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Improved Corrosion Protection of Aluminum Alloys by Electrodeposited Silanes

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Organofunctional silanes recently have emerged as outstanding, environmentally friendly corrosion protectors for metal substrates, compared with conventional chromate treatments. A simple immersion technique is typically used to coat the metal surface with silane films. However, the thickness and uniformity of the films are uncontrolled in this process. This paper proposes a new deposition technique for the silane films on the metal surface, i.e., by electrodeposition. Hydrolyzed silanes are water-soluble, ionized molecules, so they can be deposited on metals by electrodeposition. Various combinations of silane mixtures were tested at different voltages, pH values, bath concentrations, and exposure times on panels of alloy aluminum and mirror-polished ferro-plate. The surface structure was characterized by scanning electron microscopy (SEM) and ellipsometry. The resistance of the film to corrosion was investigated by direct current (DC) polarization and electrochemical impedance spectroscopy (EIS) techniques. Electrodeposition results in a more organized and uniform film with fewer pores, compared with immersed or dipped films.

Keywords aluminum, coatings, corrosion, electrodeposition, organofunctional silanes

1. Introduction

Organofunctional silanes have recently emerged as an outstanding, environmentally friendly anticorrosion treatment for metal substrates and show potential for replacing conventional chromate treatments.[1-2] The use of chromates is discouraged, due to the carcinogenicity and environmental hazards related to the toxic hexavalent chromium ions [Cr (VI)]. Organofunctional silanes are hybrid organic-inorganic compounds having the structure $X_3Si(CH_2)_nY$, where X represents a hydrolyzed group, such as methoxy or ethoxy, and Y represents an organofunctional group. When the silane is symmetrical about the functional group Y, i.e., if there are two trialkoxy (X_3) groups in the molecule, these molecules are called bis-functional silanes, having the structure $X_3Si(CH_2)_n\ Y(CH_2)_nSiX_3$. Various techniques have been used to coat the metal surface with these silanes, i.e., immersion, spray coating, brushing, and rolling. However, these techniques produce a nonuniform, sometimes porous film at the surface, and it is of uncontrolled thickness.

This paper demonstrates a new technique for coating silanes on aluminum surfaces, i.e., by electrodeposition. Although Woo et al.[3] used this technique for depositing silanes on metal surfaces, the focus of their study emphasized the adhesive properties of the films formed. Lap shear tests were performed on the silane-treated surface to evaluate the bond strength and durability. According to the results, as the voltage was applied, hydroxyl anions were generated at the cathode, and the cationic silane was deposited on the cathode by the alkali-catalyzed condensation reaction. The results obtained were at least similar (or in some cases better) than those obtained with the immersion techniques. The data presented in this paper are concerned with the corrosion-resistance properties of the films. Because hydrolyzed silanes are water-soluble ionized molecules, they dissociate into cations and anions; thus, it should be possible to electrodeposit them. At high pH, anions are present and are attracted to the anode. Similarly, at low pH, the cations are attracted to the cathode. A typical bis silane, BTSE bis[triethoxysilyl]ethane, was tested at various voltages, pH values, bath concentrations, and exposure times on panels of 6111-T4 and 5052 aluminum (Al) and ferro-plate.

Good results were achieved at a typical voltage of 5 V and pH 4 of the silane bath. DC polarization and electrochemical-impedance spectroscopy (EIS) showed higher corrosion resistance for the electrodeposited films. Other surface characterization and optical techniques, such as scanning electron microscopy (SEM) and ellipsometry, showed greater uniformity and the presence of a brittle interface between the silane film and metal surface, as compared with the immersed silane films.

2. Experimental

2.1 Materials and Silane Treatment

2.1.1 Silane. Bis-[triethoxysilyl] ethane, also known as Y-9805 Silquest, was obtained from OSi (Greenwich, CT). This silane was used without further purification. A solvent-based silane solution was prepared by mixing 5 vol.% of the silane with 90 vol.% ethanol and 5 vol.% deionized (DI) water. The natural pH of the resulting solution was 6, and it was adjusted to 4-4.5 by the addition of concentrated nitric acid. The solution was continuously stirred for 48 h for hydrolysis.

