

Online Monitoring of Undercoating Corrosion Using Coupled Multielectrode Sensors

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Online monitoring of carbon steel corrosion under different commercial coatings was conducted utilizing coupled multielectrode sensors. The experimental results showed that the coupled multielectrode sensor is an effective tool for detecting initial defects and real-time degradation of coatings. Because of their high sensitivity, the coupled multielectrode sensors may also be used as a quick and convenient tool for optimizing the selection of proper coatings for different applications. oatings are used to protect metallic substrates from corrosion in many industries. In the U.S. alone, the total annual cost of coating applications in 1997 was estimated to be between

\$33.5 billion and \$167.5 billion.1 The corrosion protection provided by coatings depends on their quality. If the coating is deteriorated or damaged, corrosion may take place under the coating or at the flawed location. Because corrosion beneath a coating is not easily detected, an effective monitoring technique is required to detect it at an early stage to eradicate or control the undercoat corrosion. Periodically, holiday detectors are used to evaluate the coating on a metallic substrate. An online monitoring technique may provide a real-time indication of the coating performance and serve as an early warning of degradation, making it an ideal tool for detecting and controlling undercoat corrosion.

Coupled multielectrode corrosion sensors have been used as in situ or online monitors for nonuniform and localized corrosion in laboratories and industrial applications.²⁻⁵ These applications have demonstrated that the sensors can be used to continuously monitor corrosion, not only in aqueous solutions but also under solid deposits such as bio and salt deposits.³⁻⁴

In this study, coupled multielectrode corrosion sensors and a newly developed multielectrode corrosion analyzer system were used as an online monitor to detect corrosion under coatings. The detailed experimental setup is described. The results of corrosion measurements on carbon steel (CS) under different coatings are presented.

Experimental Procedures

The sensing electrodes were made from an annealed mild CS wire (concrete rebar wire), 1.5 mm in diameter, 50 mm in length, and coated with different commercial coatings. Each sensor had eight electrodes painted with the same type of coating. Each sensing electrode was

TABLE 1 COATING CONFIGURATION OF SENSORS

	Sensor 1	Sensor 2	Sensor 3	Sensor 4	Sensor 5	Sensor 6
Coating code	А	A	В	С	D	А
Coating type	Ероху	Ероху	Rust inhibitive	Enamel	Auto rust paint	Ероху
Number of coats	2	2	2	2	2	2
Initial condition	Tips of three electrodes (1, 4, and 8) mechanically damaged	Tips of all electrodes mechanically damaged	Fully covered	Fully covered	Fully covered	Fully covered
Color	Black	Black	Grey	Red	White	Black

FIGURE 1



Coupled multielectrode sensors painted with different coatings for the experiment.

FIGURE 2



Experimental setup: Six sensors were connected to the coupled multielectrode corrosion analyzer system.

abraded to 320 grit and rinsed with distilled water and acetone before the coating was applied. Four types of commercial coatings were evaluated in this study.

Figure 1 shows the six sensors used in the experiment. Table 1 gives their coating configurations. Sensors 1, 2, and 6 were coated with the same type of epoxy. The tips of three electrodes (Electrodes 1, 4, and 8) in Sensor 1 and all electrodes in Sensor 2 were mechanically scratched to simulate the initial defects (pinholes) on the coating. All sensors were immersed in simulated seawater and tested at 26°C. The simulated seawater was prepared with 3% sea salt and distilled water. A nanoCorr[†] A-50 Coupled Multielectrode Corrosion Analyzer⁶ was used. This analyzer has a high current resolution (10^{-12} A) and allows the measurement of coupling currents from up to 50 electrodes (Figure 2). Six sensors were con-

[†]Trade name.

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Responses of the sensor signals to simulated initial defects and degradations of the coatings in simulated seawater. Sensors 1 and 2 had induced coating-damaged electrodes, and all other sensors had intact coatings on all electrodes prior to the test.



Appearances of Sensor 2 electrodes after 7 days of immersion in simulated seawater. Coatings at the tips of all electrodes contained initial defects prior to the test. The tips of the electrodes had rusted after 7 days and were severely corroded after 17 days of immersion.

nected to the analyzer and measured at the same time. The common coupling joint² of each sensor was connected to a large type 304 stainless steel (SS) (UNS S30400) cathode (surface area 30 cm²) so that each of the sensing electrodes would be an anode when the coating on it failed. A notebook computer and the factorysupplied software, CorrVisual[†], were used in conjunction with the multielectrode

[†]Trade name.

analyzer. The currents from each sensor's electrode, the electrochemical potential of each sensor against a saturated calomel reference electrode (SCE), and the temperature were logged at a user-specific interval (usually 20 to 120 s) and saved in a computer file. Processed signals, such as the localized corrosion current and cumulative charge for each sensor, were saved in a separate file. Other processed signals, such as the corrosion rate and cumulative corrosion damage (penetration depth), were also recorded in the processed data file if the surface areas of the damaged coating on the sensing electrodes were known. During the measurements, all of the directly measured currents, the statistical values of the measured currents for each sensor, the temperature, and other useful parameters for data acquisition were also displayed dynamically on the computer screen in both numerical and graphical forms.

Results and Discussion

Figure 3 represents the corrosion signal changes measured from the six coated sensors in response to the initial defects and degradation of the coatings. The signal for each sensor was automatically calculated by the software based on the current from the most anodic (corroding) electrode among the eight electrodes in the sensor. The results are discussed below.

