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Surface modification of passive iron by alkyl-phosphonic acid layers

A. Paszternák[a], S. Stichleutner[b], I. Felhősi[a,1], Z. Keresztes[a,1], F. Nagy[b], E. Kuzmann[b], A. Vértes[b], Z. Homonnay[b], G. Pető[c], E. Kálmán[a,*,1]

[a] *Chemical Research Center of the Hungarian Academy of Sciences, 1025 Budapest, Pusztaszeri út 59-67, Hungary*
[b] *Research Group for Nuclear Methods in Structural Chemistry, Hungarian Academy of Sciences, Institute of Chemistry, Eötvös Loránd University, 1117 Budapest, Pázmány P. sétány 1/a, Hungary*
[c] *Research Institute for Technical Physics and Materials Science of the Hungarian Academy of Sciences, 1121 Budapest, Konkoly Thege út 29-33, Hungary*

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Abstract

Phosphonate layer formation on passive iron surface has been investigated by electrochemical, conversion electron Mössbauer spectroscopy (CEMS) and atomic force microscopy (AFM) techniques. Electrochemical methods revealed that the prepassivation of iron surface results in stabilization of the phosphonate layer exhibiting favorable corrosion resistance. The rate of anodic dissolution is continuously decreasing due to the time-dependent formation of a protective phosphonate layer.

The large R_{ct} values of 1–20 MΩ cm^2 indicate rather high blocking effect of metal dissolution by the phosphonate layer. The phosphonate layer formation has been also followed by the decrease of capacitance. CEMS investigations were carried out to evaluate the differences in the composition of the passive layer as a result of the phosphonate treatment. Mössbauer spectroscopy indicated the presence of iron phosphonate. Changes in morphology due to the phosphonate layer formation have been observed.
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1. Introduction

The use of organic phosphorous compounds, e.g., phosphonic acids in corrosion inhibitor formulations for cooling water has been started in the 1960s [1,2]. Phosphonates, in general, are anodic inhibitors; they protect steels mostly in neutral and slightly alkaline solutions in the presence of dissolved oxygen. The inhibitor films build up over several hours or, in some cases, days, depending on the corrosivity of the environment [2]. Phosphonates are good complex-forming reagents. They can easily form complexes with different metal ions. The polynuclear complexes have usually low solubility and their formation at the interface can inhibit the metal dissolution. The effect of complex formation on the corrosion of metals was discussed in detail by Kuznetsov [3].

Thin layers of alkyl-phosphonic acids have been also applied as protective films against corrosion of different metals, such as iron [4–6], aluminium [6–8] and zinc [8,9]. The adsorption layer formation of mono-phosphonic acids with different alkyl chain length has been investigated and discussed in our previous work [4]. The phosphonate layer formation proved to be a spontaneous process that could be accomplished by simple immersion into the aqueous solution of phosphono compounds. Significant corrosion protection was observed, markedly decreasing the anodic dissolution of substrate metal. The inhibitor layer is supposed to have a continuous and dense structure. It was also observed, that the oxide plays an important role in the adsorption of phosphonates on iron [4,5]. The formation of stable M–O–P bonds has also been shown for alkyl *N*-aminodimethylphosphonate on mild steel [10].

The importance of oxides on phosphonate binding to surface has been also emphasized in other studies, dealing with adsorption of alkyl-phosphonic acids on oxide-covered surfaces, such as zirconium, tantalum, niobium and titanium. It has been shown

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[*] Corresponding author. Tel.: +36 1 438 1166; fax: +36 1 438 1164.
E-mail address: erika.kalman@chemres.hu (E. Kálmán).
[1] ISE member.

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that phosphono groups interact strongly with oxide, mostly through the formation of stable M–O–P bonds [11,12].

In order to develop an outstanding protective phosphonate layer forming a more defined M–O–P bond, a known oxide layer formation would be desirable on the metal surface before the inhibitor treatment. The electrochemically formed passive layer on iron surface is proposed for this purpose.

The aim of our work was to characterize the phosphonate layer formation and to determine its composition on passive iron oxide layer. The layer formation of octyl-phosphonic acid has been followed by electrochemical impedance spectroscopy, and the chemical composition of the surface has been determined with conversion electron Mössbauer spectroscopy (CEMS). The morphology of passive iron and its changes due to the phosphonation has been investigated by AFM.

2. Experimental

2.1. Sample preparation

ARMCO iron disc samples (19 mm diameter) 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 in ethanol bath using ultrasound between each polishing step. Mirror-like surface was obtained with this polishing method.

Simultaneously, samples were also prepared for the conversion electron Mössbauer spectroscopy measurements when iron enriched in ^{57}Fe (90%) was vacuum deposited on the polished ARMCO iron substrates using evaporation equipment (Hochvakuum-Bedampfungsanlage B30.2, Dresden) at pressures of 2×10^{-3} Pa in about 14 nm thickness.

The adhesion of the deposited ^{57}Fe layer on the substrate is normally very poor and can be easily pilled off. To improve the adhesion many method can be used as heat treatment during deposition and different chemical cleaning, etc. However, these methods are rather effective they cannot be used in this experiment. Instead we used a rather peculiar treatment. The main idea is that if the film deposited onto a substrate is ion bombarded with suitable ion and energy the adhesion can be improved tremendously because of the mixing between the substrate and the film induced by the bombarding ions. The mixing process needs certain energy, namely where the projecting range ions is roughly equal to the thickness of the film. This the main condition for this treatment. As an ion surface interaction induce erosion of the surface (re-sputtering) depending on the dose of ions it should be minimized to avoid the removing of the very thin ^{57}Fe surface layer however the mixing is linearly dependent of the bombarding ion dose. That means that the dose of bombarding ions it should be optimized. The next requirement to avoid the ion induced chemical reaction. That could be fulfilled using noble gas ions. According to these considerations was used the Ar ion irradiation in an ion implanter with rather low voltage (40 keV and dose 10^{14} at/cm^2). The obtained adhesion was around 100 kp/cm^2 measured by direct pull 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 [13]. In the second step potentiostatic passivation was carried out at 400 mV (versus SCE) 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 for different times between 10 min and 100 h. The pH of the phosphonate solution was adjusted to 7.0 with adding NaOH solution. The selection of pH has two reasons; firstly, in acidic solutions the dissolution rate of iron is high, corrosion is taking place; and secondly, 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 [14].

2.4. Electrochemical potentiostatic 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.

2.5. Electrochemical impedance measurements

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 ten 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 diagrams were recorded in the investigated phosphonate solution (pH 7.0).

2.6. ^{57}Fe conversion electron Mössbauer spectroscopy

^{57}Fe conversion electron Mössbauer spectroscopy (CEMS) measurements were performed on the samples at room temperature [15]. ^{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

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