Electrochimica Acta 55 (2010) 804–812

Contents lists available at ScienceDirect

Electrochimica Acta

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

Surface analytical characterization of passive iron surface modified by alkyl-phosphonic acid layers

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ARTICLE INFO

Article history:
Received 10 June 2009
Received in revised form 7 September 2009
Accepted 7 September 2009
Available online 15 September 2009

Keywords:
Corrosion protection
Passive iron
Alkyl-phosphonic acid
CEMS
XPS

ABSTRACT

Surface modification with self-assembled alkyl-phosphonic acid layers is a powerful technique for corrosion protection of different metals. In the present study, passivated, native (covered with air-formed oxide) and metallic iron surfaces were used as substrates. The influence of the oxide on the phosphonate layer formation; the corrosion protective effect of the phosphonate layer and the structure of the modified surfaces were investigated. The layer formation process was monitored directly in the phosphonate-containing solution. It was found that the phosphonate layer formation process depends on the conditions applied during iron passivation, and the oxide layer has an important role in the stability of the protective layer, while the bare metallic iron surface is disadvantageous for phosphonate bonding.

Conversion electron Mössbauer spectroscopy (CEMS) and X-ray photoelectron spectroscopy (XPS) proved the presence of phosphonate layer on the top of the passive iron surface, with the thickness around monolayer.

1. Introduction

Layers of amphiphilic organic molecules that form spontaneously on substrate surface by adsorption from solution have been intensively studied as an advantageous technique of surface modification and functionalization. Protection of metal surfaces by organic self-assembled monolayers (SAMs) is a new way to fight against corrosion.

Papers have been published already on the application of alkanethiol SAMs on iron [1,2] and copper [3,4] surfaces. Thiols form a well-ordered layer on metallic surfaces. Organosilicon protective layers were also extensively investigated [5] similarly to phosphoric acids [6–8], carboxylic acids [9,10], hydroxamic acids [8,11], imidazole compounds [12] and sulfonic acids [8], which bond preferably to oxidized surfaces.

Highly ordered films of alkyl-phosphonic acids can be used also to modify the chemical and physical properties of different metal surfaces in a wide range of applications including corrosion protection [6,7,13–17]. The protective effect of phosphonate layers for iron has been discussed in our previous papers [18–22]. Alkyl-phosphonic acid molecules might be able to replace environmentally restricted, e.g., chromate surface treatments. The phosphonate layer formation proved to be a spontaneous process that could be accomplished by simple immersion into the aqueous solution of the phosphono compounds. Significant corrosion protection was observed, markedly decreasing the anodic dissolution of substrate iron. Our previous studies were done on passive (potentiostatically passivated [19]) and on native (covered with air-formed oxide [21]) iron. It was proved that the presence of oxide at the iron surface plays a significant role in the phosphonate layer formation. It has also been shown by other authors that phosphono groups interact strongly with several metal oxides, mostly through the formation of stable M–O–P bonds [11,23].

The aim of the present study is to characterize the influence of the surface oxide on the phosphonate layer formation. In order to reveal the role of the oxide, several samples has been prepared, and potentiostatic passivation has been performed in borate buffer solution in the potential range between −400 and 800 mV (versus SCE). Passivated samples were compared also to native (covered with air-formed oxide) and metallic (cathodically reduced) iron surfaces. The layer formation process has been monitored directly in the phosphonate-containing solution by measuring the open circuit potential and the electrochemical impedance spectra. The corrosion protection effect of phosphonate layer has been investigated in a neutral solution of 0.1 mol dm^{-3} of $NaClO_4$. Attention was also paid to the investigation of the phosphonate layer structure. The structure and composition of surface film on modified iron were determined with conversion electron Mössbauer spectroscopy (CEMS) and X-ray photoelectron spectroscopy (XPS). The question was: Is the alkyl-phosphonic layer really a monolayer on the pre-passivated iron surface?

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doi:10.1016/j.electacta.2009.09.023

2. Experimental

2.1. Sample preparation

ARMCO iron disc samples (19 mm diameter for electrochemical and CEMS measurements, 10 mm diameter for XPS) were mechanically polished first with silicon carbide polishing paper (220, 600, 1200, 2000, 4000) then with diamond suspension (9, 6, 3, 1, 1/4 μm). The iron surface was washed with distilled water and cleaned by ethanol in ultrasound bath between each polishing step. Mirror-like surface was obtained with this polishing method.

2.2. Passivation of iron

The iron samples were passivated in a borate buffer solution of pH 8.4 made from 0.15 mol dm^{-3} H_3BO_3 and 0.0375 mol dm^{-3} $Na_2B_4O_7{\cdot}10H_2O$. The solution was deaerated with argon gas bubbling prior to the beginning of the experiment. The polished iron specimens placed into a plastic (PVDF 1000) electrode holder were first galvanostatically reduced at −40 μA/cm^2 until all air-formed oxide was removed from the surface [24]. In the second step potentiostatic passivation was carried out at different potentials for 1 h.

