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Atmospheric corrosion mapping of copper surfaces from diffuse light scattering measurements by an optoelectronic sensor system

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Abstract: A novel light scattering technique for mapping metal surface corrosion is presented and its results on copper exposed to atmosphere are reported. The front end of the instrument is made up of a sensor module comprising a thin beam light emitting diode (LED) illuminating a small spot on the metal surface, and a matched pair of photodetectors, one for capturing the reflected light and the other for sampling the scattered light. The analog photocurrent signals are digitized and processed online by a personal computer (PC) to determine the corrosion factor defined in terms of the two current values. By scanning the sample surface using the light beam and by computing the corrosion factor values simultaneously, a three dimensional graph and a two dimensional contour map are generated in the PC using Matlab tools. The values of the corrosion factor measured in different durations of exposure to atmosphere, which obey a bilogarithmic law, testify to the validity of our mathematical model.

Key words: Light scattering, Optoelectronic sensor, Atmospheric corrosion mapping
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INTRODUCTION

Most of the metals, when continuously exposed to atmosphere, form a thin film of corrosion products on their surfaces. The behaviour of copper surrounded by air is of interest because of its wide usage in industrial boilers, monuments, architectural objects, etc. The passive oxide layer formed on copper during the initial stage of its corrosion process is called patina. At this stage, the patina layer is transparent and gradually changes in colour from salmon-pink to red brown. As time passes, the thickness of the oxide layer further increases, and its color becomes dark brown. After exposure to aggressive environments for a few years, the colour of the patina turns to a pleasing greenish hue (Roberge, 1999; Cramer and Covino, 2003).

Several researchers have investigated the atmospheric corrosion of copper using various methods such as differential reflectometry, metallographic studies, X-ray diffraction, the photoacoustic technique, and conventional electrochemical techniques.

Shanley *et al*.(1980) studied the characteristics of copper oxides formed in laboratory atmosphere using differential reflectometry. They observed the growth patterns of the oxide from the interference peaks in the reflectograms. The differential reflectometry technique was also used by Urban *et al*.(1982) to investigate the characteristics of oxide films of various metals, produced due to high temperature oxidation.

Franey and Davis (1987) carried out metallographic studies of copper patina, formed in atmosphere over hundreds of years. They studied various compounds present in the oxide film and the variations in colour of the patina layer. Mansfeld and Tsai (1980) conducted electrochemical and weight loss measurements for calculating the corrosion rate of metals under simulated atmospheric conditions in laboratory.

The non-destructive photothermal beam deflection method was utilized by Salnick *et al*.(1995) to study the characteristics of thermal properties of the patinated copper layer. Periodic deflections of a laser beam due to the refractive index gradient of air caused by variations in temperature, captured by a position sensitive optical detector, gave the measure of the thermal properties. Veleva *et al*.(1997) carried out non-destructive photoacoustic measurements to study the thermal properties of metal samples exposed to marine environments and correlated the measured thermal conductivity with the thickness of the corroded layer. Air chamber oscillations due to periodic heating of the sample, detected by a sensitive microphone, measure the thermal properties of metal surfaces.

Fonseca *et al*.(2004) presented a comparative study on initial stages of atmospheric corrosion of copper at two sites in two different seasons. X-ray diffraction and scanning electron microscope (SEM) analysis were used to study the chemical composition, morphology and kinetics of copper corrosion. Fitzgerald *et al*.(1998) and El-Mahdy *et al*.(2005) studied the atmospheric corrosion of copper using the X-ray diffraction technique in combination with the electrochemical measurement method and the weight loss method. They analyzed the corrosion products and their distribution on the surface.

The corrosion processes investigated by the above methods employed a complex experimental setup, and the measurements were limited to laboratory environments. This paper reports the design and implementation of a compact, non-destructive optoelectronic instrument based on the light scattering principle to measure the atmospheric corrosion of metal surfaces. The optical sensor assembly comprising a light emitting diode (LED) and two matched photodetectors scanned the sample surface using a computer numerically controlled (CNC) machine driven platform. A successive area of 1 mm diameter on the sample surface was illuminated, and the reflected and the scattered lights were captured separately by two identical detectors. A factor derived from the values of reflected and scattered intensities represents the degrees of corrosion in a normalized scale from 0 to 100. The values of the corrosion factor measured in different durations as surface is exposed to atmosphere were found to obey a bilogarithmic law, which is in conformity with previous experiments (Veleva *et al*., 1997; Marcus, 2002; Fonseca *et al*., 2004). The corrosion mapping of the entire sample surface is represented by a 3D graph as well as by a 2D contour map using Matlab tools.

