Corrosion Monitoring for Protected Systems Using Thin-Film Electrical Resistance (TFER) Sensor

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This study has been conducted to monitor the corrosion rate of cathodically protected structure and corrosion inhibited system using multi-line thin-film electrical resistance (TFER) sensor in various environments. The field test data of TFER sensor for the corrosion monitoring of cathodically protected underground pipeline in soil environments and of corrosion inhibited gas heaters were also presented. The sensor was found to be a powerful method to commit the sensitive pick-up of small corrosion rate which can be observed in the cathodically protected and corrosion inhibited systems.

Keywords: multi-lined thin-film electrical resistance (TFER) sensor, cathodic protection, corrosion rate, CP potential, AC interference, corrosion inhibitors, gas heater

1. Introduction

Today, cathodic protection (CP) systems for buried pipelines are monitored mainly using pipe-to-soil (P/S) potential measurement in which the voltage between the pipeline and a reference electrode in contact with the earth's surface near the pipeline is measured. A value of -0.85 V vs. a saturated copper/copper sulfate electrode (CSE) is considered to be adequate for corrosion protection by regulation.¹⁾ P/S potential measurements, though usually adequate under controlled laboratory conditions, have been found inadequate under field conditions in some cases. Some in-service pipelines whose potential consistently met the -0.85 V/CSE criterion have failed due to corrosion.^{2),3)} For example, the corrosion state of the pipeline near electric train railway undergoing interference is hard to be determined from the potential due to the transient nature of the potential.

The gas heater as a heat exchanger has been corrosion-protected by adding some chemical agents. The corrosion inhibited system has been regularly examined by analyzing the media containing the chemical agents. However, it is a time-consuming off-line test and needs a quite lead time to alarm the symptoms for inefficient

In the previous work, the authors enhanced the sensitivity of ER probe to very low rate and non-uniform corrosion by using thin-film and multiple narrow patterns. The response of the multiple-line thin film electrical resistance (TFER) sensor was investigated and proved to effective for corrosion monitoring. In this report, the TFER sensor was applied for monitoring of cathodically protected pipeline and corrosion-inhibited gas heater facility. The detailed behavior of TFER sensor in various situations was reported and the feasibility of application of ER probes for underground pipeline was confirmed by field application.

2. Experimental

2.1 Fabrication of thin film corrosion sensor

The steel thin film of $0.6~\mu m$ was deposited by DC magnetron sputtering of carbon steel target (ASTM A108-1045) onto a slide glass or alumina (Al₂O₃). The schematic diagram of fabricated TFER sensor is shown in Fig. 1. Detailed fabrication condition and procedures are described elsewhere.³⁾

inhibiting action. Therefore many industries have strongly been requiring accurate and reliable techniques for corrosion monitoring.

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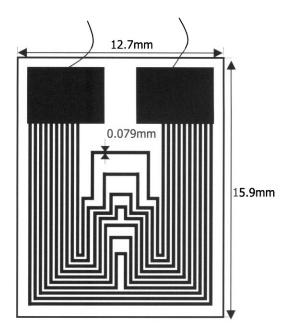


Fig. 1. Schematic diagram of multiple-line patterned TFER sensor.

2.2 Measurement of corrosion rate

The corrosion rate was determined by two methods. One was direct measurement of the probe resistance and the other was the measurement of the current through the probe at potential difference of 20 mV across the probe. The average thickness was determined by comparing the measured value to the initial value. The fraction of remained thickness to initial thickness is used to calculate corrosion rate of the probe. No compensation was made for temperature variation. For the application to corrosion monitoring of cathodically protected steel, the probes were connected to the structure which was protected by independent cathodic protection circuit. For comparison, coupon was used to measure weight loss. For the application to inhibitor added system, it was immersed in the test vessel containing the media and then the relative resistance or current was measured.⁵⁾ In some cases, glass frits were overlapped to the TFER sensor to simulate the crevice condition.

