

Investigation of Cerium-Lithium Sealing Treatment of Cobalt-based Conversion Coatings Formed on Aluminum Alloys

Shubai LI¹, Di MA^{2*}, Zhenzhen XU², Pei YAO¹, Yuan LIU¹, Yutao SUN¹

¹ Department of Chemical Engineering, Changzhou Institute of Engineering Technology, Changzhou 213000, China

² School of Chemistry & Environmental Engineering, Jiangsu University of Technology, Changzhou 213000, China

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A study was conducted to examine methods of adjusting cerium-lithium sealing process parameters in order to improve the corrosion protection capabilities of a cobalt-based chemical conversion film. In order to seal the pores of the cobalt-based conversion coatings, samples were treated in a cerium-lithium deposition bath in optimal process conditions. The optimal treatment condition was determined by examination of finished samples using the scanning electron microscope (SEM) and electrochemical test measurements. The corrosion behaviors of the sealing coatings were studied using an open circuit potential-time monitoring technique (OCPT), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization tests in 3.5 wt.% NaCl solution. It was found that the best treatment process for the cobalt-based conversion coating was sealed in the cerium-lithium sealing solution for 2 h at 90 °C.

Keywords: cerium, sealing treatment, aluminum alloy, corrosion resistance.

1. INTRODUCTION

Chromate treatments have superb corrosion resistance and have been the most commonly used technology for surface anti-corrosion pre-treatments. The technology had two major advantages: 1) Chromate treatment ensured that the metallic surfaces had a reliably tight protective film, and 2) The hexavalent chromium in the chromate film was partially soluble and was able to repair discontinuities in the film [1–4]. However, many countries have introduced strict rules and regulations on the use of hexavalent chromium ions [5–8] because hexavalent chromium ions can cause cancer in humans and improper handling can cause serious environmental pollution. Additionally, the wastewater treatment process is demanding.

Environmentally friendly alternatives to chromate treatments for protecting aluminum alloys have been investigated in the surface treatment field [9, 10]. One area that has been researched extensively in recent years is the use of rare-earth salt conversion coatings for the corrosion protection of aluminum alloys [11–13]. Another alternative that has been widely studied is cerium compounds because they are non-toxic and relatively low-cost [14, 15]. However, the surface oxide film is created by anodic oxidation or chemical oxidation of the porous structure and the film has poor corrosion resistance. The oxide film requires a sealing treatment to form cerium conversion coatings on the porous film of anodized aluminum [16–21].

There is an urgent need to develop chromium-free chemical oxidation technologies in order to produce reliable and effective aluminum alloy surface treatments because of the severe environmental contamination that is created during the conventional chromate chemical oxidation process [22, 23]. Ever since the first proposal for

preparing salt conversion films for aluminum alloy surfaces appeared [24], extensive research has been carried out around the world on the film forming mechanism and on the film forming processes for aluminum alloy rare earth conversion coatings [25]. Rare earth conversion coatings have proven to be ideal coatings for use as alternatives to chromate conversion coatings [26]. Although the cobalt salt conversion process was developed relatively earlier than other processes, it is considered a new technology in chromium-free conversion and has many advantages. And the approach already has been used for surface treatments in aerospace, electronics, and communications products [27–30].

Aluminum cobalt salt conversion technology was proposed for the first time by Schriever, working for Boeing [31]. The main components of the conversion fluid in this method, were cobalt salt (trivalent cobalt valence stabilizer), ligand, and an accelerator agent. The use of the ligand is a key factor in this method, as it can affect the life and cost of the cobalt salt conversion coating. Earlier, NH₃ was the ligand of choice, but more recently anionic ligands such as NO₂⁻, CH₃COO⁻, and HCOO⁻ have been used.

Nevertheless, improvements need to be made to the corrosion resistance of cerium-based sealing of porous film. In consequence, researchers have been studying cerium-based sealing of cobalt-based conversion coatings. The purpose of the present investigation was to examine methods for changing the sealing process parameters in order to improve the corrosion protection of cobalt-based chemical conversion films.

2. EXPERIMENTAL

Coupons of 1020 pure aluminum sheet, 100 mm × 30 mm × 0.5 mm, were used as the substrate for the cobalt-based conversion coating process. The specimens were cleaned with ethanol and polished with 1.5 mol/L NaOH. HNO₃ were used to adjust the pH to the

* Corresponding author. Tel.: +86-15951207428.
E-mail address: madi@jsut.edu.cn (D. Ma)

required value and the solution was kept at a desired temperature. The pre-treated aluminum sheet was put into the solution of 20 g/L NaNO₂, 30 g/L Co(NO₃)₂·6H₂O and 20 g/L NaClO₃ to form conversion coatings on aluminum surfaces. Three different test parameters based on Ce(NO₃)₃ and LiNO₃ were performed by immersing the cobalt-based conversion coating under the conditions described. Scanning electron microscopy (SEM) was used to study the morphology of the cobalt-based conversion coating that had been formed by the above procedure. The apparatus used was a Hitachi S-3400NII SEM working at 15 KV.

