The Investigation of Formation Reactions for Cerium Conversion Coatings Deposited on Porous Film of Anodized Aluminium Under Cathodic Polarization

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Abstract

Cerium-rich conversion coatings could be deposited on porous film of anodized aluminium by cathodic polarization in a solution containing 2.68 mol/m^3 $CeCl_3.7H_2O$ and 10 dm^3/m^3 H_2O_2. The electrochemical and chemical reactions of coating formation have been studied using electrochemical methods such as cyclic voltammograms and galvanostatic/potentiostatic polarization. It was revealed that the formation of cerium conversion coatings involved a dissolution process of anodized film and an electrodeposition process of cerium compound. Before cathodic potential reached the hydrogen evolution potential, reduction of H_2O_2 was considered to be the major reasons for the occurrence of those processes by changing the local pH at surface of anodized film.

1. Introduction

Cerium conversion coatings as an attractive alternative to chromate conversion coatings for the corrosion protection of aluminium alloys have been recognized widely because cerium compounds are non-toxic and relatively cheap. To date several methods have been used to form cerium-rich film on aluminium alloys. Typical processes included: (i) exposure to aerated aqueous solution of 1000 ppm $CeCl_3$ and 100 mol/m^3 NaCl for up to a week [1,2], (ii) immersion of the aluminium alloys in a aerated solution containing cerium salts and film formation accelerant such as H_2O_2 and $KMnO_4$ for various time which are usually less than 30 minutes depending on different process [3-7], (iii) Ce-Mo process described by Mansfeld *et al* [8-13]. It should be noted, however, that among these processes almost all cerium conversion coatings were deposited directly on matrix of aluminium alloys and little attention was made to its application in anodizing of aluminium alloys [14].

In our recent works, the cerium conversion coatings with yellow appearance were deposited successfully on porous films of anodized aluminium by cathodic polarization in a stirred solution of 2.68 mol/m^3 $CeCl_3.7H_2O$ and 10 dm^3/m^3 H_2O_2. Characterization of the cerium conversion coatings was carried out using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and X-ray diffraction (XRD) etc., and a possible mechanism of coating formation has also been proposed on the basis of experimental results [15]. According to the mechanism, the electrochemical and chemical processes of coating formation involved major contributions from the reduction of hydrogen peroxide (equation (1)) and limited contributions from oxygen reduction (equation (2)). The cathodic reactions created a local high pH along cathode diffusion layer. When the pH value increases up to larger than 8, then chemical dissolution of porous anodized film (equation (3)) and electroreduction of $Ce(OH)_2^{2+}$ (equation (4)) occurred, which resulted in a deposition of colloid $Ce(OH)_3$ on anodized film.

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (1)$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$
$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2^- + H_2 \quad (3)$$
$$Ce(OH)_2^{2+} + OH^- + e^- \rightarrow Ce(OH)_3 \quad (4)$$

Consequently, the aim of the present work is intended to confirm such electrochemical and chemical processes and to gain deep understanding of mechanism for coating formation by electrochemical methods.

2. Experimental Details

2.1 Materials

LY12 Al-alloy (Al-4.48Cu-0.64Fe-0.41Mn) sheets were used for the studies. The sheets were cut into strips of $1cm^2$ (thickness: 2mm), then sealed in epoxy resin to leave only a geometrical face, and finally were polished with emery paper to 1000 grit for subsequent anodizing.

2.2 Preparation of Anodized Film

All specimens were anodized in a stirred bath of $100dm^3/m^3$ H_2SO_4 at current density of $1.5A/dm^2$, and temperature of 20°C for 30 minutes.

2.3 Electrochemical Measurements

For all measurements, the saturated calomel electrode and a smooth platinum plate of $2.25\ cm^2$ were used as reference and counter electrodes respectively. Besides the solution for formation of cerium conversion coatings mentioned above, another two aqueous solutions were also adopted as electrolytes (Table 1). In some cases, a magnetic stirrer was used to stir electrolytes.

Table 1: Electrolytes used for electrochemical measurements.

