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# **Study on the Initial Atmospheric Corrosion Behavior of Copper in Chloride-Containing Environments**

*Chenxi Yi<sup>1</sup>, Xiaoqing Du<sup>1</sup>, Yumeng Yang<sup>1</sup>, Yu Chen<sup>1, 2</sup>, Guangyuan Wei<sup>3</sup>, Zhongnian Yang<sup>4</sup>, Zhao Zhang<sup>1,\*</sup>* 

<sup>1</sup> Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang 310027, China

<sup>2</sup> School of Aeronautics and Astronautics, Zhejiang University, Hangzhou, Zhejiang 310027, China

<sup>3</sup> School of Earth Science, Zhejiang University, Hangzhou, Zhejiang 310027, China

<sup>4</sup> Department of Chemical Engineering, Binzhou University, Binzhou, Shandong 256603, China <sup>\*</sup>E-mail: zhangzhao@zju.edu.cn

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The initial atmospheric corrosion process of copper (in 1 hour) was investigated by quartz crystal microbalance (QCM), SEM, XRD and AFM techniques. As a kind of electrochemical noise, the QCM data had been analyzed by Fast wavelet transform technique (FFT). The results showed that, both the  $Q \sim t$  curves deduced from QCM data and XRD patterns confirmed the initial atmospheric corrosion products of copper is Cu<sub>2</sub>O, and which corrosion severity increased with both the concentration of NaCl and corrosion time. A new parameter named electrochemical active energy ( $E_c$ ) was proposed from the FFT analysis of QCM data, which is not only in direct proportion to the corrosion severity (such as weight loss), but can also be used to deduce the corrosion mechanism appropriately.

Keywords: Copper; Electrochemical noise; Fast wavelet transform technique; Atmospheric corrosion

## **1. INTRODUCTION**

Copper and its alloys have been widely used as architectural materials due to their good machinability and high atmospheric corrosion resistance [1], however, they still suffer from serious damage during their long time serving processes, especially in highly aggressive environments (such as marine [2,3] and industrial environments [4]). Meanwhile, the heterogeneous structures among base metal and different corrosion products (such as patina) can also accelerate the atmospheric corrosion by producing both the microbatteries and the intercrystalline stresses.

Metal atmospheric corrosion process usually occurs in a layer of very thin electrolyte [5,6], which thickness and composition simultaneously depend on the surrounding relative humidity (RH),

the physicochemical properties of the corroding metals and the deposited contaminants (such as hygroscopic salt), while the corrosion rate and the composition of corrosion products will be influenced by the thin electrolyte. Aastrup and his coworkers found the copper in damp was carpeted with water and its atmospheric corrosion rate rise with increasing RH from 40% to 80% [7], and the composition and structure of copper corrosion products are mainly related with the gaseous pollutants dissolved into electrolyte [8]. The similar discovery was also founded by Dante and Kelly [9] while the RH ranged from 15% to 95%. The chloride ion (Cl<sup>-</sup>), which is the main corrosive particles in marine environment, possess a great influence in the atmospheric corrosion of copper [2,10]. With the increase of Cl<sup>-</sup> concentration (C>10<sup>-3</sup> M), the corrosion potential of copper shifts negatively and the corrosion current increases gradually [11].

The critical relative humidity (CRH) is a professional term, in a broad sense, it is defined as the RH of the surrounding atmosphere (at a certain temperature) at which the salt begins to absorb moisture from the atmosphere; but for metal atmospheric corrosion, the CRH is regarded as a boundary while above which the corrosion rate increases significantly and below which the rate is insignificant for many practical purposes [12]. When studying the atmospheric corrosion process with salt particles deposited, the experimental RH value was usually chosen above the CRH of salt [13,14]. However, by using mass gain measurements to determine the mass loading, Chen and his coworkers [15] pointed out that copper with NaCl particles deposited suffered from significant corrosion attack at 55% RH, which lay far below the deliquescence point of NaCl (75% at 25°C). The thickness of the adsorbed water film is synergistically affected by both the hygroscopicity of salt particles and the absorptivity of metal surface. Since a thin water layer of few molecules will be formed on metal surface even at low RH value, which is enough for electrochemical reaction [9], using the so-called "critical humidity" to judge the onset of atmospheric corrosion is meaningless in an absolute sense.

