned in acetone, alcohol, distilled water and then dried. After drying in warm air, the sample was mounted on the substrate holder and transferred to the process chamber.

The MoO_3-SiO_2 nanocomposite coatings were prepared onto the polished 316L SS substrates using a double cathode glow discharge system. The base pressure in process chamber was evacuated to less than 5×10^{-4} Pa prior to deposition. Before the onset of deposition, both the substrate and target were etched with Ar ions for 20 min at a bias potential of −600 V and an Ar gas pressure of 20 Pa. A mixture of high-purity argon and oxygen used as the working gas was introduced into the process chamber via mass flow controllers. The working pressure during deposition was kept at 35 Pa with an Ar:O_2 flux ratio of 20:1. During sputtering deposition, a bias voltage of target and substrate electrodes was maintained at −850 V and −300 V, respectively; the distance between the target and the substrate holder was 15 mm; a deposition temperature of 750 °C and a deposition time of 3.5 h. The sputtering target, with a stoichiometric ratio of $Mo_{50}Si_{50}$, were prepared by sintering mixed Mo (99.99% purity) and Si (99.99% purity) powders in air at 900 °C for 60 min.

2.2. Microstructural characterization

The crystallographic structure of the as-deposited coating was characterized by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer using Cu-Kα radiation (λ = 1.54056 Å) (using a beam energy and current of 35 kV and 40 mA, respectively) over scanning 2θ angles that ranged from 20° to 90°, with a step rate of 0.05° per second. The composition and cross-sectional morphology of the coating were observed using a field emission scanning electron microscope (FESEM; Hitachi, S-4800, Japan) to which an