Steel surface treatment with three different acid solutions and its effect on the protective properties of the subsequent silane coating

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ARTICLE INFO

ABSTRACT

Surface treatment of steel before application of silane coating plays important role to provide better corrosion protection. This work aims to evaluate the effect of steel surface treatment with acid solutions on the protective properties of subsequent organosilane coating. For this purpose, sulfuric, phosphoric and hydrochloric acid solutions were prepared at pH 3. The change in surface chemistry and morphology of mild steel surface after acid treatment was assessed by FE-SEM, XPS and water contact angle measurements. After surface treatment with acid solutions, a silane coating was applied on the steel samples. EIS measurements on the silane coated samples showed that the one treated by sulfuric acid solution provided better protection compared to the rest of samples.

1. Introduction

Steel is the most widely used metal in industries and construction specially in petroleum industries [1]. Various methods has been practiced to reduce the corrosion of mild steel, among them silane sol-gel coating is a green approach; and it is widely introduced as replacement of toxic chromate conversion coatings [2–5]. Silane compounds usually contain hydrolysable alkoxy groups (Si−OR), e.g. methoxy and ethoxy and a non-hydrolysable function e.g. methyl, ethyl, acrylate, etc. providing specific chemistry for the final silane coating [6,7]. Film formation of silane coatings generally occurs through formation of silanol groups (S−OH) through hydrolysis of alkoxy groups and condensation of silanol groups [8,9]. However, the application of silane coatings are sensitive to the substrate condition due to their high surface tension as water-based coatings [10]. In addition, they usually form a strong covalent bonding through condensation reaction between silanol groups on the silane molecule and hydroxyl groups on the substrate to form a metallo-siloxane bond (Me-O-Si). Therefore, presence of adequate amount of hydroxyl groups on the surface is essential to achieve final protective properties [11,12]. Therefore, surface treatment plays important role for silane coatings application. Van Ooij et al. [13] have summarized the impact of surface treatment condition on the silane coatings properties in a review. They reported that the treated metal surfaces should be completely wettable by water, which is essential for wetting of metal surface by water-based silane coatings. In addition, it was reported that treated metal surface have to be fully covered by hydroxide groups. In order to provide dense hydroxide groups on the surface, alkaline cleaners were reported to be more suitable than acid or neutral cleaners [13].

The effect of four different types of pre-treatment comprising: solvent degreasing; alkaline degreasing followed by alkaline or acid etching or both, alkaline degreasing followed by acid etching and oxide thickening in boiling water on the corrosion protection of sol-gel coating on EN AW 6063 alloy was studied. It was demonstrated that the best anticorrosive performances were achieved by the coatings applied on the substrates treated by the combination of acid etching with oxide growth [14].

Supplit et al. [15] used different acids, namely nitric acid 3.3%, hydrofluoric acid 12%, phosphoric acid 50%, and acetic acid 20%, for surface treatment of AZ31 alloy prior to application of silane sol-gel coating. They found that acetic and hydrofluoric acids provide better corrosion protection compared to the rest of acids. In addition, they showed that inclusion of organic corrosion inhibitors e.g. triethylphosphate or 1,2,4-triazole to acid solution in the surface treatment step led to more decrease in the corrosion rate of silane coated samples.

