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Atmospheric Corrosion of Copper Exposed in a Simulated Coastal-Industrial Atmosphere

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The corrosion behavior of copper exposed in a simulated coastal-industrial atmosphere has been investigated using weight loss measurement, scanning electron microscopy, X-ray diffraction, potentiodynamic polarization and in-situ electrochemical impedance spectroscopy (EIS) with micro-distance electrodes. The results show that corrosion kinetics follows the empirical equation $D = At^n$. The main corrosion products are composed of Cu_2O , $\text{Cu}_2\text{Cl}(\text{OH})_3$ and $\text{Cu}_4\text{Cl}_2(\text{OH})_6$. A two-layer structure comprising a loose outer layer and a compact inner layer forms the corrosion products during corrosion process. SO_2 has been found to promote the formation of $\text{Cu}_4\text{Cl}_2(\text{OH})_6$.

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1. Introduction

Copper is widely employed as an outdoor building material for fabricating statues, sculptures and monuments, because of its aesthetic qualities, good mechanical properties and corrosion resistance. This metal is also used for electric conductors due to its high conductivity, which is an important property in communication and electronics. However, in these service environments, copper would inevitably become exposed to the atmosphere, with possible occurrence of corrosion. For that reason, the atmospheric corrosion of copper has become a subject of great interest. Studies on the atmospheric corrosion of copper and its alloys have been performed through natural outdoor exposure^[1-3] and laboratory testing^[4-6].

The field exposure of materials provides actual information on their atmospheric corrosion behavior, and it is the most important method for atmospheric corrosion studies. However, actual field exposure tests for investigating the atmospheric corrosion behavior of materials are time-consuming^[7,8], hence several investigations are conducted using accelerated indoor testing techniques, such as salt spray tests, wet-dry cyclic accelerated testing, etc^[9-11]. Among these methods, wet-dry cyclic accelerated testing can better reproduce the key characteristics of the atmospheric environment, wherein relative humidity and temperature, which are the most important factors

with regard to the atmospheric corrosion of metals, alternate by day and by night. Such accelerated indoor tests are, however, only valid if there is good correlation with outdoor field exposure tests, particularly with respect to relative humidity and temperature settings. In marine environments for instance, it is known that sea salt aerosols remain wet even below 20% RH, which is far lower than 80% RH threshold signifying actual wetting conditions^[12]. Corrosion rates actually increase with thinning of the liquid film on the metal surface and attain maximum values at the transition state from the wet to the dry. Metals corrosion is accelerated by increasing the frequency of alternation of the relative humidity.

As the corrosion process is essentially an electrochemical reaction, techniques involving instantaneous monitoring of atmospheric corrosion based on electrochemical measurements have become quite popular. These include atmospheric corrosion monitors (ACM)^[13,14], Kelvin probes^[15,16], etc. However, some of these methods are not suitable for actual field monitoring, while others just give the severity of the corrosion but cannot provide direct information on the prevailing electrochemical processes. On the contrary, in-situ EIS technique, as a non-destructive procedure for the study of atmospheric corrosion, can provide instantaneous and direct information on the corrosion behavior of metals^[17-20].

In the present work, the corrosion behavior of copper exposed in a simulated coastal-industrial atmosphere, where relative humidity and temperature are set according to the actual atmosphere, has been investigated using weight loss measurement, scanning electron microscopy, X-ray diffraction, potentiodynamic polarization and

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in-situ electrochemical impedance spectroscopy with micro-distance electrodes.

2. Experimental

2.1. Sample preparation

A high purity Cu (>99.99 wt%) was used in this investigation. Four parallel samples (three for weight loss measurement and one for rust layer analysis) were cut into sizes of 50 mm × 25 mm × 2 mm. The samples for weight loss measurement were ultrasonically cleaned in acetone, dried, weighed and stored in moisture-free desiccator prior to use. The samples for potentiodynamic polarization experiments were cut into 10 mm × 10 mm × 2 mm coupons and then were embedded in epoxy resin, leaving an exposed working area of 1 cm². The electrochemical test samples were ground to 2000 grit SiC paper and then degreased by acetone, dehydrated with alcohol and finally dried for 24 h.

