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Environmentally compliant silica conversion coatings prepared by sol–gel method for aluminum alloys

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Abstract

Chromate conversion coatings have been widely applied for the corrosion protection of aluminum alloys. However, the waste containing Cr^{6+} has many limitations due to environmental considerations and health hazards. Silicates are among the proposed alternatives to chromating. A series of specimens were prepared under the following conditions: (a) as polished, (b) directly treated with silica, (c) etched, (d) oxide thickened and, (e) etching followed by oxide thickening. After surface preparation, the specimens were dipped in two different silica solution prepared via the sol–gel method. Electrochemical impedance spectroscopy (EIS) and polarization measurements have been used to evaluate the coating performance in 3.5% NaCl. The optimum conditions under which silica treatments can provide good corrosion protection to the aluminum substrate were determined. The surface preparation prior to silica treatment was found to have a marked effect on the corrosion protection of AA6061 T6. Generally, silica treatments improve the corrosion resistance due to formation of protective oxides that act as a barrier to oxygen diffusion to the metal surface. According to the EIS and polarization measurements, a combination between etching and oxide thickening prior to silica treatment plays an important role in the corrosion protection mechanism.
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1. Introduction

Chromate conversion coatings have played an important role for corrosion protection of aluminum alloys. However, exposure limits for humans to chromium compounds are being reduced, making it impractical to use chromate conversion coatings in the future. Therefore, alternative coating systems need to be developed [1].

Many attempts have been made to find alternatives to chromating such as manganese [2–5], molybdenum [6–11], vanadium [12–14], cerium [15–20] and silica [21–24].

Several techniques have been applied for protecting aluminum alloys against corrosion. Electrochemical passivation [6], inhibition by soluble or adsorbed species [25–28] as well as formation of a protecting coating system on the surface [29,30] are among the reported methods.

Sol–gel coating is one of the relatively new approaches proposed for corrosion inhibition [31]. The most important advantages of sol–gel processing over conventional coating methods are easier fabrication of crack-free films or coatings of complex oxides and easier control of composition and microstructure of the deposited films or coatings [32,33]. The basic principle of the sol–gel process is to form a solution of the elements of the desired compound in an organic solvent, polymerize the solution to form a gel, and dry and heat-treat this gel to displace the organic components and form a final inorganic oxide [34]. Thin oxide films can be deposited on a substrate at much lower temperature than traditional ceramic methods. Such oxides can provide protection against corrosion by creating an inert barrier between the metal surface and its environment.

Sol–gel-processed oxide films such as silica, zirconia and titania have been tested for corrosion protection [35,36]. They

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have all shown promise, but have been of limited use due to poor interfacial adhesion and shrinkage. In a previous work [21], we studied the effect of silicate conversion coatings prepared by conventional method on the corrosion behavior of aluminum composites in NaCl. We found that silicate conversion coatings improve the corrosion resistance due to the formation of protective oxides that act as a barrier to oxygen diffusion to the metal surface. Moreover, silicate plays an important role in the pitting repairing process by forming thin silicon oxide to block the pits. However, the surface revealed some pits and micro-cracks.

Based on the ability of sol–gel method to fabricate crack-free films, the effect of silicate conversion coatings prepared by sol–gel method on the corrosion behavior of aluminum will be studied. We will also try to improve the corrosion resistance by "modifying" the metal surface before applying sol–gel coating. This will include different surface preparation prior to sol–gel application. Accordingly, the effect of pre-etching and oxide thickening, on the corrosion protection performance of Al 6061 T6 in 3.5% NaCl solution will be studied using EIS and DC polarization techniques. Surface examination will be performed by scanning electron microscopy (SEM) and Energy-dispersive X-ray (EDS) analysis.