A three-electrode test configuration was used for the electrochemical experiments. A working electrode area (1 cm × 1 cm) was retained on the aluminum samples. The reference electrode was a saturated calomel electrode (SCE) and the counting electrode was a platinum electrode. The test solution was 0.5 wt.% NaCl solution. A CHI660C type Electrochemical Analyzer/Workstation was used to record electrochemical measurements at the open circuit potential. The scan time was 400 s, the sampling interval was 0.1 s, the high potential was limited to 1 V and the low potential was limited to -1 V. The electrochemical impedance measurements were conducted at the open circuit potential, the high frequency was 100 kHz, the low frequency was 0.1 Hz, and the applied perturbation amplitude was 0.01 V. The standing time was 60 s, and the instrument was operated in autoranging mode. In Tafel curve measurements, the scanning speed was 0.5 mV/s, and the sensitivity was automatically adjusted to avoid over flow.

3.1. SEM morphological analyses

The rare earth conversion coating from cobalt salts was prepared on a pure aluminum surface. This coating was colorless and transparent to the naked eye. The morphology of the samples was examined using the SEM in order to gain a better understanding of the structure of the cobalt salt conversion coating on the aluminum alloy sealed by Ce(NO₃)₃ and LiNO₃ at different temperatures. In the film formation process, the reaction produces gas that causes cracks in the surface of the film. Subsequent different conditions in closed treatment conditions make the cracks smaller or they may even disappear. When the samples were sealed within the temperature range of 20 – 60°C, the surfaces of the coatings had many voids and some cracks (Fig. 1 a and c) and these were most pronounced for the sealing treatment at 60 °C. When the samples were sealed at 40 °C, the surface of the coating was smooth, and a number of small pores were observed on the surface (Fig. 1 b). The sealing treatment effects were lessened because the coating was relatively loose. The cracks and pores showed that the lower temperature of the sealing treatment was not able to close completely the pores on the coating surface; i.e. the sealing treatment was not completely effective when the samples were sealed at 40 °C (Fig. 1 b). No pores were observed at 80 and 100 °C (Fig. 1 d and e). However, there were some fine cracks in the surface. The film surface consisted of uniformly distributed pores, which can be seen in the SEM observation chart (Fig. 1 f).

