Preparation of Superhydrophobic Coatings on Zinc as Effective Corrosion Barriers

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ABSTRACT Stable superhydrophobic films with a contact angle of $151 \pm 2°$ were prepared on zinc substrates by a simple immersion technique into a methanol solution of hydrolyzed $1H,1H,2H,2H$-perfluorooctyltrichlorosilane [$CF_3(CF_2)_5(CH_2)_2SiCl_3$, PFTS] for 5 days at room temperature followed by a short annealing at 130 °C in air for 1 h. The superhydrophobic film provides an effective corrosion-resistant coating for the zinc interface when immersed in an aqueous solution of sodium chloride (3 % NaCl) for up to 29 days. The corrosion process was investigated by following the change of the water contact angle over time and by electrochemical means. The results are compared to those of unprotected zinc interfaces.

KEYWORDS: superhydrophobic coating • zinc • corrosion inhibition

1. INTRODUCTION

Zinc coating is one of the most commonly used ways of protecting steel against corrosion processes (1). The cathodic protective nature of zinc-coated or galvanized steel on coating defects is linked to the formation of a thick and porous film of zinc corrosion products, which influence the reduction mechanisms and the rate of oxygen reduction on the zinc interface. It is generally established that, in the pH range 4−11, oxygen reduction is the major cathodic reaction next to anodic dissolution of zinc (2, 3). To extend the lifetime of steel constructions, big efforts have been put into the optimization of zinc-coating composites (4, 5) and the improvement of the performance of the zinc coating. Phosphate conversion coatings (6−8), passivation treatments based on silanes (9), polymer materials (10, 11), and the formation of insoluble organometallic compounds using organic chelation materials (12) are some examples of zinc protective layers. The formation of self-assembled monolayers of water-repelling molecules is an attractive alternative. It can serve as an effective barrier to keep water, moisture, and atmospheric oxygen from reaching the base metal. In addition, it acts as a dielectric film that electrically insulates zinc, slowing down the process of corrosion of the coating. Long-chain aliphatic acid monolayers (e.g., phosphonic and diphosphonic compounds) linked to metal and metal oxide/hydroxide surfaces have been exploited as corrosion-resistant coatings (13). More recently, superhy-drophobic films (surfaces with a water contact angle higher than 150 °C) on copper and aluminum have been successfully used as corrosion inhibitors (14, 15). In a recent report by some of us, it was found that superhydrophobic coatings on copper and galvanized iron substrates can be easily prepared by a simple solution-immersion process (16, 17). Here, we have applied the same technique to form a superhydrophobic film on a metallic zinc foil and studied the corrosion behavior in a 3 % NaCl aqueous solution.

2. EXPERIMENTAL SECTION

Materials. Zinc foil (99.9 %, 0.25 mm thick), $1H,1H,2H,2H$-perfluorooctyltrichlorosilane [$CF_3(CF_2)_5(CH_2)_2SiCl_3$, PFTS], methanol, ethanol, isopropyl alcohol, and sodium chloride were obtained from Aldrich and used without further purification.

Preparation of Superhydrophobic Zinc Interfaces. The zinc substrates (1 cm × 1 cm) were first cleaned ultrasonically in ethanol, isopropyl alcohol, and distilled water (5 min, two times each). The clean specimens were dried under a stream of nitrogen. Subsequently, a methanol solution of PFTS was hydrolyzed by the addition of a 3-fold molar excess of water at room temperature. The dried specimens were immersed in the hydrolyzed PFTS solution for 5 days at room temperature, then rinsed with ethanol and water, and finally heated at 130 °C in air for 1 h.

Instrumentation. Linear sweep voltammetry (LSV) was performed using an Autolab potentiostat 30 (Eco Chemie, Utrecht, The Netherlands). The zinc substrates were sealed against the bottom of a single-compartment electrochemical cell ($V = 5$ mL) by means of a rubber O-ring (the electrical contact was made to a copper plate through the zinc). A platinum sheet and a AgCl-modified silver wire were used as the counter and reference electrodes, respectively. LSV tests were performed by scanning the potential at a rate of 1 mV s^{-1}. The cathodic and anodic fields were recorded separately.

