

STUDY REPORT

SR 212 (2010) Novel Corrosion Sensors Zhengwei Li



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Novel Corrosion Sensors

BRANZ Study Report SR 212

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Abstract

BRANZ has noted that the application of corrosion sensors in buildings is not as popular as in other industrial or engineering sectors.

This research has confirmed that custom-designed sensors, measuring the electrical resistance of a metallic element, could be suitable for in-situ corrosion monitoring of metallic building components.

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1. INTRODUCTION

Metallic materials are used extensively in building and construction. Their corrosion performance, influenced by many environmental factors, is critical to the durability of buildings. Field exposure tests may provide basic corrosion data for design, construction and maintenance schemes. However, the real situation under which they deteriorate might be quite different. This is because the design features and the unique characteristics of the built environment may significantly influence the corrosion process. Simple exposure tests have difficulty in reproducing these phenomena and simulating the initialisation and progress of corrosion in a real building is challenging

Due to limited accessibility, corrosion in building cavities cannot be revealed, assessed and repaired with ease. This can lead to premature failures. Continuous monitoring of material degradation could provide vital information to evaluate the performance and durability of building components. An extensive range of techniques and systems for detecting, measuring and predicting corrosion have evolved. These have now expanded into the domains of real-time data acquisition, process control, knowledge-based systems, smart structures and condition-based maintenance. However, BRANZ has noticed that the application of corrosion sensors in buildings is not as popular as in other industrial or engineering sectors.

2. DISCUSSION

The weight loss coupon is probably the simplest and longest established method of monitoring corrosion. This technique requires a long exposure to yield accurate results, and so has considerable limitations in the detection of processes that change quickly. It is desirable that corrosion sensors offer: (1) quick response to changes of corrosion rate or mechanism; (2) ease of measurement and data interpretation; and (3) provision of corrosion rate.

BRANZ has confirmed in this research that sensors measuring the electrical resistance of a metal could meet the above requirements and be a suitable candidate for corrosion monitoring of metallic building components in cavities. The fundamental premise of this type of sensors is simple: the electrical resistance of a current path increases as its cross-sectional area is reduced. Any mass loss due to corrosion can then be detected by measuring the change in electrical resistance of a metal exposed to a corrosive environment. Real-time corrosion rates can be determined through periodic or continuous resistance change measurements. It has been reported that the nominal minimum thickness loss that can be detected by electrical resistance sensors is on the order of 1 µm. However, a sufficient amount of corrosion is still required for a measurable resistance change to occur. In general, it would take more than 60–70 hours to register a corrosion rate change of 0.025 mm/year with conventional electrical resistance sensors. Hence, it is difficult to measure the corrosion rate in a mild corrosive environment. Sensor response to high dynamics of steel corrosion is also poor.

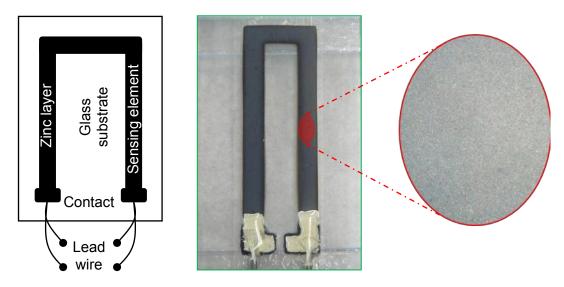
This research also identified that low profile electrical resistance sensors (using thin metallic films as sensing elements) would provide a possible solution for the detection of initialisation, progress and interruption of corrosion in building cavities. The fact is that the sensitivity of an electric resistance sensor is governed by the

thickness of the sensing element; the thicker the sensing element is, the slower the response time. Advanced thin film technologies can produce metal or alloy films with a well-controlled thickness, typically from a few tens of nanometers to a few tens of micrometers. Therefore, the sensitivity of thin film electrical resistance sensors can be manipulated over a wide range. Recently, thin film electrical resistance sensors have been used to measure the corrosion rate of steels embedded into soil. A change in corrosion rate of the order of 0.01 mm/year or less could be detected. The general kinetic equation for steel corrosion at a specific location can also be obtained within a short period compared to conventional weight loss measurement techniques using corrosion coupons.