2. Experimental

2.1. Materials

The specimens of AA6061 T6 alloy, in the form of 60×30 mm taken from a sheet of 3 mm thick, were abraded to 800 finish with SiC grit papers, degreased in acetone, washed with distilled water, and dried in dry air. The nominal composition was as follows (wt.%): 0.35 Cu; 0.95 Mg; 0.70 Fe; 0.50 Si; 0.15 Mn; 0.15 Cr; 0.25 Zn; 0.15 Ti; remainder Al.

2.2. Sol–gel coatings

The following analytical-grade reagents and high-purity raw materials were used to prepare SiO_2 sol:tetraethyl orthosilicate (TEOS) 98% Si $[OC_2H_5]_4$ Aldrich Chemical Co. and ethyl alcohol absolute.
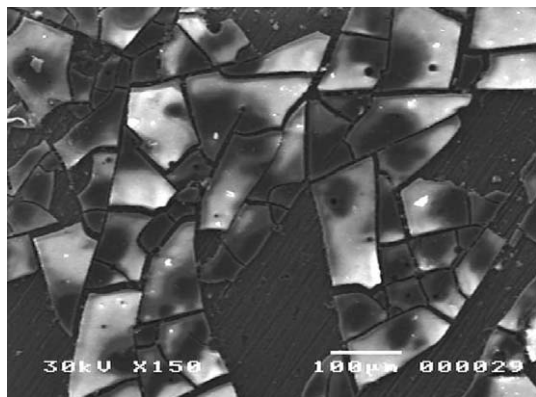

Fig. 1. SEM of directly treated (DT) specimens after 30 days of immersion in 3.5% NaCl solution.
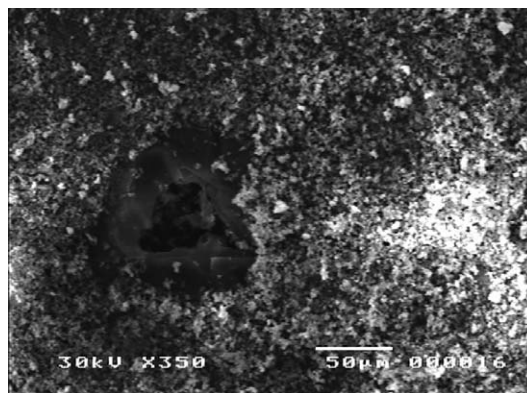

Fig. 2. SEM of etched specimens (K) after 30 days of immersion in 3.5% NaCl solution.

Two SiO_2 sols were prepared under the following conditions: TEOS/H_2O/C_2H_5OH/HCl as molar ratios were 1:4:5:0.25. 30 ml TEOS was added to 32 ethyl alcohol and 0.1 ml HCl (1M) as catalyst and then 17 ml H_2O was added for hydrolysis. The second solution was prepared from the same precursors but silica diluted to half concentration of the first solution. The mixture was stirred for 30 min at room temperature to complete hydrolysis then forming the sol. Soon after, the beaker containing sol was adequately covered with a plastic film to prevent chemical/solvent evaporation.Four groups of specimens were prepared under the following conditions:

1. As-polished specimens (DT).
2. Etching in 0.01 M KOH solution for 10 min (K).
3. Oxide thickening in boiling distilled water for 1 h (B) to form thick Al-hydroxide layer.
4. Etching in 0.01 M KOH solution for 10 min followed by oxide thickening in boiling water for 1 h (KB).

After the surface preparation, the specimens were dipped into the SiO_2 sol for 10 min, dried at 110 °C for 30 min and heat treated at 500 °C for 30 min. As-polished sample without any surface treatment (WT) will be used as a reference.

In an attempt to reduce the amount of silica used as sol–gel coating, a new sol with half silica concentration was prepared. The metal was treated following the treatment conditions that showed the best corrosion resistance from the first solution. A comparison will be made between the corrosion resistances obtained from the two solutions.

2.3. Methods

The corrosion behavior of the previous specimens was monitored using electrochemical impedance spectroscopy (EIS) and DC polarization techniques during immersion in 3.5% NaCl solution open to air and at room temperature for up to 30 days.

