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Cerium oxide as conversion coating for the corrosion protection of aluminum

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Abstract

CeO₂ coatings were formed on the aluminum after Al surface preparation, by dripping the ceria sol, previously prepared by forced hydrolysis of Ce(NO₃)₄. The anticorrosive properties of ceria coatings were investigated by the electrochemical impedance spectroscopy (EIS) during the exposure to 0.03% NaCl. The morphology of the coatings was examined by the scanning electron microscopy (SEM). EIS data indicated considerably larger corrosion resistance of CeO₂-coated aluminum than for bare Al. The corrosion processes on Al below CeO₂ coating are subjected to more pronounced diffusion limitations in comparison to the processes below passive aluminum oxide film, as the consequence of the formation of highly compact protective coating. The results show that the deposition of ceria coatings is an effective way to improve corrosion resistance for aluminum.

Keywords

Ceria, Coatings, Corrosion, Microstructure.

Introduction

It is well known that chromate-based chemical conversions were used for corrosion protection of aluminum for decades. On the other hand, because of toxic and carcinogenic properties of chromium, this kind of coatings should be soon withdrawn from all industrial processes [1,2].

Many researchers tried to find alternative for chromate conversions; it is believed that rare earth elements (cerium, lanthanum, neodymium and yttrium) could effectively inhibit the corrosion of aluminum. Hinton *et al.* [3,4] introduced the application of lanthanide compounds for this purpose. The reported results showed that these barrier coatings simply prevent contact between aluminum surface and corrosive species. The best degree of corrosion inhibition is achieved with cerium [5-8].

Based on these findings, the aim of this study was to examine efficacy of ceria based coating for corrosion protection of aluminum, by means of the scanning electron microscopy (SEM) and the electrochemical impedance spectroscopy (EIS).

Experimental

Materials

The aluminum panels, 20 mm×18 mm×1 mm in size, were used as substrates. The surface of specimens was mechanically polished by 800, 1200, 2400 and 4000 grit emery papers. To remove the surface contamination the panels were degreased in alkaline solution containing: NaOH, Na₃PO₄·12H₂O, Na₂SiO₃ and ethoxylate of nonylphenol with nine molecules of ethylene oxide, during 1 min at 70 °C. Finally, the panels were rinsed by distilled water and dried in air at room temperature.

For the investigation in this study ceria sol which was obtained by forced hydrolysis of 1 N Ce(NO₃)₄ aqueous solution was used. The ceria sol was synthesized by Gulicovski *et al.* [9] according to the reported procedure. The main characteristics of the synthesized ceria sol are: pH value of synthesized sol, 0.66, average particle size, 71 nm, and solid phase content, 0.51 mass%. In order to obtain the stable and pure ceria dispersion, nitrates were removed from the prepared sol by ultrafiltration. The final pH of the sol was around 4.

The CeO₂ coatings were formed on the aluminum panels by dripping method. The ceria sol was applied in the quantity of 2×30 μl. Between the two applications, dispersing medium was evaporated at 35 °C.

Methods

The corrosion behavior of the ceria-coated aluminum was determined by the electrochemical impedance spectroscopy (EIS). EIS data were recorded at the open circuit potential using a Gamry, Reference 600 potentiostat/galvanostat/ZRA.

To examine the surface morphology of the coatings, scanning electron microscope (SEM) JOEL, model JSM-5800, at 20 kV was used.

Results and Discussion

Surface morphology of bare Al and Al/CeO₂

Figure 1 shows typical SEM images of the Al and Al/CeO₂ specimens before and after prolonged exposure to 0.03% NaCl solution. An uniform pattern of the Al surface can be seen after mechanical polishing and degreasing (Figs. 1a and 1b). A highly porous film consisted of uniform μm-sized grains is observed at the Al surface after immersion in NaCl solution (Figs. 1c and 1d), *i.e.*, native homogeneous surface has been destroyed and a new layer of corrosion products was produced.

