

# MICROSTRUCTURE AND CORROSION PERFORMANCE OF SILICA COATINGS ON ALUMINUM SURFACE PREPARED BY PLASMA ELECTROLYSIS TECHNIQUE

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**Abstract** Silica phases were precipitated on aluminum surface by potentiostatic plasma electrolysis technique. Aqueous sodium silicate solutions with different concentrations were used for this purpose. SEM, EDS, XRD, surface profiles and polarization curves were used to study coatings properties. The results showed that the growth of the silica containing phases on aluminum surface was promoted by increasing sodium silicate content of the electrolyte. However, in very high concentration solutions, the morphology of the oxide films changed and the roughness of the coating increased. Moreover, the amorphous compounds were substituted for crystalline phases. Coated specimens showed high corrosion resistance in 3.5 % NaCl media.

**Keywords** Plasma Electrolysis, Silica Coating, Surface Profile, Polarization Curves

**چکیده** به منظور ایجاد پوشش سیلیسی روی آلومینیوم به روش الکترولیز پلاسمایی پتانسیواستاتیک از محلول آبی سیلیکات سدیم در غلظت های مختلف به عنوان الکترولیت استفاده شد. SEM، EDS، XRD، پروفیل سطح و منحنی های پلاریزاسیون جهت ارزیابی خواص پوشش مورد استفاده قرار گرفت. نتایج نشان داد که رشد فازهای حاوی سیلیس با افزایش غلظت سیلیکات سدیم در الکترولیت تقویت می شود. البته در غلظت های بسیار زیاد، مورفولوژی فیلم های اکسید تغییر نمود و خشنی سطح پوشش افزایش یافت و نیز فازهای پوشش از حالت بلورین به حالت آمورف تبدیل شدند. نمونه های پوشش داده شده مقاومت به خوردگی بالایی در محلول آبی کلرید سدیم ۳/۵٪ نشان دادند.

## 1. INTRODUCTION

Plasma electrolysis is a relatively novel technique in surface treatment of metals. In this process, spark or arc plasma micro-discharges in an aqueous solution are utilized to ionize gaseous media from the solution such that complex compounds are synthesized on the metal surface through the plasma chemical interactions [1,2]. Plasma electrolytic oxidation (PEO), also called micro-arc oxidation (MAO) or anode spark precipitation (ASP) is the most important branch of plasma electrolysis. It's a technique to produce hard and thick ceramic coatings on metals, such as aluminum, titanium, magnesium, niobium and their alloys [3-5]. This process usually is carried out in

alkaline solutions [6-9]. Different current regimes such as DC pulsed unipolar current, amplitude modulated AC or pulsed bipolar current can be used [10].

Recently, several researches outlined alumina growth on aluminum surface by plasma electrolysis. Aluminum and its alloys have been well used in special chemical processes. However, their thermal and corrosion resistance are much lower than those of ceramic materials. Alumina coatings can provide corrosion protection to the base metal from a corrosive environment by acting as barrier films. Also, the development of crystalline phases, such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> on aluminum surface can provide high hardness [11,12]. Although alumina is considered to be one of the most versatile

materials that resist corrosive attack by acids, alkalis, molten salts, as well as oxidizing and reducing gases, even at high temperatures, its pitting susceptibility, especially in chloride containing media, limits the application of Al and its alloys in seawater and marine atmospheres. Silica is extremely corrosion resistant to many environments (the notable exception is hydrofluoric acid). Moreover, inherent hardness of silica makes it resistant to erosion corrosion [13]. Monfort, et al believes silica deposition on aluminum surface under sparking conditions and formation of  $\text{Al}_2\text{SiO}_5$  and  $\text{Al}_6\text{Si}_2\text{O}_{13}$  phases is promoted by increased time of anodizing and concentration of metasilicate compounds in electrolyte. They showed that at sufficiently high concentration of metasilicate and pH, when more extreme voltage fluctuations accompany breakdown, the two-layered nature of coatings is replaced by a mixture of aluminum-rich and silicon-rich regions throughout the coating thickness [14]. However, systemic investigations on the precipitation of silica-rich phases on aluminum and the structure, composition and corrosion performance of the films were seldom reported.

The purpose of this work is to reveal the growth process of silica coatings produced by electrolytic plasma on aluminum surface and study the phase composition, morphology and corrosion behavior of the coated specimens. DC current was used for establishment of the electrolytic plasma.