3. THIN FILM CORROSION SENSORS

BRANZ has investigated the fabrication and performance of electrical resistance sensors using thin zinc films as the sensing element. These zinc films were deposited onto substrates using direct-current magnetron sputtering (with the support of researchers at the University of Auckland), a popular method of physical vapour deposition (PVD).

A typical single-lined electrical resistance sensor produced during the research is shown below. The thickness of the zinc film is around $5-10~\mu m$. After deposition, wires were attached to the pads using silver paste. To minimise the influence of the resistance of the wires on the measurement of the resistance of the thin film, a four-point configuration was adopted.

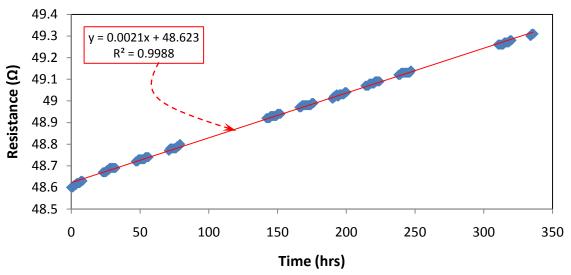


Single-lined electrical resistance corrosion sensor

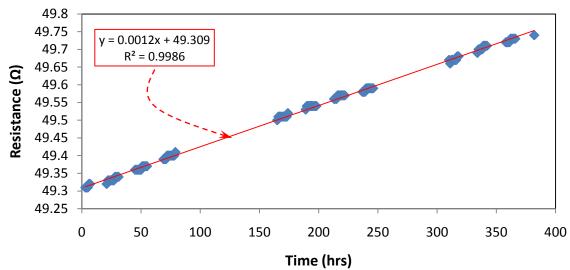
Testing of the sensor was performed in an environmental chamber. The electrical resistance of the sensing element was measured and recorded continuously with a multimeter.

At this stage, the change in electrical resistance was not converted into film thickness reduction with time. The response of sensors to the change in environmental condition was monitored as a resistance change (increase) of the sensing element with time.

The results clearly indicate that the single-lined zinc thin film sensor shows a relatively high sensitivity to the variation of environmental conditions e.g. temperature (T) and relative humidity (RH), two important factors affecting the corrosion of metals. Typical results are given in the following figures.



Change in electrical resistance of the sensor exposed to an atmosphere of $T = 20^{\circ}$ C and RH = 60%

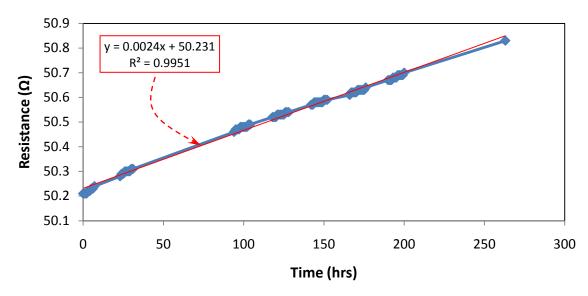


Change in electrical resistance of the sensor exposed to an atmosphere of $T = 20^{\circ}$ C and RH = 50%

It can be seen that in an atmosphere of $T = 20^{\circ}\text{C}$, an increase of RH from 50% to 60% (i.e. 10% increase in absolute or 20% in relative) led to an increase of the slope of the curve from 0.0012 Ω /hr to 0.0021 Ω /hr (corresponding to an increase of 75%). This trend agrees well with the general characteristics of corrosion of metal in humid atmospheres under given temperature conditions; an atmosphere with a higher humidity will generally corrode metal more quickly.

Similarly, it was observed that when the RH was kept constant, an increase of environment temperature from 20°C to 25°C (25% increase) significantly increased

the slope from 0.0012 to 0.0024 Ω /hr (100% increase). Obviously, temperature also accelerates the kinetics of the corrosion process.



