

Influences of the main anodic electroplating parameters on cerium oxide films



Yang Yang^a, Yumeng Yang^a, Xiaoqing Du^a, Yu Chen^a, Zhao Zhang^{a,*}, Jianqing Zhang^{a,b}

^a Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, China

^b State Key Laboratory for Corrosion and Protection of Metals, Shenyang 110016, China

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ABSTRACT

Cerium oxide thin films were fabricated onto 316 L stainless steel via a potentiostatically anodic electrodeposition approach in the solutions containing cerium(III) nitrate (0.05 M), ammonia acetate (0.1 M) and ethanol (10% V/V). The electrochemical behaviors and deposition parameters (applied potential, bath temperature, dissolving O₂ and bath pH) have been investigated. Results show that, the electrochemical oxidation of Ce³⁺ goes through one electrochemical step, which is under charge transfer control. The optimum applied potential for film deposition is 0.8 V. Bath temperature plays a significant effect on the deposition rate, composition (different colors of the film) and surface morphology of the deposits. Due to the hydrolysis of Ce³⁺, cerous hydroxide is facility to form when the bath temperature is higher than 60 °C. The electroplating bath pH is another key role for the anodic deposition of cerium oxide thin films, and the best bath pH is around 6.20. N₂ or O₂ purged into the bath will result in film porosities and O₂ favors cerium oxide particles and film generation.

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Introduction

Cerium oxides have raised many interests because of their good properties in solid oxide fuel cells [1], polishing agents for chemical mechanical and planarization processes [2], catalysts for three-way catalysis of exhaust gas from automobiles [3], and as leading candidates to replace highly toxic chromium coatings for corrosion protection of metallic materials [4–10].

Generally, ceria powders or coatings can be prepared by chemical [11,12] or electrochemical [11,12] vapor deposition, precipitation method [13], hydrothermal precipitation [14,15], solid state reactions [16], sol–gel method [17], electroplating [18–23] and others techniques [24,25]. Among them, electroplating is an attractive method for film preparation and possesses many advantages, such as low processing temperature, normal handling pressure, and high purity of deposits. Recently, cerium oxide films have been produced by either cathodic [26–28] or anodic [22,23,29] deposition in aqueous solutions. In the case of cathodic deposition, CeO₂ films are deposited following the so-called base generation mechanism [18,19,27], which applies a more negative bias than

the hydrogen evolution potential of H₂O and raises the pH value near the electrode surface, then the generated OH[−] reacts with Ce³⁺ to form a layer of hydroxide (Ce(OH)₃) on the electrode surface, which finally transforms to CeO₂ through dehydration and oxidation. Consequently, the deposited film obtained by the cathodic electroplating method is composed of mixed Ce(III)/Ce(IV) oxidation states. Martínez et al. [30] demonstrated the composition of the cathodically deposited surface layers by different spectroscopic methods and found that the coatings are mainly composed of defective cerium oxide. Both Ce(III) and Ce(IV) species are present in the coating. In addition, hydroxides, carbonates and nitrates are also present, together with adsorbed water. In the case of anodic deposition [20,23], Ce³⁺ can be directly oxidized to soluble Ce(OH)₂²⁺, the supersaturated Ce(OH)₂²⁺ at the anode surface is deposited as solid CeO₂. Therefore, it is believed that anodic deposition is more appropriate to fabricate pure CeO₂ film.

The quality of the electrodeposited ceria film can be affected by many factors. Bouchaud et al. [31] developed a diagram showing the distribution as well as the relative amount of Ce(III)/Ce(IV) species in aqueous media as a function of the pH range, which can predict the relevant precipitation mechanisms and species involved during the growth of cerium-containing films. The Pourbaix diagram for cerium [20,32] shows that at solution pH value above 7, Ce(OH)₃ precipitate (gray–green) forms toward reducing voltages and CeO₂ precipitate (yellow) forms at oxidizing voltages. Kulp et al.

* Corresponding author. Tel.: +86 13805751827/+86 571 85615190;

fax: +86 571 87951895.

E-mail addresses: eaglezzy@zjuem.zju.edu.cn, eaglezzy@zju.edu.cn (Z. Zhang).