A three-electrode setup described elsewhere [37] was used with impedance spectra being recorded at the corrosion potential E_{Corr}. A saturated calomel electrode (SCE) was used as the reference electrode. It was coupled capacitively to a Pt

wire to reduce the phase shift at high frequencies. EIS was performed between 0.01 Hz and 65 kHz frequency range using a frequency response analyzer (Autolab PGSTAT 30, Eco-Cheime, The Netherlands). The amplitude of the sinusoidal voltage signal was 10 mV.

DC polarization tests of specimens previously immersed for 30 days in 3.5% NaCl solution were made at a scan rate of 0.07 mV/s in the applied potential range from -0.15 V_{SCE} to 0.7 V_{SCE} with respect to E_{Corr} using an Autolab PGSTAT 30 galvanostat/potentiostat (The Netherlands). The exposed surface area was 2.54 cm^2. All curves were normalized to 1 cm^2.

SEM images were obtained using a digital scanning electron microscope Model JEOL JSM 5410, Oxford Instruments, Japan. Microprobe analysis was performed using energy-dispersive spectrometry, EDS, Model 6587, Pentafet Link, Oxford micro-analysis group, UK. XRD analysis was performed using Bruker axs, Model D8, Germany.

3. Results and discussion

A thick layer of Al-oxide was formed after immersion of the as-polished specimen in NaCl solution. This layer increased the insulating power of the material surface in addition to hindering the ion diffusion through the surface. Unfortunately, this layer could not protect the surface completely, and hence, severe localized corrosion took place (5,6,14,15).

The specimens of group 1 which were directly treated with silica (without any surface pretreatment) and the etched specimens of group 2 showed severe cracked surface areas and pitting corrosion (Figs. 1 and 2). This may be due to the formation of a rigid glassy-like layer of silicates which can favor the propagation of cracks through which the localized corrosion takes place. Moreover, the failure of the protective layer is considered to be a sequential process with the breakdown of the individual oxide/silicate and oxide layers by the action of chloride and initially also hydroxide released from the silica
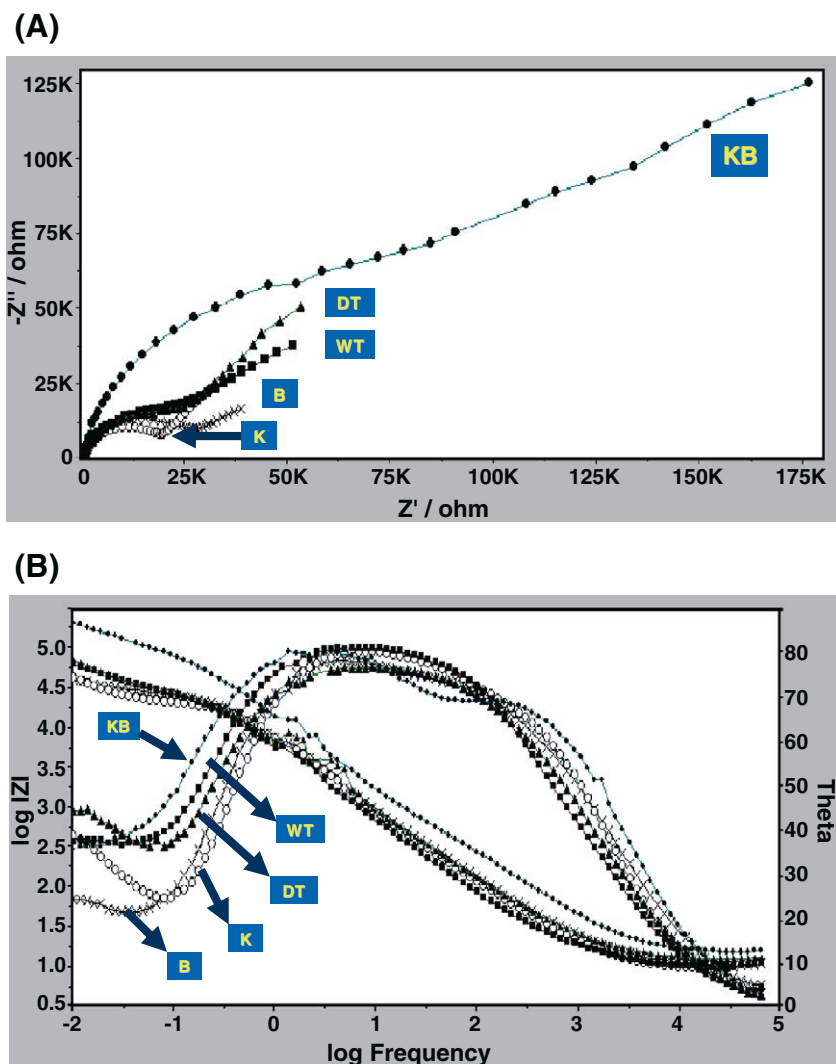