2.1.2 Substrate. Unpolished 6111 Al panels (10 × 10 ×

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0.06 cm) were obtained from ACT laboratories (Hillsdale, MI). Mirror-polished ferro-plate sheet (61 × 61 × 0.08 cm) was obtained from Regal Arkay (Milwaukee, WI) and mirror-polished 5052 Al sheet (61 × 61 × 0.08 cm) from McMaster-Carr (Aurora, OH).

2.1.3 Power Supply. The voltage supply required for electrodeposition was built by Sanction Electronics (Trenton, OH).

2.1.4 Substrate Preparation. The 50.8 × 50.8 × 0.89 mm samples of 6111 were degreased in hexane and ethanol ultrasonically for 5-7 min and 3-4 min, respectively. The substrates were then dipped in a dilute alkaline cleaner (AC1055, provided by Brent PLC, Lakebluff, IL) at 60-70 °C for 5-7 min, after which they were rinsed with DI water and air dried. The same cleaning procedure was also used for the ferro-plate and 5052 panels (50.8 × 25.4 × 0.89 mm).

Immersion. Panels of cleaned 6111, polished ferro-plate, and polished 5052 were immersed in the silane solution for 1 min. After immersion the 6111 and ferro-plate substrates were dried at 100 °C for 60 min in an oven, but the 5052 panel was immediately transferred to an ethanol bath in an ultrasonic cleaner and kept there for 5 min. After that it was dried in an oven at 120 °C for 30 min. An ethanol bath was used to remove the film from the surface.

Electrodeposition. The setup comprised an electrolytic cell with the silane solution as the electrolyte, the metal substrate as the cathode (negative), and graphite as the anode (positive). A 0-30 V power supply was used for applying the voltage through the electrodes. A constant 5 V voltage was applied to 6111 for 60 min, to the 5052 for 30 min, and to the ferro-plate for 1, 10, 30, and 60 min. Timed electrodeposition on ferro-plate was done to evaluate the variation of film thickness with time, as the 6111 substrate was unpolished and caused a problem in thickness evaluation during modeling. Also, voltages higher than 5 V led to vigorous hydrogen evolution near the metal substrate. After electrodeposition, the 6111 and ferro-plate substrates were dried at 100 °C for 60 min in an oven. The 5052 substrate was transferred to ethanol bath in ultrasonic cleaner for 5 min and then dried in the oven at 120 °C for 30 min.

2.2 Electrochemical Techniques

2.2.1 DC Polarization Test. Blank, immersed, and electrodeposited 6111 samples kept immersed in 3.5 vol. % NaCl solution for 2 h, after which a DC polarization test was performed.

2.2.2 Electrochemical Impedance Spectroscopy (EIS). EIS measurements on 6111 substrates were carried out in 3.5 vol.% NaCl aqueous solution, using an SR 810 frequency-response analyzer and a Gamry CMS 100 (Warminster, PA) potentiostat. Impedance data were recorded at frequencies ranging from 10^{-2} to 10^{5} Hz, with an alternating current (AC) voltage amplitude of ±10 mV. A commercial saturated calomel electrode (SCE) served as the reference electrode, coupled with a graphite counter electrode. An area of 5.3 cm^2 of the specimen was exposed to the electrolyte during the EIS measurement. All EIS spectra were recorded after immersing one sample of each kind (blank, immersed, electrodeposited) in the 3.5 vol.% NaCl solution for different intervals of time. With such data, pore resistance of the film was evaluated.