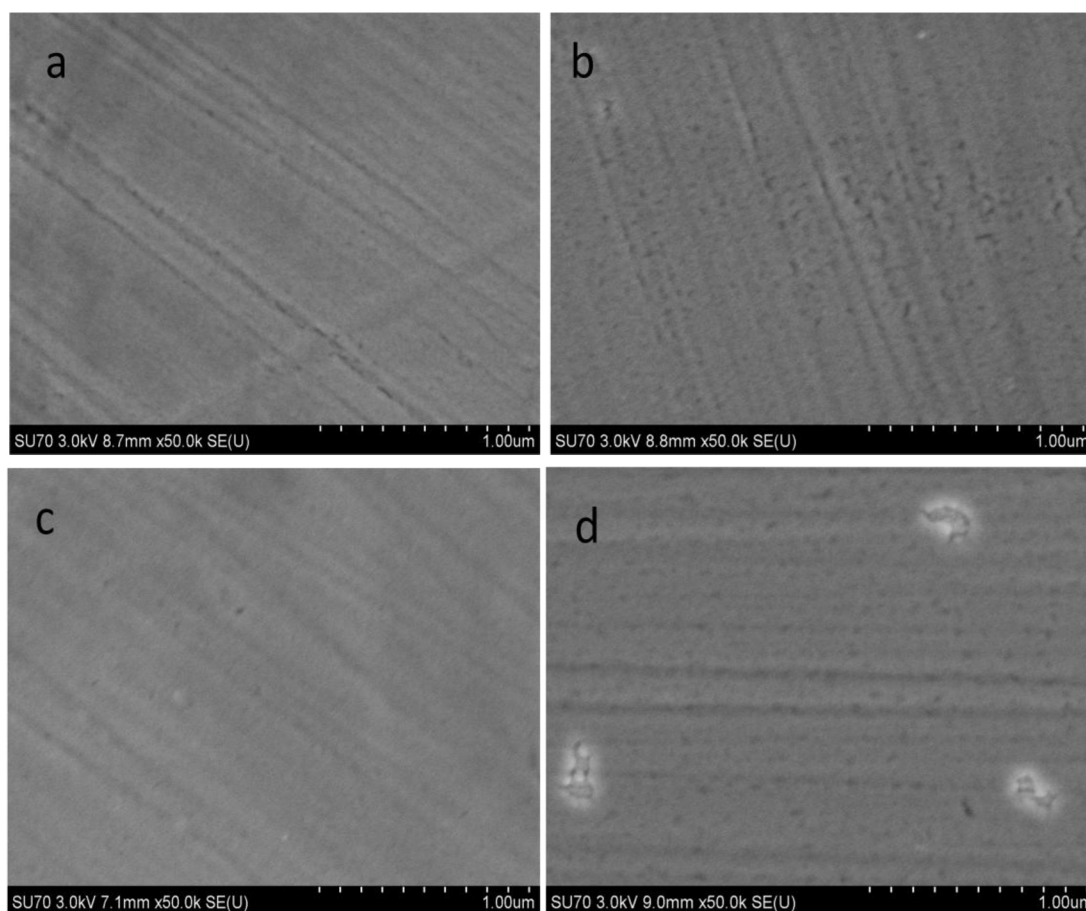


Fig. 1. SEM surface morphology of the films deposited at different potentials in the system of 0.1 M $\text{CH}_3\text{COONH}_4$ + 0.05 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ + 10% (V) $\text{CH}_3\text{CH}_2\text{OH}$ (pH = 6.20). $T = 50^\circ\text{C}$, $t = 40$ min, $r = 500$ rpm. (a) 0.25 V, (b) 0.50 V, (c) 0.80 V, (d) 1.00 V.

[33] pointed out that low positive potential facilitated the formation of compact CeO_2 film, and the cracked films were formed at the potentials higher than 1.1 V (vs. Ag/AgCl). Switzer et al. [18,19] reported that the grain size of the deposited CeO_2 film varied from 6 to 16 nm with increasing bath temperature (from 299 to 353 K) or decreasing current density (from 30 to 5 A/m²). Hamlaoui et al. [34,35] reported that the increase of the bath temperature brings about significant modifications of the surface morphology, the crystallite size and the content of oxygen vacancies that are suspected not to confer adequate protection. In contrast, the addition of polyethylene glycol to the solutions will inhibit the development of the carbonated green rust and the corrosion resistance impaired. The addition of some ionic liquid into the electroplating electrolyte can influence the morphology, the growth rate and crystallinity of the electrodeposited ceria film [36]. And the addition of ethyl alcohol into the electroplating electrolyte can both promote the particle coagulation and the gel ($\text{Ce}(\text{OH})_2^{2+}$) formation [26,28] because that, ethyl alcohol can reduce the solubility of the deposits and lead to the homogeneous and continuous coatings with reduced cracks and porosities. Our previous work also found that ceria film with the optimum quality is obtained in the deposition solution containing 10% V/V ethanol [37].

The aim of the present work is to systematically investigate the influences of the main deposition parameters, including anodic deposition potential, bath temperature, pH and the dissolving O_2 in the electrolyte on the anodic deposited ceria thin films.

Experimental

A classical 3-electrode cell was used for all electrochemical experiments. A 316L stainless steel rod (SS, working area 0.50 cm²) was adopted as the working electrode. Before each experiment, the working surface was polished to mirror using 2.5 μm diamond paste, rinsed with acetone and double-distilled water. The treated steel was dried with nitrogen gas (N_2) and then dipped into the electrochemical cell for use. A saturated calomel electrode (SCE) connected through a salt bridge was used as reference, and a large platinum foil (25 × 25 × 0.2 mm) as counter electrode. All potentials were referred to SCE unless otherwise stated.

The electroplating bath consisting of 0.05 M $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Analytical reagent (AR), 0.1 M $\text{CH}_3\text{COONH}_4$ (AR) as a complex agent, 10% (V) $\text{CH}_3\text{CH}_2\text{OH}$ (AR) and double-distilled water that was further purified with a Milli-Q purification system (Millipore, resistivity, 18.2 MΩ cm). All electroplating solutions are naturally aerated unless otherwise specified. The deposition was carried out using electrochemical workstation (CHI630D, China) at 0.25 V, 0.50 V, 0.80 V and 1.00 V. The temperatures were controlled by thermostat water bath at 30 °C, 40 °C, 50 °C, 60 °C and 70 °C. The pH of the electroplating bath solution was adjusted to basic using 0.01 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ (AR) and to acidic using 1 M CH_3COOH (AR). After deposition, the samples were washed with double-distilled water and dried by N_2 gas and then stored in a desiccator for further examination.

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