Atmospheric corrosion is a well-known electrochemical process in nature [1,5,16,17]. Therefore, electrochemical methods in coupled with IRAS (infrared reflexion absorption spectroscopy) [18], SEM (scanning electron microscope), XRD (X-ray diffraction) [6] and XPS (X-ray photon spectroscopy) [19] techniques, have been widely adopted to study atmospheric corrosion process. Unfortunately, the traditional transient-state techniques such as cyclic voltammetry and chronoamperometry exert great disturbances to the investigated systems, the quasi-steady-state method, such as electrochemical impedance spectroscopy (EIS), needs an equivalent circuit mode beforehand, whilst SEM, XRD and XPS techniques cannot be used for in-situ corrosion determination [20]. Moreover, all electrochemical techniques have to be performed in an electrochemical cell of two or three electrodes [21-23], which cannot represent the true atmospheric corrosion processes [24], especially at its initial stage. Some steady-state methods such as electrochemical noise (EN) may be appropriate, but a thin electrolyte layer system with two or three electrodes is precondition for many researchers [25-27].

In order to in-situ investigate the atmospheric corrosion of copper in chloride-containing environment, especially at its initial stage continuously, the quartz crystal microbalance (QCM) technique, which is based on the piezoelectric effect of the quartz crystal and possesses high sensitivity (better than 10<sup>-9</sup> g), has been adopted [28]. Compared with XPS, SEM and electrochemical techniques

[6], QCM can in-situ monitor the atmospheric corrosion process, and without the demands of two or three-electrode systems.

The data obtained by QCM technique is directly related with the mass variation of the corroding metal, which is essentially a kind of electrochemical noise [29-31]. Therefore, the aim of this paper is to monitor the initial atmospheric corrosion process (in 1 hour) of copper by QCM technique, and make attempts to analyze the obtained QCM data by using wavelet analysis method to extract the energy distribution plot (EDP, which is widely regarded as the "fingerprints" of EN signal [32,33]) to characterize the corrosion process.

#### 2. MATERIAL AND METHODS

The resonant frequency of quartz crystal was measured by QCA-922 quartz crystal analyzer (SEIKO EG&G), which was interfaced with a computer. AT-cut quartz crystals of  $f_0 = 9$  MHz, which were covered with high purity (>99.9%) gold (Au) or copper (Cu) film of 0.1256 cm<sup>2</sup>, (Wanshihe Electronics Co., Ltd., China) were used as the investigated substrates. Before tests, the surfaces of Au and Cu quartz crystals were successively purged with deionised water, ultrasonically cleaned in acetone for 3 min, and then rinsed with double-distilled water again and finally dried with nitrogen gas (N<sub>2</sub>). The corrosion solution of  $6.47 \times 10^{-3}$  M NaCl was prepared by dissolving NaCl into the mixed solvent of ethanol and water ( $V_{water}$ : $V_{ethanol}$ =1:9). All chemical reagents used in this paper were analytical grade.

After the metal (Cu or Au) was distributed with a layer of quantitative NaCl solution by a micro syringe, it was transferred into a low-pressure vessel (absolute pressure less than 0.01MPa) for 20 minutes to volatilize the mixed solvent. Then, a layer of NaCl particles was deposited on the metal surface. The total weight of NaCl deposited on the metal surface was determined by the volume of NaCl solution, hereinafter, the parameter  $C_{NaCl}$  was used to represent the deposited NaCl weight per unit area (the unit is  $\mu g \cdot cm^{-2}$ ). Lastly, the quartz crystal was positioned horizontally in a closed chamber (GP-GDS50, China) with constant temperature and RH without disturbance, and connected with QCM analyzer. The interval sample time of the QCM analyzer was 0.1 second.

After tests, the residual NaCl particles on metal surface were removed by rinsing the surface with double-distilled water several times slightly. SEM (SU-8010, HITACHI) was adopted to characterize the corroded morphologies. The specimen's surface roughness and the stereoscopic topography information were obtained by AFM (Multimode-8, Bruker Nano Inc) with a scan rate of 0.5 Hz and scan size of 100  $\mu$ m. Lastly, the identification of the present phases were performed using an X-ray polycrystalline diffractometer (Ultima IV, Rigaku) with 20°-80° scanning range which data were further analyzed using the Joint Committee on powder Diffraction Standards (JCPDS) database.

