ONLINE MONITORING OF UNDERCOATING CORROSIONS UTILIZING COUPLED MULTIELECTRODE SENSORS

Xiaodong Sun Corr Instruments, LLC San Antonio TX, USA

ABSTRACT

Online monitoring of carbon steel corrosion under different commercial coatings was conducted, utilizing coupled multielectrode sensors. The experimental results showed that the coupled multielectrode corrosion sensor is an effective tool for detecting initial defects and real-time degradation of the 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.

Key words: multielectrode, corrosion sensor, localized corrosion, corrosion undercoating, corrosion monitoring, online sensor, real-time sensor

INTRODUCTION

Coatings are used to prevent metallic substrates from corrosion in many industries—including infrastructure, transportation, military, and industrial process equipment. In the United States alone, the total annual cost of coating applications in 1997 was estimated to be between \$33.5 billion and \$167.5 billion, according to a recent NACE report.¹ The corrosion protection provided by the coatings depends on the quality of the coatings. If the coating is deteriorated or damaged in a given environment, corrosion may take place under the coating or at the flawed location. Such corrosion can cause severe problems—even catastrophic failures—if it is not identified and mitigated at an early stage. Because corrosion beneath a coating is not easily detected, an effective monitoring technique is required to detect it at an early stage, in order to eradicate or control the undercoat corrosion. Periodically, inspection tools, such as 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. Therefore, an online corrosion monitor is 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 corrosions, 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-deposits 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 corrosions under coatings. The detailed experimental setup is described. The results of corrosion measurements on carbon steel under different coatings are presented.

EXPERIMENTAL

The sensing electrodes of the coupled multielectrode sensors are made from an annealed mild carbon steel wire (concrete rebar wire), 1.5 mm in diameter and 50 mm in length, and coated with different commercial coatings. Each sensor had 8 electrodes painted with the same type of coating. Each sensing electrode was 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 6 sensors used in the experiment. Their coating configurations are given in *Table 1*. Sensors #1, #2 and #6 were coated with the same type of epoxy. The tips of 3 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 a simulated seawater and tested at 26°C. The simulated seawater was prepared with 3% sea salt (Vigo Importing Co., Tampa, Florida, USA) and distilled water.

A nanoCorr^{TM*}–50 Coupled Multielectrode Corrosion Analyzer⁶ manufactured by Corr Instruments (San Antonio, TX, USA), was used in the experiment. This coupled multielectrode analyzer has a high current resolution (10^{-12} Å) and allows the measurement of coupling currents from up to 50 electrodes. Figure 2 pictures the experimental setup during the measurement. Six sensors were connected to the coupled multielectrode corrosion analyzer and measured at the same time. The common coupling joint² of each sensor was connected to a large stainless steel (UNS S30400) cathode (surface area 30 cm^2) so that each of the sensing electrodes would be an anode, when the coating on it failed. A notebook computer and the factory supplied software, CorrVisual^{TM*}, were used in conjunction with the multielectrode analyzer. The currents from each electrode of the sensors, the electrochemical potential of each sensor against a saturated calomel reference electrode (SCE), and the temperature were logged at a user-specified interval (usually 20 to 120 seconds) 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), would be 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 statistic values of the measured currents for each sensor (minimum, maximum, mean, and cumulative charge), the electrochemical potential of 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 DISCUSSIONS

Figure 3 presents the corrosion signal changes measured from the 6 coated sensors in response to the initial defects and the degradation of the coatings. The signal for each sensor was automatically calculated by the software based on the current from the most corroding electrode (or the most anodic electrode) among the 8 electrodes in the sensor. The results in *Figure 3* are discussed as follows:

^{*} nanoCorr and CorrVisual are trade names of Corr Instruments, LLC.

