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Effect of surface topological structure and chemical modification of flame sprayed aluminum coatings on the colonization of *Cylindrotheca closterium* on their surfaces

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ABSTRACT

Biofouling is one of the major problems for the coatings used for protecting marine infrastructures during their long-term services. Regulation in surface structure and local chemistry is usually the key for adjusting antifouling performances of the coatings. In this study, flame sprayed multi-layered aluminum coatings with micropatterned surfaces were constructed and the effects of their surface structure and chemistry on the settlement of typical marine diatoms were investigated. Micropatterned topographical morphology of the coatings was constructed by employing steel mesh as a shielding plate during the coating deposition. A silicone elastomer layer for sealing and interconnection was further brush-coated on the micropatterned coatings. Additional surface modification was made using zwitterionic molecules via DOPA linkage. The surface-modified coatings resist effectively colonization of *Cylindrotheca closterium*. This is explained by the quantitative examination of a simplified conditioning layer that deteriorated adsorption of bovine calf serum proteins on the zwitterionic molecule-treated samples is revealed. The colonization behaviors of the marine diatoms are markedly influenced by the micropatterned topographical morphology. Either the surface micropatterning or the surface modification by zwitterionic molecules enhances antimicrobial ability of the coatings. However, the combined micropatterned structure and zwitterionic modification do not show synergistic effect. The results give insight into anti-corrosion/fouling applications of the modified aluminum coatings in the marine environment.

1. Introduction

As one of the persistent problems for marine infrastructures, biofouling causes huge negative impacts on marine economy [1,2]. Biofouling is a complex process in which the settlement of diatoms plays an important role in deciding the following colonization of other fouling species, such as barnacles, bryozoans and polychaetes [3]. In response to the vast demands for antifouling techniques, a variety of antifouling systems were developed. Yet, none of the available antifouling systems, either toxic antifouling paints or environment-friendly fouling-release coatings, has the capability of effectively preventing the settlement of marine diatoms [4]. Hence, emerging ongoing research efforts have been devoted to developing diatom-resistant systems for marine applications.

To control the settlement of marine diatoms, it is essential to inspect the microenvironmental variables that crucially determine the fate of the diatoms contacting the surfaces of the marine materials. Surface topological structure [3,5–7] and local chemistry [8,9] are the two major factors among those that have been extensively examined. The surface topographies with varying geometry like meshes, pillars, grooves, bumps or holes were fabricated by mimicking the natural topographies of marine organisms [10,11]. Recent studies show that antifouling properties of the artificial structures do not follow a linear relationship with the size of the topographical feature [12,13]. Available studies on the influence of local chemistry of a submerged surface, which is another important factor mediating the settlement of diatoms, are usually based on the use of polymeric materials. Polyethylene glycol (PEG) modified surfaces have shown a competent restriction against protein adsorption, in turn resisting effectively the settlement of marine fouling organisms [14]. However, the intrinsic property limitation is a major hurdle for long term application of the PEG modified surfaces. Recently,

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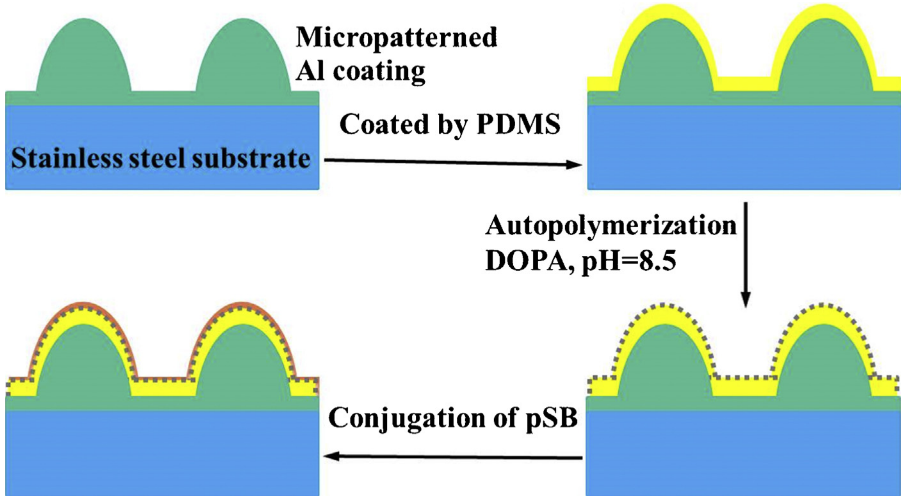

Fig. 1. Schematic depiction showing the construction of the micropatterned Al coatings with additional surface modification.

