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The corrosion protection mechanism of rust converters: An electrochemical impedance spectroscopy study

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ABSTRACT

Oxide converters represent an interesting alternative for the protection of steel surfaces that have some degree of rust. Although the mechanism of these converters is not clear, it is assumed that they react with iron oxides and generate new compounds that may have a passivation effect on the steel surface. This last point is not well established, and several authors have even spoken of an accelerating effect of these compounds.

We present here a study of the electrochemical behaviour of iron oxides immersed in the rust converter. The modulus of the impedance increases significantly after a certain time of immersion, suggesting that the electronic conductivity and, consequently, the rate of the cathodic reaction tend to decrease.

1. Introduction

Most rust converters are based on tannic and phosphoric acids, which are not problematic from the viewpoint of the environment, unlike the toxic inhibitors such as red lead or zinc chromate. However, there is considerable controversy about their effectiveness. Depending on the experimental conditions, the results may even be contradictory. Several reasons may explain this fact, among them, the different nature of the layer of iron oxide to convert (type, density, thickness, etc.) [1–4], pH, and concentration or origin of the tannic solution [5–8] appear to be the most important. However, neither the reaction mechanism nor the transformations taking place at the oxide layer are clearly established. There is some agreement that the rust converter reacts with crystalline iron oxides leading to an amorphous layer [9]. The reaction occurs quickly with lepidocrocite (γ-FeOOH), a little slower with magnetite (Fe_3O_4) and much slower with goethite (α-FeOOH) [10].

Concerning the mechanism of protection, some authors [11] point out that the formation of the conversion layer is accompanied by an increment of film tightness, which is responsible for the protection afforded. However, other authors [8,12] have concluded that the use of tannic acid solutions does not improve the anticorrosion properties of rust. There are even authors suggesting that the effect of tannates may be harmful in environments with high chloride content [13].

It was also shown that the effectiveness of the rust converter is strongly dependent on the history of rust formation [14]. Good converter behaviour of the converter is only found on corroded surfaces showing a homogeneous distribution of the corrosion products. The conversion layer formed seems to follow the distribution of the rust layer.

The aim of this work is to analyze the transformation of iron oxides when they are in contact with a rust converter and determine how it can affect their electrochemical behaviour.

2. Experimental

The activity of the rust converter was studied using the oxide obtained from mild steel plates corroded in a salt spray chamber as base material. Mild steel plates (150 mm × 100 mm × 2 mm) were exposed for 500 h in a NaCl salt spray chamber operated according to the ASTM B-117 standard. At the end of the exposure period the oxide layer was removed using a metallic brush. Once dried, 50 g of the oxide was mixed with 100 ml of a commercial rust converter (oxi-no®) based on tannates and phosphates, according to the technical information supplied by the producer. Then the mixture was aged for 13, 47 and 167 days, keeping the container at room temperature.

Prior to electrochemical testing, all the samples were dried in oven for 24 h at 40 °C and milled in agate mortar in order to obtain a homogeneous powder.

The physic-chemical characterisation of materials and mixtures was performed using:

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(a) A JEOL 5410 scanning electron microscope (SEM) (JEOL, Akishima, Tokyo, Japan) equipped with energy dispersive X-ray microanalysis (EDX) for surface morphology observations and elemental analysis.
(b) X-ray diffraction (XRD) using a Siemens D5000 powder diffractometer with the monochromatised Cu K_α radiation ($\lambda = 1.54$ Å) from $2\theta = 5^\circ$ up to $2\theta = 70^\circ$ for characterisation of the crystalline compounds.
(c) Fourier transform infrared (FTIR) using Thermo Nicolet 6700 spectrometer in the wave number range of 4000–500 $\mathrm{cm^{-1}}$ for characterisation of the chemical bonds formed during the contact time between the oxide and the rust converter.
(d) Differential scanning calorimetry (DSC) using a Mettler Toledo 822e/400 apparatus, from 20 °C up to 200 °C with a heating rate of 10 °C in a stream of N_2 (flow: 50 $\mathrm{ml\,min^{-1}}$) for characterisation of humidity content in samples.

Electrochemical impedance spectroscopy (EIS) was used for electrochemical characterisation. Configurations of two electrodes and three electrodes were employed, according to the arrangements shown in Fig. 1. The two-electrode arrangement was used for the characterisation of the electrical properties of the sample (oxide powder with or without rust converter), no electrolyte was added. In the three-electrode arrangement the mix oxide-rust converter was applied on a glassy carbon electrode and 1 M NaCl solution was employed as electrolyte to study the electrochemical properties of the mix.

For the two-electrodes measurements a HP4194A impedance analyser was used. The frequency was scanned from 40 MHz down to 10 Hz taking 17 frequencies per decade, and 20 mV rms signal amplitude. For the three electrodes configuration, the measurements were performed with a potentiostat Autolab® PGSTAT 30, from 10 kHz down to 10 mHz, taking 7 frequencies per decade, and 10 mV rms signal amplitude. All the measurements were performed under potentiostatic control, at null dc current.