3. Results and discussion

3.1 Laboratory tests for corrosion monitoring feasibility

The resistance change of fabricated probe in various mediums was monitored by current measurement across the probe under constant voltage difference of 20 mV. Fig. 2 shows the responses of TFER sensor in various deaerated solutions.⁶⁾

It is apparent that the responses of each probe were

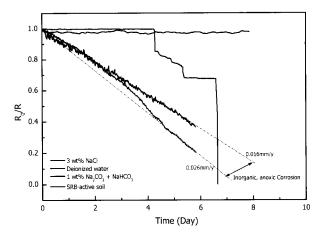


Fig. 2. The responses of multiple-line TFER sensor in deaerated environments at 25°C. ⁶⁾

quite different. From these results, the corrosion behavior of carbon steel can be divided as three categories in the absence of oxygen, i.e., 1) anaerobic inorganic corrosion, 2) the precipitation of protective films (carbonate/bicarbonate), and 3) microbiologically-induced corrosion by sulfate-reducing bacteria. The elaborations for these mechanisms are described in the previous work.⁵⁾

This ER technique seems to be very effective to investigate the change of corrosion behavior, and the localized corrosion characteristics as well as the uniform corrosion characteristics, within relatively short period compared with conventional electrochemical methods. Corrosion rate change was monitored at different cathodic protection levels to confirm the possibility of monitoring cathodic protection effectiveness with the thin film probes. The probes were immersed in the NaCl solution with the resistivity of 100 ohm · cm and the potential have been controlled. The results were shown in Fig. 3.

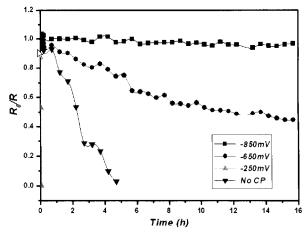


Fig. 3. The corrosion rate change of the sensor probe under the CP potentials in NaCl aqueous solution with electrolyte resistivity of $100 \, \Omega$ cm.

At the potential of -850 mV/CSE, most of the initial thickness of the probe maintained after the experiment. Slight decrease had been observed after long exposure. This slight decrease was found to be attributed to the corrosion during the measurement. The CP system had been interrupted for a while and the accumulated corrosion during measurement decreased the conductance. By altering the measuring interval to several hours, this conductance change had been eliminated. The corrosion rates were increased with the increase of the potential. At the potential of -250 mV/CSE, which was much higher than natural corrosion potential, the corrosion rate was high enough to corrode entire probe within a few minutes. The results showed that the performance of the CP system could be determined successfully by the TFER within 12 hours. As the test did not depend on any potential measurement, any kind of interference could be monitored with this sensor. It means that the consequence of stray current from unknown sources could be estimated within reasonable period.

3.2 Field application 1 (Cathodically protected system)

The TFER sensors were installed at five sites with metal coupon of 1 cm² area for comparison purpose. These sites were selected especially to identify the influence of alternating current interference which was hard to evaluate by routine P/S potential measurement. One of the examples of the P/S potential taken from a site is shown in Fig. 4.

As shown in Fig. 4, AC wave was observed as one of single 60 Hz, 180 Hz and mixed harmonics at a site close to electricity transmission utility. The corrosion rates at those situations were measured. The corrosion rates have been measured with TFER probes and weight loss coupon recovered after 6 months of exposure. A typical data obtained from the sites was shown in Fig. 5 at a day interval.

The corrosion rates were summarized in Table 1. The current flowing through a coupon of 1 cm² area was measured and also listed in the Table.



Fig. 4. Typical Pipe-to-Soil Potential Profile (Vertical grid: 10V, Horizontal grid 5ms)

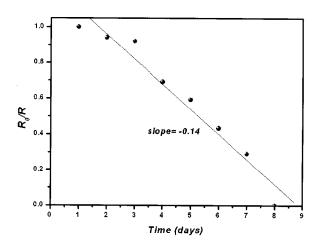


Fig. 5. A Typical Response of the Probe from Application 1

Table 1. The Summary of the Corrosion Rate observed from Field Application¹

Site	Corrosion rate by ER (mpy)	Corrosion rate by coupon (mpy)	AC current (mA)	Domination frequency (Hz)
1	1.20	3.3	3.2	180
2	0.17	0.4	2.8	180
3	0.91	5.5	2.5	60
4	0.13	2.5	0.75	60
5	0.27	1.1	1.2	180

The corrosion rates determined from weight loss coupon was higher than that from the probe. There could be many reasons about this discrepancy. One of the causes could be related to the improper insulation of the weight loss coupon. At the edge and corner of the square coupon, the current was concentrated and masking paint layer was disbonded. The weight loss at the disbonded edge was major portion of the weight loss in heavily corroded coupons. Therefore, it was concluded that the use of probe provide more relevant corrosion rate without artifact from imperfection of the preparation of the coupon.