Coatings with Initial Defects

Signals from sensors #1 and #2, with simulated initial defects on coatings (sensor #1 had 3 coating-damaged electrodes, and sensor #2 had 8 coating-damaged electrodes), increased instantaneously from the lower detection limit $(2x10^{-11} \text{ A})$ to more than $1x10^{-6} \text{ A}$, when the sensors were immersed in the simulated seawater. The corrosion current signals for sensors #1 and #2 remained above 1×10^{-6} A throughout the test, in the simulated seawater. As shown in *Figures 4 and 5(A)*, corrosion of the sensing electrodes with initial defects on coatings was apparent after 7 days of immersion in the simulated seawater. Figure 5(B) indicates that the electrodes of sensor #2 were severely corroded after 17 days of immersion in the simulated seawater. Figures 6 and 7 show 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 stainless steel cathode, the measured potential for each sensor was slightly higher than the free immersion potential or open circuit potential (-0.62 to $-0.70 V_{SCE}$) of a carbon steel wire in the same solution. The coupling of the sensor electrodes to the stainless steel electrode was made to ensure that each sensing electrode would act as an anode, when the coating on it was degraded or flawed. However, some electrodes 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 due to the variations of the open circuit potential 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 2 orders of magnitude in approximately 20 hours, after the first and the second immersions in the brine solution, and stabilized at a constant value, after the 20 hours of test. The initial change in the measured signal was due to 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 17-day immersion test (Figure 9). The gradual increase in the sensor signal, upon the first (day 1) and the 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 faster 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 hours) on day 6.

Coatings of High Quality

The signal from sensor #5 remained at the background noise value $(2.2 \times 10^{-11} \text{ A})$ (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 (Figure 9).

Coatings Degraded During Measurements

The signal of sensor #4 remained at the background noise value in the first 16 hours (Figure 3) of immersion in the brine solution and suddenly changed, by approximately two orders of magnitude (from 1.8×10^{-11} to 3×10^{-9} A). This abrupt change was apparently due to a rapid degradation, such as the cracking of the coating on the sensor electrode. A similar sudden increase occurred on day 5. A visual examination of the sensor electrodes, after the 7 days of immersion, verified the failure of the coating. A small peeling-off area was noted (Figure 8A). 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 in the brine solution. This behavior was also evident from the responses 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 was not always immediately after the immersion, because the degradation usually took some time to develop.

Coatings with Poor Initial Quality and Degraded During Measurements

The response of the signal from sensor #3 is between those of sensors #6 and #4; for instance, there were both an initial gradual increase and then further changes after the signal was stabilized. The initial change was due either to the poor quality of the paint or to minor initial defects; the subsequent increase was due 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 (Figure 9). This underscores the significance of real-time monitoring, which enables warnings of coating failures or defects long before it can be visually detectable.

CONCLUSION

This experiment demonstrated that coupled multielectrode sensors are effective online tools for monitoring the performance of protective coatings on carbon steel surfaces. The measurement was realtime 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. As 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 carbon steel materials.

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	Sensor #1	Sensor #2	Sensor #3	Sensor #4	Sensor #5	Sensor #6
Coating Code	Α	Α	В	С	D	Α
Coating			Rust		Auto Rust	
Туре	Ероху	Ероху	Inhibitive	Enamel	Paint	Ероху
Number of	2	2	2	2	2	2
Coats						
Initial Condition	Tips of 3 electrodes (#1,#4 and #8) mechanically damaged	Tips of all electrodes mechanical ly damaged	Fully covered	Fully covered	Fully covered	Fully covered
Color	Black	Black	Grey	Red	White	Black

 Table 1. Coating Configuration of Sensors



Figure 1. Coupled multielectrode sensors painted with different coatings for the experiment.

