Materials Chemistry and Physics 113 (2009) 650–657

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

# Cathodic electrodeposition of cerium-based oxides on carbon steel from concentrated cerium nitrate solutions

## Part I. Electrochemical and analytical characterisation

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ARTICLE INFO

*Article history:*
Received 8 January 2008
Received in revised form 19 June 2008
Accepted 3 August 2008

*Keywords:*
Cathodic electrodeposition
Cerium oxide films
Rinsing media
Composition
Morphology
Green rust

ABSTRACT

In this work the elaboration by cathodic electrodeposition of cerium-based oxides on carbon steel from relatively concentrated cerium nitrate solutions is investigated. In particular, the study presented here (Part I) focuses on the electrochemical and analytical characterisation of the films and on the correlations between the electrochemical features and the characteristics of the layers. The effect of other parameters such as concentration, temperature, pH and additives to improve the behaviour of the film against corrosion will be investigated in part II of the study.

The electrochemical characterisation will reveal that Ce(IV)–steel interactions can be responsible for some weak electrochemical waves appearing in the cyclic voltammograms that often are attributed to oxygen or nitrates reduction. This results from the oxidation of Ce(III) solutions to Ce(IV) in contact with air. Furthermore, the deposits strongly depend on the applied current density. Low current densities do not render fully covering deposits on the steel and a carbonated green rust will appear. On the contrary, the increase of the current density leads to denser layers of relatively small crystallite size that readily covers the steel surface. The deposits have a needle-like morphology and the Ce content achieves a plateau of about 20–22 at.%. However, a significant network of cracks appears probably occurring during the deposition process itself. The differential scanning calorimetry (DSC) results indicate that the deposits are not fully crystalline after 550 °C in contrast with the X-ray diffraction (XRD) patterns that unambiguously show a fluorite-type $CeO_2$ phase whose crystallite size decreases with increasing the current density. The rinsing medium also brings about different features of the films. Rinsing with water allows to incorporate more nitrates and to adsorb $CO_2$ than when rinsing with ethanol. However, R-OH bonds will be trapped in the latter.

## 1. Introduction

Cerium containing salts have been long investigated as environmentally friendly alternatives to the use of Cr(VI) baths for the protection of steels [1,2]. Cathodic electrodeposition has been claimed to become an important method on the processing of this ceramic because of the low cost of equipment and of precise control of deposited thickness [3–6]. Also, the films can be obtained on a vast variety of metallic substrates as aluminium and aluminium alloys [7–9], magnesium alloys [10,11], stainless steel [5,6,12–14], and galvanised and Zn-plated steels [15–22]. To this end, low precursor concentrations (between $10^{-3}$ and $10^{-2}$ M) seem to be required but the use of relatively high concentrations has only been investigated by Arurault et al. [13] using an electrochemical cell with a diaphragm. Similarly, very few works have been devoted to the deposition of Ce-based coatings on low carbon steel [23,24]. This is however widely employed as the substrate for Zn-based coatings (galvanised or Zn-plated). Therefore, some protection should be conferred upon the storage period prior to coating or in the case the coating showed significant defaults. Moreover, the rinsing medium and its viability to eliminate water and incorporated nitrates in the film is not yet understood.

The aims of this study are therefore to elaborate and to characterize the films of cerium-based oxides electrodeposited from relatively high precursor concentrations using a classic three-electrode cell. The correlation between the electrochemical features in the cerium nitrate solutions and the characteristics of the layers developed on an A366 low carbon steel is established

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doi:10.1016/j.matchemphys.2008.08.027

through polarisation experiments, Raman spectroscopy, X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) coupled to energy dispersive spectrometry (EDS). As the rinsing medium may play a role on the morphology and compactness of the deposits [25,26] the differences between ethanol and water as rinsing media will be also addressed in this work. Furthermore, the appearance of a corrosion product will raise the question on how to inhibit its development and growth. The effect of other parameters such as concentration, temperature, pH and additives to improve the behaviour of the film against corrosion will be therefore investigated in part II of the study.

## 2. Experimental

### 2.1. Materials

Plates of 2-mm thick of A366 cold-rolled steel were cut to produce discs of 14 mm of diameter. The low carbon steel nominal composition – according to SAE 1008/1010 – is: 0.13 C, 0.041 Mn, 0.040 S, 0.012 N, 0.55 Cu (wt.%) and Fe balance. The samples were mechanically abraded from coarser to finer 2400 grit SiC emery paper, rinsed with water then cleaned in an ultrasonic bath of ethanol and finally dried with pulsed hot air immediately before the deposition of the films.

### 2.2. Experimental set-up for cathodic electrodeposition

The electrochemical baths were composed of 0.01, 0.1 and 0.25 M $Ce(NO_3)_3{\cdot}6H_2O$ solutions at room temperature. The electrodeposition was realised using a classical three-electrode experimental set-up, with the steel sample being the cathode, a platinum grid as the counter electrode and a saturated calomel electrode (SCE) served as the reference one. The deposition experiments were carried out in the galvanostatic mode without stirring the solution. Cyclic voltammetry was recorded from −0.6 to −2.5 V under various scanning rates. After electrodeposition, the samples were rinsed in ethanol and dried in a desiccator overnight before any further subsequent analysis.