Electrolyte	Compositions		pH
A (i.e. coating solution)	$CeCl_3.7H_2O$ H_2O_2	$2.68\ mol/m^3$ $10\ dm^3/m^3$	Adjust pH value to 3.1 with HCl.
B	NaCl H_2O_2	$8.04\ mol/m^3$ $10\ dm^3/m^3$	
C	$CeCl_3.7H_2O$	$2.68\ mol/m^3$	

The measurements of cyclic voltammograms and cathodic polarization curves were carried out in all electrolytes by combining a potentiostat, a function generator and an X-Y recorder.

The measurements of Potential (E) –t (time) and Current Density (j)-t curves under galvanostatic and potentiostatic conditions respectively were carried out in A electrolyte by only combining a potentiostat/galvanostat and an X-Y recorder.

3. Results and Discussion

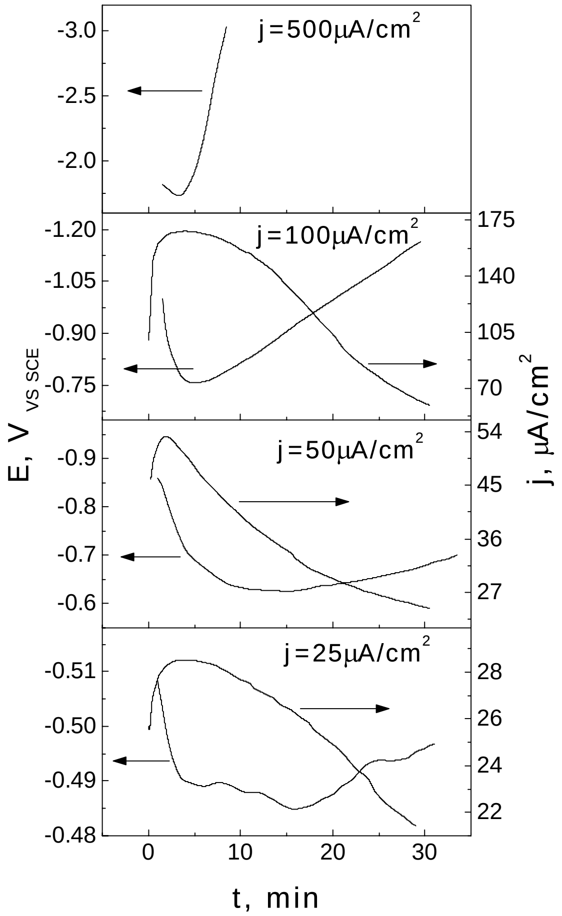

Figure 1: E-t and j-t curves for anodized film in A electrolyte at different potential and current density respectively.

Figure 1 shows E-t and j-t curves for anodized film in A electrolyte (i.e. formation solution) at different current density and potential respectively. For the measurement of j-t curves, the potential under which the starting responsive current density equalled to the current density noted in corresponding E-t curves was chosen as the constant potential. In general, owing to development of electrochemical polarization and concentration polarization or deposition of conversion coatings on anodized film, it could be expected that the overvoltage increased with time under galvanostatic conditions and responsive current density decreased with time under potentiostatic conditions. However, the appearance of the peak and the trough in the j-t and E-t curves respectively (Figure 1) indicated that there was a depolarization process in the incipient stage of coating formation. It was most likely that this is due to dissolution of the anodized film under local high pH resulting from reactions of Eq.1 and Eq.2 [2]. In the incipient stage of coating formation, the rate for dissolution of anodized film might be higher than that for deposition of conversion coatings, so overall resistance of cathodic reactions decreased. Because gradual formation of conversion coatings can restrain the dissolution of anodized film, as polarization time increased, the rate for deposition of conversion coatings would go beyond that for dissolution of anodized film [15]. In this case, it thus appeared that overvoltage increased or responsive current density decreased with time. It also could be seen from E-t curves that times for overvoltage beginning to increase shortened with polarization current density increasing. This implied that the rate for deposition of conversion coatings became faster when current density was increased.

