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Fabricating protective silica/PMDS composite films for Mg alloy: Correlating bulk silica reinforcement with barrier performance

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ABSTRACT

Despite numerous innovative research ideas and advances in coating manufacturing and testing, the phenomenon surrounding cathodic blistering in primers and top-coats is still unclear, especially in hypersaline media. In this work, we have discussed a new silica/polydimethylsiloxane synthetic route for Mg coating, and have also probed the fate of ionic/molecular migration within coating variants with varying crosslink densities in saturated NaCl solution. Corrosion resistance is observed to increase with silica content, and the optimum amount of tetra alkoxide needed to prepare an efficient corrosion resistant coating has been established. Improved corrosion resistance is attributed to the compact coating network with reticulate internal ceramic structures as well as the hydrophobic character of their polydimethylsiloxane (PDMS) moiety. These protective silica-modified composite coating materials were synthesized using two end-capped PDMS molecules bearing reactive groups, epoxypropoxypropyl terminated PDMS and aminopropyl terminated PDMS, added in a fixed ratio, in combination with tetraethoxysilane. Their barrier properties on Mg alloy were examined by electrochemical impedance spectroscopy while the extent of coating degradation and blistering were probed using scanning electron microscopy after chloride-induced treatment.

1. Introduction

The use of protective coatings has been widely explored as an efficient mitigation technique against metal corrosion [1]. A number of innovative research ideas have led to the developments some interesting primers and top-coats in recent years, with a combination of organic-inorganic hybrid precursors as an exquisite option [2]. Related works have witnessed the use of organosiloxanes (e.g. polydimethylsiloxanes, PDMS) as coupling adhesion agents between organic and inorganic materials for coating applications [3–6]. Precursors with hydrolysable alkoxysilyl chemical groups readily react to form metallosiloxane (M—O—Si) bonds that promote enhanced coating/metal interfacial adhesion, bulk rigidity, corrosion resistance, etc. within inorganic phases. Those with organic moieties foster improved surface and mechanical properties (e.g. hydrophobicity, flexibility, etc.) [1]. Consolidants composed of tetraethoxysilane (TEOS) and PDMS are common among precursors for numerous protective materials due to their reduced viscosity and stable silica (Si—O—Si) networks [7]. However, some protective silica-type coatings synthesized from this class of precursors are susceptible to bulk shrinkages upon ageing. This poses significant challenge on their barrier properties as uptake of corrosion species (oxygen, water, etc.) is intensified due to the presence of inherent pores within the coatings [1]. Rapid curing of new coating materials also induces cracks which are in turn propagated by influences of solvent evaporation and capillary forces during associated condensation reaction stages [2]. To suppress the propagation of these cracks within coatings, attention has been drawn to various chemical modification processes involved in strengthening the internal bonding networks inherent within internal coating structures, with and without the encapsulation of appropriate nanofillers. Coating modification by introduction of a second compact phase further improves mechanical strength and toughness, and depending on the crosslinking densities within coating networks, bulk reinforcement leads to superior corrosion resistance [8]. Crosslinking between neighboring chemical species and units within these organic-inorganic hybrid systems results in dense and closely-packed coating structures with superior barrier properties, hence ionic migration is appreciably delayed. In line with Mayne hypothesis of ionic migration via coatings, since rate of percolation is electronically (and kinetically) controlled, the nature of charge is predetermined by the polymer structure within the coating [6]. However, ionic transportation processes through coatings become more complex when the anode and cathode co-exist within a single interface [6]. The design and fabrication of reticulate and highly crosslinked PDMS/amine-cured hybrid resin structures, using more than one compatible

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precursor is needed [1]. Recently, some authors have reported on the corrosion barrier performance of some reinforced PDMS derived hybrid coating systems for metal substrates in various media. Surca et al. [2] have investigated the protective performance of polyhedral oligomeric silsesquioxane (POSS)/bis-(3-(3-(3-triethoxysilyl)propyl)thioureido) propyl terminated PDMS coatings on AA 2024. Authors linked the enhanced corrosion and mechanical stabilities of this hybrid coating composite to its epoxy and POSS contents. Corrosion resistance of this coating in 0.5 M NaCl was also attributed to its tightly packed coating structure in the presence of these organic additives; Raman imaging with a detection range of 150 lines per image was deployed to ascertain their molecular distributions within the coating matrix. Protective coatings prepared from the epoxy ring-opening reactions involving amino-terminated PDMS curing agent have been widely reported in the literature [9–12]. Rauter et al. [10] have reported the reaction between three aminopropyl-terminated siloxane curing agents ((3-aminopropyl) trimethoxysilane, aminopropyl-heptaisooctyl POSS and aminopropyl-terminated PDMS) and (3-glycidoxypropyl)trimethoxysilane. Coating synthesis was performed with acetic acid catalyst, and at the end of the test, the resultant coatings from each amine hardener was applied to AA 2024 alloy via dip coating technique and cured at 150 °C. The degree of corrosion resistance of each coating variant was measured by potentiodynamic polarisation technique, and their resistance to corrosion was linked with the nature of their hydrophobic PDMS surfaces. Wu et al. [11] have investigated the barrier properties of a protective coating synthesized from TEOS, 3-glycidoxypropyltrimethoxysilane with an amino-terminated siloxane compound for AA 2024-T3 and AA 6061-T6. This hybrid polymer film was coated on aluminum alloy and tested for its thermal and barrier properties using potentiodynamic polarisation technique. The resistance of the film against Al corrosion was attributed to its dense silica content. Eduok et al. [12] have studied the anticorrosion/antifouling potentials of a coating synthesized from TEOS in combination with 3-glycidoxypropyltrimethoxysilane and 6–7% (aminopropyl methyl siloxane)-dimethylsiloxane copolymer. Modified with Zn-based corrosion inhibitor pigments, the corrosion resistance of this coating on mild steel was enhanced due to its compact internal structure upon encapsulation of these inorganic additives. The coating materials, also modified with *Bacillus licheniformis* endospores, were observed to significantly reduce marine biofouling due to the secretion of antibiotic γ-polyglutamate from the bacterial biofilm. The fabrication of PDMS coatings modified with nanofillers have also witnessed series of developments and anticorrosion applications in recent times [13–16]. These nanoscale materials have played significant roles in enhancing the corrosion resistance of silica coatings by reducing bulk porosity and narrowing diffusion pathways. Several of them have been reported within nanocomposite coatings: Epoxy/ZnO on cold-rolled mild steel [13], perfluorodecyltrichlorosilane/ZnO on Q235 steel [14], and Epoxy resin/SiO_2 on cold-rolled mild steel [15]. To the best of our knowledge, the application of reinforced silica/PDMS hybrid coatings for Mg protection is scare [16], though some related works on other reinforced hybrid coatings are detailed in the literature [17–21]. Why Mg alloy? With the growing interest and demand for weight-saving materials in automobile, electronic and aeronautics applications, Mg alloys have been identified as candidate materials with favorable strength-to-weight ratio [22]. In the past decades, some structural components and mechanical parts were successfully fabricated from Mg, but their multifunctional potentials have also been marred by low corrosion resistance [22,23]. With its significantly robust mechanical strengths as the lightest structural metal, Mg has potentials for multiple mechanical applications and could be further harnessed for suitable applications if coated with appropriate protective films.