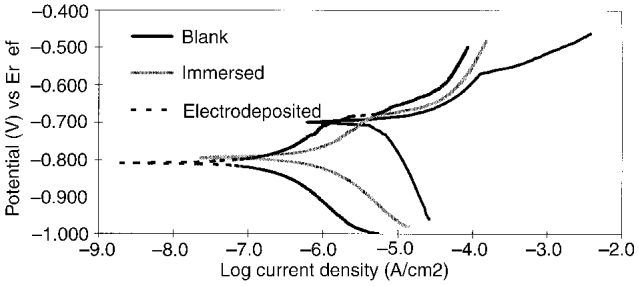

Fig. 1 DC polarization curves showing the comparison of blank, immersed, 5 V electrodeposited silane film. The samples were tested after 2 h of immersion in 3.5% NaCl solution (silane used is BTSE 5/5/90 on Al-6111 panels)

2.3 Optical Technique

2.3.1 Ellipsometry. A variable-angle spectroscopic ellipsometer W-VASE 32 (J.A. Woollam Co., Inc., Lincoln, NE) was used to measure the thickness of the silane film formed on the ferro-plate surface. The measurement was done at two different spots on the same surface, at three angles of incidence (75°, 80°, and 85°), with wavelengths in the range of 300-800 nm. The same technique was applied on the 5052 panels at four angles of incidence, 60°, 65°, 70°, and 75°, using the same wavelength range.[4-5]

2.4 Electron Microscopy

2.4.1 Scanning Electron Microscopy (SEM). A Hitachi S3600 (Hitachi HighTechnologies America, Inc., Pleasanton, CA) scanning electron microscope was used to observe the silane film structure on the immersed and electrodeposited polished ferro-plate surface. SEM examination was done on samples that had been immersed for 1 min and electrodeposited for 10, 30, and 60 min. In situ EDX was also done to determine the elemental constituents of the film.

3. Results and Discussion

3.1 DC Polarization Results

The DC curves for blank, immersed, and electrodeposited 6111 samples are shown in Fig. 1. The 5 V curve shows a higher shift toward the left, when compared with immersed curve; this finding clearly indicates that electrodeposited samples have a corrosion current value less than that of the immersed samples. Because I_{corr} (corrosion current) is directly proportional to the corrosion rate, a lower corrosion rate is observed in the electrodeposited samples, as compared with the immersed films.

3.2 EIS Results

The results of DC polarization were bolstered by the EIS test. These results are shown in Fig. 2. The curves show higher value of impedance for electrodeposited films than for the immersed ones for the 6111 panels. The phase-angle curve

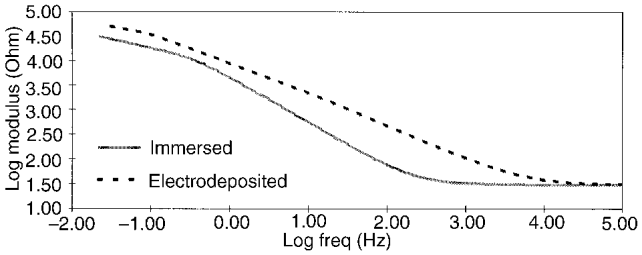

Fig. 2 Impedance curves showing the comparison of blank, immersed, 5 V electrodeposited samples after 8 h of immersion in 3.5% NaCl solution (silane used is BTSE 5/5/90 on Al-6111 panels)

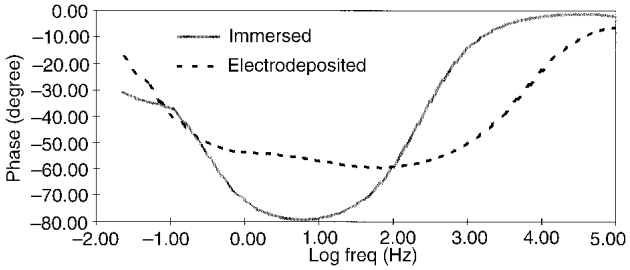

Fig. 3 Phase-angle curves showing the comparison of blank, immersed, 5 V electrodeposited samples after 8 h of immersion in 3.5% NaCl solution (silane used is BTSE 5/5/90 on Al-6111 panels). TC, time constant; W, Warburg impedance