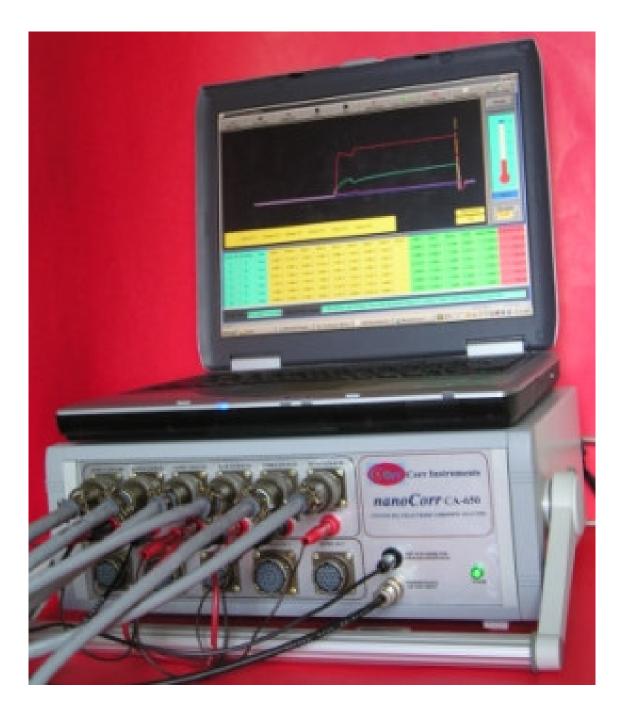


Figure 2. Experiment setup: Six sensors connected to the coupled multielectrode corrosion analyzer system.

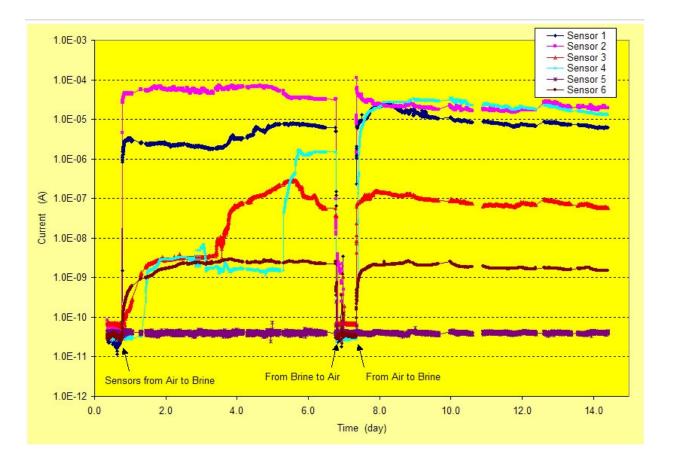


Figure 3. Responses of the sensor signals to simulated initial defects and degradations of the coatings in simulated seawater. Sensors #1 and #2 had induced coating-damaged electrodes and all other sensors had intact coatings on all electrodes prior to the test.



Figure 4. Appearance of sensor #1 electrodes, after a 7-day immersion in brine solution. Coatings at the tips of three electrodes had initial defects prior to the test. Rust developed on these three electrodes after the 7-day immersion. Only one of the three electrodes can be seen in front of this photograph.

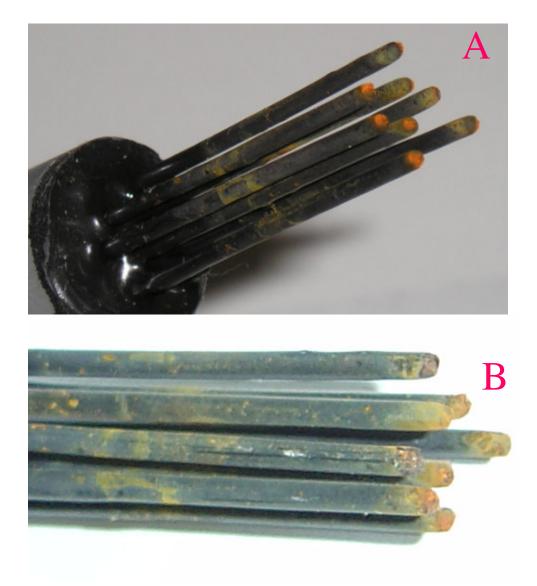


Figure 5. Appearances of sensor #2 electrodes, after 7 days (A) and 17 days (B) of immersion in a brine solution. Coatings at the tips of all electrodes contained initial defects prior to the test. The tips of the electrodes had rusted after 7 days and were severely corroded after 17 days of immersion.