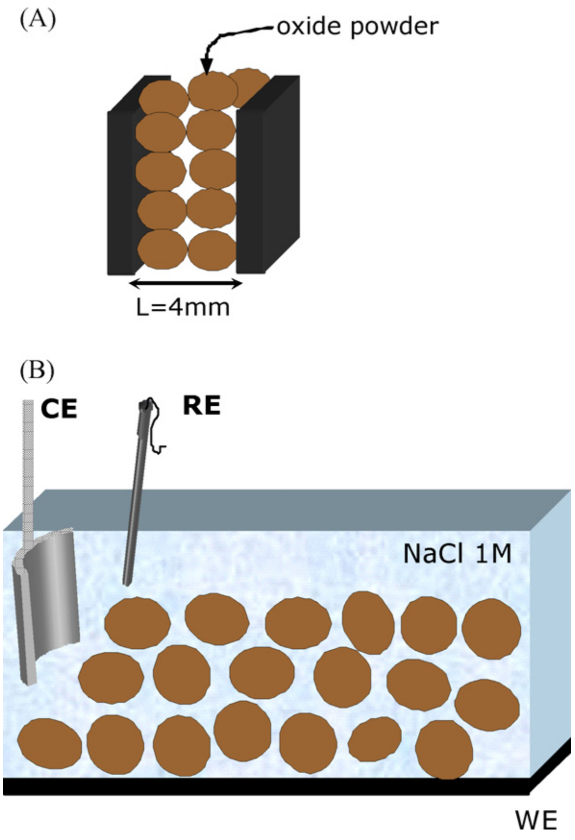

Fig. 1. Electrode configurations for the impedance measurements. (A) Two electrodes. (B) Three electrodes. The counter electrode, CE, and the working electrode, WE, are 1.57 $\mathrm{cm^2}$ glassy graphite platelets.

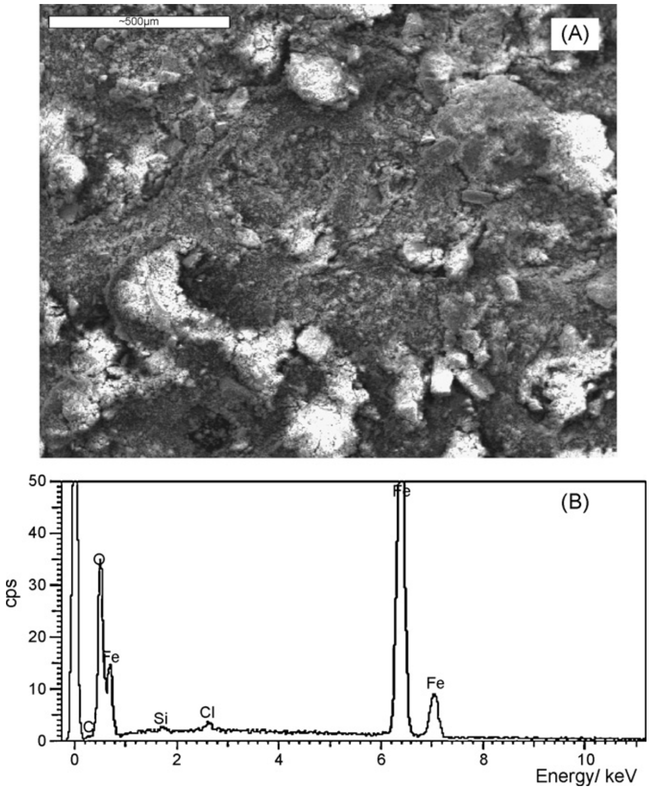

Fig. 2. (A) SEM image showing the initial morphology of the rust. (B) EDX microanalysis performed on the whole SEM image showing the presence of oxygen and traces of chlorine, typical of the iron hydroxychlorides present in these rusts.

The experimental impedance data were treated using a SIMPLEX-based procedure described elsewhere [15].

3. Results and discussion

3.1. Chemical characterisation

Fig. 2 shows the original appearance of the rust powder, which is heterogeneous, and shows differences in electronic conductivity between different areas. The lighter areas correspond to low-conductivity corrosion products that remain charged under the electron beam. The EDX analysis of Fig. 2B shows traces of chlorine, indicating the presence of oxo-hydroxides and hydroxychlorides, which are typical corrosion products in salt spray tests [14].

Fig. 3A shows the typical morphology of the oxides after 13 days in contact with the converter. The comparison with Fig. 2A reveals a more homogeneous structure and the presence of faceted particles. The homogeneity of the structure refers to electrical properties: non-conducting electrically charged areas, bright spots, are less in Fig. 3A. The presence of phosphorus, carbon and traces of copper are evident in Fig. 3B. Copper is not characteristic element in most rust converter formulations; nevertheless, its presence here will help to explain the electrochemical behaviour observed, as it will be shown later. The reaction between the rust converter and the oxide layer is suggested by the decrease of peaks corresponding to goethite, lepidocrocite and magnetite observed in Fig. 3C. The IR spectra presented in Fig. 3D also support this thesis because of the emergence of bands of phosphates and iron tannates with immersion time. All those facts evidence the existence of a chemical reaction between the rust converter and the oxide layer.