(Fig. 3) shows the presence of a time constant at high frequency and a second one at low frequency during the initial hours of testing for electrodeposited film. No second time constant is observed in case of immersed films. The second time constant is due to the presence of an interfacial layer between the silane film and the metal substrate, as subsequently verified by ellipsometry. This interfacial layer is absent in case of immersed films. The trend was observed continuously for 12 days. Based on the trend, film-pore resistance (R_{po}) was calculated for both electrodeposited and immersed films by modeling the EIS curve.[6-7] The fitting process was done by developing an equivalent circuit model (Fig. 4, 5) from the software. Pore resistance (Fig. 6) of the electrodeposited silane film was primarily equivalent to that of the immersed film; however, the pore resistance of the interfacial layer in case of electrodeposited film was extremely high and decreased with time as the electrolyte penetrated it.[8-14]

3.3 Ellipsometry

The film on the immersed ferro-plate panel was 227.5 nm thick, with a nonuniformity of 55% at three different points. The mean standard error (MSE) for this measurement was 9.8. The silane film thickness is independent of time for the immersion samples; however, in the case of electrodeposited films, the thickness increased with time. The electrodeposited film at 1 min had a thickness equal to 214.1 nm, with a nonuniformity of 20% and MSE 8.4. After 10 min of electrodeposition, the thickness increased to 242 nm with the nonuniformity equal to 7%. The MSE was equal to 20.8. The same trend continued for 30 and 60 min, with thickness reaching 275.4 and 272.7 nm, respectively. The nonuniformity remained the same at 7%, with MSE reaching values of 9.2 and 10.5, respectively. Figure 7 shows a linearly increasing film thickness in the initial time period, leading to a plateau at longer times. These results indicated that, unlike on the immersion panels, electrodeposited film thickness increases with time. In the 5052 panels, the immersed panel showed a thickness of 0 nm on both the spots examined, whereas the electrodeposited sample showed thicknesses of 4.6 nm and 4.9 nm, with MSE values of 3.8 and 10.5, respectively. These results revealed the presence of a highly cross-linked interfacial layer of 5 nm or more in thickness on the electrodeposited substrate, which was not washed away in the ethanol bath as was the case for the immersed film.

The appearance of a second time constant in Fig. 3 is due to the presence of this interfacial layer. Figure 8 and 9 show a

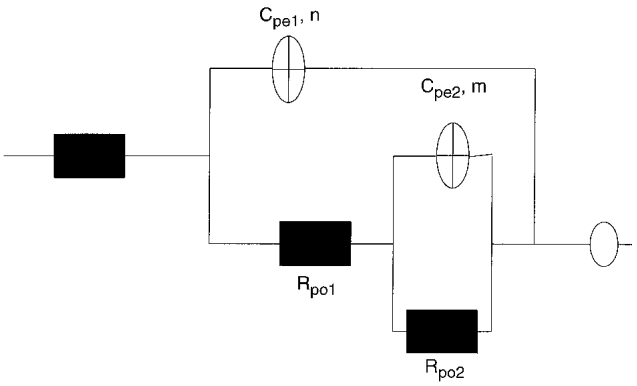

Fig. 4 Equivalent circuit model for EIS data fitting for electrodeposited Al-6111 panels. R_{so} is the uncompensated solution resistance, C_{pe1} is the silane-coating capacitance, R_{po1} is the pore resistance of silane film, C_{pe2} is the capacitance of interface, and R_{po2} is the pore resistance of interface

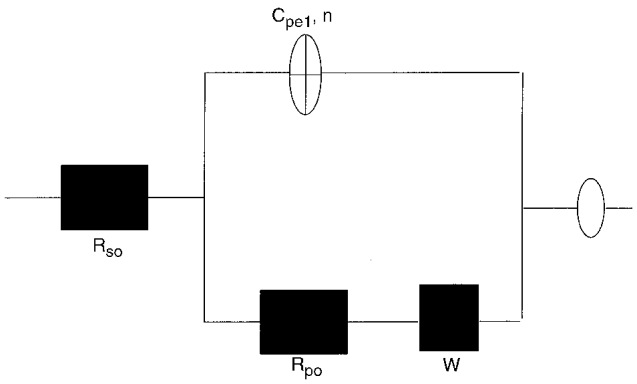

Fig. 5 Equivalent circuit model for EIS data fitting for immersed Al-6111 panels. R_{so} is the uncompensated solution resistance, C_{pe1} is the silane-coating capacitance, R_{po} is the pore resistance of silane film, and W is the Warburg impedance