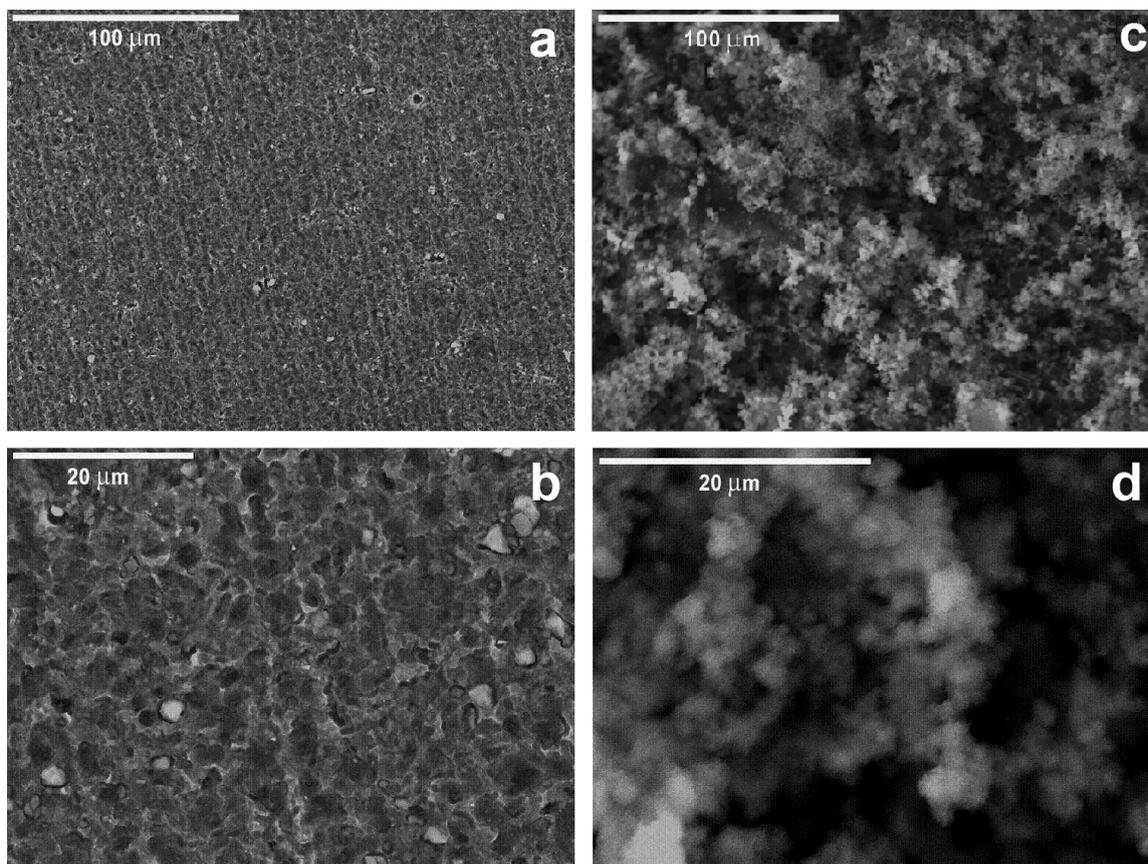


Figure 1. Typical scanning electron micrographs of Al sample at two different magnifications: before (a and b) and after exposure to 0.03% NaCl (c and d).

Typical surface morphology of a cerium oxide coating deposited onto Al panel is shown in Fig. 2. Narrow cracks and sparing pits are visible (Figs. 2a and 2b); however, no signs of the peeling were detected. The cracks are typical for rather thick conversion film and it is the result of the stress induced in the film during the drying process. SEM micrographs of the film surface after immersion in 0.03% NaCl solution (Figs. 2c and 2d) revealed presence of agglomerates of corrosion products (Fig. 2c). The agglomerates appear to lay over compact granular structure (Fig. 2d), uniformly consisted of μm-sized fluffy grains.

Corrosion behavior

The corrosion behavior and stability of prepared Al/CeO₂ sample were investigated by EIS after different times of the exposure to 0.03 % NaCl. The data registered after 24 h of exposure are shown in Fig. 3 as complex plane and Bode phase shift spectra and compared to the data of Al reference sample. The complex plane spectra are consisted of at least three semicircles. The semicircle at lowest frequencies (below 0.4 Hz) is more pronounced for Al/CeO₂, whereas it is only weakly indicated in the spectrum of Al (below 0.3 Hz). The peaks corresponding to two the high frequency semicircles appear clearly in the phase shift spectra, whereas low frequency semicircle can be observed only as a shoulder around 0.1 Hz for Al/CeO₂. However, phase shifts at low frequencies for both Al/CeO₂ and Al are similar, around 20°. The semicircles are larger for Al/CeO₂, especially two of them appearing at lower frequencies. This indicates good corrosion protection of the applied ceria coating, since this kind of the spectra, usually observed for the corrosion of aluminum, are assigned to the passive Al-oxide film (high frequency data) and corrosion-related charge transfer processes beneath (low frequency data) [10-12].