Contact-angle measurements were measured using deionized water using a remote computer-controlled goniometer system (DIGIFROP by GBX, France) under static conditions. The ac-

FIGURE 1. Schematic illustration of the formation of the superhydrophobic coating on the zinc interface.

FIGURE 2. SEM images of zinc substrates before (A) and after coating with the perfluorosilane polymer (B). The insets correspond to water contact angles (droplet volume = 6 μL) and zoom-in modified zinc.

curacy is ±2°. All measurements were made in an ambient atmosphere at room temperature.

Scanning electron microscopy (SEM) images were obtained using an electron microscope ULTRA 55 (Carl Zeiss, France) equipped with a thermal field emission emitter, three different detectors (EsB detector with a filter grid, a high-efficiency In-lens SE detector, an Everhart-Thornley secondary electron detector), and an energy-dispersive X-ray analysis device (EDX analysis).

3. RESULTS AND DISCUSSION

The preparation of superhydrophobic zinc interfaces is based on the hydrolysis of perfluorooctyltrichlorosilane molecules. The hydrolysis reaction of Si—Cl into Si—OH bonds generates HCl and results in a pH decrease (pH = 1−2 of the hydrolyzed PFTS solution) (17). Zinc is catalytically oxidized in the acidic medium to yield next to semiconducting zinc oxide (ZnO), simonkolleite [$Zn_5(OH)_8Cl_2*H_2O$], and zinc hydroxide [$Zn(OH)_2$] (2). Figure 1 illustrates a possible reaction mechanism for the reaction under investigation. First, hydrolysis of the trichlorosilane precursor takes places, followed by interfacial condensation and polymerization reactions occurring between the hydroxyl groups of zinc and the silanol groups, resulting in a covalent linkage between the organic layer and zinc. The possibility of silane polymerization in solution followed by precipitation onto the surface can be excluded because superhydrophobic interfaces cannot be formed on any interface of choice (e.g., silicon oxide, steel, etc.) using the same reaction conditions

as those employed for zinc (19). Figure 2 displays SEM images of the zinc interface before and after coating with the superhydrophobic polymer. The clean zinc substrate is relatively smooth. After immersion of the clean zinc substrate in the hydrolyzed PFTS solution for 5 days, the roughness of the surface largely increased. Contact-angle measurements were used to follow the changes in the surface wetting properties. It is well-known that the wettability of a solid depends on both the roughness and the chemical composition of the surface. The unmodified and clean zinc substrate displays a water contact angle of 64 ± 2°. The chemically modified zinc interface exhibits a maximum water contact-angle value of 151 ± 2° after 5 days of immersion in the hydrolyzed PFTS solution (insets in Figure 2). The successful formation of a superhydrophobic interface is believed to be an interplay between the presence of fluorine, the most effective element for lowering the surface free energy because of its small atomic radius and the largest electronegativity among all atoms, and the roughness of the oxidized zinc interface (18). The success of the surface modification was furthermore. confirmed by EDX analysis (spectrum not shown). The surface consists mainly of Zn (61.67 wt %), O (3.01 wt %), Si (0.87 wt %), F (27.12 wt %), C (5.37 wt %), and Cl (1.96 wt %) elements. The presence of Cl in the EDX spectrum suggests that not all of the Si—Cl bonds are hydrolyzed.
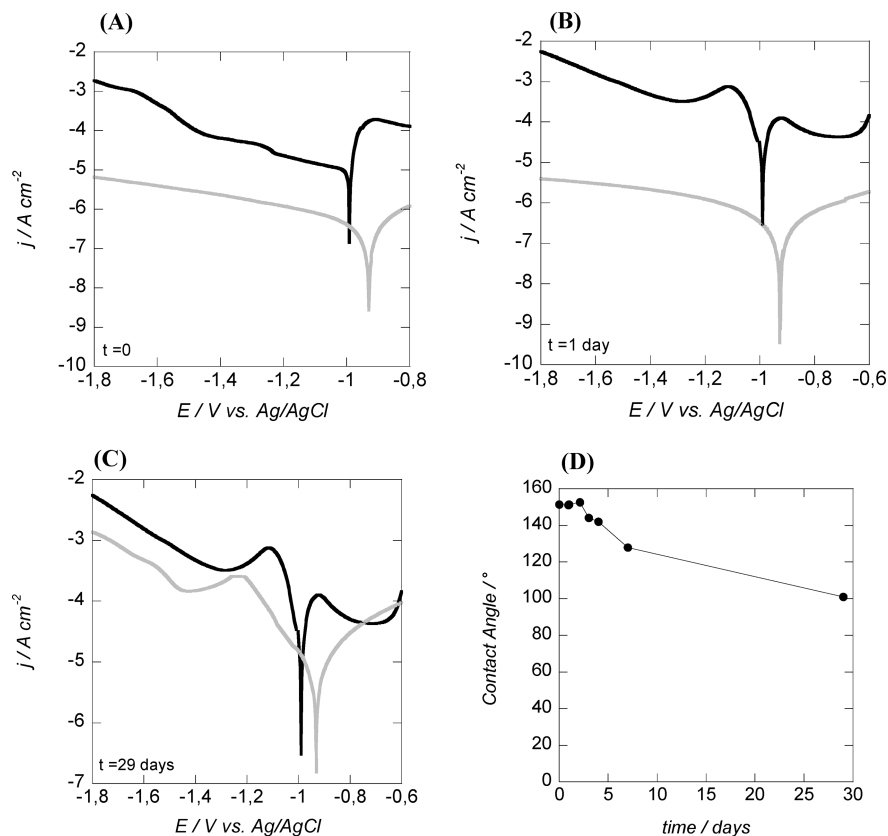
FIGURE 3. Potentiodynamic polarization curves of an unmodified zinc substrate (black line) and a zinc substrate coated with a superhydrophobic film (gray line) immediately after immersion (A) and after 1 day (B) and 29 days (C) in a 3% NaCl aqueous solution. (D) Change of the contact angle over time of the zinc substrate coated with a superhydrophobic film upon immersion in a 3% NaCl aqueous solution.