schematic representation of film formation after the electrodeposition and ethanol rinse, respectively. After electrodeposition, two layers are present on the metal surface: A is the silane layer, while B is the interfacial layer. The total thickness is about 255 nm, including the 5 nm interfacial layer. After an ethanol rinse, the silane film is washed away, but the 5 nm

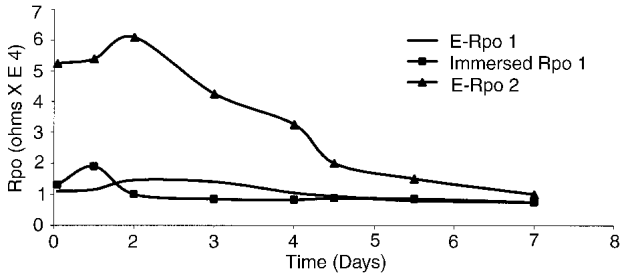

Fig. 6 Pore resistance versus number of days for immersed and electrodeposited Al-6111 (silane used is BTSE 5/5/90)

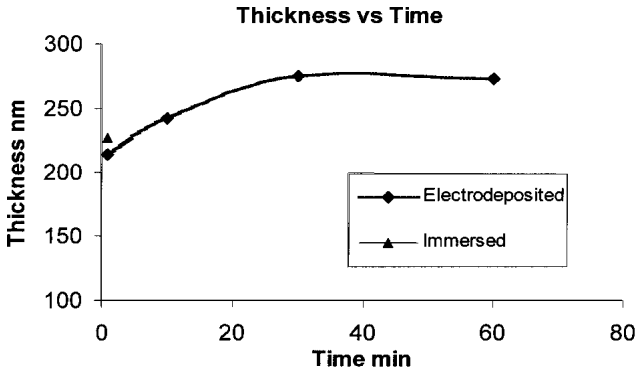

Fig. 7 Thickness versus time, for electrodeposited silane films (silane used is BTSE 5/5/90 on ferro-plate panels)

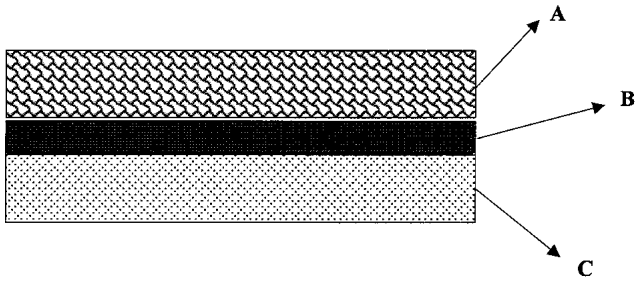

Fig. 8 Metal surface structure after electrodeposition; A, silane film (250 nm); B, cross-linked interfacial layer (5 nm); C, metal substrate

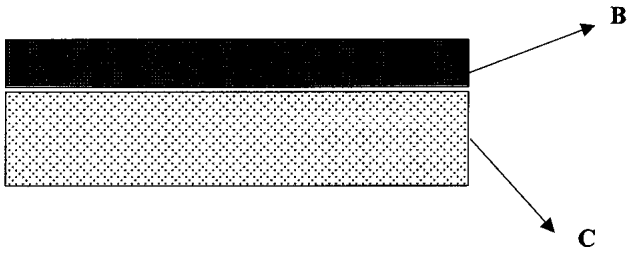

Fig. 9 Electrodeposited metal surface structure after ethanol rinse; B, cross-linked interfacial layer (5 nm); C, metal substrate