THEORY

According to light scattering theory (Fig.1), an ideally smooth metallic surface reflects the incident light at an angle equal to the angle of incidence. Here θ_i and θ_r are the incident and reflected angles, respectively; J_s and J_r are the scattered and reflected light intensities, respectively.

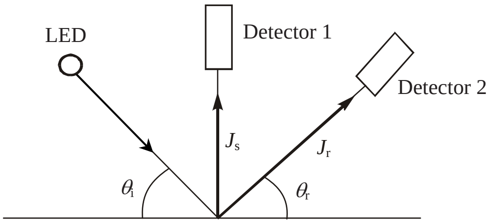


Fig.1 Light scattering by a metal surface

The oxide molecules, the corrosion products of the atmosphere exposed metal surface, form the scattering centers, which scatter the incident light in directions other than that of the metal reflected light depending on the disorientation of the oxide molecule with respect to the crystal orientation. Thus the scattering is isotropic for a large number of randomly oriented oxide molecules. The degree of corrosion in a given area may be defined by the ratio of the number of oxide molecules to the number of metallic atoms originally prevalent there. This, in turn, can be calculated in terms of the scattered and the reflected light intensities from the illuminated area. As the cross sectional area (B) of the incident light beam covers both pure metallic area (A_m) and corroded area (A_c), the corrosion factor may be defined as the ratio of the corroded area to the total area covered by the incident light beam, i.e.,

$$C = S\frac{A_c}{A_c + A_m}, \tag{1}$$

where S is the scaling factor, which may be taken as 100, for example.

Let the power of the incident beam be

$$P_{\mathrm{in}} = J_{\mathrm{in}} B, \tag{2}$$

where J_{in} is the intensity of the incident light, and $B=A_{\mathrm{c}}+A_{\mathrm{m}}$.

Power of the reflected light at the specular angle is

$$P_{\mathrm{r}} = A_{\mathrm{m}} P_{\mathrm{in}} / B\,. \tag{3}$$

The average intensity of the reflected beam in the specular direction is

$$J_{\mathrm{r}} = P_{\mathrm{r}} / B = J_{\mathrm{in}} A_{\mathrm{m}} / B. \tag{4}$$

For the incident light of wavelength in the near infrared region and for the thin corrosion layer on a metal surface, the absorption of light is negligible (Degueldre *et al*., 1996). Hence, the total power of light scattered from an area of B is

$$P_{\mathrm{s}} = P_{\mathrm{in}} A_{\mathrm{c}} / B = J_{\mathrm{in}} A_{\mathrm{c}}. \tag{5}$$

If the absorption is significant as in the case of UV region and a thick corrosion layer, an appropriate factor should be included on the right hand side of Eq.(5).

Substituting the values of A_{m} and A_{c} from Eqs.(3) and (5) into Eq.(1) leads to the following expression of the corrosion factor:

$$C = S\frac{P_{\mathrm{s}} / J_{\mathrm{in}}}{P_{\mathrm{s}} / J_{\mathrm{in}} + P_{\mathrm{r}} / J_{\mathrm{in}}} = S\frac{P_{\mathrm{s}}}{P_{\mathrm{s}} + P_{\mathrm{r}}}. \tag{6}$$

If a photodetector D1 is placed at the specular angle, the current I_{D1} is proportional to the reflected and scattered light intensities incident on the detector:

$$I_{\mathrm{D1}} = kJ_{\mathrm{D1}} = k\left(\frac{J_{\mathrm{r}} B + J_{\mathrm{s}} A_{\mathrm{D1}}}{A_{\mathrm{D1}}}\right). \tag{7}$$

Hence the reflected power

$$P_{\mathrm{r}} = J_{\mathrm{r}} B = \frac{A_{\mathrm{D1}} I_{\mathrm{D1}}}{k} - J_{\mathrm{s}} A_{\mathrm{D1}}. \tag{8}$$

The scattered intensity incident on a detector D2 placed at an arbitrary angle is related to the photocurrent as $I_{\mathrm{D2}}=kJ_{\mathrm{s}}$.