### 2.3. Characterisation of the films

The morphologies of the films were first investigated by optical microscopy then more thoroughly by scanning electron microscopy (JEOL 5410 LV) coupled to EDS analysis (Rontec detector). The X-ray patterns were obtained in a Bruker AXS D8-Advanced diffractometer using Cu Kα radiation ($\lambda = 1.5406$ nm) at a scan rate of 0.04° $s^{-1}$ in the symmetric configuration. The crystallite size "$D$" was calculated from the Scherrer equation ($D = 0.9\lambda/\beta\cos\theta$) applied to the diffraction peak corresponding to the (1 1 1) reflections (where $\lambda$ is the wavelength of the X-ray, $\theta$ is the diffraction angle and $\beta$ is the full width at half maximum of the peak). The Raman spectra were recorded with a LabRam HR8000 spectrometer equipped with a confocal microscope using an incident beam of 632.82 nm emitted by a HeNe laser. The deposits were also scraped then milled and further analysed by XRD and differential scanning calorimetry (DSC) in a Q100 of TA Instruments between 30 and 550 °C with a heating rate of 10 °C $min^{-1}$ under nitrogen. This atmosphere confers to the deposit a better microstructural order and a longer oxidation time than in oxygenated atmosphere [27]. The infrared measurements were performed with a Thermo Nicolet FT-IR Nexus spectrometer using a KBr beamsplitter, a DTGS detector and a diffuse reflectance accessory. The spectra were recorded with the Omnic software at a resolution of 4 $cm^{-1}$, with 128 scans and a gain of 8. The samples were diluted with KBr.

## 3. Results and discussion

### 3.1. Electrochemical characterisation

Fig. 1 presents the cyclic voltammetry responses of the A366 electrodes immersed in increasing (0.01, 0.1 and 0.25 M) concentrations of fresh aqueous cerium nitrate solutions. The variation of the current density can be in principle related to the following reactions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

$$NO_3{}^- + H_2O + 2e^- \rightarrow NO_2{}^- + 2OH^- \quad (2)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (3)$$

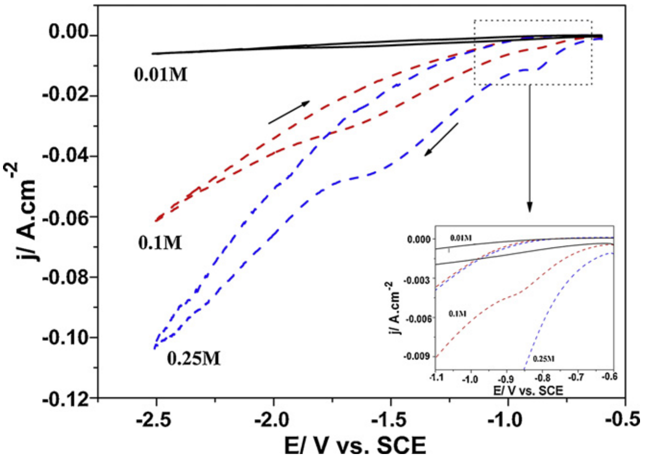

**Fig. 1.** Cyclic voltammograms performed on the uncoated steel at different concentrations of Ce(III) nitrate at room temperature (scanning rate: 20 mV $s^{-1}$).

The hysteresis observed during the reverse scan indicates that the surface of the electrode is modified during the cathodic polarisation especially in the more concentrated solutions. As the concentration is increased, the solution pH lowers (4.5, 3.8 and 3.3 for the 0.01, 0.1 and 0.25 M concentrations, respectively). Therefore, the corresponding thermodynamic potentials for the reaction (1) should be −1.06, −1.01 and −0.96 V/SCE. However, the experimental curves show that the potential values have moved towards less cathodic values with overpotentials of about 200 mV. This would suggest that the reduction reaction occurs rapidly.

Furthermore, during the cathodic scanning, a peak of weak intensity is observed at −0.86 and −0.89 V/SCE for the 0.1 and 0.25 M concentrations, respectively, but it does not appear at 0.01 M, hence suggesting that it depends on the cerium nitrate concentration. The same peak was also observed in previous works [28,29] and was attributed to the nitrate reduction, the reduction of oxygen or to a catalytic reaction. In principle, three interactions could explain the origin of this peak: reduction of nitrates, reduction of oxygen and evolution of the cerium species. The reduction of nitrates has been investigated by comparing the cyclic voltammograms of the substrate in 0.1 M $KNO_3$ and in 0.1 M $CeCl_3{\cdot}7H_2O$ solutions (Fig. 2). It can be observed in the enlarged area of Fig. 2 that the peak appears in the cerium chloride solutions but not in the potassium nitrate ones. Therefore, the role of the reduction of nitrates can be disregarded.

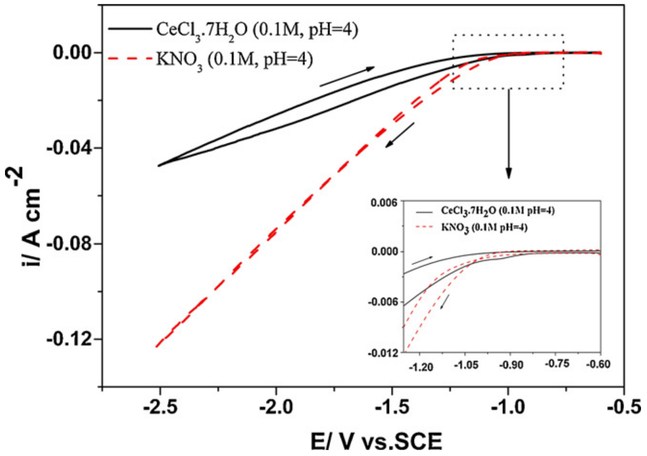

**Fig. 2.** Cyclic voltammograms performed on the uncoated steel in 0.1 M $CeCl_3{\cdot}7H_2O$ and in $KNO_3$ solutions at room temperature (scanning rate: 20 mV $s^{-1}$).