Fig. 3. (A) Nyquist plots and (B) Bode plots after 30 days of immersion in NaCl. Blank (WT) as-polished (without treatment), Group 1 (DT) directly treated in silica (without surface pre-treatments), Group 2 (K) etching followed by silica treatment, Group 3 (B) boiling water for 1 h followed by silica treatment, Group 4 (KB) etching followed by boiling water for 1 h followed by silica treatment.
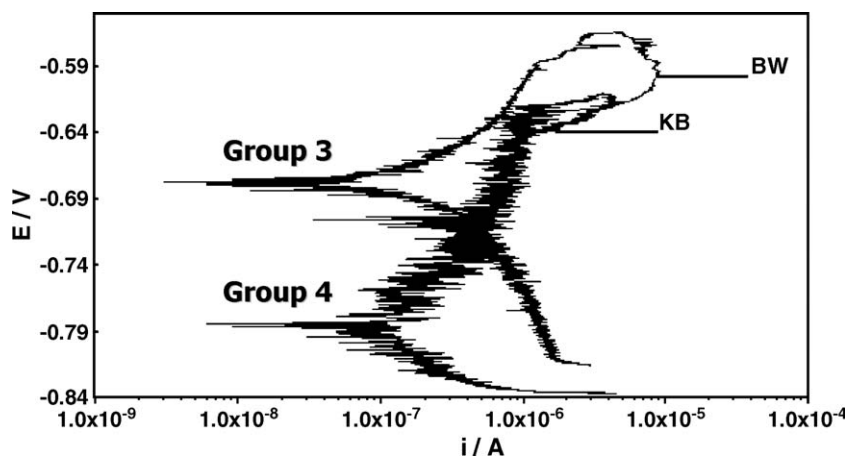
Fig. 4. Potentiodynamic curves after 30 days in NaCl. Group 3 (B) Boiling water for 1h followed by silica treatment, Group 4 (KB) etching followed by boiling water for 1h followed by silica treatment.

treatment. This allows progressively more chloride and oxygen through the barrier oxide layer allowing pitting to occur.