In the initial stages when the corrosion layer is thin, the scattering may be assumed to be isotropic and hence the total scattered power is

$$P_{\mathrm{s}} = 2\pi r^2 I_{\mathrm{D2}}, \tag{9}$$

where r is the radius of the hemisphere containing the detectors.

Substituting Eqs.(8) and (9) into Eq.(6), we have

$$\begin{aligned} C &= S\frac{2\pi r^2 I_{\mathrm{D2}} / k}{2\pi r^2 I_{\mathrm{D2}} / k + A_{\mathrm{D1}} I_{\mathrm{D1}} / k - J_{\mathrm{s}} A_{\mathrm{D1}}} \\ &= S\frac{I_{\mathrm{D2}}}{I_{\mathrm{D2}} + \dfrac{A_{\mathrm{D1}}}{2\pi r^2}(I_{\mathrm{D1}} - kJ_{\mathrm{s}})}. \end{aligned}$$

The corrosion factor is

$$C = S\frac{I_{\mathrm{D2}}}{I_{\mathrm{D2}} + \dfrac{A_{\mathrm{D1}}}{2\pi r^2}(I_{\mathrm{D1}} - I_{\mathrm{D2}})}. \tag{10}$$

INSTRUMENTATION

The experimental setup (Fig.2) consists of an optical sensor assembly comprising an LED of wavelength 930 nm and a small emission spot of 400 μm with an output power of 2 mW (infrared LED L2791 series from Hamamatsu Photonics, Japan) and two matched photodetectors (Silicon Pin Photodiode S4707-01 from Hamamatsu Photonics, Japan) with a photosensitivity of 0.5 A/W, one placed at an angle of reflection (135°) and the other in a direction normal to the surface. The sensor unit is contained in a black hemispherical box placed at a distance of 4 mm, very close to the sample surface to avoid noise due to ambient light. The CNC machine (MTAB-Starturn, Japan) controls the 2D motion of a platform holding the samples, against the fixed sensor assembly.

A 2-channel 8-bit analog-to-digital converter (ADC 0809) with a multiplexer samples and digitizes the analog signal output from the detectors in synchronization with the scan step size of 0.5 mm and feeds the signals through a parallel port interface to a personal computer. The digitized signal values are read from the parallel port using C Program, and the 3D mapping is done using Matlab.

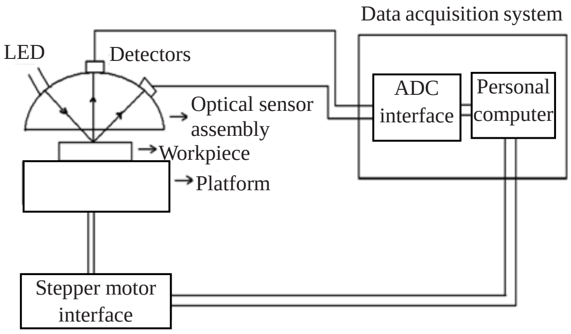


Fig.2 Experimental setup for corrosion measurement

EXPERIMENT

The experiment consists of the following two stages.

1. Test sample preparation

Copper plates (99% purity) of size 50 mm× 60 mm were fine polished using silicon carbide papers to a minimum roughness. The initial roughness factor was measured using the same experimental setup developed for corrosion measurement. The suitability of the same technique used for measuring the roughness factor was tested by different samples and their results were compared with those obtained by a standard technique. Then the samples were exposed to a normal atmosphere for various periods ranging from 3 to 21 d.

2. Measurement of the corrosion factor

The light from the LED illuminated an area of 1 mm^2 on the sample surface. The reflected light was captured by a detector placed at the specular angle, and the scattered light was captured by a second detector placed at an angle of 90° to the surface. The sample was placed on a movable platform driven by the CNC machine in X direction with a step size of 0.5 mm and in Y direction with a step size of 1 mm.