Figure 2 shows cathodic polarization curves for the anodized film in the three electrolytes. When cathodic potential became negative enough, the current density began to increase rapidly. This was thought to be associated with the occurrence of hydrogen evolution. It is apparent that the overvoltage for hydrogen evolution is highest in A electrolyte. It might be due to the argument that the deposition of cerium conversion coatings on anodized film increases polarization resistance of hydrogen evolution. In addition, according to Figure 2, it is easy to conclude that the sharp jump of electrode potential after about three minutes cathodic polarization at current density of 500μA/cm^2 depicted in E-t curve of Figure 1 was due to total concentration polarization of reactants rather than rapid deposition of cerium conversion coatings.

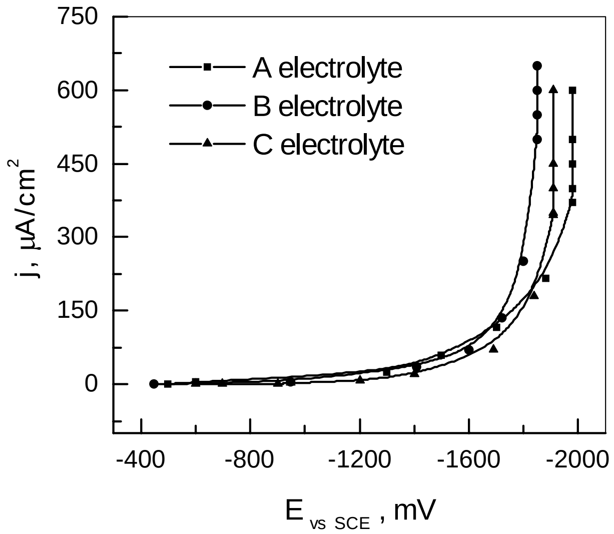

Figure 2: Cathodic polarization curves for anodized film in three kinds of quiescent electrolytes. The scan rate was 10 mV/S.

The results obtained from cyclic voltammograms could be used to further demonstrate the electrochemical and chemical processes during coating. Figure 3 shows the cyclic voltammograms for anodized film in three kinds of electrolytes under stirred conditions. The scan rate was 1.667mV/min. According to the results revealed from Figure 2, it was apparent that hydrogen evolution was impossible in all electrolytes at the potential range used in the cyclic voltammograms. Therefore, in C electrolyte cathodic responsive current must be the result of the reduction of oxygen, while in B electrolyte major cathodic reaction was the reduction of hydrogen peroxide, with minor contribution from reduction of oxygen. Further, for first cycle of cyclic voltammograms, responsive current density at back-scan (i.e. the potential scan going positive) was larger than that of positive-scan (i.e. the potential scan going negative) in A and B electrolyte in contrast C electrolyte. The results further supported the argument that the dissolution of anodized film owing to local pH increases, reduced the polarization resistance for the cathodic reaction. For B electrolyte, responsive current density at back-scan became lower than that at positive direction scan only after the first cycle, which suggested that the effect of concentration polarization on polarization current have overrun that of dissolution of anodized film. For A electrolyte, however, the case was not so. That transition didn't appear until the fifth cycle (Figure 3 (a)). Apparently, with or without a reaction of forming cerium conversion coatings must have been the major reason for the difference. In A electrolyte, the gradual increase of pH value due to reaction of Eq.1 and Eq.2 during positive-scan enabled reaction of Eq.4 to take place as well as resulted in the dissolution of anodized film during back-scan [16,17]. If the current contributed from reaction of Eq.4 was dominant while comparing to the decrease of current due to accumulation of concentration polarization, the increase of overall current could be expected. The discussion together with the fact of cerium being predominantly in the 3-valent state in cerium conversion coatings, which resulted from XPS analysis [15], indicated that indeed the cerium conversion coatings was formed by electroreduction of 4-valent state cerium compound rather than chemical precipitation.