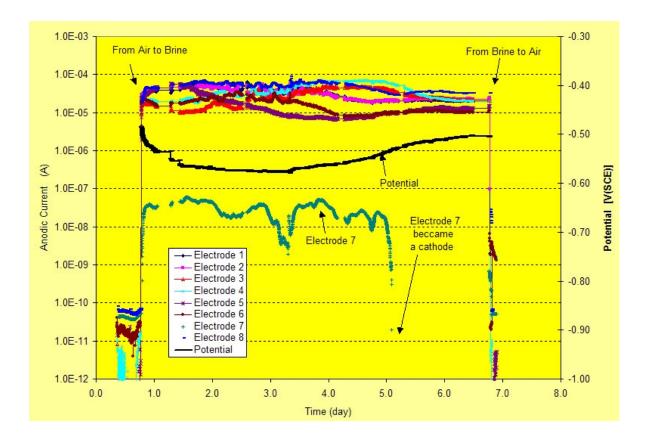


Figure 6. Currents from the different electrodes and the potential of the coupling joint of sensor #2 during the initial 7-day measurement. Most of the coating-damaged 8 electrodes acted as anodes, except electrode 7, which became a cathode on day 5.

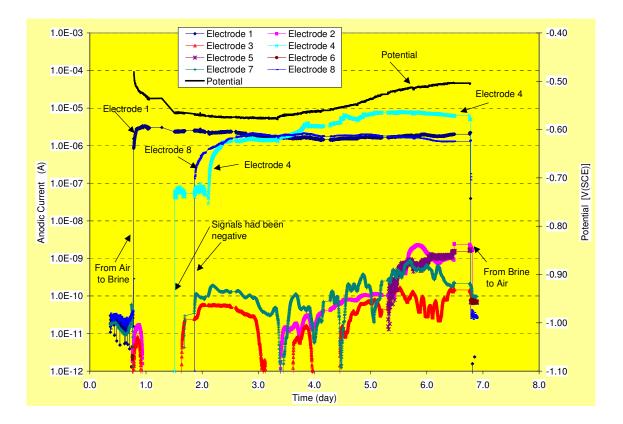


Figure 7 Currents from the different electrodes of sensor #1 during the initial 7-day measurement. The anodic currents from the 3 coating-damaged electrodes (1, 4, and 8) are significantly higher than those from the other electrodes, except for the first two days.

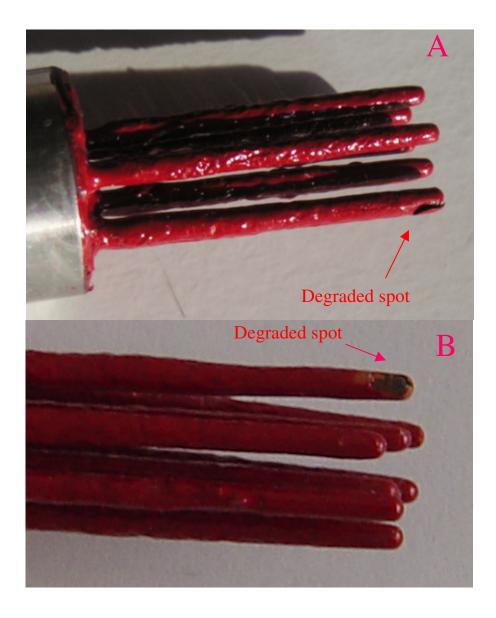
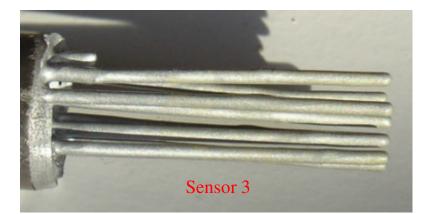
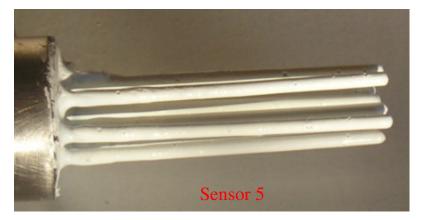


Figure 8. The appearances of sensor #4 electrodes, after 7 days (A) and 17 days (B) of immersion in a brine solution. The coating at the tip of an electrode had peeled off with the first 7th day and was severely corroded after the 17th day.





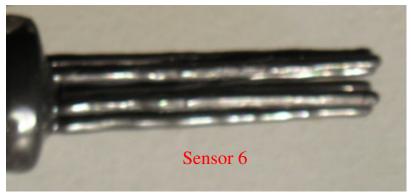


Figure 9. Appearances of the electrodes of sensors #3, #5, and #6, after 17-day immersion in brine solution. No degradation was visible on any of the electrodes.