3. RESULTS AND ANALYSIS

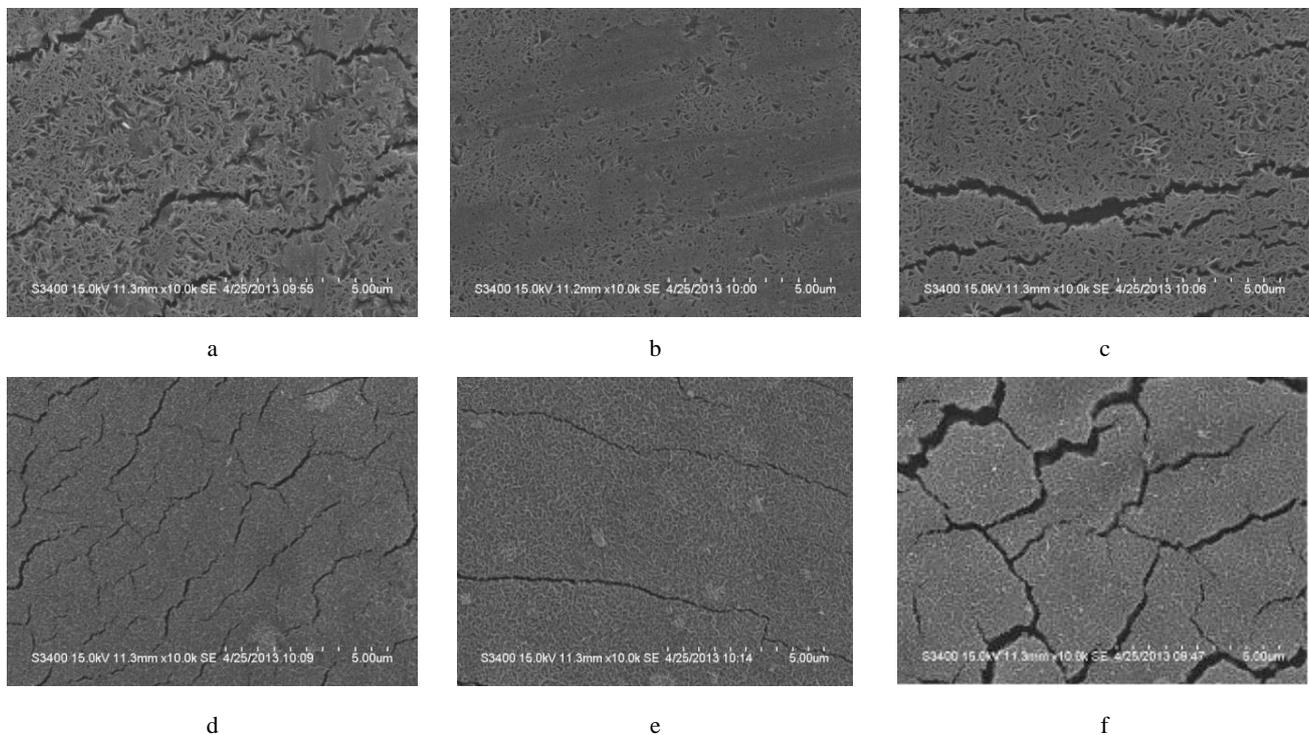


Fig. 1. SEM micrographs showing the morphology of sealing treatment at: a–20 °C; b–40 °C; c–60 °C; d–80 °C; e–100 °C; f–cobalt chemical conversion coating on pure aluminum

In summary, when the temperature was increased from 60 to 100 °C (Fig. 1 c, d and e), the effects of the sealing treatment were improved, as evidenced by the SEM results. After applying the sealing treatment, the crack width on the film surface became smaller, but the cracks were not removed completely.

3.2. Oxidation-protective properties of the coating

The electrochemical measurements were conducted at the stabilized open circuit potential. Plots of the open circuit potential time monitoring (OCPT) curves for different sealing coatings at different temperatures and sealing times concentration of the LiNO₃ sealing treatment are shown in Fig. 2. From the OCPT curves for the sealing coatings performed at different temperatures while keeping constant the sealing time and the solution concentration (Fig. 2 a). The values of the steady state open circuit potential (E_{OC}) for these three electrodes were between -1.05 and -1.15 V. The sealing coating that was prepared at 40 °C showed a lower E_{OC} , possibly because the pores of the coating were not closed during the sealing treatment. The OCPT curves were used to determine the temperature that would provide the best sealing treatment. When the sealing treatment was at 100 °C, the E_{OC} was the largest and the sealing coating had an optimal corrosion protection performance. However, after an initial potential decay, the electrode sealed at 60 °C. This potential decay was associated with a change in the surface morphology, as revealed by SEM. The unsealed pores of the sealing coating surface caused poor corrosion resistance in the electrode so that the E_{OC} was lower than when the sealing treatment was at a higher temperature. The changing trends of the OCPT curves (Fig. 2 b) show that, with the sealing time enhanced the corrosion resistance of the conversion coatings and the E_{OC} of the electrodes that were sealed for 1.5 h was highest when the potential trend changed. When LiNO₃ was added to the sealing solution, the potential trace tended to flatten at about 250 s (Fig. 2 c). This was because lithium oxide in the sealing coating exhibits self-healing properties. When the potential reached equilibrium, the E_{OC} of the electrodes was highest for those samples that were sealed with 5 g/L LiNO₃ added to the sealing solution. If the proportion of LiNO₃ increased beyond this concentration the sealed coatings had poorer corrosion resistance. Through analyzing the OCPT curves it was

found that the optimum process for the treatment of the sealing coat was 1.5 h at 100 °C with 5 g/L LiNO₃ added to the cerium sealing solution.

EIS measurements were performed in 3.5 wt.% NaCl solution at the E_{OC} in order to investigate the influence of the sealing treatment as a function of the differences in the corrosion resistance of the cobalt-based conversion coatings. The impedance spectra recorded all the Nyquist curves in the low-frequency range when coating sealing was performed at different temperatures, sealing times, and concentrations of LiNO₃ (Fig. 3). The EIS data were analyzed using Nova software (issued by Metrohm Autolab). The corrosion resistances of the sealing coatings were characterized by the radius size of semi-circular arc curves at lower frequencies. Larger radiuses of the Nyquist curves were associated with greater resistances (indicative of lower corrosion rate), and therefore higher corrosion resistance of the sealed coatings. With the increase of temperature, arc diameter was basically on the rise. This showed that the increase of temperature increased corrosion resistance of the sample surface. Better corrosion resistance of the electrodes was obtained using a sealing treatment at 80–100 °C. The diameter of the main Nyquist arc increased, and the corrosion resistance of the sealing coatings was better when the sealing time was extended (Fig. 3b). However, as the addition of LiNO₃ to the cerium sealing solutions gradually was increased, the diameters of the Nyquist arcs became smaller (Fig. 3 c). When the sealing solution had a certain cerium quality, 5 g/L LiNO₃ could improve the corrosion resistance of the sealed coating.