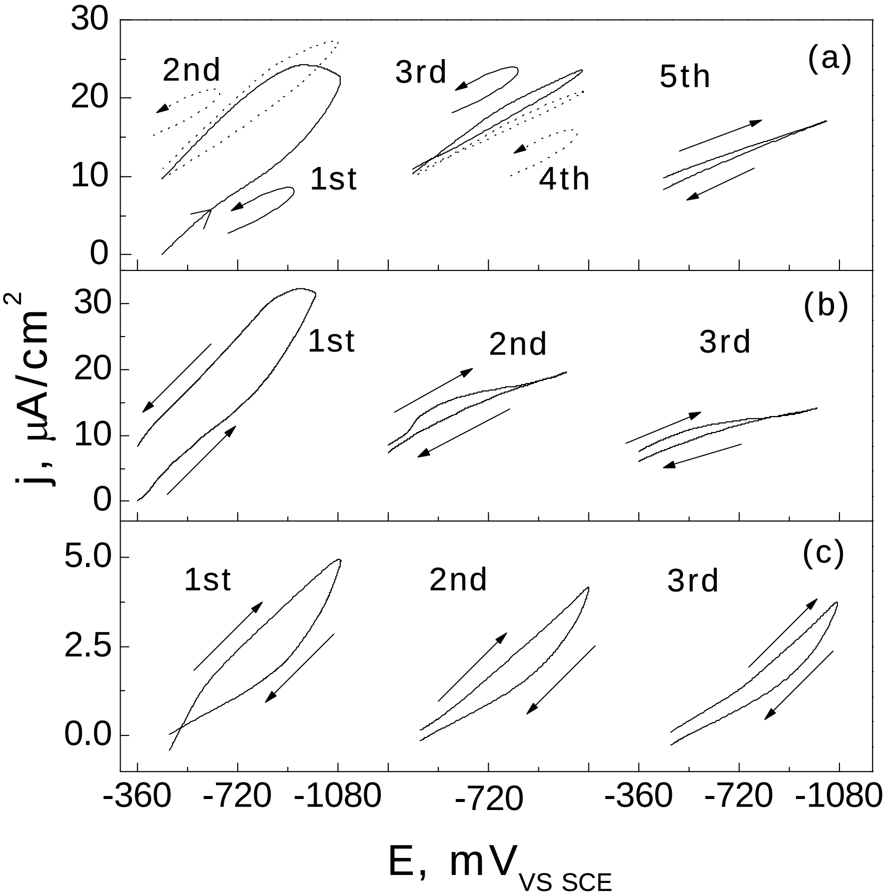

Figure 3: The cyclic voltammograms for anodized film in (a) A electrolyte, (b) B electrolyte and (c) C electrolyte under stirred conditions. The scan rate was 1.667mV/S. Arrow direction indicates potential scanning direction.

Figure 4 shows the cyclic voltammograms for anodized film in A electrolyte at different scanning rate, and with or without stirring. It can be seen that the responsive current density to increased with scanning rate, which was not expected. This might be due to the fact that scanning rate affected the degree of local pH increase and therefore the degree of dissolution of anodized film. For a high scanning rate of 100mV/S, high current density might be expected owing to very thin diffusion layer and large diffusion flux. On the other hand, however, due to very thin diffusion layer and quite short times for each cycle, the local pH value of diffusion layer might be not high enough to give rise to dissolution of anodized film. So the current density for back–scan was lower than that for positive-scan (Figure 4 (a)). When the scanning rate was reduced to 10mV/S, apparently diffusion layer became thicker and diffusion flux became less. This would result in a decrease of overall responsive current density of all cathodic reactions (Figure 4 (b)). But in this case, local high pH might bring about a small quantity of dissolution of anodized film and enable the reaction of Eq.4 to take place, which was thought to be the reasons of depolarization. Then there is no difficulty in understanding that the amount of current increase contributed from depolarization had gone beyond that of current decrease resulted from reduction of diffusion flux at scanning rate of 1.667mV/S (Figure 4 (c)). Hence the overall responsive current density at the scanning rate of 1.667mV/S was higher than that scanning rate of 10mV/S. Because stirring mainly affected the thickness of diffusion layer too, its effect on responsive current was similar with that of scanning rate. For example, the responsive current density in quiescent electrolyte was higher that in stirred electrolyte only at scanning rate of 1.667mV/S after second cycle (Figure 4 (c)).