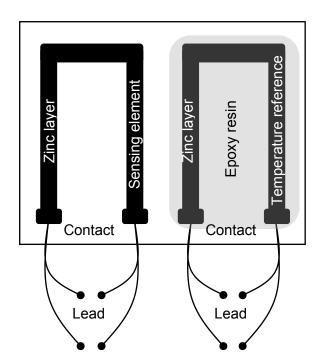
Change in electrical resistance of a sensor exposed to an atmosphere of $T = 25^{\circ}$ C and RH = 50%

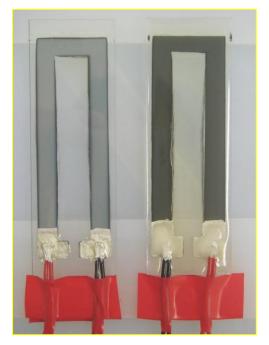
These results also indicate that these thin film electrical resistance sensors have reasonably good output stability. During exposure (up to 15 days) to a constant atmosphere (temperature and *RH*), their resistance output with time could be fitted with a linear regression line with a R-squared value very close to 1.

Temperature has a strong influence on electrical resistance. Zinc has a temperature coefficient of resistance (TCR) of 0.0037/K. To achieve accurate measurements of corrosion rate in a wide range of environments, electrical resistance sensors need to be configured so that the resistance of the sensing element will be fully compensated. This can be achieved by using an identical element that is completely protected from environmental attack.

In this research, two single-lined sensing elements of identical dimension were prepared in one sputtering deposition run so that their compositions and thicknesses were almost exactly the same. Post-deposition measurements also confirmed that they had very similar initial electrical resistances. One element was then completely encased in epoxy resin.

Subsequent characterisations indicated that it is critical to choose the right type of epoxy resin for reliable isolation of metallic sensing elements from the atmosphere. It was recognised that a suitable epoxy resin should have the characteristics of: a fast curing process, low permeability for vapour, high stability in a moist environment at temperature, very limited interaction (chemically) with metal, low air bubble trapping probability and reasonably high thickness build-up. Otherwise, the underlying metallic component will undergo slow oxidation, resulting in a gradual increase of the electrical resistance of the sensing element.

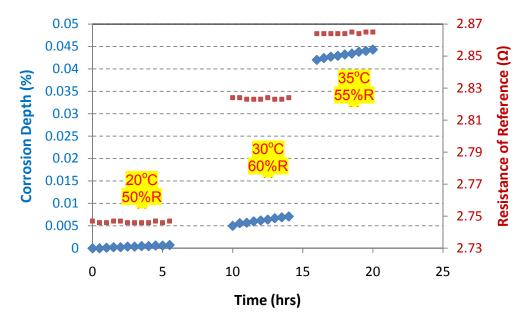




Schematic and photo of a corrosion sensor with a temperature reference

BRANZ tested three types of epoxy resins. The changes in the electrical resistance of the sensing elements covered by these coating layers were monitored continuously. Two epoxy resins were immediately proved to be inappropriate for this application. The high density of air bubbles trapped inside and their slow curing made the electrical resistance output unstable. The other epoxy resin showed a slightly better performance. Measurements showed electrical resistances over short time periods were relatively stable. However, the electrical resistance of the metallic zinc layer covered by this coating still showed a very slow increase with time. After several days of exposure in an atmosphere between 20–35°C and 50–60% *RH*, the surface of this epoxy resin coating also changed from clear, transparent to rough and dull. This indicated deterioration, which may explain why the electrical resistance of zinc layer increased gradually over long exposures.

Due to time constraints, the single-lined Zn thin film covered with this type of epoxy resin was used as the temperature reference for a corrosion sensor exposed to an atmosphere of varying temperature (20–35°C) and relative humidity (50–60%). The preliminary results shown below indicate that with this configuration it was possible to continuously monitor the corrosion progress of a metallic sample in a varying environment.



Response of a thin zinc film corrosion sensor with a temperature reference upon exposure to an atmosphere of varying temperature and relative humidity

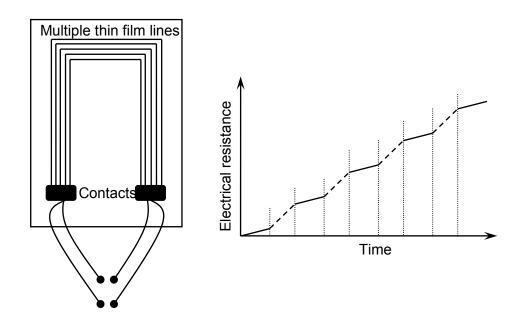
4. MULTI-LINED THIN FILM SENSORS

Localised corrosive attack, such as pitting, cannot be easily detected and is therefore of higher risk to the durability of building components. Conventional electrical resistance sensors have very limited capabilities (low sensitivity and reliability) in detecting localised corrosion. One reason for this is that this type of corrosion only causes insignificant metal loss over limited areas. Thus, the conductivity change is negligible and sensors with enhanced sensitivity and the ability to detect localised corrosion are needed.

