EIS examination of mill scale on mild steel with polyester–epoxy powder coating

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Abstract

Mill scale exists as a thin layer on mild steel. This layer is unstable and cracks easily under mechanical and thermal shocks and this may lead to serious damages in the organic coatings, which have been applied on it. In this study, effects of mill scale removal on performance of a polyester–epoxy powder coating were investigated, using two corrosion test methods: electrochemical impedance spectroscopy (EIS) and open circuit potential (OCP) in function of time. These tests were performed in a 3.5% w/w NaCl solution.
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1. Introduction

Steel is an important part of the modern world and most of the structural steel that is used today for heavy construction such as marine, chemical and petrochemical industries contains varying amounts of mill scale on the surface. Mill scale can be formed on the steel structure through chemical oxidation of iron with oxygen at high temperature during the rolling process [1,2].

Since mill scale potential is more positive than bare steel, when cathodic reaction specimens such as oxygen, water and also ions reach the coating/metal interface, galvanic cell can be formed between mill scale and bare metal. Corrosion products are the result of electrochemical reactions, which are more voluminous than original metal. This is likely to remove mill scale from the substrate. This problem also exists created when mill scale is painted over. The mill scale is then unstable and when it comes in contact with a aggressive environment tends to release adhesion from the metal surface. When painted over, this reaction results in loose areas of coating with blistering or cracking in these areas [1]. One of the latest methods of coatings is powder coating that has superior techno-economical benefits the conventional coatings, like being free of solvent. Solvent emission is considered as a great problem through all parts of the paint and surface coating industry.

There are several ways to examine corrosion phenomenon. One is electrochemical impedance spectroscopy (EIS) which is a non-destructive test method [3–8]. Qualitative and quantitative data can be obtained from EIS using applied sine wave via three electrodes known as working electrode (WE), auxiliary electrode (AE) and reference electrode (RE) [9–15]. The applied current passes through WE and AE while the potential is taken between RE and WE. The purpose of ac impedance is to model the corrosion process in terms of circuit elements such as resistor, capacitor and inductor. Therefore, it is possible to make conclusions about characteristics of the corrosion process.

Circuit element which simply changes the signal amplitude is a resistor. Capacitors and inductors introduce a delay in the response and therefore a phase angle. In the measurement of impedance, the independent variable is the frequency of the signal. The result is given by two numbers: (1) modulus and phase angle of the impedance or (2) the magnitude of the real and imaginary components.

In this study, EIS and open circuit potential (OCP) of polyester–epoxy powder-coated mild steel were measured in the presence of mill scale and also when mill scale had been removed by acid pickling.

2. Experimental

All test panels used in this study were mild steel (Q-panel). Two surface treatments were applied on the samples

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including (1) solvent degreasing and acid pickling and (2) only solvent degreasing. Solvent degreasing and acid pickling were achieved by immersion of panels in acetone and hydrochloric acid, respectively, afterwards the polyester–epoxy powder coating was applied to a thickness of $45 \pm 3\,\mu$m using an electrostatic spray gun. The curing schedule used for each powder-coated panels was 20 min at 180 °C. Electrical contact for each sample was achieved by drilling a hole on top of the samples, connecting a conductive wire by means of a nut and bolt to each. For obtaining a constant and known surface area and also omitting the chance of edge and bimetallic corrosion the samples were coated with a 3:1 mixture of beeswax and colophony resin back and round the edges leaving a central area of 36 cm^2 unmasked.

The sample, an Ag/AgCl electrode and a platinum counter electrode were placed in the sodium chloride solution with a concentration of 3.5% w/w. The ac impedance measurements were performed at the open circuit potential, Ecorr, using a sine wave of 20 mV amplitude peak to peak for the samples. The frequency range was usually from 10 kHz down to 0.01 Hz. The working, counter and reference electrodes were connected to the terminals of an ACM impedance machine model ac Gill. The open circuit potential (OCP) was also measured between saturated calomel electrode (SCE) and working electrode over 70 days immersion in 3.5% w/w NaCl.

3. Results and discussion

In the measurements of impedance, the result is expressed by modulus and phase angle of the impedance or the magnitude of the real and imaginary components. Typical Niquist diagram for the coating systems is shown in Fig. 1.

The elements were selected through a model equivalent circuit to represent the systems under study. It was found the systems were under charge transfer control according to the circuit as it is shown in Fig. 2 where R_s represent solution resistance, R_p coating resistance, C_c coating capacitance, R_{ct} charge transfer resistance and C_{dl} double layer capacitance.

Figs. 3–6 show parameters such as coating resistance, coating capacitance, charge transfer resistance and double layer capacitance after 7 and 50 days immersion. The analysis of ac impedance data was performed by using Boukamp
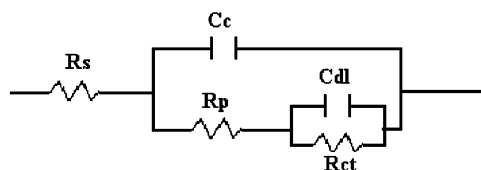

Fig. 2. Electrical equivalent circuit for the polyester–epoxy coating on the different surface treatments of Q-panel mild steel.

software [16]. It is necessary to note that in all figures, dimension of resistance and capacitance is Ω cm^2 and F/cm^2, respectively.