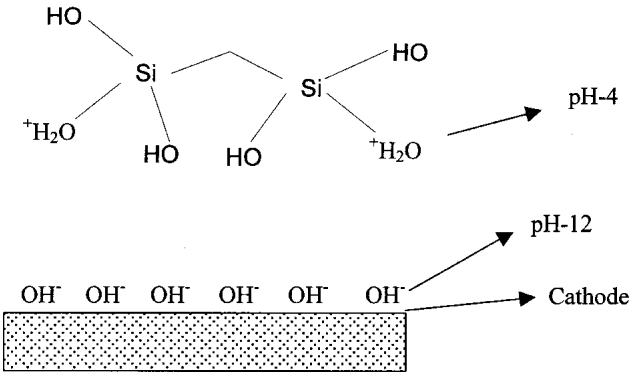

Fig. 10 Schematic of silane metal interaction for electrodeposition

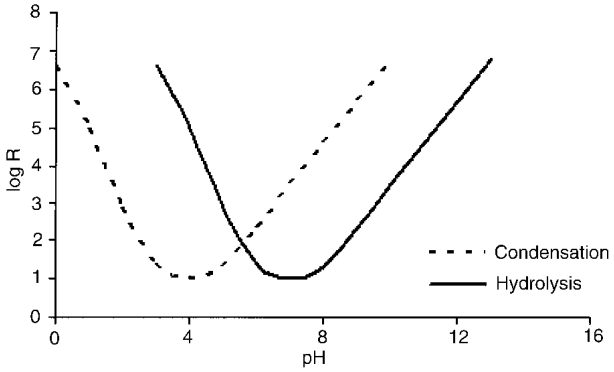

Fig. 11 Condensation and hydrolysis rate versus pH for BTSE

interfacial layer (Fig. 9) remains, clearly indicating the high degree of cross-linking that occurs, which is resistant to any external electrolyte penetration. The curve E-R_{po2} in Fig. 6 represents this interfacial layer B. The entire mechanism of film formation during electrodeposition can be explained from the silane solution chemistry. At low pH, BTSE silane molecules dissociate into H_2O^+ ions. With the application of voltage, these ions move toward the cathodic metal substrate where OH^- ions are generated as a result of water decomposition and hydrogen gas evolution (Fig. 10). These OH^- ions increase the pH to 12 in the vicinity of the substrate and make it highly alkaline, thereby catalyzing the condensation and leading to the formation of a strong complex near the surface. However, this phenomenon is not useful in a high pH silane solution because the hydrolysis rate is less and the condensation rate is high (Fig. 11). When voltage is applied in this solution, the SiO^- ions move toward the anodic metal substrate, where H^+ ions are generated. However, this reaction is much slower and solution stability is at stake. This result is the reason BTSE performs well at an optimum pH of approximately 4.

3.4 Scanning Electron Microscopy

The SEM image for the immersed silane film (Fig. 12) shows haphazard clots on the surface, which lead to higher nonuniformity (as indicated by ellipsometry studies). EDS on these clots shows a higher Si peak (Fig. 13), whereas no Si peak is observed on the rest of the surface (Fig. 14). Figure 15 shows an SEM image of a 10 min electrodeposited silane film. The electrodeposited film is more uniform than the