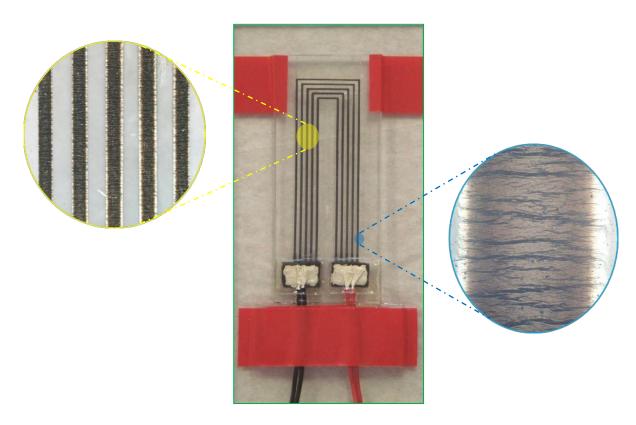
BRANZ identified multi-lined thin film sensors as a promising candidate for this purpose. In a simple design, parallel thin metallic lines are connected together at their ends. The total resistance is then:

$$\frac{1}{R_{total}} = \frac{1}{R_1} + \frac{1}{R_2} + \dots + \frac{1}{R_{n-1}} + \frac{1}{R_n}$$

When one or more lines (the line must be narrow enough so that a small pit can break it) are broken, the resistance of the sensor will increase abruptly (as shown below).



Schematic of a thin film electrical resistance sensor with a multi-lined configuration and its resistance change induced by localised corrosion with time



A multi-lined corrosion sensor fabricated on a polymeric substrate (optical images inserted showing the physical defects in the lines)

In this research, multi-lined zinc thin films were deposited onto polymeric substrates using a pre-fabricated stainless steel mask. Unfortunately, measurements showed that the sensor had a very high initial electrical resistance and showed an extremely

low response to environmental changes during testing. A closer examination of the surface morphology of the sensor lines, using an optical microscope, revealed that there were many fine cracks perpendicular to the sensor lines. The presence of these physical defects explained the high initial resistance. It is believed that these cracks were caused by the heat-induced deformation of the polymeric substrate during deposition. No further attempts were made to address this problem due to time limitations.

5. RECOMMENDED FURTHER WORK

The results obtained within this research demonstrate that it is possible to develop electrical resistance sensors using thin metallic films for the detection of corrosion in the built environment. BRANZ believes that future studies should be focused on the following:

- Metallic thin films prepared using various technologies (such as evaporation, sputtering and chemical or electrochemical deposition) may have different compositional, structural and electrochemical properties in comparison with a bulk metal. Surface characteristics of a metal also affect its corrosion behaviour. The correlation between the corrosion performance of thin film and bulk samples under identical conditions should be established. With this fundamental information, the corrosion rates measured with thin film sensors can then be used for more accurate service life prediction for real structures.
- ➤ The thickness of the sensing element is critical to the sensor's sensitivity and service life. The balance between these two important parameters should be defined according to the aggressivity of the environment where the sensor will be installed and the durability requirement of the component to be monitored.
- The protective coatings for use in isolating the reference element of the sensor from the environment should be researched and optimised according to their long-term environmental durability, output stability and sensitivity to temperature variation.
- The width of the sensing lines is critical to the detection of localised corrosion. The lines must be narrow (and thin) enough so that that the lateral growth of a pit can break them quickly. For this purpose, photo-lithographic etching, commonly used in circuit manufacturing, would be a more suitable technique for the fabrication of multi-line sensors. In addition, other substrates, with a higher physical stability in the sputtering atmosphere (such as glass and ceramic) should be used in future studies.