Fig. 3 shows the coating resistance after 7 and 50 days immersion in 3.5% NaCl solution for the coating systems, which were degreased and acid pickled.

It is concluded from the mentioned previous rates and figures on the diagram that the coating resistance for the acid pickled specimens is higher than for the degreased samples. This indicates that lower ionic resistance and a higher number of pores exist in the coating samples which were degreased. Corrosion products caused by galvanic cell between mill scale and bare metal at the interface could provide the driving force to develop the number of conductive paths which would cause a reduction in the coating resistance for coating samples which were degreased. It is reasonable that the value of the coating resistance is inversely proportional to the average cross-section of the conduction channels.

Coating capacitance for the different samples are shown in Fig. 4. The coating capacitance determines the total amount of water in the coating. After 7 and 50 days immersion in electrolyte, the value of the coating capacitance for the samples with degreasing treatment is higher than for the samples with acid pickling treatment, indicating that the absorption of water in the coating is higher. Absorption of water causes an increase in the dielectric constant of the coating with a corresponding increase in the coating capacitance. There are corrosion products which absorb more water through the film and increases the dielectric constant of the coating for the specimens which have been degreased.

In Fig. 5, it is clearly shown that after 7 and 50 days immersion in 3.5% w/w NaCl solution the charge transfer resistance of the samples treated with acid pickling is higher than the charge transfer resistance of samples degreased. This indicates that the corrosion rate is higher for the samples
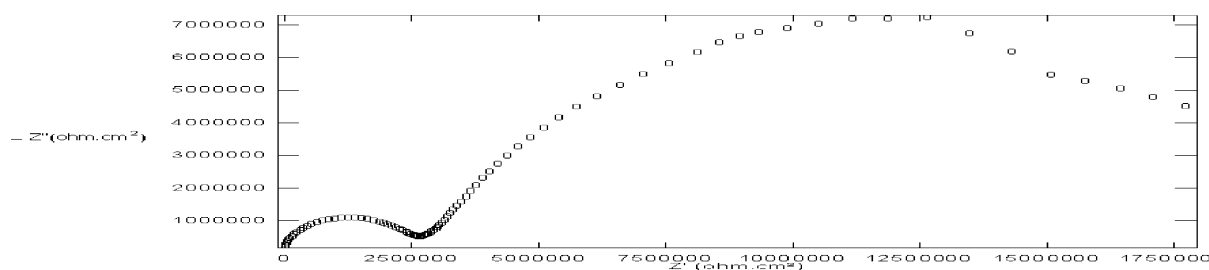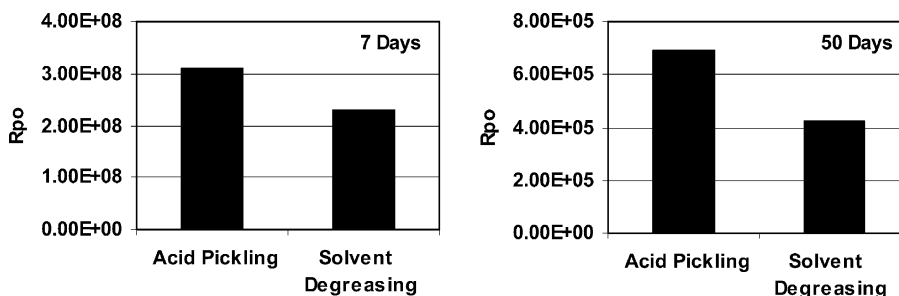

Fig. 1. Typical Nyquist diagram.

Fig. 3. Coating resistance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days.
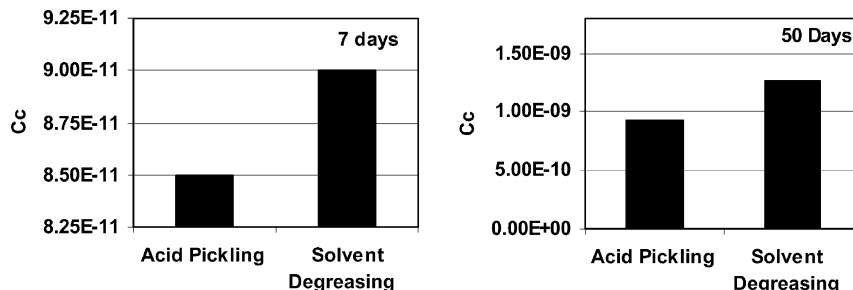

Fig. 4. Coating capacitance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days.
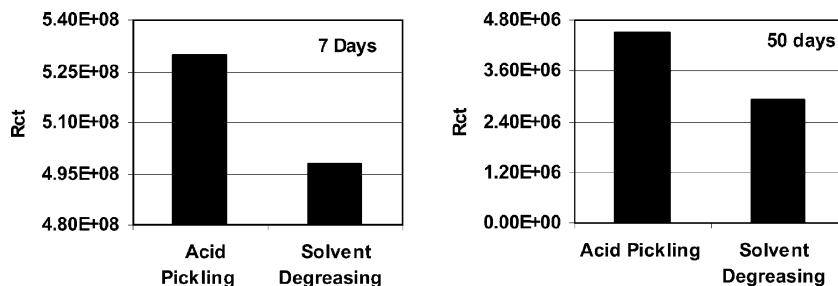

Fig. 5. Charge transfer resistance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days.

treated with solvent [17]. The easy access of aggressive ionic species to the interface though the pores and the galvanic cell between mill scale and bare metal could be the reasons for having higher corrosion rate.