According to the EIS results (Fig. 3A and B) and visual inspection, group 4 (KB) showed the best corrosion protection performance. The surface resistance of the as-polished samples (WT) is 2.5×10^4 Ω cm^2. The surface resistance increased about one order of magnitude (1.75×10^5 Ω cm^2) for the specimens of group 4 (KB). Although the surface resistance of groups 1, 2 and 3 is almost with the same order of magnitude as the as-polished samples (WT), the pitting resistance of the silica-treated samples was generally improved which was confirmed by the relaxation of the impedance spectra (Fig. 3A, B). This may be due to formation of silicate layer that acts as a barrier to oxygen diffusion to the metal surface thereby impeding but not preventing corrosion [24]. Localized corrosion is the predominant corrosion species in the as-polished samples. Conversely,
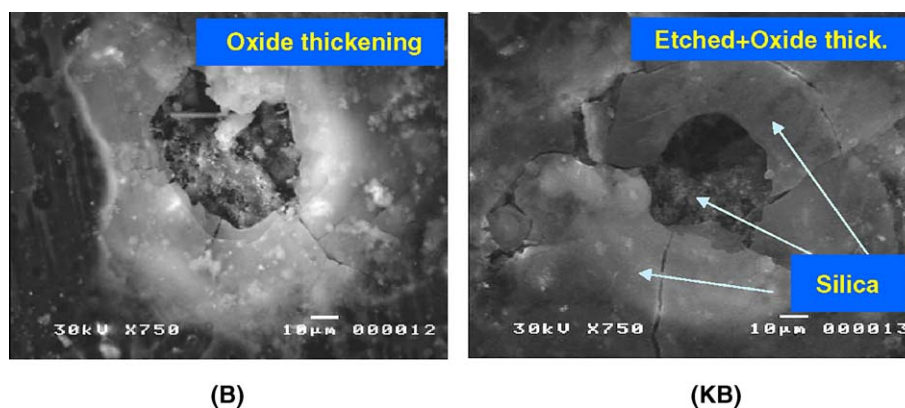

Fig. 5. SEM of group 3 (B) and group 4 (KB) after 30 days in NaCl (pitting auto-repair by forming a dense silica layer over the pitted area).
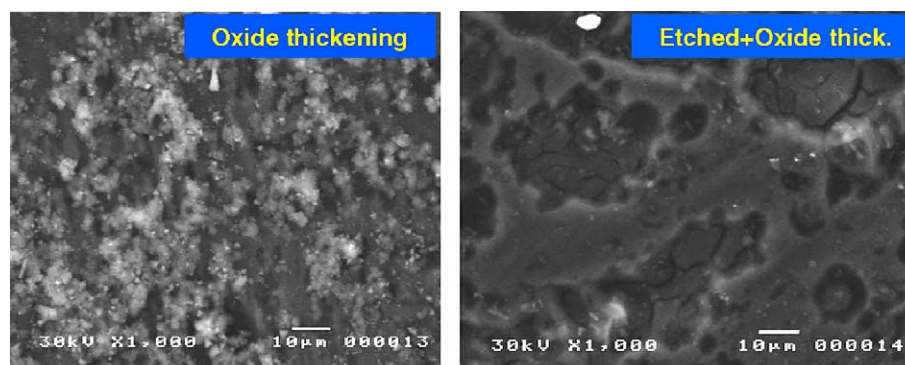

Fig. 6. SEM of group 3 (B) and group 4 (KB) before corrosion (surface distribution).

Table 1
Atomic ratios of Si/Al and Cl/Al for some silica-treated specimens after 30 days in NaCl

| Type of treatment	Al_2O_3 ratio (%)	Si/Al Atomic ratio	Cl/Al Atomic ratio
Group 1 (DT)	23.66	12.98	0.88
Group 2 (K)	36.64	1.42	4.14
Group 3 (B)	37.36	1.50	0.57
Group 4 (KB)	34.87	3.55	0.68

the most predominant corrosion species in groups 1, 2 and 3 is the general corrosion. The surface resistance is the summation of pitting and general corrosion resistances. This can explain why the values of surface resistance are close to each other in all cases.

According to the Bode plot (Fig. 3B), the samples of group 1, 2 and 3 showed a dramatic decrease of the impedance in the capacitive region, which is characteristic for the pitting process on Al. In addition, the phase angle (θ) tended toward zero at low frequencies, indicating that the resistance of the barrier layer was being approached. An additional maximum

of θ was observed for the above-mentioned samples, as evident in Fig. 3B. These changes of the spectra at very low frequencies indicated the occurrence of pitting and were in agreement with the visual and SEM inspection. On the other hand, group 4 (KB) showed very stable impedance behavior even after 30 days of immersion in NaCl solution, indicating that etched and oxide thickened provided superior corrosion-resistant layer.