An ADC controlled by the same computer sampled the signal from the output of the detectors at an interval of 500 ms to synchronize the sample movement by a step size of 0.5 mm, and the digitized signals were fed to the computer. The corrosion factor was calculated using Eq.(10) at each point, and the entire surface was corrosion mapped and represented as a 3D graph (Fig.3) and also as a contour map (Fig.4) using Matlab tools.

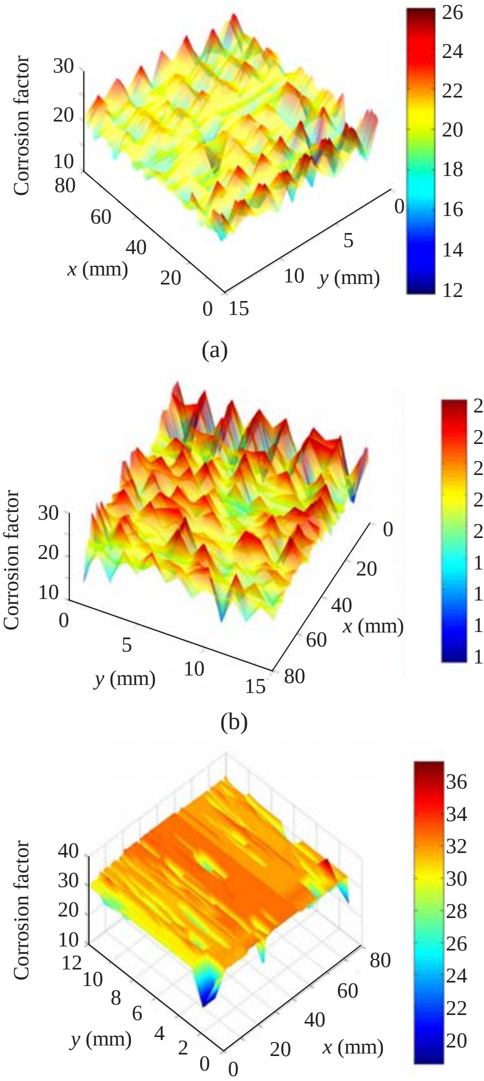
RESULTS AND DISCUSSION

Figs.3a~3c present the corrosion maps of copper samples exposed to atmosphere for 6, 9, and 18 d, respectively. In the initial days the corrosion developed and grew faster in selected areas as indicated by higher peaks. As days passed by, the growth of corrosion was more evenly spread out on the surface.

Figs.4a~4c present contour maps of copper samples exposed to atmosphere for 6, 9, and 18 d, respectively. In the early stages, the corrosion increased rapidly in some portions of the surface as indicated by the prominent colour, and gradually the corrosion grew more uniformly throughout the surface.

Fig.5 presents the corrosion factor (averaged over the surface of each sample) as a function of time of exposure to atmosphere. The experimental points conform to a bilogarithmic fit $C=At^B$, where A=9.7, B=0.438, and t is the time of exposure. The initial high growth rate of corrosion governed by the coefficient A contributes to the rapid lateral growth of the oxide film covering the metal surface. The slow rate of corrosion at a longer time of exposure, as determined by the coefficient B (<0.5), is due to the onset of passivity characteristics of the oxide layer being protected by a hydroxide layer. These results are in conformity with the results of previous experiments on copper (Veleva, 1997; Fonseca, 2004). A maximum deviation of 5.94% in the measured corrosion factor value from the bilogarithmic law is observed for the 3-d exposure sample.

The method was applied to the measurement of the corrosion factor of stainless steel sample surfaces (inhomogeneous sample surface) corroded in various concentrations of nitric acid, and the results are presented in Fig.6. The bilogarithmic behaviour ($C=am^b$, where a=13.01, b=0.831, and m is the concentration of nitric acid in normality) observed is found to be in agreement with theory (Roberge, 1999).