3.3 Field application 2 (Corrosion inhibited system)

The second field application was made on the corrosion inhibited system, i.e., gas heaters. Fig. 6 shows the sensor response directly exposed to an aqueous corrosion inhibitor. In the Figure, the sensor exhibits two staged behavior. Right after the exposure to the solution, the initial corrosion during the depletion of oxygen by the action of the inhibitor agent appears, while the stable corrosionless behavior can be observed later. However, the corrosion rate would considerably increase under the crevice

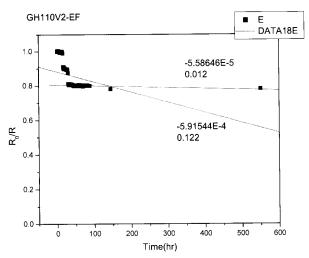
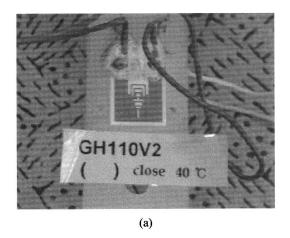


Fig. 6. Corrosion behavior of TFER sensor in pure chemical inhibitor at 40°C.

TFER sensor can be thus thought to be a very sensitive device to detect the abnormal state of corrosion protected system.

For the field application 2, some actual gas heater systems were selected, which were inferred to have exhausted inhibitors based on the laboratory analysis results regularly made, to demonstrate the ability how to promptly show the performance of the inhibitors. Fig. 8 illustrates the corrosion behavior of the sensors immersed at the gas heater. Free exposed sensor showed a stepwise decrease of relative resistance within a span, that is, the occurrence of corrosion whereas the sensor with crevice condition revealed the drastic collapse of the resistance, which means the more fast corrosion. This is substantiated by the photographs as shown in Fig. 9. The rust can be seen on the surface of the sensor under the crevice condition.



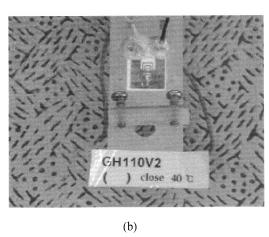
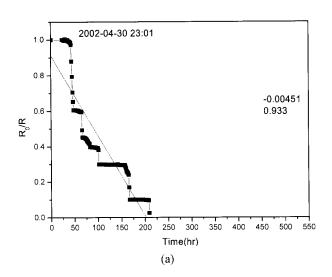


Fig. 7. Sensors after the immersion tests under (a) free exposure and (b) crevice condition.

condition even in the pure corrosion inhibitor system. This fact can be understood from the photographs with the corroded surface of the sensors as shown in Fig. 7. The



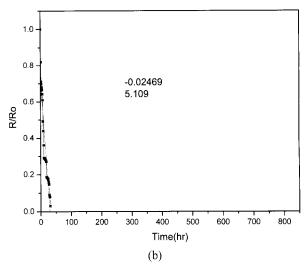


Fig. 8. Corrosion behaviors of the TFER sensors equipped at the gas heater facility under (a) free exposure and (b) crevice condition.

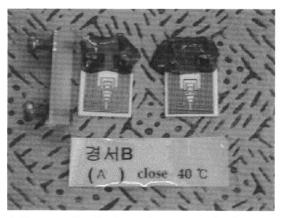
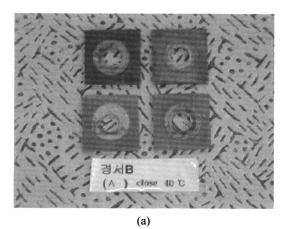


Fig. 9. Sensors after the immersion tests under free exposure (right) and crevice condition (left). The sensor under the crevice condition shows slight corrosion.



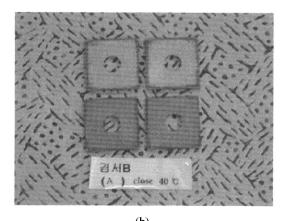


Fig. 10. Coupons extracted from the heater for the comparison; (a) creviced coupon, (b) free coupon.

The prompt and reliable response of the TFER sensor can be confirmed by comparing the status of corrosion coupons, which had been installed in the heater for a long-term monitoring. From these Figures, one can find the effect of crevice condition on corrosion, and the TFER sensor can provide the prompt and reliable testimony for the corrosion occurrence or the running out of the inhibition ability.

4. Conclusion

Application of the TFER probe for underground pipeline with CP and gas heater under corrosion inhibited action to measure the corrosion rate was demonstrated in this study. The corrosion rate of the cathodically protected pipeline could be determined with the TFER probe. The time required to register corrosion rate of pipeline under interference varied from few minutes to days which was much smaller than conventional weight loss coupon method. The presence of interference and its impact on CP system could be monitored successfully by installation of the probe connected to the pipeline. And the successful application was found to be made on gas heater to predict the efficiency or exhaustion of the inhibitor.

Acknoeledgement

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