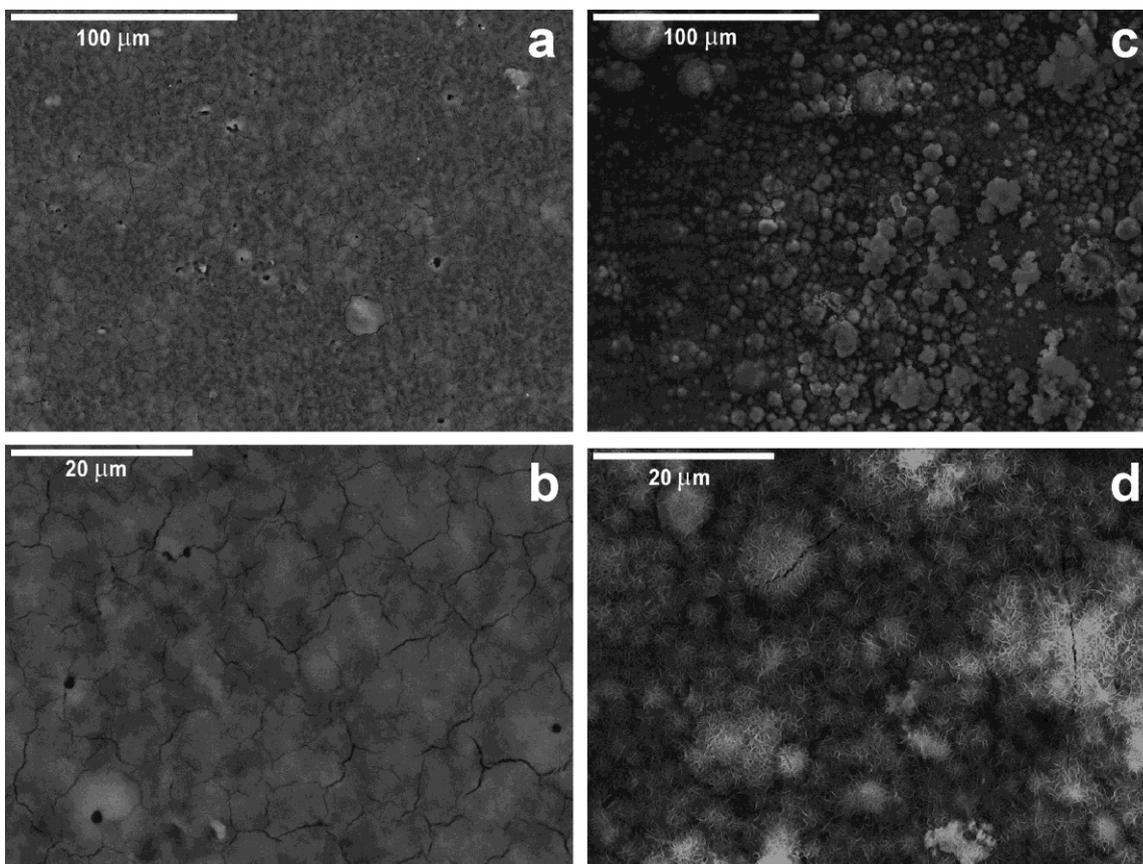


Figure 2. Typical scanning electron macrographs of Al/CeO₂ sample at two different magnifications: before (a and b) and after exposure to 0.03% NaCl (c and d).