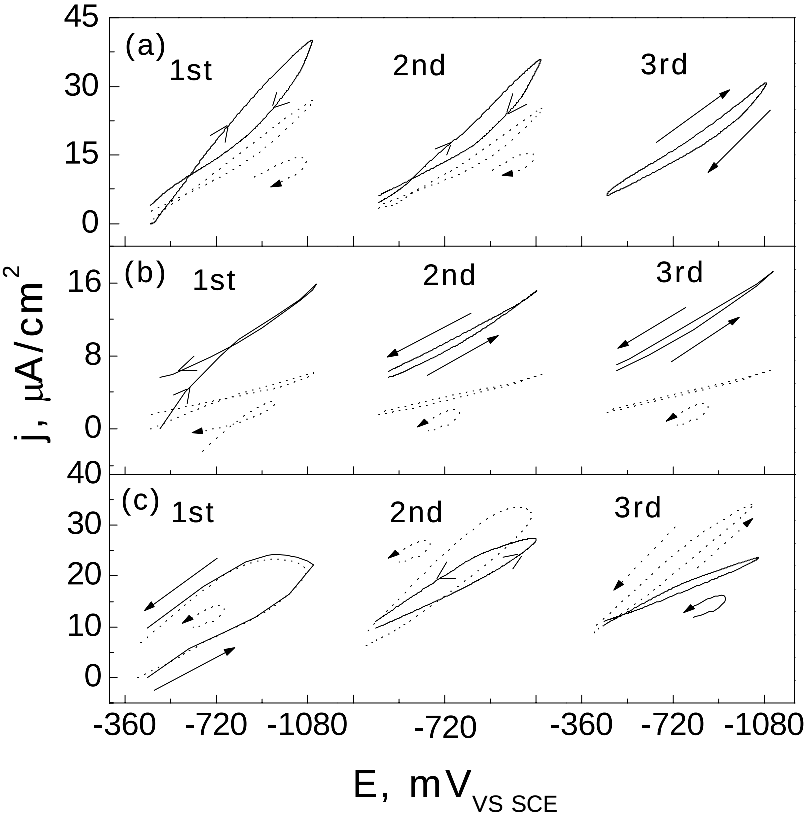

Figure 4: The cyclic voltammograms for anodized film in A electrolyte at scan rates of (a) 100 mV/S (b) 10 mV/S and (c) 1.667 mV/S. Solid lines indicate stirring conditions and dotted lines indicate quiescent conditions. Arrow direction indicates potential scanning direction.

Figure 5 and Figure 6 may support the argument fully that the depolarization function resulted from increase of local pH was associated with the thickness of diffusion layer and cathodic reaction concerned. Figure 5 shows the first cycle of cyclic voltammograms of stirred B electrolyte at various scanning rates. The effects of scanning rates on responsive current and depolarization were good agreement with the first cycle of cyclic voltammograms in A electrolyte (Figure 4). Figure 6 was the cyclic voltammograms for anodized film in C electrolyte at different scanning rate, and with or without stirring. It was clear that reduction of oxygen could not result in depolarization in any case. This suggested, in the other hand, that before cathodic overvoltage increased up to the overvoltage for hydrogen evolution, cathodic polarization could not result in the formation of cerium conversion coatings on anodized film in C electrolyte.

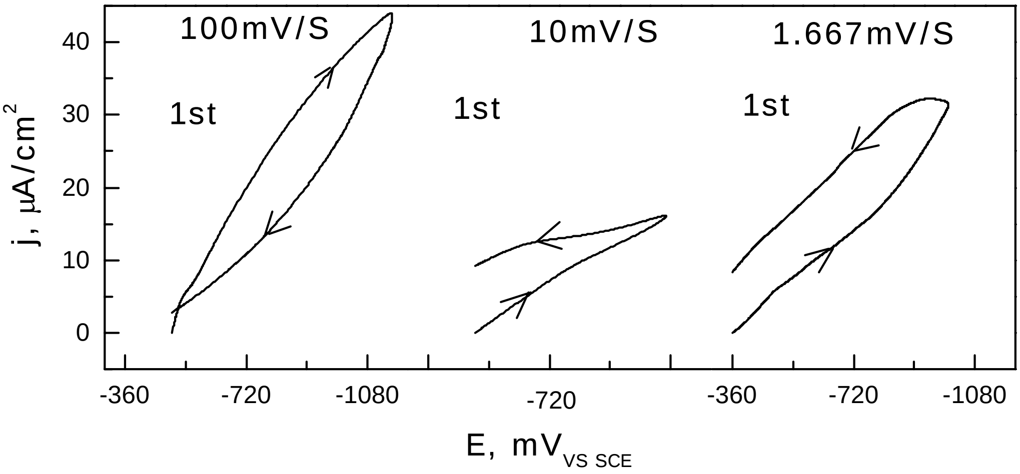

Figure 5: The first cycle of cyclic voltammograms for anodized film in stirred B electrolyte at various scanning rates.

