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Effect of ZrO_2 on corrosion behaviour of chromium coatings

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Abstract

To study the effect of ZrO_2 particles on corrosion behaviour of Cr coating, steel samples were plated in Cr(VI) baths without and with ZrO_2. The corrosion behaviour of plated samples was studied at different exposure times in a solution containing 0.01 mol l^{-1} H_2SO_4 + 0.5 mol l^{-1} Na_2SO_4 using cyclic voltammetry and impedance spectroscopy. The equivalent circuit model $R_e(Q_cR_{pore})(Q_s[OR_s])$ was proposed to fit the corrosion process and the parameters $Y_0(Q_c), Y_0(Q_s)$ and R_{pore} reflecting corrosion behaviour of samples were evaluated. From the results, it was found that samples plated in bath containing ZrO_2 exhibited improved protective properties as a result of the structural characteristics of the coatings obtained; namely, the size and shape of pores.

Keywords: A. Chromium coating; A. ZrO_2 particles; A. Steel; B. Cyclic polarization; B. Impedance spectroscopy

1. Introduction

Conventional chromium coatings have many defects, which may be described as pinhole and microcrack defects. It is generally accepted that defects in the coating may be the reason of poor protection of steel surface against corrosion. The use of the coatings with different defect levels may highly influence the corrosion process. To improve corrosion resistance of Cr plated on steel, it is needed to modify the structure of Cr coating. The presence of particles in the electrolyte leads to extensive modifications of the structure of the metal matrix even if they are not incorporated into the deposit [1]. This may promote deposition of coatings with an excellent corrosion resistance. According to the data published before [2–4], the dispersion particles affecting the microstructure of the chromium coatings remarkably improved corrosion resistance of the coatings.

To investigate protective properties of the coatings, the impedance spectra (IS) in a wide range of frequencies for various coating exposure times to the aggressive solution are widely used [5–7]. For the interpretation of the electrochemical behaviour of a sample, it is necessary to find an appropriate physical model of the electrochemical process occurring on the electrode. The electrochemical process may be represented by an equivalent circuit model, which consists of resistances, capacitors and other circuit elements and provides the most relevant corrosion parameters for the electrode/electrolyte system [8]. Impedance measurements are fast and enable to detect the initial corrosion at the metal/coating (via pinholes) interface. In particular, the modelling of IS to the equivalent circuit model made it possible to reveal correlation between the corrosion behaviour and microstructure of the coating [6]. The variation of some parameters extracted from the equivalent circuit model can be attributed to the processes or changes occurring in the coating or at the coating/substrate (via pinholes) interface with immersion time, even when the appearance of the coating is obviously unchanged [6,7]. Corrosion behaviour of steel/hard-coating systems studied by the electrochemical polarization and IS methods

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is discussed in [9] where the current flow through coating pinholes is shown to be eliminated and the galvanic attack at the coating/substrate (via pinholes) interface is reduced owing to the microstructure features of the coating.

The corrosion behaviour of Cr coating deposited from the Cr(VI) bath has been studied and discussed elsewhere [10]. The data obtained have shown that appearance of the active dissolution region during the anodic scan coincided with that characteristic of the supporting steel. This is interpreted as evidence of penetration of the aggressive solution to the substrate.

The aim of this work was to study the effect of ZrO_2 particles added to the Cr(VI) bath on the electrochemical behaviour and corrosion properties of the Cr coating obtained.

2. Experimental

The samples were plated on steel containing 99.4% iron (Steel-3) in the electrolyte containing 120 $g\,l^{-1}$ of chromic anhydride (CrO_3), 2.5 $g\,l^{-1}$ of Limeda Ch-3 additive, which is a mixture of the fluoride-containing complexes and sulphate compounds [11] and additionally ZrO_2 particles were used. The size of particles was about 0.5–1.0 μm. The solution was agitated prior to electrolysis for over 4 h. The steel cathode was mechanically polished, degreased with magnesium oxide, rinsed thoroughly, activated in diluted (1:1) hydrochloric acid and then rinsed with deionised water. A bath with a volume of 1 l with two vertical anodes and a steel cathode between them was maintained at constant temperature and agitated with a 150 l h^{-1} flow of compressed air. The samples were plated at a current density (i_c) of 40 A dm^{-2} and a temperature of 50 °C.