Polarization curves confirmed this result where as-polished specimens did not show any passive perfect zone. Conversely, an onset passive zone amounted to 40 and 120 mV for group 3 and group 4, respectively, was observed (Fig. 4). Although the pitting potential, E_{pit}, of the specimens of group 3 is 40 mV higher than the group 4, and the corrosion potential, E_{Corr}, of group 3 is 100 mV more noble than group 4, the pitting area under the loop of group 4 is too small to that obtained from group 3. The difference between the pitting corrosion potential (E_{pit}) and the corrosion protection potential ($E_{protect}$) of group 4 is almost one third of group 3 indicating that the chance for pitting corrosion to occur is very low compared with group 3. Furthermore, when pitting started, the ability to repair the pits is
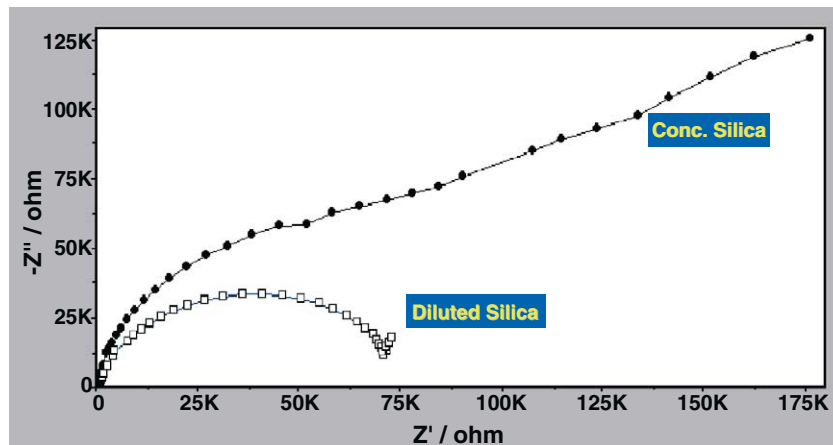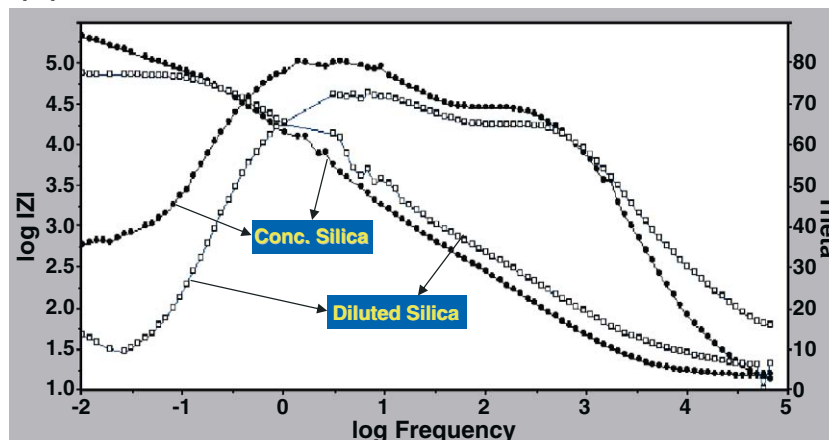

Fig. 7. (A) Nyquist plots and (B) Bode plots after 30 days of immersion in NaCl. Group 4 (KB) etching followed by boiling water for 1 h followed by silica treatment at different concentration.

very fast in group 4 compared with group 3. The presence of long perfect passive zone beside the distinct pitting auto-repair (Fig. 5) for group 4 suggests that the film formed is relatively thicker and more uniformly distributed than group 3 and consequently; group 4 is more effective in reducing the number of pits. These results confirm the important role of the etching together with the oxide thickening processes to improve the localized corrosion resistance.

The corrosion potential, E_{Corr}, of groups 3 and 4 was shifted to more noble ones. However, localized corrosion and microcracks are still present. This confirms what we mentioned before that silicate layer acts as a barrier to oxygen diffusion to the metal surface thereby impeding but not preventing corrosion.