The polarization curves of the sealing coatings (for sealing treatments performed at different temperatures, sealing times, and concentrations of LiNO₃ in the cerium sealing solution) are shown in Fig. 4. The values of the corrosion current density and corrosion potential can be obtained from the potentiodynamic polarization curves via Tafel region extrapolation. As can be observed from the plots, there was a significant difference in the polarization response when the sealing condition was changed because the porous morphology of conversion coatings was not completely closed when the samples were sealed under different sealing conditions.

In addition, the sealing coating with high corrosion potential had the highest corrosion resistance.

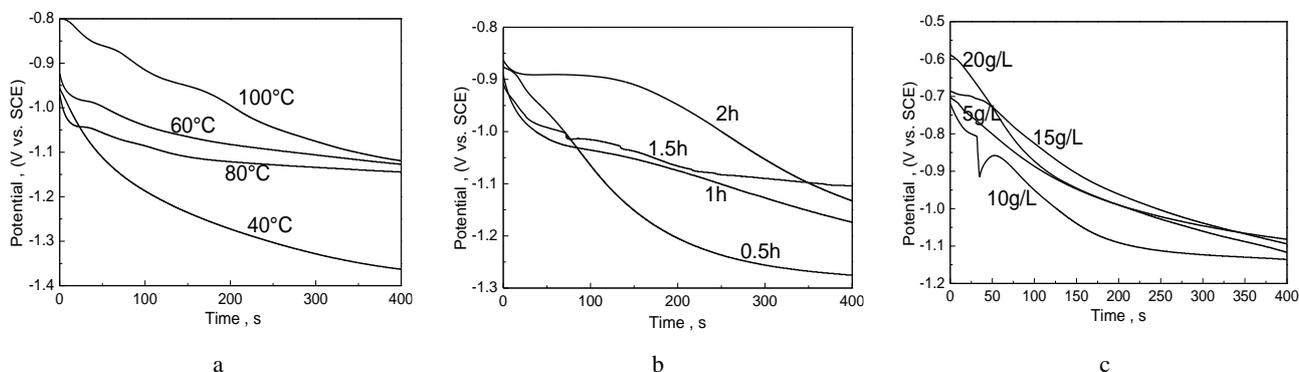


Fig. 2. a – experimental OCPT curves for the sealing treatment at 40, 60, 80 and 100°C; b – sealing treatment for 0.5 h, 1 h, 1.5 h and 2 h; c – sealing treatment in solutions with different LiNO₃ concentrations

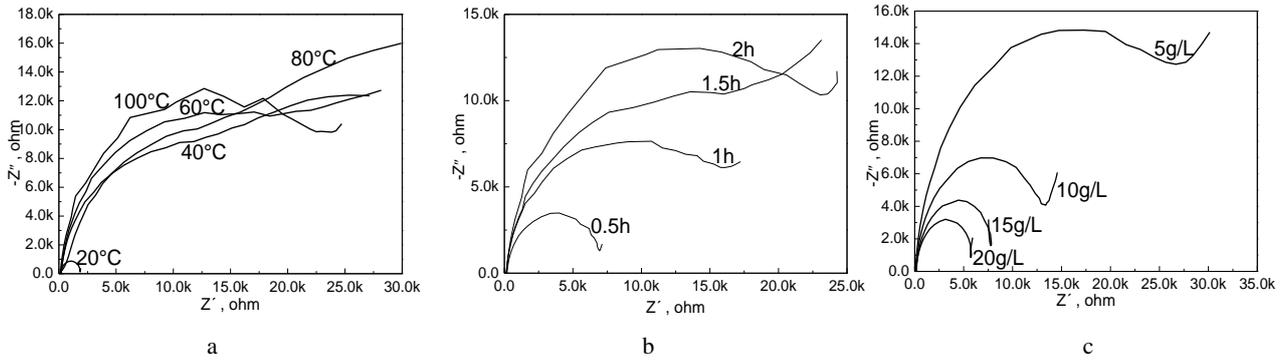


Fig. 3. a – experimental Nyquist curves for sealing treatment at 20, 40, 60, 80 and 100°C; b – sealing treatment for 0.5 h, 1 h, 1.5 h and 2 h; c – sealing treatment in different concentrations of LiNO₃