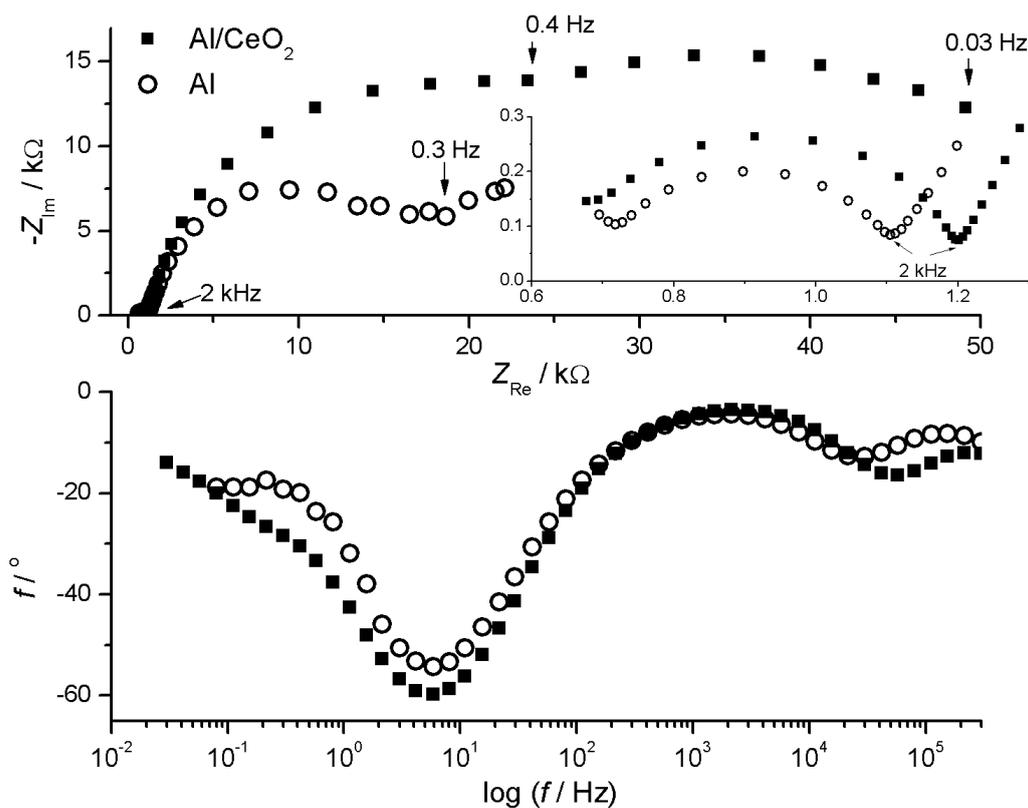


Figure 3. Complex plane and Bode plots of Al and Al/CeO₂ sample registered at open circuit potential after 24 h exposure to 0.03 % NaCl. Inset: high frequency parts of the complex plane spectra.

In order to examine the effect of exposure time on the characteristic features of the EIS spectra, they were recorded at prolonged exposure times. Typical complex plane and Bode plots of EIS data are presented in Fig. 4 by those registered after 312 h of exposure.