2.3. Phosphonate film formation

Phosphonate layers were produced by immersion of the passivated iron specimens into the aqueous solution of 10^{-3} mol dm^{-3} 1-octyl-phosphonic acid (C8P) for different times (24, 96 h). The pH of the phosphonate solution was adjusted to 7.00 by adding NaOH solution. The selection of this pH value has two reasons; first, in acidic solutions the dissolution rate of iron is high, corrosion starts immediately; and second, the dissociation of protons in phosphono groups is necessary for corrosion inhibition by phosphonates. Phosphonic acids, in general, inhibit steel corrosion in neutral and slightly alkaline solutions [25].

2.4. Electrochemical potentiostatic and impedance measurements

Electrochemical potentiostatic measurements were performed with Solartron 1286 ECI and PAR potentiostat/galvanostat Model 283. The counter electrode was a platinum net, and the reference electrode was a saturated calomel electrode (SCE). All of the potentials presented in the paper are given relative to this reference electrode.

Electrochemical impedance measurements were carried out using Solartron 1286 Potentiostat and 1250 Frequency Response Analyzer. Impedance spectra were measured at the open circuit potential in the frequency range of 30 kHz to 1–10 mHz, with 10 points per decade. The applied frequency range of spectra and waiting time between the EIS measurements was optimized to the shift of OCP in time in our systems. A sine wave with 10 mV amplitude was used to perturb the system. The impedance spectra were recorded in phosphonate solution (pH 7.0).

2.5. ^{57}Fe conversion electron Mössbauer spectroscopy (CEMS)

CEMS measurements [26] were performed on the samples at room temperature. ^{57}Co/Rh radioactive source with 1 GBq activity, a conventional constant acceleration mode Mössbauer spectrometer (WISSEL) and He–4%CH_4 gas flow CEMS detector (RANGER) were applied for the Mössbauer measurements. The spectra were evaluated by the least-square fitting of spectral lines using the MOSSWINN program [27]. The isomer shifts are given relative to α-iron.

2.6. X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out using an electron spectrometer manufactured by OMICRON Nanotechnology GmbH with an EA125 energy analyser. The photoelectrons were excited by Al Kα (1486.6 eV) radiation. Spectra were recorded at normal emission in the constant analyser energy mode: for survey spectra 50 eV pass energy was used, while detailed scans of the relevant peaks were measured at 30 eV pass energy, with resolution better than 1 eV. Spectra were evaluated by fitting with Gaussian–Lorentzian sum peaks after removing a Shirley or linear background. Binding energies were referenced to the main component of the C 1s spectrum (285.0 eV binding energy), which was confirmed by the metallic Fe 2p$_{3/2}$ component (707.0 eV) and the Fermi edge (0.0 eV) of the underlying metal substrate. Measured data were quantified using the XPS MultiQuant software [28].

3. Results and discussion

3.1. Electrochemical investigation of passive iron surfaces modified with alkyl-phosphonic acid layers

3.1.1. Passive oxide layer formation on iron, influence of the passivation potential

As it was proven in the literature, the presence of oxidized surface is an important requirement for the chemical bonding of phosphonate compounds. The bond strength depends on the interaction between metal oxide and phosphonate group. Therefore, in order to investigate the layer formation of phosphonate on iron, passive oxide films with well-defined structure were formed by potentiostatic passivation in borate buffer of pH 8.4. This solution has emerged as the preferred electrolyte because the surface oxide film forms with a current efficiency of nearly 100% without significant Fe dissolution, and can be described as a true passive film [29,30].

The current density–time transient measured during passivation of iron electrode at different potentials for 1 h is shown in Fig. 1. The linear relationship between log *i* and log *t* with the slope of −1.0 between 10 s and 1 h confirms that dense passive oxide film was formed with logarithmic film growth mechanism. Assuming a current efficiency of 100%, the charge obtained with integration of current density transients, and the estimated thickness of passive oxide films are listed in Table 1. Passive film thickness values were calculated to the geometric surface area assuming a density of 5.2 g/cm^3 [31]. These results are in a good agreement with the literature data obtained in similar experimental conditions [32,33].

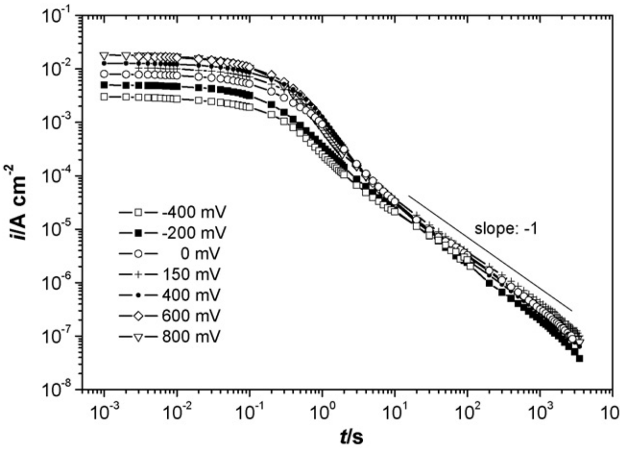

Fig. 1. Anodic current density versus time transient of iron electrode at different passivation potentials obtained in borate buffer (pH 8.4).