The superhydrophobic film on the zinc interface should form a successful barrier against moisture/water diffusion through the perfluorooctyl layer to the underlying zinc interface, where corrosion can be initiated. Prior to the investigation of the corrosion behavior of zinc substrates coated with superhydrophobic films, the stability of the coating in acidic and alkaline pH was studied. Superhydrophobic zinc substrates were immersed in 0.1 M H_2SO_4 and 0.1 M NaOH aqueous solutions, and the contact angle was measured at room temperature. No change in the water contact angle was observed over a time period of 24 h, suggesting a good chemical stability of the superhydrophobic coating.

The effect of the superhydrophobic dielectric layer on the corrosion behavior of zinc was investigated using LSV in parallel with contact-angle measurements. Figure 3 shows the anodic and cathodic polarization curves of freshly prepared zinc substrates without and with a superhydrophobic coating and after 1 and 29 days of immersion in a 3% NaCl aqueous solution. In a neutral chloride solution, oxygen reduction is the major cathodic reaction on untreated zinc. Oxygen is reduced in two distinct two-electron steps (eq 1) (2), characterized by two plateaus in the potential range from -1.0 to -1.5 V. At potentials lower than -1.5 V, the reduction of water becomes dominant, leading to a progressive increase in the current density (eq 2).

$$O_2 + H_2O + 2e \rightarrow HO_2^- + OH^-$$
$$HO_2^- + H_2O + 2e \rightarrow 3OH^-$$
(1)