The effect of silica treatment as a sealing step into thick porous aluminum oxide layer prepared by immersion in boiling distilled water for 1 h was also investigated using SEM-EDS. SEM (Fig. 6) showed that the specimen surface of group 4 had a smooth appearance which suggested that the silicate filled the pores of cellular oxide structure. Such behavior was not observed for group 3 where SEM revealed presence of Al_2O_3 agglomerates at the metal surface indicating that the etching process has an important effect on the distribution of silica over the specimen surface.

Another confirmation was obtained by EDS analysis where the amount of SiO_2 in the specimens of group 4 is higher than that observed in the other groups (Table 1). Although the amount of SiO_2 identified in the specimens of group 1 is much higher, SEM showed that this high amount of silica is present as large cracked areas attached to and not incorporated into the metal surface (Fig. 1). On the other hand, no silicon peaks were identified using XRD in all groups. These results, together with the results of EDS analysis, indicate that a porous Al-oxide film incorporated with silica was formed in group 4, and this film is relatively thin to be detected by XRD. The presence of silica-rich Al-oxide film at the metal in group 4 can explain the improvement of corrosion resistance using such type of treatment. Accordingly, it seems that the pitting auto-repair process takes place only when silica-rich Al-oxide film is present.

According to Nyquist plot (Fig. 7A), reducing silica concentration to half affects negatively the corrosion resistances. The surface resistance decreased more than one order of magnitude from 1.75×10^5 Ω cm^2 to 0.75×10^5 Ω cm^2.

For the silica-diluted sample (Fig. 7B) a dramatic decrease of the impedance in the capacitive region was observed, which is characteristic for the pitting process on Al. In addition, the phase angle (θ) tended toward zero at low frequencies, indicating that the resistance of the barrier layer was being approached. An additional maximum of (θ) was observed, as evident in Fig. 7B. These changes of the spectra at very low frequencies indicated the occurrence of pitting and were in agreement with the visual and SEM inspection. On the other hand, the samples that treated with concentrated silica showed very stable impedance behavior, indicating that silica concentration plays an important role to provide high corrosion protection.

Table 2
Polarization data after 30 days in NaCl

Sample	E_{corr} (mV)	Passive current (A)	E_{pit} (mV)	Perfect passivity domain
As-polished	778	3×10^{-6}	740	Not present
Diluted silica (KB)	764	1×10^{-6}	643	Not present
Concentrated silica (KB)	780	5×10^{-7}	619	≈ 140 mV

Polarization measurements (Table 2) confirmed these results where diluted silica treated specimens did not show any passive perfect zone. Conversely, concentrated silica treated specimens showed an onset passive zone of about 140 mV. The pitting potential, E_{pit}, of concentrated silica is 25 mV more noble than the diluted one. The corrosion potential, E_{corr}, of concentrated silica is also 15 mV more noble than the diluted one. The pitting area under the loop of concentrated silica is too small to that obtained from diluted silica. The presence of a long perfect passive zone beside the distinct pitting auto-repair (Fig. 5) for concentrated silica-treated samples suggests that the film formed is relatively thicker and more uniformly distributed than the diluted one, and consequently, concentrated silica is more effective in reducing the number of pits.

4. Conclusions

1. Generally, silica treatments improve the pitting resistance due to formation of protective oxides act as barrier to oxygen diffusion to the metal surface.
2. Corrosion protection is mainly due to the formation of silica-rich Al-oxide film. Silicon incorporates in the pores of Al-oxide film to form a high corrosion-resistant layer.
3. Etching together with the oxide-thickening processes play a vital role in the mechanism of corrosion protection of aluminum alloys in NaCl.
4. Silica concentration plays an important role to provide high corrosion protection. The film formed is relatively thicker and more uniformly distributed than the diluted one, and consequently; concentrated silica is more effective in reducing the number of pits.

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