## 2. EXPERIMENTAL

**2.1. Materials** Rectangular specimens of pure Al (Cu 0.009, Fe 0.04, Mn 0.005, Si 0.02 in wt % and Al-balance) with dimensions of 25 mm × 30 mm × 1 mm were used as the substrate. The specimens were ground successively with SiC papers to 1500 grit, degreased in absolute ethanol and then rinsed with distilled water. The specimens were hanged in the electrolyte using a rigid catch contact and were insulated against arcs using proper glue and a plastic jacket. Aqueous solutions of sodium silicate at concentrations of 10, 20, 30 and 90 g/l were prepared using analytical grade chemicals (Merck).

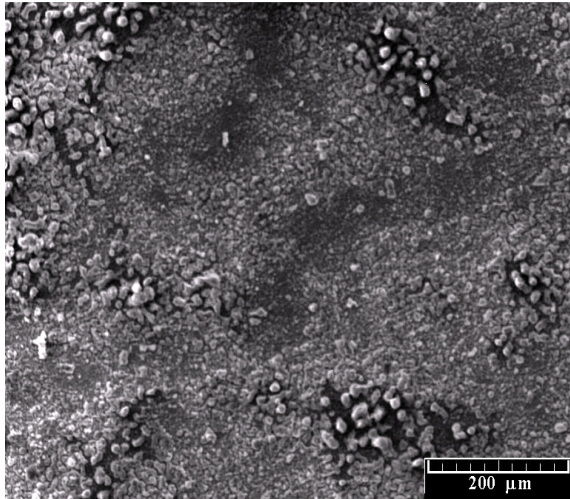
**2.2. Methods** The process was carried out with

conventional electrolytic plasma electrolytic oxidation equipment consisting of a DC power supply and a stirring-heating system. The magnetic stirrer prevented localized temperature overshooting of the electrolyte adjacent the anode. To obtain reproducible data, voltage was increased immediately up to 500 V. In 1 minute duration of each experiment, the current density of the specimen changed and spontaneously decreased in the range of 530-120  $\mu\text{A}/\text{cm}^2$ . After the treatment, the specimens were rinsed carefully with distilled water and then dried in air.

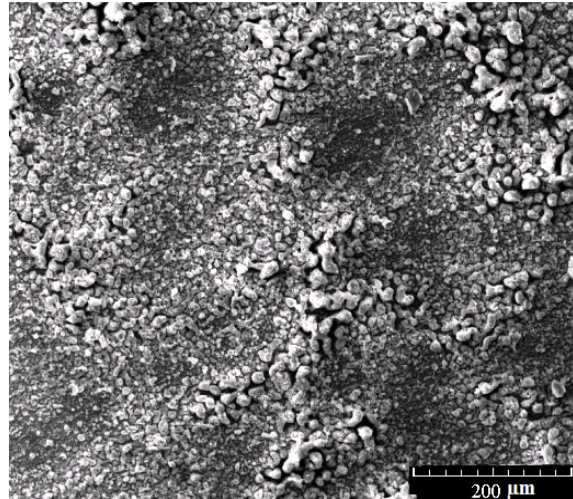
**2.3. Equipment** The microstructure and phase composition of the coatings were studied using scanning electron microscope (SEM), CamScan MV2300 and X'Pert Pro system x-ray diffractometer (XRD), respectively. Also, roughness of the coatings was examined by obtaining surface profiles with the same SEM. The observations were complimented with an energy dispersive x-ray spectroscopy (EDS) for analysis of elemental distributions across the surface as well as cross-section of the coated specimen. An EG and G Princeton Applied Research Model 263 A potentiostat was used for electrochemical corrosion and potentiodynamic polarization curves were recorded in 3.5 wt % NaCl solution in the potential range of  $\pm 250$  mV versus OCP at a sweep rate of 1 mV/s. A platinum electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. A Luggin capillary having a porous tip was employed for minimizing the contamination, preventing potential variation of the reference electrode, and positioning it in the desired point of the cell. For confirming the results reproducibility, each measurement was carried out three times in the same condition and the mean value was reported.