$$2H_2O + 2e \rightarrow 2OH^- + H_2$$
(2)
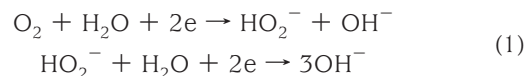
The positive effect of the presence of the superhydrophobic layer on zinc is seen by (i) the anodically shifted corrosion potential ($E_{corr} = -0.93$ V vs Ag/AgCl), as compared to $E_{corr} = -0.99$ V vs Ag/AgCl for the unmodified zinc and (ii) the decrease of the anodic and cathodic currents due to a restricted supply of oxygen and water-limiting oxygen and water reduction (eqs 1 and 2). Consequently, the corrosion currents are largely reduced to $j_{corr} = 1.62 \times 10^{-7}$ A cm^{-2} for a zinc substrate coated with a superhydrophobic film, while $j_{corr} = 1.09 \times 10^{-5}$ A cm^{-2} is obtained for a noncoated zinc substrate. The anodic dissolution current does not increase sharply with overpotential as in the case of pure zinc, indicating that the dissolution of zinc and the transport of Cl$^-$ are strongly restricted by the superhydrophobic film. The stability of the superhydrophobic film was tested by recording LSV experiments after immersion of the coated interface for 1−29 days in a 3% NaCl aqueous solution. In the case of unprotected zinc, increased cathodic and decreased anodic currents are detected after immersion of the interface for only 1 day (Figure 3B). The increase in the current densities as a function of time of nonmodified zinc is, at first sight, unusual. Indeed, as the surface becomes
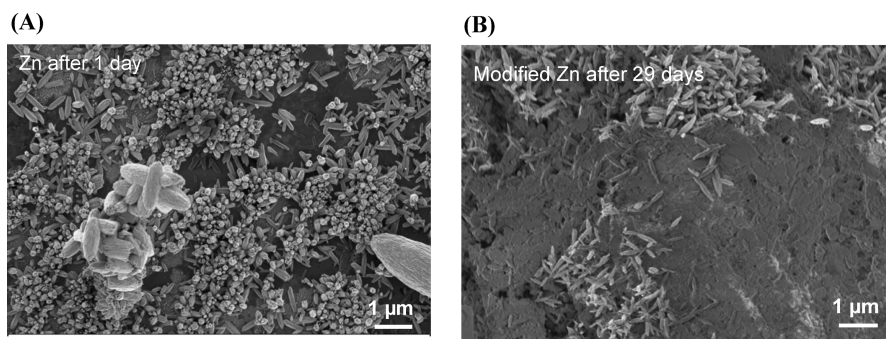
FIGURE 4. SEM images of unmodified zinc (A) and zinc coated with a superhydrophobic film (B) after immersion in a 3% NaCl aqueous solution for 1 and 29 days, respectively.

covered by corrosion products, a partial blocking of the surface could be expected and, hence, smaller current densities. A similar behavior was observed by Yadav et al. (2), who postulates two possibilities for the increase in the current density: (i) increased surface roughness and (ii) a change of the mode of oxygen reduction. The superhydrophobic interface, on the other hand, showed no change in the potentiodynamic polarization curve after 1 day. It took about 29 days for a significant change in the anodic and cathodic polarization curves to be recorded (Figure 3C). The electrochemical results are corroborated with the change in the water contact angle (Figure 3D). After 5 days of immersion of the zinc surface coated with a superhydrophobic film in a 3% NaCl aqueous solution, the contact angle decreased to 140° and reached ~100° after 29 days. Furthermore, EDX analysis of the zinc substrate coated with a superhydrophobic layer after 29 days of immersion in 3% NaCl consisted mainly of Zn (73.17 wt %), O (15.17 wt %), Si (1.57 wt %), F (7.58 wt %), C (1.38 wt %), and Cl (0.58 wt %), where the O content has increased and the F amount has decreased, compared to uncorroded modified zinc. This indicates a degradation of the perfluoroalkyl chain, enabling the penetration of water to the underlying zinc interface where corrosion is initiated. Finally, SEM analysis of an uncoated zinc substrate after immersion in a 3% NaCl aqueous solution for 1 day shows the formation of a dense film of ZnO structures all over the surface (Figure 4A). These structures are only visible in certain areas on the superhydrophobic zinc interface immersed in the same solution for 29 days (Figure 4B). This clearly indicates that the reduced contact area between the superhydrophobic surface and water restricts the corrosion process. However, the presence of defects in the superhydrophobic layer may be responsible of the observed behavior.

4. CONCLUSION

We showed here the possibility for the formation of a superhydrophobic film on a metallic zinc interface using a simple solution immersion technique. The aim of this work was to evaluate the chemical stability of zinc interfaces covered with a thick superhydrophobic film when immersed in alkaline and acidic media as well as in a strongly saline aqueous solution (3% NaCl). The modified interface proved to be stable in 0.1 M H_2SO_4 and 0.1 M NaOH, and no degradation of the superhydrophobic character was ob-

served. In parallel, such interfaces showed higher corrosion resistance properties when immersed in a 3% NaCl aqueous solution, as compared to an uncoated zinc substrate. However, besides protection against corrosion, superhydrophobic coatings find potential applications as anti-snow-sticking interfaces, for electrowetting-based applications (20, 21), and for surface self-cleaning processes (22).

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