In spite of the numerous years of coating testing applications, failure mechanisms in protective coatings are still obscure and there is no explicit understanding of the modes of ionic migration across underfilms during coating disbonding from metal surfaces (particularly when involving Mg alloy) [6]. In this work, we have developed predictive coating models for studying the effect of changing silica content on coating performance. TEOS is deployed as the silica source within this highly crosslinked sol–gel derived hybrid coating network. Reinforcement towards improved barrier protection is achieved by varying the moles of TEOS needed to synthesize a protective material with significantly enhanced cohesion/adhesion between coating layers on Mg surface. The acid-catalyzed hydrolysis-condensation of TEOS is accompanied by a ring-opening type reaction between two end-capped PDMS molecules bearing reactive groups; di-epoxy/diamine chemical groups, respectively, added in a fixed ratio. The PDMS and TEOS precursors ascribe a synergy of unique physical properties to the hybrid coating molecular network. For instance, while the hydrophobic character of the PDMS chains induces water repellency, the compact internal silica network serves as an auto-barrier against ionic migration [24–27]. We have undergone in-depth investigations of the degree of corrosion resistance of resultant silica/PDMS hybrid coating variants on Mg alloy in 4 wt% NaCl medium. The impact of corrosive ionic ingression on the metal substrate via each coating has also been assessed after prolong exposure to the saline electrolyte. In the end, limited molecular/ionic flow paths within superior coatings aided in proposing possible corrosion protection mechanisms from the trend of results obtained from surface analyses and electrochemical corrosion studies. While scanning electron microscopy (SEM) was used in examining the effect of the colloidal silica content on the barrier characteristics of every coating model, the hydrophobic nature of each coating surface was quantified by contact angle goniometry. These surface properties were examined prior to and after exposure to the saline electrolyte at 30 °C.

2. Experimental procedures

2.1. Materials and reagents

A test metal substrate is a Mg alloy (N5018-3 Mg-X-Ca grade) with the chemical composition: Zn (1%), Ca (0.2%), Nd (0.5%), Si (0.01%), Mn (0.01%), Fe (0.02%), Mg (balance). Several 10 cm × 10 cm × 1 cm coupons were cut out from a large metallic mass; they were precleaned, sonicated in 99.9% ethanol (Sigma-Aldrich) and treated with 10% NaOH (Sigma-Aldrich). They were later stored in an air-free desiccator before coating application. The coating variants deployed within this work were prepared from as-received reagents without further purification. The three main coating precursors: 98% TEOS (molar mass: 208.329 g/mol) epoxypropoxypropyl terminated PDMS (8–11 cSt; > 97% purity) and aminopropyl terminated PDMS (10–15 cSt; 95–100% purity) purchased from Sigma-Aldrich and GELEST, respectively. Propanol (*n*-PrOH; 99.5% purity) and acetic acid (AcOH; 99.9% purity) were also obtained from Sigma Aldrich and used as diluent and catalyst, respectively, for the sol–gel reaction.

2.2. Synthesis of the hybrid composite coatings

The preparation procedures of this coating model are consistent with a sol–gel type process. We have carefully varied the amounts of TEOS needed to synthesize stable coating structures in an attempt to correlate internal structural reinforcement with corrosion resistant performance. Their net performances will significantly depend on inherent inter-phase interaction and compactness of the inorganic domains as well as the extent of crosslinking between inorganic silica (Si—O—Si) networks [28,29]. In line with this, the presented synthesis protocol in Fig. 1 takes into account the volume concentrations of TEOS at the initial reaction stages. This precursor, measured into five different beakers (0.5 to 2 ml), was allowed to undergo simultaneous hydrolysis/condensation reactions in the presence premixed water and AcOH solution (1:1 ratio). PrOH acted as a diluent in dissolving the colloidal sol in a premixed suspension of two end-capped PDMS molecules (Epoxy-PDMS and Amino-PDMS) added in a 1:1 ratio at 45 °C.

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