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Synthesis and characterisation of thin cerium oxide coatings elaborated by cathodic electrolytic deposition on steel substrate

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Abstract

Cerium oxide films are widely studied as a promising alternative to Cr(VI) based pre-treatments for the corrosion protection of different metals and alloys. This paper deals with the deposition and characterisation of cerium oxide films deposited onto mild steel substrates by cathodic electrolytic deposition via Ce(III) chloride aqueous and mixed water–ethyl alcohol solutions with and without hydrogen peroxide as a precursor. The major role of this precursor is to increase the deposition rate of the oxide films allowing smooth and adherent hydrated cerium oxide films to be obtained. However, the evolution of the composition of the bath with time leads to a non-reproducibility of the morphology and composition of the thin films. The deposited oxide films are composed of small particles of hydrated Ce(IV) oxide with a significant amount of amorphous phase. In the absence of a precursor, only the mixed water–ethyl alcohol solution permits cerium oxide films to be deposited. The influence of the deposition parameters such as applied cathodic current density, deposition time and composition of the bath was also investigated. The deposits exhibit a quite developed crack network, which is highly dependent on the deposition parameters and the drying process. Moreover, the incorporation of chloride ions during the deposition has been observed. The protection efficiency of these films was examined during extended immersion tests in 3% NaCl solution. The deposits allow the cathodic reaction kinetics to be reduced by acting as a cathodic inhibitor. However, the presence of large defects or cracks induces an accelerated local degradation of the steel substrate, removing partially the oxide deposit, whereas a thin crack network can rapidly be sealed by corrosion products without deterioration of the deposit.

Keywords: Cerium oxide film; Cathodic electrodeposition; Protection efficiency

1. Introduction

Chromium(VI) compounds are largely used to create a conversion layer that provides an improved corrosion resistance for many metallic alloys. The use of rare earth (RE) salts is nevertheless studied as an environmentally friendly alternative to the use of Cr(VI) based pre-treatments. An enhancement of the corrosion resistance for different alloys such as aluminium alloys [1–3], zinc alloys [4–8] or steels [9–11] has been reported. The different mechanisms suggested in literature show that the role of the rare earth conversion films is not well understood. The main mechanism of action for the RE elements seems to be based on the reduction of the rate of the cathodic process acting as cathodic inhibitors [1,6]. However, Montemor et al. [5] recently showed that RE elements act as mixed inhibitors, reducing both cathodic and slightly anodic activity on hot dip galvanised steel substrates.

Ceria (CeO_2) has a considerable interest as a promising material in corrosion protection. Different techniques such as laser beam evaporation ion [12], chemical vapour deposition, sol–gel processing, immersion [1–9] and electrodeposition [10,11,13–15] have been used to obtain cerium oxide films. Electrodeposition is an attractive method for the preparation of thin films since it offers the advantage of low processing temperature, controlled thickness of the film and low cost process. Cerium oxide films

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have been obtained by cathodic or anodic deposition on different substrates [1,10,11,13–18]. In the cathodic electrolytic deposition, hydroxide ions are formed at an electrode surface by a cathodic process and metal ions or complexes are then hydrolysed by the electrogenerated base. Zhou and Switzer [11], Zhitomirsky and Petric [13,14] and Arurault et al. [9] have used a solution of Ce(III) nitrate in order to deposit thin oxide films. The reduction of nitrate ions into nitrite or ammonia ions also produces hydroxide ions, which promote a rapid increase of the pH at the interface. The electrogenerated base induces the formation of colloidal particles of Ce(III) hydroxide or hydrous oxide [11,13,14], or also the formation of a ionic species [$Ce(OH)_2^{2+}$], that can be hydrolysed into ceria. Different authors [13,14,19] suggest that the use of a precursor like hydrogen peroxide (H_2O_2) prevents the accumulation of nitrite or ammonia ions that provokes deposition instabilities. Zhitomirsky and Petric [13] have shown that, using a Ce(III) chloride solution, associated to hydrogen peroxide precursor, leads to more adherent and uniform oxide films than Ce(III) nitrate solution.