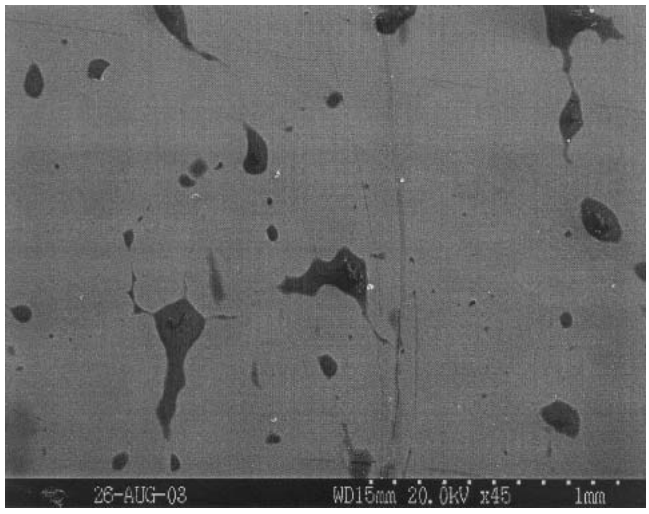

Fig. 12 SEM image of immersed film on ferro-plate

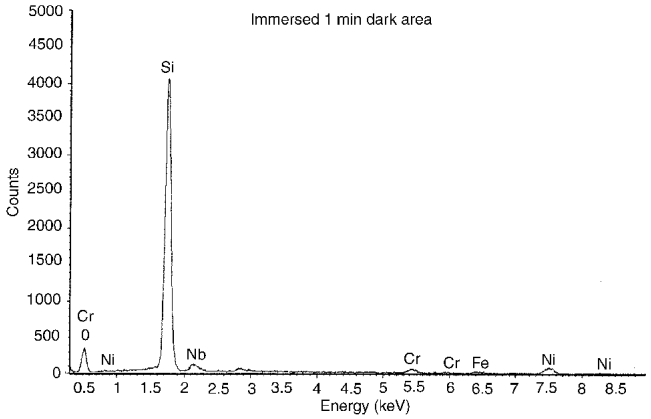

Fig. 13 EDS of dark clots on the immersed ferro-plate

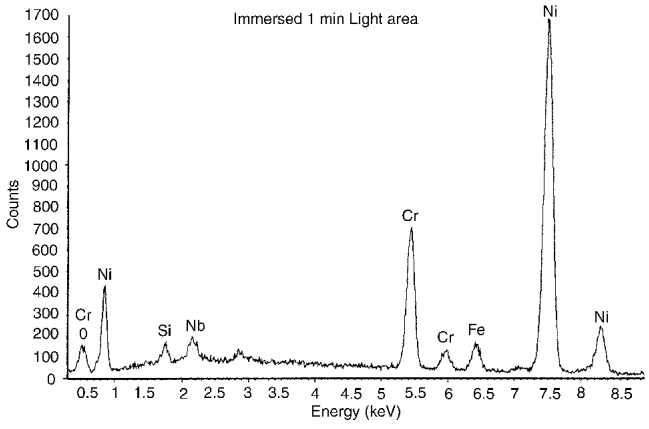

Fig. 14 EDS of the immersed ferro-plate surface without any clots

immersed one, but it is torn at certain locations. The long streaks were caused by cleaning the surfaces with "tissue wipes," using a rubbing motion. EDS of the torn portion (Fig. 16) shows no silane peak, whereas on the rest of the surface, an