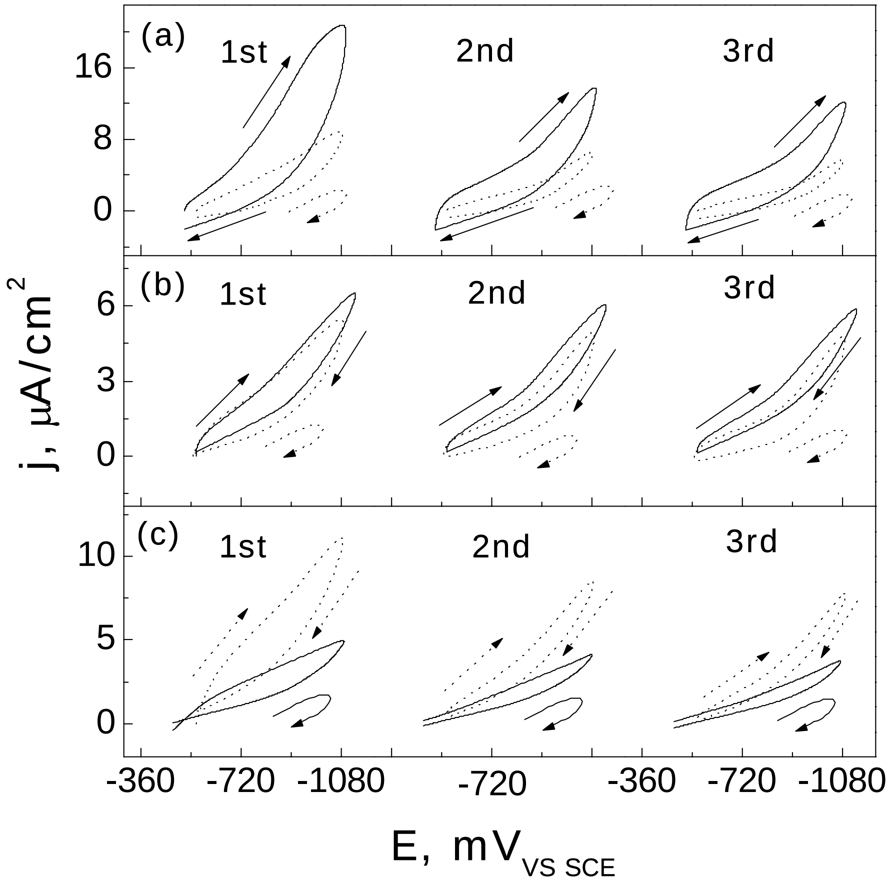

Figure 6: The cyclic voltammograms for anodized film in C electrolyte at scan rates of (a) 100 mV/S (b) 10 mV/S and (c) 1.667mV/S. Solid lines and dotted line indicate stirring and quiescent condition respectively. Arrow direction indicates potential scanning direction.

4. Conclusions

The formation of cerium conversion coatings on porous film of anodized aluminium by cathodic polarization in A electrolyte was thought to include a process of dissolution of anodized film and a process of electrodeposition of cerium conversion coating. Whether the two processes take place depends on the local high pH value resulted from cathodic reaction of hydrogen peroxide and oxygen reduction. The higher polarization current, the thicker diffusion layer and the longer polarization time, the more likely or rapidly the two processes will proceed. In B electrolyte, reduction of hydrogen peroxide may give rise to only the dissolution of anodized film, while in C electrolyte, reduction of oxygen can not result in significant dissolution of anodized film and electrodeposition of cerium conversion coatings.

Acknowledgments

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