The aim of this study was to characterise ceria coatings elaborated on a carbon steel substrate by cathodic electrolytic deposition from Ce(III) chloride aqueous and mixed water–ethyl alcohol solutions. The influence of hydrogen peroxide precursor is discussed and the corrosion resistance of coated steel is investigated in saline solution through extended immersion tests.

2. Experimental procedure

Electrochemical experiments were carried out in a classical three-electrode glass cell. The working electrode was a 36NiCrMo16 (EN 1083-1) steel disk with an area of 0.78 cm^2. Before each experiment, the steel surfaces were polished with silicon carbide (particle size 5 μm), sonicated for 2 min, rinsed thoroughly with Milli-Q water and dried.

The reference electrode was a saturated calomel electrode (SCE). The counter electrode was a large platinum grid. The experiments were performed at room temperature with an AMETEK 263 A potentiostat system, driven by Softcorr 3 software. The steel electrodes were left at the open circuit potential for 30 s prior to the potential scans.

The cerium oxide films were deposited by cathodic electrolytic deposition (CELD) via two electrolytic baths of $CeCl_3 \cdot 7H_2O$. Their compositions are presented in Table 1.

Table 1
Composition of the (A) aqueous and (B) mixed water–ethyl alcohol (1:9 volume ratio) solution for the deposition of thin solid films

Composition	Aqueous solution		Mixed water–ethyl alcohol solution		
	A1	A2	B1	B2	B3
$CeCl_3 \cdot 7H_2O$	0.8 mM	0.8 mM	0.8 mM	10 mM	0.8 mM
H_2O_2 (30 %)		25 mM			25 mM

Table 2
Deposition conditions of thin ceria films from both A and B solutions

Conditions	Aqueous solution		Mixed water–ethyl alcohol solution	
	A1	A2	B1 and B3	B2
Duration (min)	10	10	10	10
	20	20	20	
j (mA/cm^2)	0.005	0.005	0.01	0.1
	0.01	0.01	0.1	0.25
	0.1	0.1	0.25	
			1	
			5	

All the reagents were Sigma-Aldrich maximum purity chemicals.

Cyclic voltammetry, performed from −0.55 V/SCE to −1.8 or −2.5 V/SCE at the scan rate of 20 mV/s, was used to characterise the electrochemical reactions. The deposits were obtained in galvanostatic mode in unstirred solutions at room temperature. The deposition conditions are summarised in Table 2. After deposition, the samples were carefully washed in order to prevent the detachment of the thin films and dried during 24 h in air at room temperature.

The morphology of the samples was studied using optical microscope and scanning electron microscope (SEM JEOL 5410 Low Vacuum), coupled to X-ray energy dispersive spectroscopy (EDS). The cerium oxides were also analysed by X-ray diffraction (XRD) with a classical powder diffractometer (Bruker AXS D8-Advance), using Cu-$K_{\alpha 1}$ wavelength ($\lambda = 1.5406$ nm) in Bragg-Brentano geometry. Raman spectra were recorded with a LabRam HR spectrometer, equipped with a confocal microscope, using an incident beam of 632.82 nm emitted by an argon laser. Differential scanning calorimetry (DSC TA Instrument Q100) was carried out in air between 40 and 550 °C at a heating rate of 20 °C/min. UV–visible absorption spectra of the tested Ce(III) chloride aqueous and mixed water–ethyl alcohol-based solutions containing H_2O_2 as a precursor were obtained using a Helios β-UNICAM spectrometer.

The protection efficiency of the coatings was investigated via experiments performed in aerated and stirred 3% NaCl solution (pH = 6). The open circuit potential (OCP) and polarisation resistance (R_p) of the coated substrates versus time were recorded during long immersion tests (around 65 h). The polarisation resistance measurements were estimated via a linear polarisation experiment performed at a scan rate of 0.16 mV/s about ±20 mV/OCP. Polarisation curves $i(t)$ were recorded at a scan rate of 0.16 mV/s after 1 h of immersion in saline solution.

3. Results and discussion

3.1. Synthesis and characterisation of cerium oxide powder

The synthesis of cerium oxide by precipitation was performed by addition of sodium hydroxide solution in