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Short Communication

A cathodic delamination study of coatings with and without mechanical defects

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ABSTRACT

It has been demonstrated that the surface defects of carbon steel, when protected with a coating in good conditions, cause an advance of the cathodic delamination front as fast as that caused by forced cathodic polarization where the coating is damaged.

For this and because the potential difference between cathodic and anodic areas in the crevice corrosion process is much smaller than the polarization promoted by the anodic areas beneath the damaged coating, it is suggested that diffusion prevails over migration as controlling parameter in the forward speed of the process.

Trending were confirmed by Scanning Kelvinprobe and Scanning Vibrating Electrode Technique.

1. Introduction

In the middle 1980s, Leidheiser's works [1,2] summarized much of the information that was already available, and provided new results that led to the clarification of the general mechanism for the cathodic delamination process. In the 1990s, Pommersheim et al. published results and models [3,4] which clarified details of the mechanism involved in the processes of degradation of organic coatings. In the same decade, Stratmann's team [5,6] validated those of the Pommersheim's and studied the advancing front of the delaminated area using Scanning Kelvinprobe (SKP) to measure the potential corrosion beneath the coating surface.

In the past decade, Allahar et al. [7] took into account the Stratmann results to propose a one-dimensional mathematical model for predicting the delamination front based on pH gradients.

Although there have been advances to slow down the cathodic delamination phenomenon, and almost to disrupt it [8], the consequences of these alternatives still have not proved to be more beneficial for the metallic substrate.

Despite the number of publications on the subject, there has been minimal research [9] on the influence of metallic surface (defects or roughness) on this phenomenon. Quite the contrary, despite the known and accepted gradual penetration of water and oxygen through the coating it is accepted [5,10] that while the coating is not damaged the substrate corrosion and the delamination can be minimized.

This short communication shows that, regardless of the physical condition of coating, if the steel surface has pores or crevices, that can be polarized anodically, then the delamination may occur even when only minimal amounts of water and oxygen diffuse through the coating.

2. Experimental

Commercial mild steel square panels (5 cm × 5 cm × 0.1 cm) were used as metallic substrates. The steel panels were modified with cylindrical inlays of Zn, Cu and Ag of 1 mm diameter (purchased from GoodFellow™). After the inlays were coupled to the steel coupons the surface was prepared by abrasion with 1000 grit paper, degreased, rinsed in methanol and stored in desiccators before applying the organic coatings.

A model transparent vinyl varnish was applied by the dip-coating method on the steel samples at a constant withdrawal rate of 1.35 mm/s. In this way, homogeneous organic films were obtained. The applied dry film thickness was 20 ± 2 µm.

Artificial defects of 0.15 mm diameter were produced on the coating with a needle. The size and quality of such defects was controlled using an optical microscope.

The Zn inlays were used to polarize the adjacent surface of the steel and so to locally promote the cathodic delamination. The inlays of Cu were coupled to the steel leaving a crevice intentionally while the well coupled silver electrodes were used as a control of what was happening under the surface of intact coating.

Owing to the fact that the specimens had a non-conductive coating and that other localized electrochemical techniques

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present some problems in working with heterogeneous surfaces [11], it was decided to use the SKP and Scanning Vibrating Electrode Technique (SVET) for verifying the visual results.

After the immersion in NaCl 0.6 M, the coated coupons were introduced into the saturated humidity chamber of the SKP at 24 °C.

For obtaining the SKP potentials a plane-ended cylindrical 80Ni–20Cr probe with a diameter of 50 μm was used as needle, which was moved with three stepping motors for *x*, *y* and *z* directions. Before performing these experiments, the SKP was calibrated by using a standard Cu/$CuSO_4$ solution to establish a relation between the work function and corrosion potential. SKP potentials are given relative to the potential of the standard hydrogen electrode (SHE). The technical specifications of the home made SKP used are reported in [13, design B].

On the other hand, the SVET from Uniscan Instruments (Model SVP370) was used with bare specimens immersed in NaCl 0.06 M. No external potential was applied, and measurements were performed in the open circuit corroding mode. The distance between the tip of the probe and the steel surface was approximately 100 μm, the vibration amplitude 10 μm, the vibration frequency 85 Hz and the reference phase 175.

3. Results and discussion

Series I in Fig. 1 shows that once artificial defects were produced in the coating both Zn electrodes caused a fairly similar delamination in their neighborhoods. Even when one of these processes started first, both average speeds of the delaminated front were very similar: 106 μm/h and 105 μm/h, respectively. These were consistent with those reported by Hausbrand et al. [12].