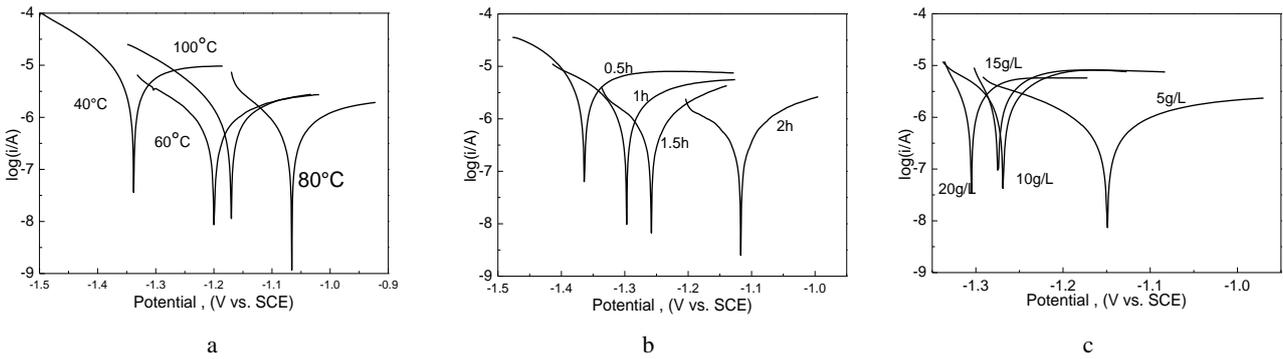
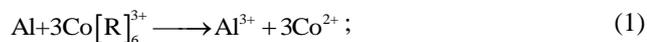


Fig. 4. a – polarization curves in 3.5 wt.% NaCl of sealing treatment at 40, 60, 80 and 100°C; b – sealing treatment for 0.5 h, 1 h, 1.5 h and 2 h; c – sealing treatment with different concentrations of LiNO₃

As can be seen in Fig. 4 a, the electrode that was sealed in a cerium sealing solution at 80 °C had a higher corrosion potential (–1.066 V) than the electrodes sealed at the other temperatures.

The order of the corrosion potentials was consistent with the AC impedance results. When the processing time of the sealing treatment was extended, the corrosion potential increased (Fig. 4 b). The highest corrosion potential was –1.117 V, which was achieved when the samples were treated in the cerium and lithium bath for 2 h. The sealing time determined the degree of sealing of the pores in the conversion coatings. Fig. 4 c illustrates the effect of the concentration of LiNO₃ on the degree of sealing. It can be observed that the electrochemical behavior of the sealing treatment did not exhibit a difference for concentrations of LiNO₃ at 10 and 20 g/L. The corrosion potential of the sample that was treated with 5 g/L LiNO₃ cerium sealing solution was higher than for other concentrations. It was observed that the corrosion resistance was better than for samples that had been treated with a sealing treatment concentration of 5 g/L. The film obtained using the above-mentioned parameters had excellent corrosion resistance and could be widely used in the surface treatment industry to increase the service life of the aluminum substrates. The electrochemical tests demonstrated that the film formed under the prescribed conditions did so by the following reactions [32]:



4. CONCLUSIONS

The pores of cobalt-based conversion coatings were successfully sealed by means of deposition in a cerium-lithium bath in optimal process conditions. SEM micrographs showed that the sealing treatments completely covered the pores of the optimal cobalt-based conversion coatings when the sealing temperatures were greater than 80 °C, but the larger cracks in the coating surface that were sealed at 80–100 °C indicated that the coating was defective. The OCPT curves showed that the sealing process was best when the treatment was sealed for 1.5 h at 100°C and with 5 g/L LiNO₃ added into the cerium sealing solution. The Nyquist curves showed that the sealing process was the best when the reaction time was 2 h, the sealing temperature was 80–100°C, and 5 g/L LiNO₃ was added to the cerium sealing solution. The polarization curves showed that the sealing process was best when the reaction time was 2 h at 80°C with 5 g/L LiNO₃ added the cerium sealing solution. In summary, the best treatment process for the cobalt-based conversion coating was obtained in a sealed cerium-lithium bath for 2 h at 90°C, and the LiNO₃ concentration of the cerium-lithium sealing solution was 5 g/L.

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