2.2. Electrode preparation

A two-electrode system with comb-like arrangement was used for EIS measurements. In order to benefit the collection of electrical signal, the comb-like micro-distance electrodes were prepared from pure copper plates with dimensions 10 mm × 10 mm × 2 mm. The plates were separated from each other by a thin insulator and then embedded in epoxy. The schematic diagram of the electrode design is illustrated in Fig. 1(a). Fig. 1(b) shows the distance between two plates to be about 60 μm. After being ground with SiC paper to 2000 grit, the micro-distance electrodes were stored in a desiccator for 24 h and then subjected to the wet-dry cyclic corrosion tests.

2.3. Wet-dry cyclic accelerated test

The wet/dry cyclic test was conducted using a Weiss-Voetsch temperature and climatic test system. The corrosion tests involved the following steps within a 24 h period: (1) wetting the sample surface with 10 μL/cm² of 0.25 mol/L NaCl + 0.05 mol/L NaHSO₃ solution (simulating a coastal-industrial atmosphere); (2) drying the sample in an oven at 40 °C; (3) wetting the samples in the chamber maintained at 35 °C and 90% RH for 60 min; (4) drying the samples in a chamber maintained at 35 °C and 60% RH for 120 min; (5) repeating steps (3) to (4) 7 times. The test samples were retrieved for analysis after 72, 144, 216, 288 and 360 h. For gravimetric experiments, corrosion products on the retrieved samples

were removed chemically by immersion in a specific solution (100 mL H₂SO₄ + 900 mL distilled water) at 20–25 °C according to ISO 8407.

2.4. Characterization of corrosion products

X-ray diffraction (XRD) analysis was used to characterize the crystalline corrosion products formed on the Cu sample surface. The XRD measurements were carried out using a Rigaku-D/max 2000 diffractometer with a CuK_α target under 50 kV, 250 mA and 2θ = 10°–85° of range at a scanning speed of 2°/min. Examination of the surface and cross-sectional morphologies of the corrosion products were conducted using a scanning electron microscope (XL30FEG).

2.5. Electrochemical measurements

For potentiodynamic polarization measurements, the corroded samples were employed as working electrode, and the measurements were performed with a PARSTAT 2273 potentiostat/galvanostat in a conventional electrochemical glass cell with a large platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The test solution used in all experiments was 0.5% NaCl solution prepared from reagent grade chemicals and distilled water. The scanning rate of the potentiodynamic polarization measurements was 20 mV/min.

The EIS measurements were also carried out using the PARSTAT 2273 potentiostat/galvanostat. The EIS spectra of the micro-distance electrodes with NaCl and NaHSO₃ particles were measured in-situ in the corrosion test chamber at RH 90%. The amplitude of AC voltage was 10 mV and the frequency range was from 10⁵ Hz to 10⁻² Hz. The frequency sweep of the EIS is always taken in a direction from high to low.

3. Results

3.1. Corrosion kinetics of copper

The corrosion kinetics can be determined by measuring the mass loss of copper before and after corrosion testing. In order to obtain a clearer view of the corrosion damage, the weight loss data obtained for the copper were converted to a thickness reduction factor (in μm) according to the following equation^[21]:

$$D = \frac{10000W_t}{\rho A} \quad (1)$$

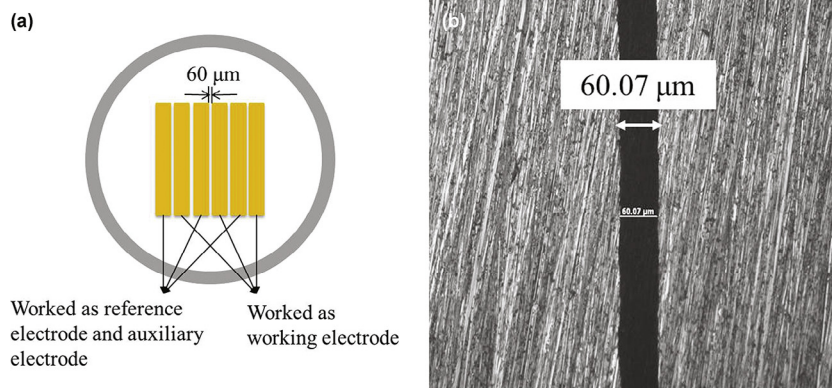


Fig. 1. Schematic diagram in illustrating the arrangement of micro-electrodes used for EIS measurement: (a) top view of the comb-like micro-electrodes; (b) optical micrograph of micro-electrodes in illustrating the distance between two copper plates.

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