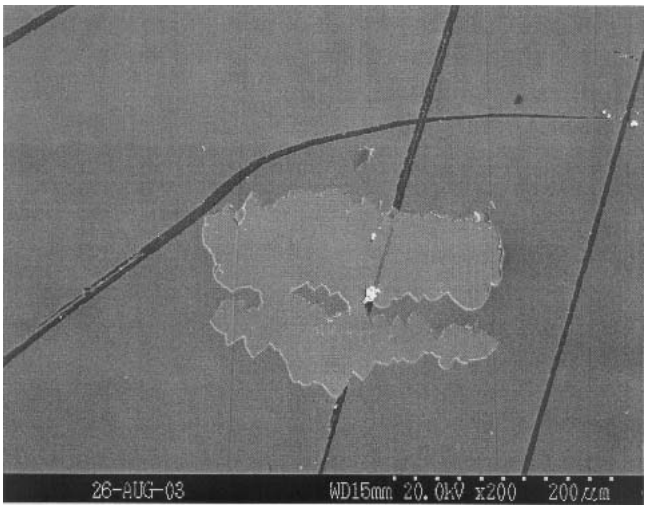

Fig. 15 SEM image of 10 min electrodeposited ferro-plate

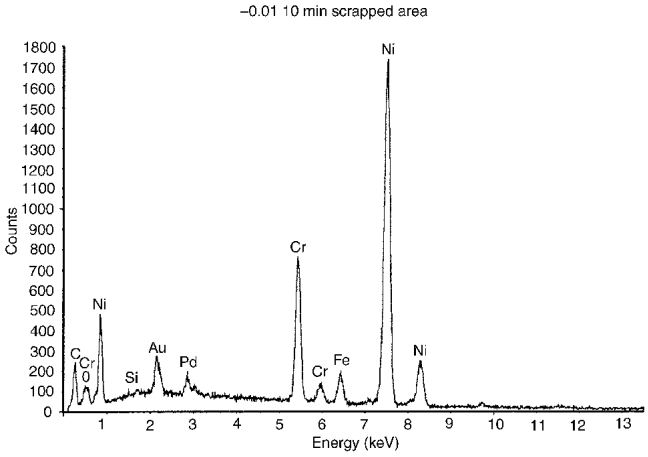

Fig. 16 EDS of the torn spot on 10 min electrodeposited ferro-plate

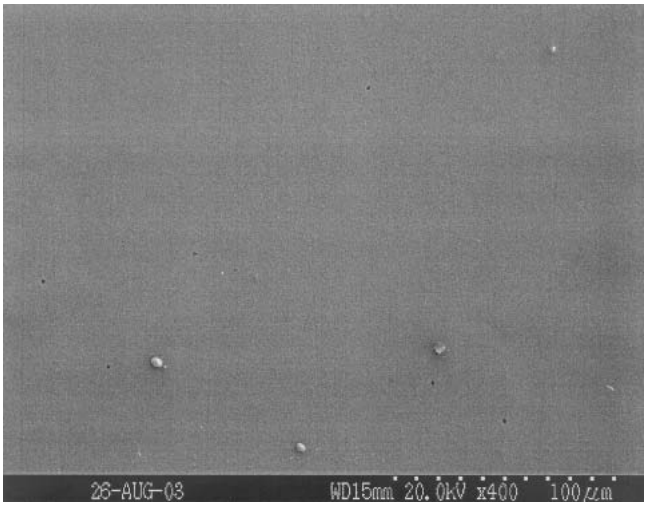

Fig. 17 SEM image of 60 min electrodeposited ferro-plate

Si peak of significant intensity is observed. As the electrodeposition time is increased to 30 and 60 min, the film heals with no torn spots, becoming highly uniform over the surface. Fig-

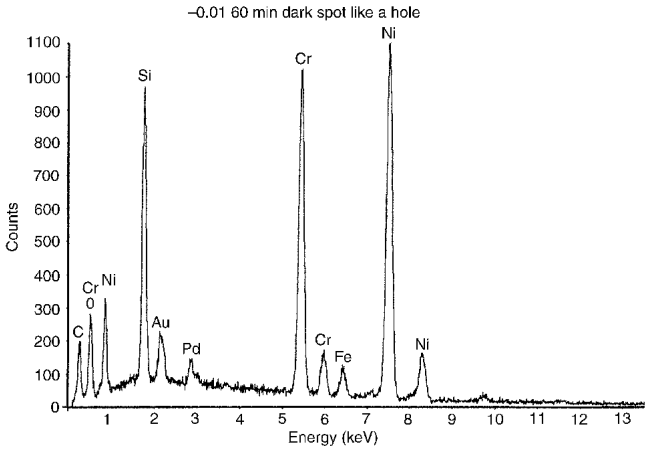

Fig. 18 EDS 60 min electrodeposited ferro-plate

ure 17 shows an SEM image of a 60 min electrodeposited silane film on a ferro-plate substrate. The visible white spots on the surface are tiny bits of tissue. EDS on the entire surface shows a moderate-intensity silane peak (Fig. 18). The reason for the moderate-intensity silane peak in the case of the electrodeposited films can be attributed to the fact that a uniform film forms over the entire surface (as compared with a large clot in case of the immersed films).

4. Conclusions

Electrodeposition of silane films results in a more organized, void-free, and uniform film with less porosity at the metal surface. The layer formed at the interface between the silane and the oxide possesses high ohmic resistance and low permeability for the electrolyte.

Acknowledgments

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