Apparently, delamination fronts grew randomly in opposite directions and formed almost perfect circular tracks after 400 min of immersion in the electrolyte. The dark color within the blisters was caused by the polarization of light film on the precipitates.

In the case of the neighborhood of the copper-electrode, the delamination footprint expanded almost at the same rate as the

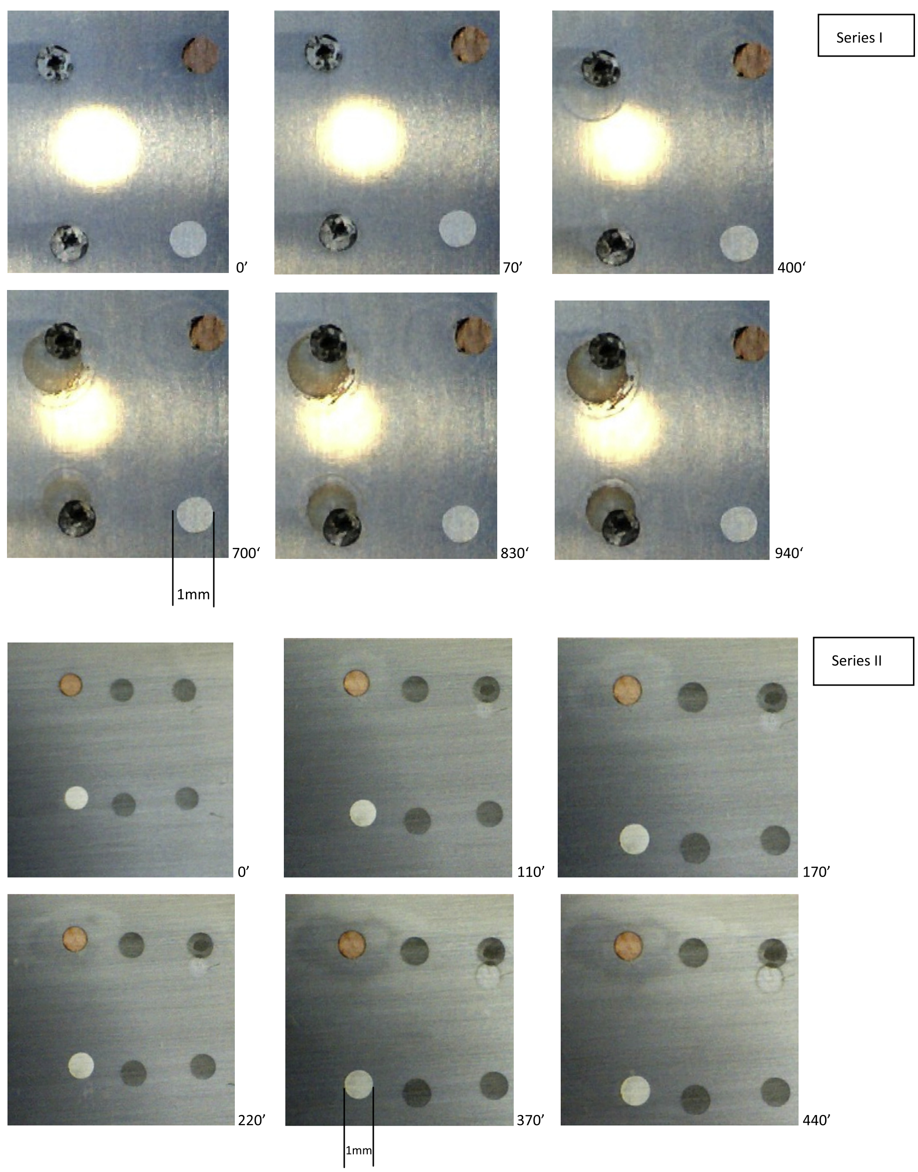

Fig. 1. Pictures of the system steel-inlays/coating in electrolyte over time. The pictures were taken using a AGPtek® digital USB microscope video camera which was programmed for taking pictures each 5 s. Series (I) Delaminated area advance around two Zn-electrodes (with a damaged coating) and around a Cu-electrode (with an intentional crevice). Silver inlay was used as a control. The circular filming light could not be avoided. Series (II) Delamination advance next to a Zn-electrode (with a damaged coating) and next to a Cu-electrode coupled with a crevice. The silver and the remainder Zn-electrodes were used as control.