In Fig. 6, the double layer capacitance of the two specimens can be seen. The double layer capacitance of the acid pickled sample is lower than that of the solvent treated one. High performance systems show low double layer capacitance. The higher the double layer capacitance the higher the disbonded area. Any factors such as pressure of corrosion products on the film and a chemical or electrochemical gradient across the coating which can increase the number of the defects in the systems and reduces the coating resistance can also increase the double layer capacitance [18]. Therefore, having mill scale at the interface, increases the disbonded area.
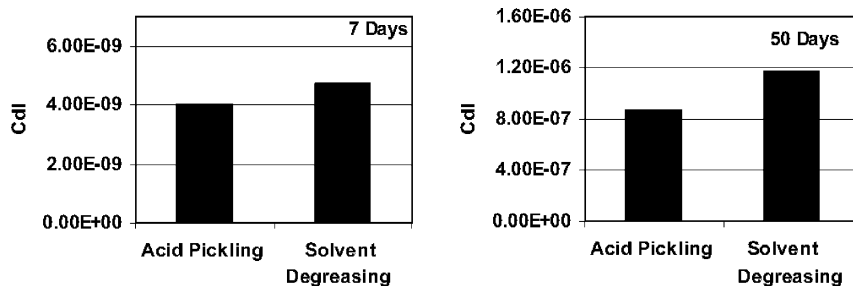

Fig. 6. Double layer capacitance of specimens with different surface treatments after immersion in 3.5% NaCl solution for 7 and 50 days.
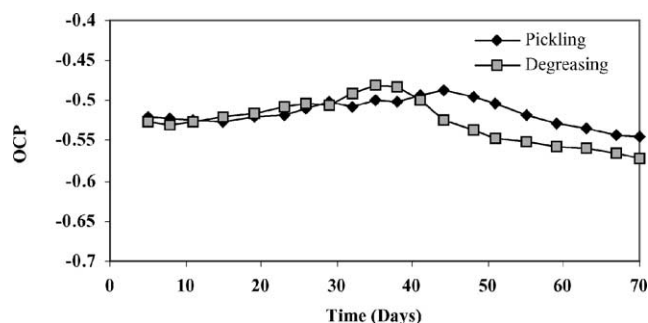
Fig. 7. Potential vs. time diagram of the two different samples including powder coating after immersion in 3.5% NaCl solution during 70 days.

According to Figs. 3–6 by increasing the immersion time, coating and charge transfer resistance decrease and coating and double layer capacitance increase.

Open circuit potential (OCP) of the two different samples are given in Fig. 7.

Mayne [19] stated that the potential of a painted specimen is a mixed potential of the interface and IR drop of the coating and it is cathodic over an unpainted sample when it is immersed in the electrolyte. On immersion of a coated sample, current must pass from the anodic area via the coating to the solution and also back through the coating to cathodic area.

The polyester–epoxy powder coating film acquires a negative charge when immersed in electrolyte and it renders the film selectively permeable to ions of opposite charge, i.e. iron ions. Consequently, the hydroxyl ions, which are produced by the oxygen reduction reaction at the interface, accumulate underneath the coating with time followed by formation of a passive layer on the metal. This causes an increase of the ratio cathodic to anodic areas with a corresponding increase in potential up to 35 days for solvent degreased samples and up to 45 days for acid pickled samples. With higher diffusion of water in the film, ionic species such as OH^- and Cl^- are able to permeate more easily through the film causing the breakdown of passive layer on the metal. This leads to an increase in the anodic reaction rate and an increase in the proportion of anodic to cathodic areas thereby OCP becomes more negative. A maximum peak of OCP occurred after a longer time for the acid pickled sample compared to the other one. This indicates that the cathodic area under the pressure of mill scale can be changed to an anodic area at the shorter time of 35 days compared to 45 days for the acid pickled samples.

4. Conclusions

By comparing the two different pretreatment of mild steel, degreasing and acid pickling, it is clearly seen that coating resistance and charge transfer resistance are higher in the acid pickled system and that the coating capacitance and double layer capacitance are lower in the acid pickled system than in the solvent degreased system.

Moreover, the period of exposure for the maximum peak of OCP is longer in the case of the acid pickled system. Therefore, in conclusion, the acid pickled system is a better choice than the degreased system and this can be attributed to not having mill scale on the mild steel which produces galvanic cell causing more diffusion of ionic species through the coating. This shows that the nature of the interface is very important to produce a high performance coating.

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