## 3. RESULTS AND DISCUSSION

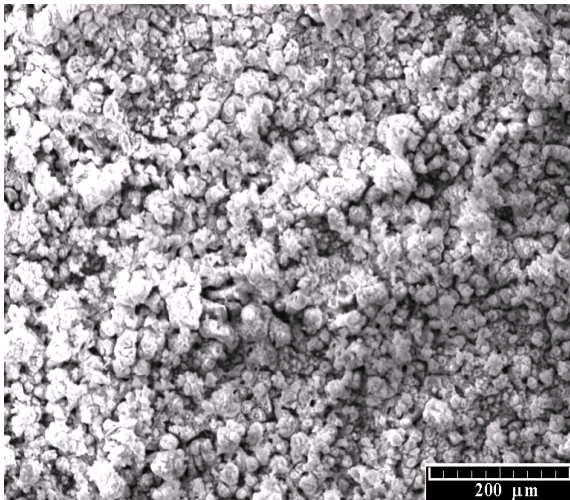
**3.1. SEM and EDS Analysis** Figure 1 shows SEM micrographs of the coatings produced via plasma electrolysis in electrolytes containing different concentrations of  $\text{Na}_2\text{SiO}_3$ . Coating was formed in all conditions. Clearly, morphology and particle size of the precipitated phases gradually changed by increasing the sodium silicate



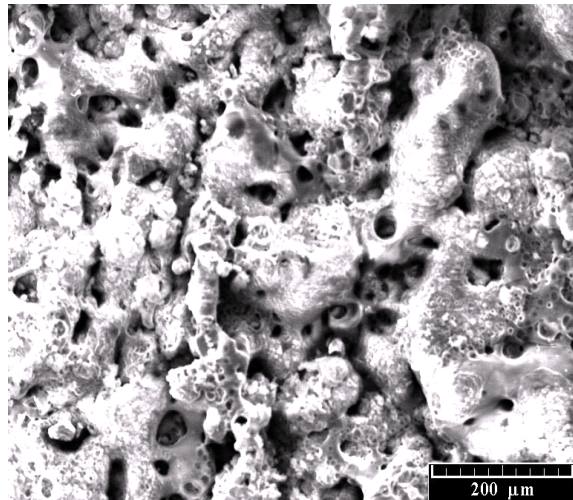
(a)



(b)



(c)



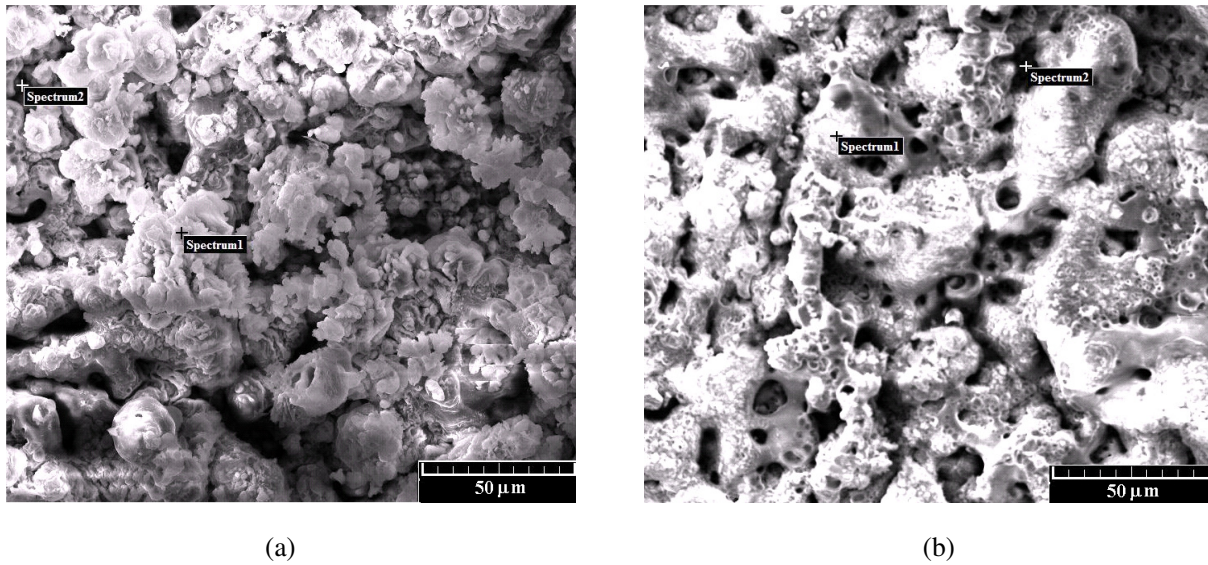
(d)

**Figure 1.** Scanning electron micrographs of the oxide films formed in silicate solutions: (a) 10, (b) 20, (c) 30 and (d) 90 g/l.