COATINGS WITH INITIAL DEFECTS

Signals from Sensors 1 and 2 with simulated initial defects on coatings (Sensor 1 had three coating-damaged electrodes and Sensor 2 had eight coatingdamaged electrodes) increased instantaneously from the lower detection limit (2 \times 10⁻¹¹ A) to more than 1 \times 10⁻⁶ A. The corrosion current signals for Sensors 1 and 2 remained above 1 \times 10⁻⁶ A throughout the test.

As shown in Figure 4, corrosion of the sensing electrodes with initial defects on coatings was apparent after 7 days of immersion. The electrodes of Sensor 2 were severely corroded after 17 days of immersion. Figure 5 shows that, indeed, most of the electrodes with initially damaged coatings had high anodic currents flowing through them during the measurement. Since the electrodes of the sensors were galvanically coupled to a nobler SS cathode, the measured potential for each sensor was slightly higher than the free immersion potential or open-circuit potential (OCP) (–0.62 to –0.70 $V_{\text{SCE}})$ of a CS wire in the same solution. The coupling of the sensor electrodes to the SS electrode was made to ensure that each sensing electrode would act as an anode when the coating on it was degraded or flawed. Some electrodes, however, were still giving low levels of negative currents and acting as cathodes, even when they were coupled with a nobler electrode. If only one single electrode had been used, the sensor would not have been able to detect the coating damage, because it might give a low-level negative signal indicating there was no corrosion. Therefore, the use of multiple electrodes in the sensor is essential to effectively detect the degradation of coatings. The behavior of these electrodes, which gave low-level cathodic currents, was caused by variations of the OCP among the different electrodes. This was probably caused either by the heterogeneity in the metallurgical microstructures among the different electrodes of a sensor or by the different localized environments surrounding the sensor's electrodes.

COATINGS OF POOR QUALITY

The signals from Sensor 6 increased gradually by two orders of magnitude in ~20 h, after the first and second immersions in the brine solution, and stabilized at a constant value after the 20-h test. The initial change in the measured signal was caused by either the poor quality of the coating or the minor initial defects. The poor quality of coating is a more likely cause because, if the sensor had initial defects, it would have continued to fail and the signal would have continued to increase during the course of the immersion test. No visually detectable damage to the coating was observed after the 17day immersion test. The gradual increase



Currents from the different electrodes and the potential of the coupling joint of Sensor 2 during the initial 7-day measurement. Most of the coating-damaged eight electrodes acted as anodes, except Electrode 7, which became a cathode on Day 5.

in the sensor signal upon the first (Day 1) and second (Day 7) immersions may have been caused by the diffusion of the electrolyte in the conducting path (or pores) in the coating. Between the two immersions, the increase upon the first immersion was much slower than that upon the second immersion because the electrolyte was not totally dried out of the conducting path when the sensor was removed for a short time (12 h) on Day 6.

COATINGS OF HIGH QUALITY

The signal from Sensor 5 remained at the background noise value $(2.2 \times 10^{-11}$ A—Figure 3) throughout the experiment. The low signal is an indication of the high quality of coatings on the sensing electrodes. A post-test visual examination showed no apparent degradation of the coating.

COATINGS DEGRADED DURING MEASUREMENTS

The signal of Sensor 4 remained at the background noise value in the first 16 h (Figure 3) of immersion and suddenly changed by approximately two orders of magnitude (from 1.8×10^{-11} to 3×10^{-9} A). This abrupt change was apparently

caused by a rapid degradation, such as the cracking of the coating on the sensor electrode. A similar sudden increase occurred on Day 5. After the 7 days of immersion, a visual examination of the sensor electrodes verified the failure of the coating. A small peeling-off area was noted. The signal change caused by the abrupt coating degradation appeared to be different from the response of a sensor with already damaged coatings. The signal from the coating-damaged sensor increased instantaneously and by a large degree after the immersion. This behavior was also evident from the response of Sensors 1 and 2 at the start of the measurement on Day 1 (Figure 3) and the response of Sensor 4 upon the second immersion on Day 7 (Figure 3). In contrast, the response to degradation did not always happen immediately after the immersion because the degradation usually took some time to develop.

COATINGS WITH POOR INITIAL QUALITY AND DURING MEASUREMENTS

The response of the signal from Sensor 3 is between those of Sensors 6 and 4; there were both an initial gradual increase



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and then further changes after the signal was stabilized. The initial change was caused by either the poor quality of the paint or by minor initial defects; the subsequent increase was attributed to the degradation of the coating during the immersion test. Even though the signal was significant, no visually detectable coating damage could be observed at the end of the 17-day test period. This underscores the significance of real-time monitoring, which enables warnings of coating failures or defects long before they can be visually detectable.

Conclusions

This experiment demonstrated that coupled multielectrode sensors are effective online tools for monitoring the performance of protective coatings on CS surfaces. The measurement was in real-

time and the signal changed as the degradation took place. Because of their high sensitivity, the sensors had the ability to give early warnings long before the failure of the coatings was visually detectable. The high sensitivity of the sensors used in this technique also enabled the discriminative evaluation of coatings with different qualities. Thus, the sensors are also ideal and quick tools for screening a prospective coating on a particular metal surface or for a particular application. Because multiple electrodes were used in the measurements, the coupled multielectrode sensors offered a high degree of reliability in detecting the quality or the degradation of coatings on CS materials.

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