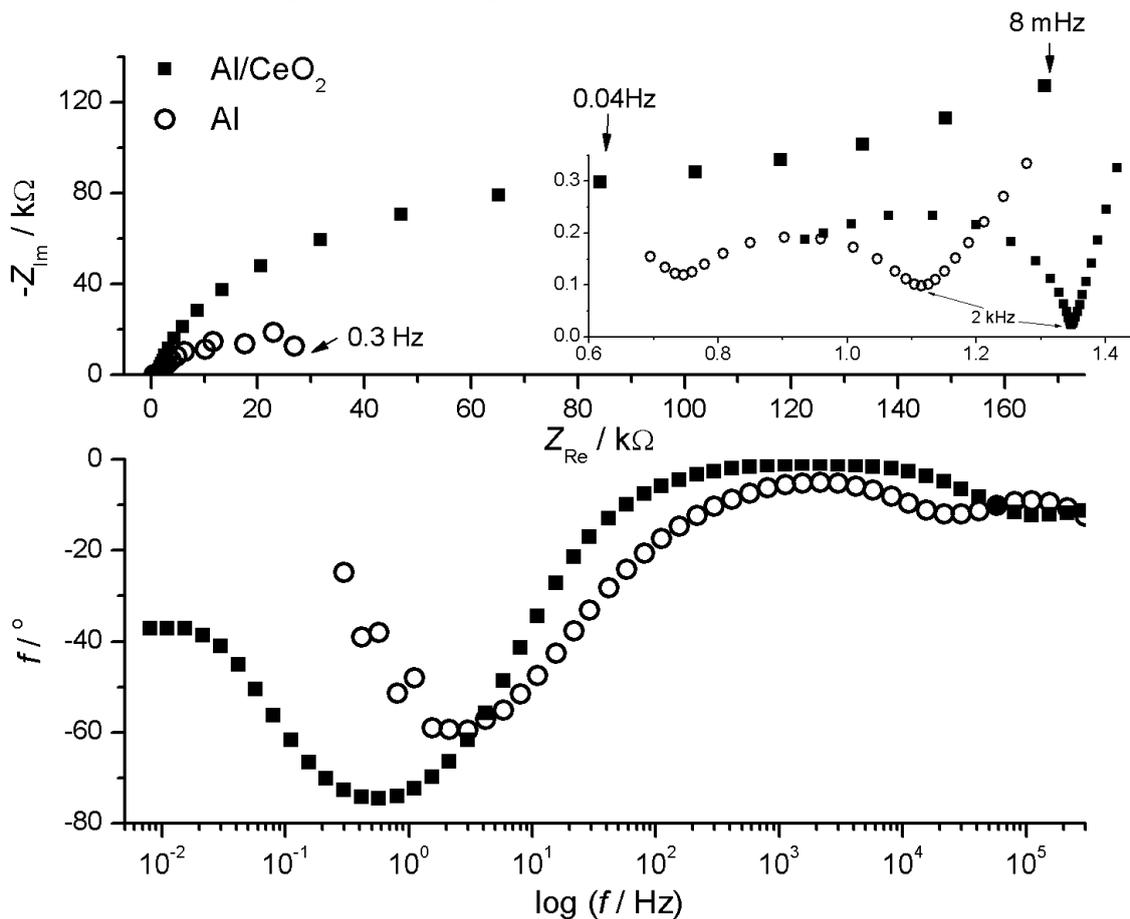


Figure 4. Complex plane and Bode plots of Al and Al/CeO₂ sample registered at open circuit potential after 312 h exposure to 0.03 % NaCl. Inset: high frequency parts of the complex plane spectra.

As Fig. 4 shows, prolonged exposure to the corrosive environment does not considerably change the characteristic features of the spectra. The comparison of Figs. 3 and 4 reveals that the spectra for both Al and Al/CeO₂ samples at high frequencies are poorly affected by the prolongation of the exposure, which indicates that 24 h of exposure is sufficiently long to allow complete formation of passive oxide layer. However, it appears that corrosion processes on bare Al are not hindered since its spectra from Figs. 3 and 4 at lower frequencies, related to the charge transfer, are similar. It follows that corrosion products formed after 24 h are not incorporated into the passive film with impedance response at high frequencies.

These observations, except those related to the high frequency semicircles and passive aluminum-oxide interlayer does not hold for Al/CeO₂ sample. It is to be noted from Figs. 3 and 4 that the semicircles for Al/CeO₂ sample in low frequency domain grow considerably upon the increase in exposure time, which can be considered as a result of increased corrosion resistance with respect to bare Al. At lowest frequencies (below 0.04 Hz), the semicircle in Fig. 4 is followed by a straight line assignable to the diffusion controlled corrosion processes. Indeed, the corresponding Bode plot reaches the values around 40°, which is quite close to the theoretical value of 45°. Well pronounced diffusion limitations are due to the presence of a compact protective film induced by CeO₂.

Conclusions

With an appropriate surface pre-treatment, ceria was formed on the aluminum panels by dripping method. These substrates were characterized by SEM and EIS methods in order to study their possible applications as protective barriers in corrosive environment.

SEM analysis confirmed formation of the oxide film on Al and Al/CeO₂ substrates after immersion in 0.03 % NaCl solution. The film is consisted of Al₂O₃ agglomerates with compact granular structure that improve corrosion resistance of the ceria coatings.

The results achieved by EIS measurements show that the semicircles obtained for Al/CeO₂ sample in low frequency domain grow considerably upon the increase in exposure in NaCl, which can be considered as a result of increased corrosion resistance with respect to bare Al.

It can be concluded that deposition of ceria coating is an effective way to improve corrosion resistance for aluminum.

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