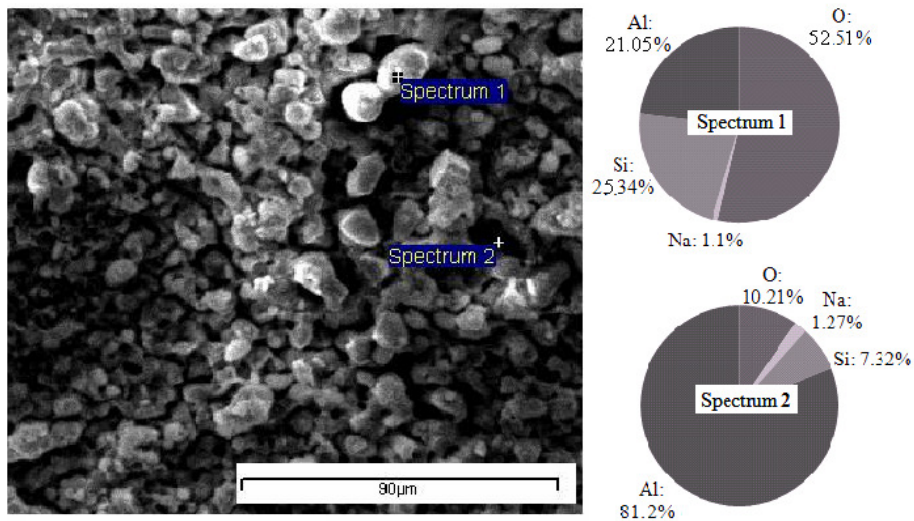
concentration. Besides, some step by step like growth, converting gradually to a porous microstructure was ascertained in the coatings produced in higher concentrations (Figure 2).

Figure 3 shows a typical EDS analysis of the produced coating in 10 g/l  $\text{Na}_2\text{SiO}_3$  solution. Detected peaks in ups and downs confirmed the discrepancy in the compounds formed in substrate/coating and coating/electrolyte interface.

EDS results showed that increase in the solution concentration enhanced nucleation of silica-rich phases on the surface and limited aluminum oxides formation. Moreover, EDS analysis demonstrated that increasing sodium silicate concentration in the solution reduced Al percentage of the oxide film even in collapses and so, promoted precipitation of a silica-rich coating on the surface. Figure 4 shows a typical EDS maps of the PEO coatings produced



**Figure 2.** Scanning electron micrographs showing growth way of the oxide films formed in high concentration silicate solutions: (a) 30 and (b) 90 g/l.



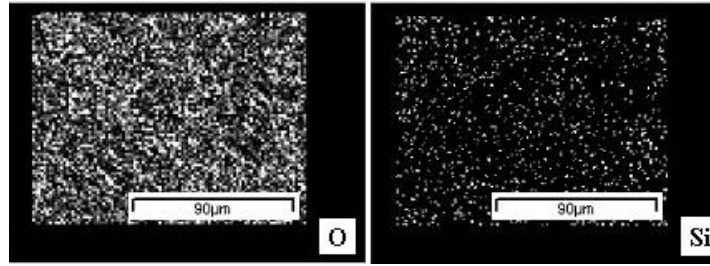
**Figure 3.** A typical EDS analysis of the oxide film formed in electrolyte containing 10 g/l  $\text{Na}_2\text{SiO}_3$ .

in high and low concentration electrolytes. It ascertained the coverage of the silica containing phases, especially in concentrated solutions.

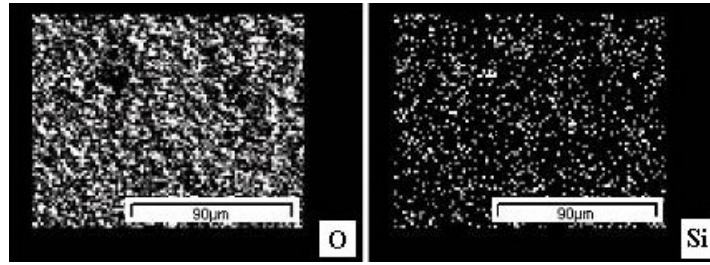
Figure 5 shows a typical cross-section of the coating/substrate interface. The results of line scans illustrated variations of aluminum, oxygen and

silicon concentrations through the cross-section.

