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# Study on the protective function of cloisite incorporated silane sol–gel coatings cured at different conditions

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ABSTRACT

In this research, cloisite incorporated silane sol–gel coatings cured at different conditions were applied on 304L stainless steel to control its corrosion in 3.5% NaCl solution. At first step, the electrochemical noise data revealed the superior barrier function of the silane coating with cloisite compared to the neat one. As confirmed by the surface analysis, this was attributed to denser structure and increased coating thickness in the presence of cloisite nanoparticles. Then, the study focused on the impact of curing procedure on the performance of the hybrid silane film. The electrochemical data and results of FTIR, water contact angle and FESEM surface analysis showed that the heat treatment at sufficient temperature and time may lead to developing a reticulated coating which functions as an effective barrier to the diffusion of aggressive species.



## 1. Introduction

In recent years, the pretreatment based on silane formulation using a sol–gel technology is emerging as a promising technology for surface modification and corrosion protection of stainless steels (Motte et al., 2012; Phanasgaonkar and Raja, 2009; Quinton and Dastoor, 1999; Trabelsi et al., 2006). In addition to ensuring the adhesion between metal substrates and organic coatings, silane layers are able to provide a thin, but efficient, barrier against diffusion of aggressive species to the metal/coating interface (Zandi Zand et al., 2011). The silanol groups, resulting from the hydrolysis of silane molecules in alcohol or water, are adsorbed on the metallic surface through the formation of hydrogen bonds between the SiOH groups and the hydroxyl groups of the metal–OH. During the curing process, the condensation reactions among silanols themselves and between silanols and hydroxylated metallic substrates can lead to the formation of Si–O–Si and Si–O–Metal covalent bonds (Cabral et al., 2005; Chico et al., 2007; Honkanen et al., 2011; Kong et al., 2010; Lixia et al., 2009). Accordingly, the reticulated coating provides a physical barrier for penetration of aggressive species towards the coating/metal interface (Motte et al., 2012; Shi et al., 2009; Fedel et al., 2014; Naderi et al., 2013a; Suegama et al., 2008; Lampke et al., 2008a). A variety of strategies have been pursued to enhance the coating barrier properties (Asadi et al., 2014a,b; Jeeva Jothi and Palanivelu, 2013; Seifzadeh and Golmoghani-Ebrahimi, 2012; Zheng and Li, 2010). It is reported that the crackability and porosity of the sol–gel films might be decreased by incorporation of nanoparticles into the hybrid matrix (Zheludkevich et al., 2005). Furthermore, the curing characterization of silane coatings has been focused by some researchers (Asadi et al., 2014b,c; Fedel et al., 2010; Franquet et al., 2003b; Lampke et al., 2008a,b). Chico et al. (2007) studied the effect of curing time on the barrier properties of two 2-types of silane, 3-aminopropyltriethoxysilane and bis-3 triethoxysilylpropylamine, applied on steel substrates, with or without the subsequent application of an alkyd-based paint. They reported that heating to high temperatures and long times reduces the silane coating reactivity, due not to loss of the organofunctional group but to conversion of the free SiOH silanol groups to Si–O–Si bonds. According to Lampke et al. (2008a), the optimum heat treatment makes the silane layer denser by drying and cross-linking the film, which improves the corrosion resistance of aluminum alloys. Furthermore, it was revealed that no further improvement occurs in the protection exceeding the optimum curing condition. Phanasgaonkar and Raja (2009) showed the significant impact of curing temperature on the morphology and composition of a silane coating, made from hydrolysis and polycondensation of tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES), on mild steel substrate. Moreover, it was reported that the addition of $SiO_2$ nanoparticles and cerium dopant can affect the optimum curing temperature of hybrid coatings. Fedel et al. (2010) highlighted that an elevation in curing temperature can enhance the barrier properties of silane coatings applied on galvanized steels. It was suggested that the high temperature of curing process may lead to formation of a dense and highly interconnected silane film. Characterizing nonfunctional silane films of bis-1,2-(triethoxysilyl)ethane (BTSE) on aluminum substrates via electrochemical method, surface analysis and optical techniques, Franquet et al. (2003b) indicated that the curing step

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**Table 1**
A brief description of the samples.

| Sample | Nanoclay concentration (ppm) | Curing time (min) | Curing temperature (°C) |
|---|---|---|---|
| C0 | 0 | 30 | 150 |
| C1 | 1000 | 30 | 150 |
| T1 | 1000 | 30 | 100 |
| T2 | 1000 | 30 | 200 |
| T3 | 1000 | 5 | 150 |
| T4 | 1000 | 60 | 150 |

performed after the coating deposition could increase the barrier properties and improve the corrosion protection by forming a denser layer. In order to improve the barrier properties of silane coatings deposited on copper and aluminum, Deflorian et al. (2006) studied the curing procedure. Regardless of the substrate type, they reported that sufficient thermal curing could enhance the barrier function.

Various parameters of silane coatings, particularly curing condition, have been evaluated in the literature with the aim of improving corrosion resistance of different metallic substrates (Deflorian et al., 2006; Fedel et al., 2010; Franquet et al., 2003a,b; Lampke et al., 2008a). In the present research, the protective performance of an eco-friendly silane coating with cloisite applied on stainless steel 304L via sol–gel route was investigated. It is widely known that stainless steel does not stain, corrode, or rust as easily as ordinary steel. However, in practical cases they tend to corrode in the presence of chlorides or other aggressive ions (Cambon et al., 2012; Kim and Hwang, 2012; Zandi Zand et al., 2012).