(a)

(b)

(c)

Fig.3 Three-dimensional corrosion mapping of copper sample surfaces exposed to atmosphere for 6 d (a), 9 d (b), and 18 d (c)

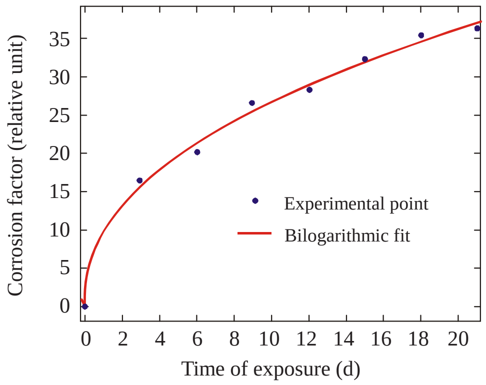
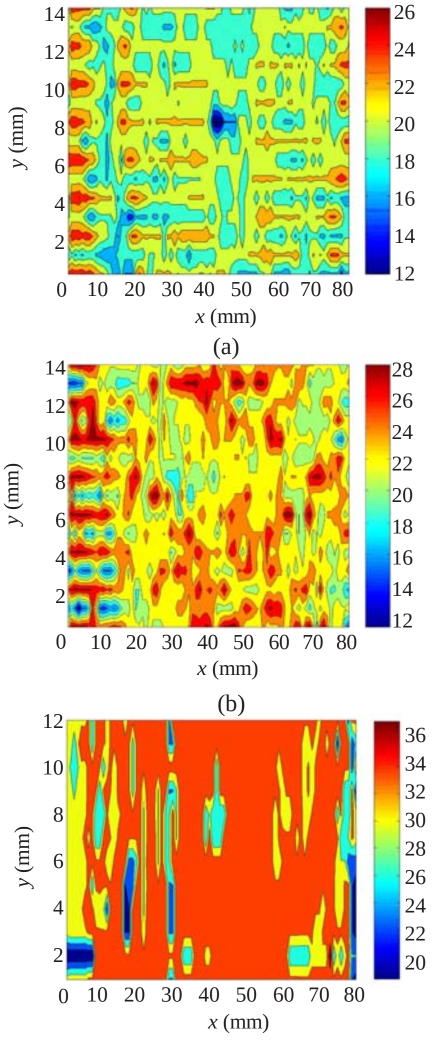


Fig.5 Relationship of corrosion factor (C) and time of exposure (t)

The experimental points conform to a bilogarithmic fit C=9.7$t^{0.438}$



(a)

(b)

(c)

Fig.4 Contour mapping of copper sample surfaces exposed to atmosphere for 6 d (a), 9 d (b), and 18 d (c)

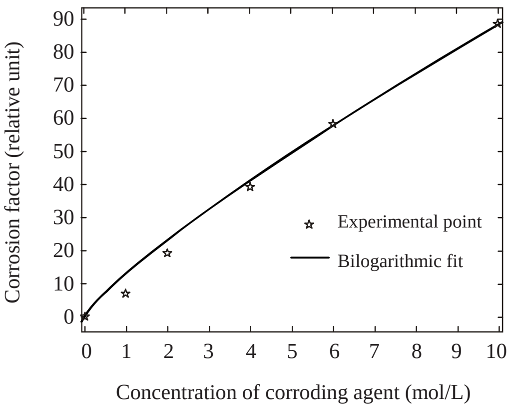


Fig.6 Bilogarithmic fit of the corrosion factor (C) for stainless steel samples as a function of concentration of corroding agent (HNO_3) (m)

The experimental points conform to C=13.01$m^{0.831}$

CONCLUSION

The copper corrosion measurement results obtained by employing the optical technique developed by the authors indicate its suitability for estimating corrosion of metal surfaces. Unlike the existing methods, the new method enables real time corrosion mapping of an entire surface in a very short span of time. The present measurement represents only the sum of all the corrosion products formed over the metallic surface. A further development of this method will be needed for identifying the presence of more than one corrosion product. The application of the present method is limited to the initial stages of corrosion till a thin corrosion layer is formed, beyond which the corrosion in metal surface should be measured in terms of thickness rather than the ratio of corroded area to total area. As the thickness of the corrosion layer further increases unevenly, the scattering will not be uniform in all directions. In this case, the actual scattering pattern should be measured using an array of detectors.

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