**3.2. XRD Patterns Analysis** Figure 6 presents XRD patterns of the coatings produced in electrolytes containing different concentrations of  $\text{Na}_2\text{SiO}_3$ . Strong diffraction peaks of silica

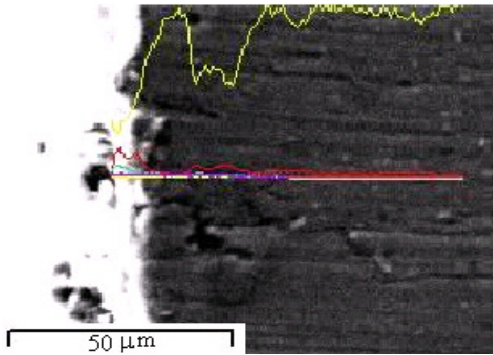


(a)

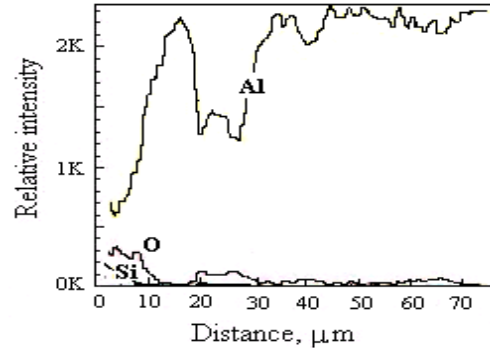


(b)

**Figure 4.** EDS maps of the PEO coatings produced in different concentrations of  $\text{Na}_2\text{SiO}_3$ : (a) 10, (b) 90 g/l.



(a)



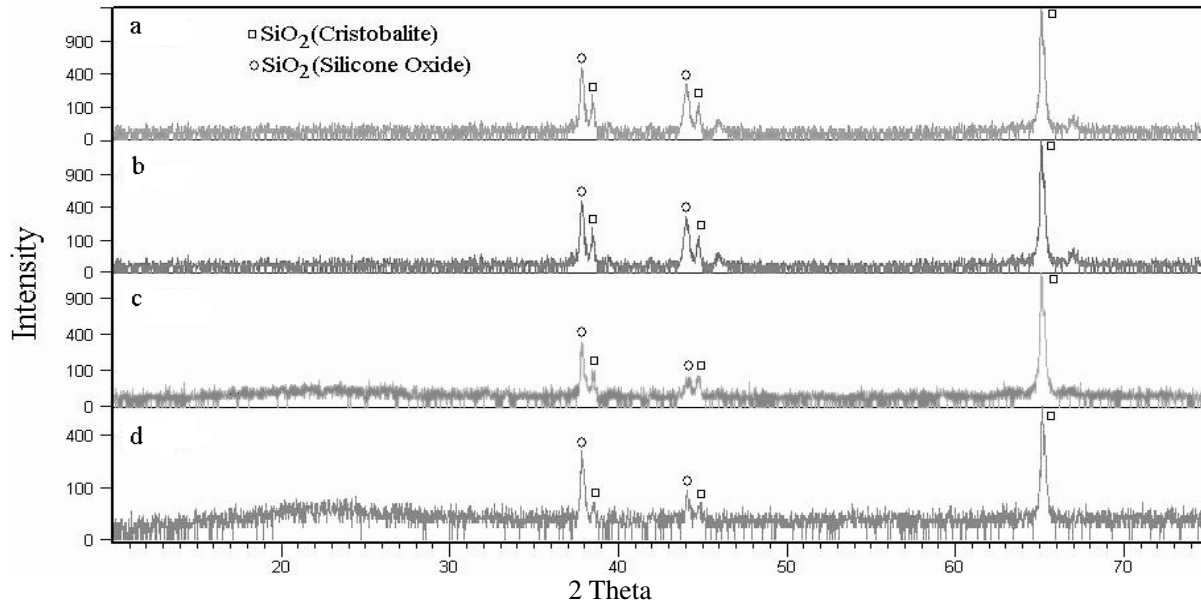
(b)

**Figure 5.** Cross-section of the coating formed in electrolyte containing 10 g/l  $\text{Na}_2\text{SiO}_3$ : (a) scanning electron micrograph, (b) relative intensity of Al, O and Si versus distance (intensity of Na is negligible).

containing phases were detected in all of the XRD patterns. The peaks confirm SEM and EDS results.