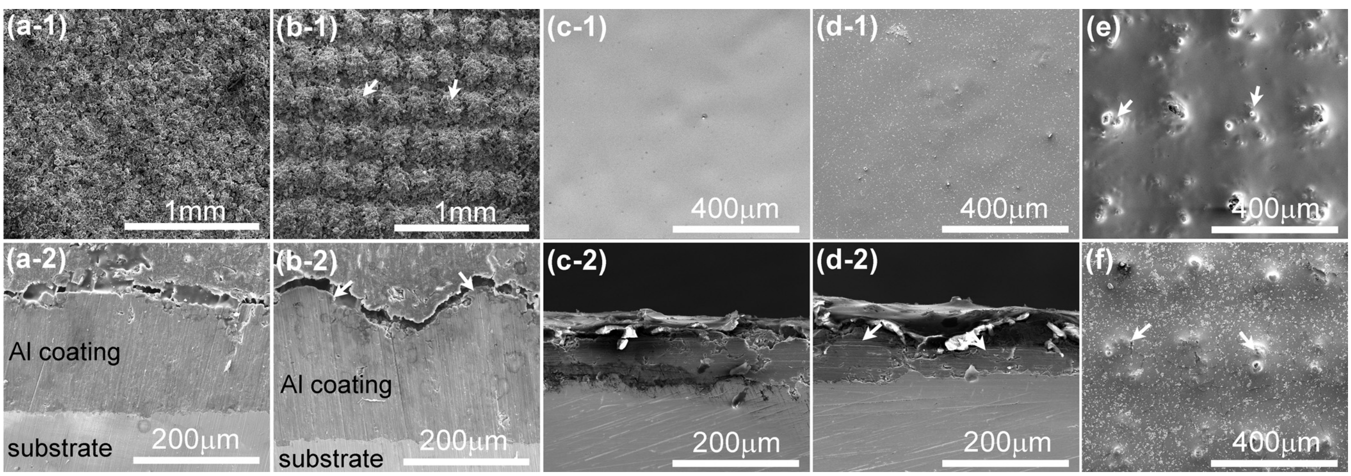

Fig. 2. SEM images of (a) the flat Al coating (a-1: surface view, and a-2: cross -sectional view), (b) the micropatterned Al (b-1: surface view, and b-2: cross -sectional view), (c) the flat Al-PDMS coating sample (c-1: surface view, and c-2: cross-sectional view), (d) the micropatterned Al-PDMS coating sample (d-1: surface view, and d-2: cross-sectional view), (e) the flat Al-PDMS-DOPA-pSB coating sample, and (f) the micropatterned Al-PDMS-DOPA-pSB coating sample. The white arrows point to typical asperities of the patterned aluminum coating.

zwitterionic molecules, such as [2-(Methacryloyloxy) ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide (pSB) which is neutrally charged in seawater, have been identified effective in reducing adsorption of proteins [15–18]. Effect of the zwitterionic molecules on protein absorption was well demonstrated. However, the mechanism of the resistance of zwitterionic molecules to the settling of marine diatoms keeps unknown. Alterations in either surface topography or surface chemistry have shown a certain success in preventing marine diatom settlement. Appropriate approaches for attaining the alterations are still lacking. Further studies are necessary for developing effective foul-resistant topographies. In addition, several studies have implied that an effective antifouling solution would require multiple physico-chemical properties of a surface [19,20]. Quantitative models involving the combined effects of both surface topography and chemistry on the adhesion tendency of *Ulva* spores have been reported [21,22]. However, to the best knowledge of the authors, there are so far few research publications focusing on the combined effect of surface topography and chemistry on diatom behaviors. This study aims to construct a new aluminum-based coating system with a multi-layered structure for enhanced antifouling performances. The surface micro-topological structure of the coatings was produced by surface micropatterning during flame spraying and further chemical modification was made by depositing a silicone elastomer layer and following zwitterionic molecules via DOPA linkage. The effect of the combined effect of micro-topography (micropattern) and chemical cue (pSB-functionalization) on the settlement of the typical marine diatom *Cylindrotheca closterium* was investigated and elucidated.

2. Experimental setup

2.1. Sample preparation

Commercial pure aluminum powder with the size range of +15 to 45 μm (Beijing General Research Institute of Mining & Metallurgy, China) was used as the starting feedstock. The Sylgard 184 silicone elastomer (Dow Corning, USA) and the zwitterionic molecule [2-(Methacryloyloxy) ethyl]-dimethyl-(3-sulfopropyl)-ammonium hydroxide (pSB) and 3,4-dihydroxyphenylalanine (DOPA) (Sigma-Aldrich, USA) were used as received. Stainless steel (316 L) plates with the dimension of 20 × 20 × 1.5 mm were used as the substrates. The Al coatings were deposited by flame spray using the FS-4 multi-functional powder flame spray torch (Wuhan Research Institute of Materials Protection, China). Acetylene was used as the fuel gas with a flow rate of 1.5 Nm^3/hr and working

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