In the first step of this work, electrochemical noise method was employed to examine the role of cloisite nanoparticles in the protective function of the silane sol–gel coating synthesized by mixing of gamma-glycidyloxypropyltrimethoxysilane (γ-GPS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES). Then, the effect of curing time and temperature on the barrier properties of the cloisite inserted hybrid film was studied with the aid of electrochemical techniques and surface analysis.

## 2. Experimental

### 2.1. Materials

Stainless steel 304L panels (composition in wt.%: Fe: base, C: 0.0349, Si: 0.591, Mn: 1.18, P : 0.0211, S< 0.00020, Cr: 18.65, Mo: 0.174, Cu: 0.138, Ni: 9.17 and Al: 0.00052) were abraded with the abrasive papers starting from 600 to 1200 grit size. The abraded samples were rinsed with distilled water and dried in air, then followed by acetone degreasing. In order to increase wettability, the samples were dipped

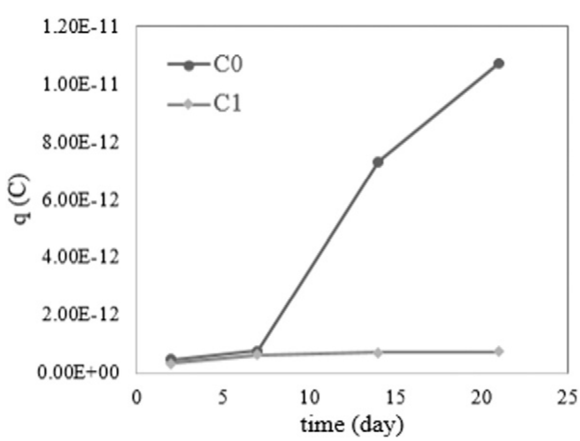


**Fig. 1.** The time variation of characteristic charge of stainless steel plates with silane coatings including 0 and 1000 ppm of NaMt nanoparticles.

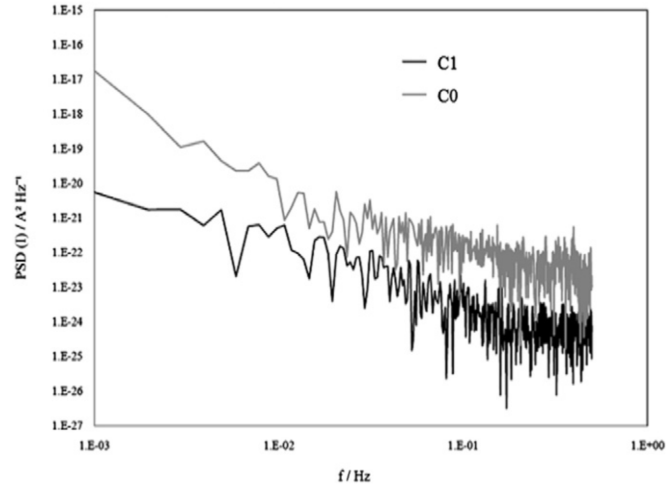


**Fig. 2.** PSD (*I*) plots of stainless steels coated with the silane films containing 0 and 1000 ppm of nanoclay after 21 days of immersion in 3.5% NaCl solution.

in 2.5 M NaOH solution at 90 °C for 15 min. The alkaline treatment leads to the formation of a high surface density of hydroxyl groups. The presence of Fe–OH bonds ensures the subsequent interaction between the metal surface and the hydrolyzed silane molecules. The substrates were then rinsed in distilled water and blow-dried with compressed air. The silane molecules were tetraethoxysilane (TEOS), methyltriethoxysilane (MTES) and γ-glycidoxypropyltrimethoxysilane (γ-GPS), supplied by Aldrich. In order to prepare the sol, 10% (w/w) of the silane mixture including an equal weight percentage of the three components was dissolved in distilled water. The pH was adjusted to 2.1 with hydrochloric acid. The mixture was then magnetically stirred at ambient temperature for 24 h at a rate of 1000 rpm. The nanoparticle incorporation was performed using ultrasonic dispersion of 1000 ppm

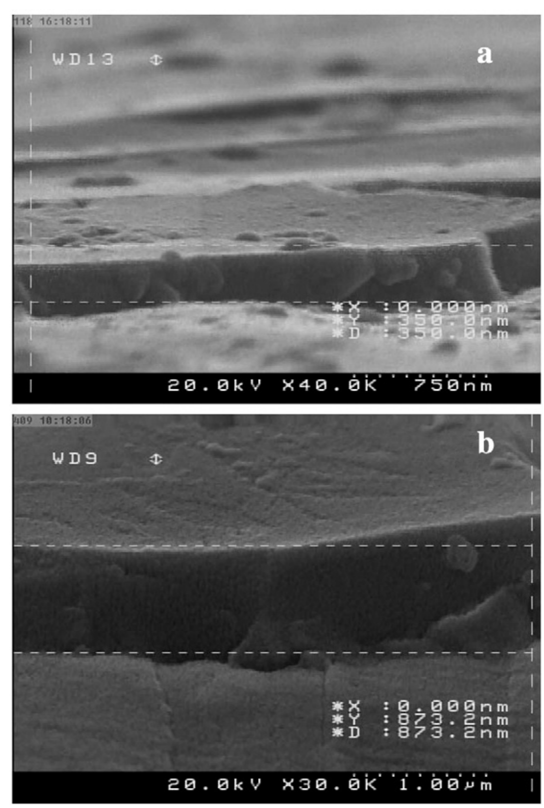


**Fig. 3.** Influence of (a) 0 and (b) 1000 ppm on of NaMt on the sol–gel coating thickness.