Also, the results of XRD patterns analysis indicated that in the coatings produced in high concentration solutions, amorphous compounds were substituted for crystalline phases. This may

be attributed to the augmentation of the numbers and intensity of the electrical discharges on the surface during the tests accomplished in concentrated solutions. It was observed that during plasma electrolysis in concentrated solutions, a halo of white light covered the specimen. Meanwhile in



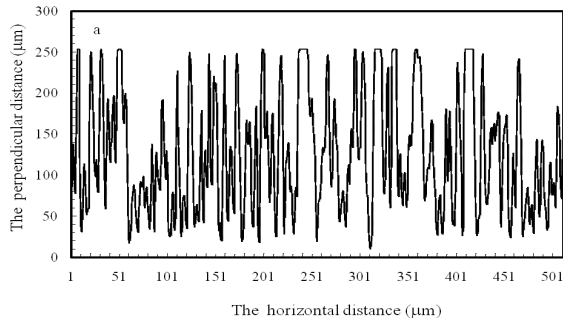
**Figure 6.** XRD patterns of the oxide films formed in silicate solutions: (a) 10, (b) 20, (c) 30 and (d) 90 g/l.

low concentration solutions, the arcs were separated and red colored. In the discharge channel, the instantaneous temperature can reach 7000 K. The melted oxide phase has an intimate contact with the cool electrolyte and the cooling velocity of it even reaches  $10^8$  K/s [4,15]. Strong electrical discharging, confronted in high sodium silicate concentration solutions, may increase temperature difference between the surface and the solution and so can raise the cooling rate of the coating [16]. Also, under the situated conditions, the contact numbers between the coating and the solution may increase due to the more disarrangement of the gaseous film around the specimen. These variations can enhance the formation of the amorphous compounds.

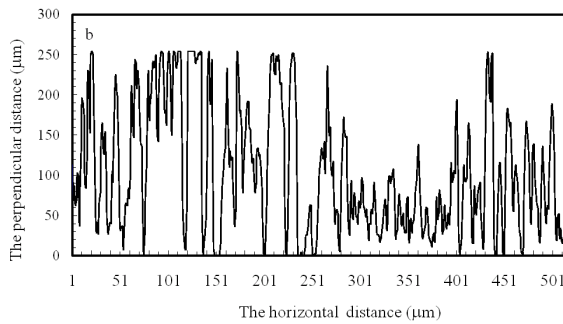
**3.3. Coatings Roughness** Figure 7 demonstrates surface profiles of the oxide films produced in sodium silicate solutions with different concentrations. Roughness severity of coatings can strongly affects their tribological properties as well as their corrosion behavior. It was observed that the fluctuations intensity of the coatings surface was diminished by increasing the electrolyte concentration. However, the coating produced in

90 g/l  $\text{Na}_2\text{SiO}_3$  solution (very high in this study) showed more roughness than one treated in 30 g/l  $\text{Na}_2\text{SiO}_3$  solution. This can be attributed to the porous nature of the film as well as the elevated growth rate of the oxide phases on the surface. As mentioned before, increase of electrical discharge intensity observed in very high concentration solutions (90 g/l) could change the coating morphology from compact nucleation and even growth to a complex and porous microstructure.

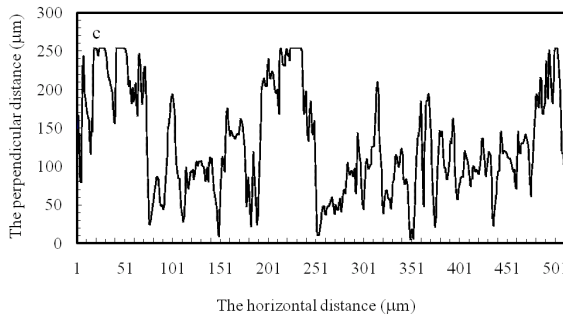
**3.4. Polarization Curves** The corrosion performance of the oxide films formed in sodium silicate solutions with different concentrations was evaluated by measuring polarization behavior of the specimens. Figure 8 shows potentiodynamic polarization curves in 3.5 wt % NaCl media for bare and electrolytic plasma treated specimens and Figure 9 illustrates the potentiodynamic polarization parameters extracted by “Softcorr 352” software. Corrosion current density ( $i_{\text{corr}}$ ) of bare aluminum electrode in this condition was  $16.54 \mu\text{A}/\text{cm}^2$ . It is clear that corrosion current density decreases in the presence of the silica coating more than two orders of magnitude for the specimen treated in the optimum concentration of sodium silicate (curve d,