Kim et al. [16] investigated the effect of various pre-treatments on bonding of bis-1,2-(triethoxysilyl) ethane (BTSE) to an aluminum alloy. Pretreatments included distilled water rinse, H_2 plasma exposure, ultrasolication in distilled water and acid treatment by a sulfuric acid and sodium dichromate solution. They showed that too many OH groups on the surface may prevent formation of Al–O–Si interfacial bonding due to etching in the BTSE solution, therefore optimized surface OH function is needed to react with silane coating. The effect of phosphating before application of silane coating on the corrosion protective
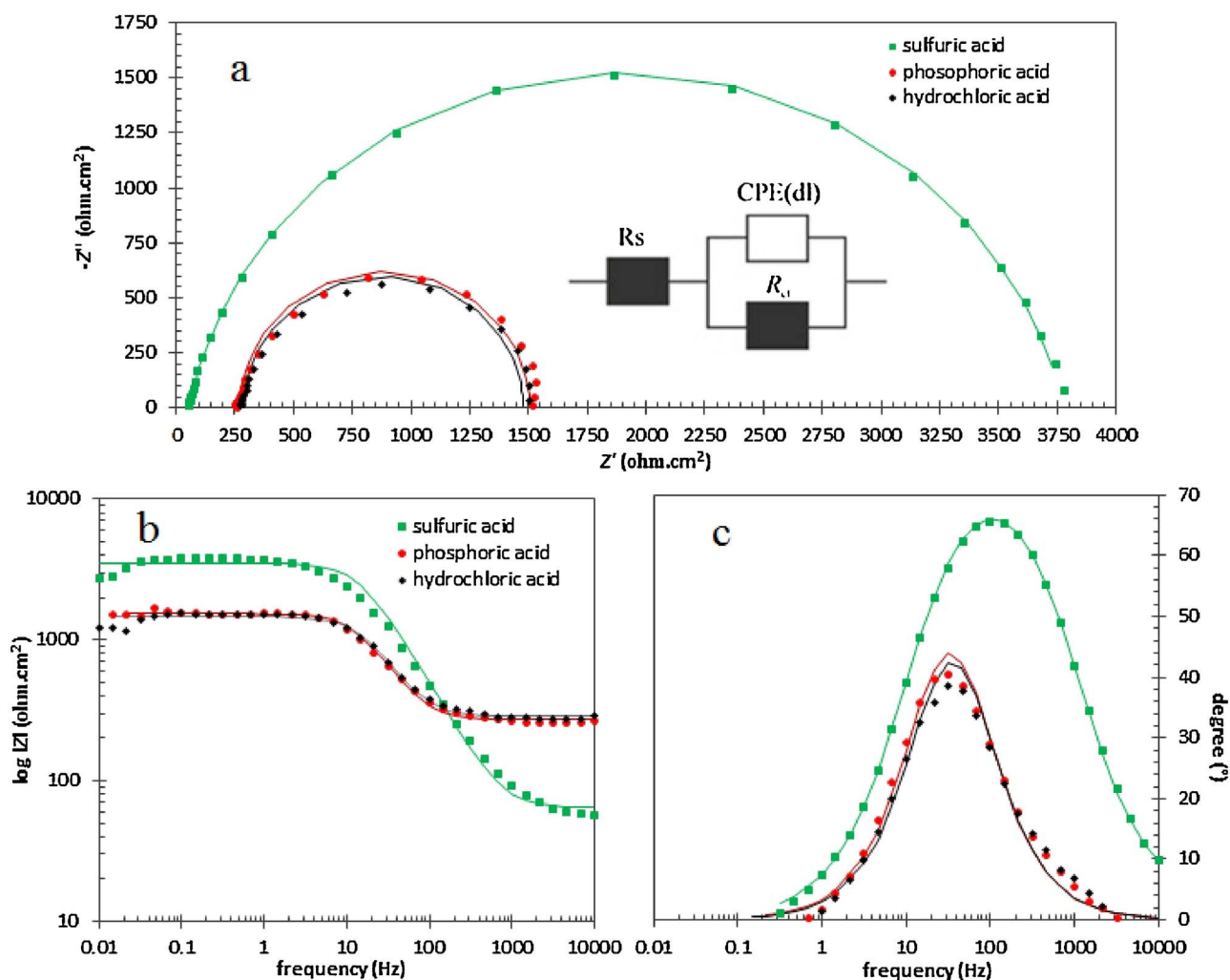

Fig. 1. The Nyquist (a), magnitude (b) and phase angle (c) Bode plots for the bare steel samples immersed in inhibited acid solutions for 30 min; the measured data are presented as symbols and the fitted curves obtained by equivalent electrical circuit are presented as solid lines.
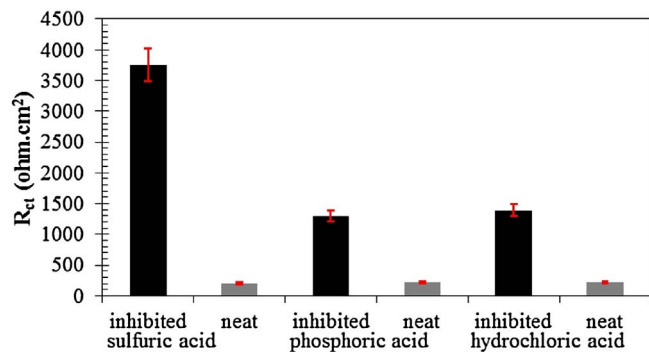

Fig. 2. Charge transfer resistance values extracted from the fitting of EIS measurements.

properties has also been reported in literature [17,18]. It was found that superior corrosion protection of silane coating on phosphate sample is due to improvement of Si-O-Si network and sealing of phosphate coating micro pores by the siloxane network.

In the previous study [19], we examined the effect of surface treatment of steel with sulfuric acid solutions containing corrosion inhibitor at different acidic pHs (1.5, 3, 4 and 5) on the protection properties of silane coating. Moreover, the results were compared with those obtained for the alkaline treated sample for the same silane coatings with the same processing conditions. It was shown that lower pH facilitated formation of surface hydroxide compared to surface

oxide groups as the solution is stronger to protonate the iron oxide film on the surface. However, at very low pH, i.e. pH 1.5, due to the sever corrosion, iron oxyhydroxide film was porous and thick causing negative effect on silane coating adhesion on mild steel. The best pH for steel cleaning with sulfuric acid was pH 3, which led to the highest corrosion protection by the silane coating. The corrosion protection performance of the silane coatings applied on steel treated at pH 3 was at least 4 times higher than that applied on alkaline treated surface reflecting the superiority of acid treatment in comparison with the conventional alkaline treatment.

Considering the results of previous study, we examined the effect of steel acid cleaning with different acid solutions at pH 3 on the corrosion protection properties of subsequent organosilane coating in this work. The barrier and electrochemical properties of silane coatings on steel substrate were evaluated by electrochemical impedance spectroscopy. Surface analysis such as FESEM, AFM, XPS and contact angle was used to investigate the chemical and physical changes on the steel substrate after acid treatment. This work is novel over the previous studies as it reveals the impact of acid type in the surface treatment step on the protection performance of subsequent silane coating.

2. Experimental

2.1. Material

Glycidoxypropyltrimethoxysilane (γ-GPS), tetraethylorthosilicate