The compositions of both the substrate and the coating in wt.% were determined by means of an X-ray electron probe microanalyzer JXA-50 A. The surface morphology of Cr electrodeposits was examined under a scanning electronic microscope (SEM). In order to choose a typical picture for each coating, three – four locations (in the central zone) were taken.

The thermal effect on the microhardness of coatings was investigated after annealing the samples at 200 and 600 °C for 6 h. The Vickers pyramide hardness (HV) was measured using a 50 g load on 20 μm thick coatings and the average value was calculated from over ten measurements.

The corrosion resistance of Cr coatings plated in baths with and without ZrO_2 particles was tested in a neutral salt spray chamber, as well. The temperature in the testing chamber was maintained at 35 ± 2 °C. The corrosion resistance of the coatings (10 μm) was evaluated as a percentage of the area of defects in the coatings according to the ISO 4540 standard [12].

The electrochemical measurements were carried out in a three-electrode cell of 100 cm^3. A steel plate covered with a chromium coating was used as a working electrode. A platinum plate and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All the potentials given are referred to the SCE. All measurements were performed in a solution containing 0.01 mol l^{-1} H_2SO_4 and 0.5 mol l^{-1} Na_2SO_4(pH 2.6). Cyclic polarization measurements were conducted under potentiodynamic conditions with a potential scan rate of 10 mV s^{-1} at a temperature of 20 ± 1 °C. The polarization was usually carried out in the positive direction and then reversed to the initial potential.

Elemental analysis of the coatings was carried out using X-ray photoelectron spectroscopy (XPS) [13]. The XPS spectra were recorded by an ESCALAB MK-II spectrometer (VG Scientific, UK) using Mg K_α anode radiation (1253 eV, a pass energy of 20 eV).

Measurements of electrochemical impedance were carried out at the open circuit potential (E_{corr}) after immersion of a sample into the studied solution for different time periods (from 0.5 h to 5 days). An Autolab combined with GPES software provided a fully computer controlled electrochemical measurement system. Frequencies were varied from 2×10^4 to 5×10^{-2} Hz. The amplitude of sinusoidal potential was 10 mV peak to peak. To interpret the EIS data, various equivalent circuits (about 10 models) describing electrochemical corrosion were used. The calculated parameters of equivalent circuit were used for simulation of impedance diagrams. Finally, the data obtained were fitted and analysed using the EQUIVCRT program written by Boukamp [14]. The use of this program made it possible to select the most accurate electrical equivalent circuit model for fitting of the experimental data.

3. Results and discussion

The SEM data in Fig. 1 show that the coating deposited from the Cr(VI) bath without ZrO_2 has a fine-grained structure with microcracks, whereas the one deposited from the bath containing ZrO_2 particles may be characterized as a spherulite with a ball-like crystals structure without visible microcracks. XPS analysis indicated that ZrO_2

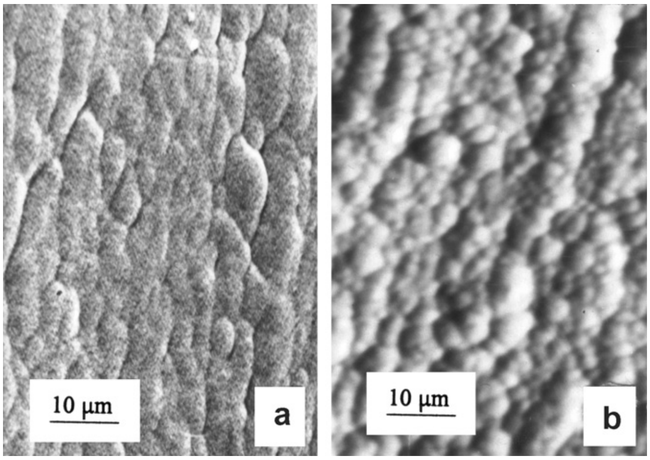

Fig. 1. Micrographs of the coatings deposited in Cr(VI) bath without (a) and with 20 $g\,l^{-1}$ of ZrO_2 particles (b).