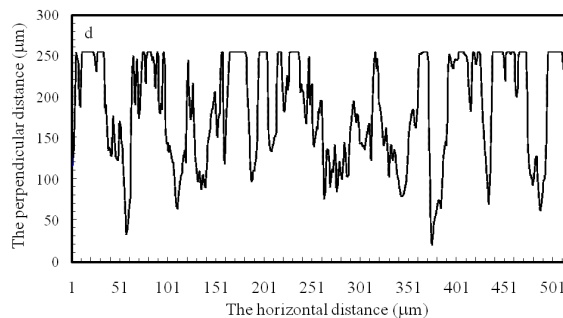
(a)



(b)

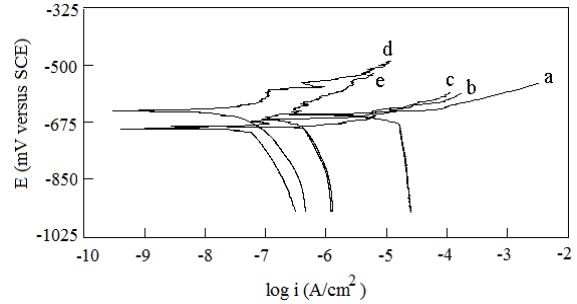


(c)



(d)

**Figure 7.** Surface profiles showing roughness of the oxide films formed in silicate solutions: (a) 10, (b) 20, (c) 30 and (d) 90 g/l.



**Figure 8.** Potentiodynamic polarization curves of the aluminum specimens coated in different concentrations of  $\text{Na}_2\text{SiO}_3$ : (a) bare, (b) 10, (c) 20, (d) 30, (e) 90 g/l. Test environment: NaCl 3.5wt%; T: room temperature.

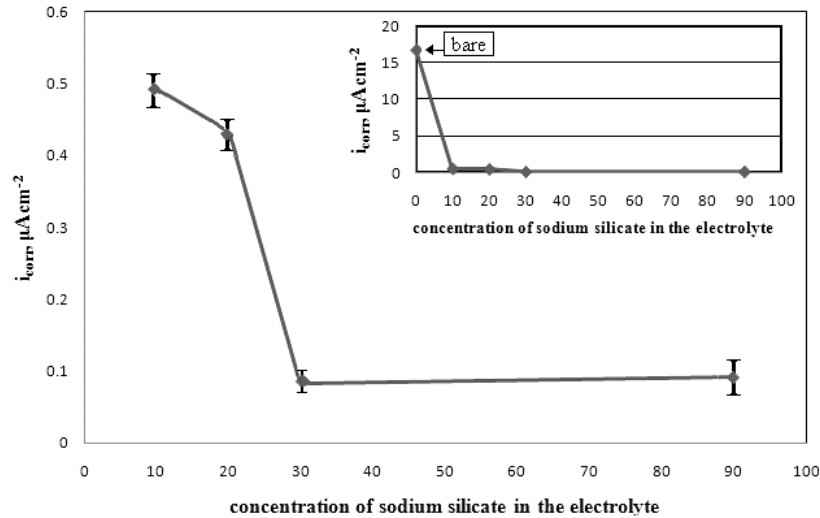
$i_{\text{corr}}=0.08\mu\text{A}/\text{cm}^2$ ). It is notable that the specimen treated in 90 g/l  $\text{Na}_2\text{SiO}_3$  solution showed slightly higher corrosion current density. This is compatible with other results and can be qualitatively explained by taking into account the microstructure and the phase composition of the oxide films.

#### 4. CONCLUSIONS

1. Silica-rich phases on aluminum surface can be produced through potentiostatic electrolytic plasma technique.
2. Roughness of the coatings decreased by increasing the electrolyte concentration. However, the coatings produced in very high concentration solutions were subjected to more roughness.
3. Formation of the amorphous compounds in high sodium silicate concentration solutions can be attributed to increasing the coating cooling rate.
4. Corrosion current density decreased in the presence of the silica coating. Coated specimens in 30 g/l  $\text{Na}_2\text{SiO}_3$  solution showed the highest corrosion resistance.

#### 5. ACKNOWLEDGEMENTS

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**Figure 9.** Variation of corrosion current density of the coating versus concentration of sodium silicate in the electrolyte of plasma electrolysis.

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