Weight loss method was used as the supplementary measurement for atmospheric corrosion evaluation, by testing the accurate copper weight loss after 80 hours exposing to 25C, 70%RH with different  $C_{NaCl}$ , which was obtained by analytical balance (AL104 METTLER TOLEDO), and the corrosion products at each  $C_{NaCl}$  were removed by rinsing in HCl solution ( $V_{HCl}$ : $V_{water}$ =1:1) about 5 min according to ISO 8407:2009.

## **3. RESULTS AND DISCUSSION**

For the rigid deposits, the change of the crystal resonant frequency ( $\Delta f$ , in the unit of Hz) is proportional to its mass variation ( $\Delta m$ , in the unit of ng·cm<sup>-2</sup>). As long as  $\Delta f$  is less than one percent of the crystal resonant frequency, the following linear relation between  $\Delta f$  and  $\Delta m$  (Sauerbrey equation, eq. 1) can be obtained [34],

$$\Delta f = -2\Delta m (f_0^2) / (n \sqrt{\mu \rho}) \tag{1}$$

where  $f_0$  is the fundamental frequency of the crystal, *n* is order of the harmonic (for rigid deposits, *n*=1),  $\mu$  and  $\rho$  are the shear modulus (2.94×10<sup>11</sup> g·cm<sup>-1</sup>·s<sup>-2</sup>) and the density of quartz (2.648 g·cm<sup>-3</sup>) respectively. In this paper,  $f_0$  of the used Cu or Au crystals equal to 9 ± 0.02 MHz, therefore, eq.1 can be rewritten as,

$$\Delta m(\mathrm{ng}\cdot\mathrm{cm}^{-2}) = -5.4774\Delta f(\mathrm{Hz})$$

In the chamber of definite temperature and humidity, the total mass change ( $\Delta m_{all}$ ) during copper corrosion process includes both the reversible and irreversible adsorption of species from surroundings [18]:

(2)

$$\Delta m_{all} = \Delta m_{water} + \Delta m_{corr} \tag{3}$$

The reversible mass change is mainly caused by the adsorbed water ( $\Delta m_{water}$ ) due to the synergetic hygroscopicity of salt particle and absorptivity of metal surface; whilst the irreversible mass change is mainly depended on the oxygen adsorption and its reaction with copper, i.e., the corrosion process of copper ( $\Delta m_{corr}$ ) [8,9]. In order to characterize the corrosion process caused by oxygen ( $\Delta m_{corr}$ ),  $\Delta m_{water}$  should be discounted from  $\Delta m_{all}$ . For the reason that, the tendency for water to cluster has been related to the similar heat values of its adsorption and vaporization on both Au and Cu [9], the association of water molecules with the metal surface or with other water molecules is energetically similar. As Au is chemical inertness in marine atmosphere,  $\Delta m_{water}$  is achieved by testing the frequency change of Au quartz crystal at the same temperature, RH and C<sub>NaCl</sub>. After subtract  $\Delta m_{water}$  from  $\Delta m_{all}$ ,  $\Delta m_{corr}$  can be obtained (Figure 1).



**Figure 1.** Different  $\Delta m \sim t$  curves at 25°C, 70% RH while  $C_{\text{NaCl}}$  is  $60 \mu \text{g} \cdot \text{cm}^{-2}$ . a -  $\Delta m_{\text{all}}$ , b -  $\Delta m_{\text{water}}$ ; c -  $\Delta m_{\text{corr}}$ 

The derivation procedure of  $\Delta m_{\text{corr}}$  is elucidated in Figure 1, which undoubtedly shows that, in the case of 25°C and 70% RH, the mass change rate of Au initially increases with the corrosion time (*t*) and then keeps almost horizontal to the time coordinate axis after 2500 seconds, whilst the mass change rate of Cu is much greater than that of Au. The increase of  $\Delta m_{\text{corr}}$  indicates that more corrosion products are formed, which consequently demonstrates the increase of the corrosion severity.

In some literatures [35,36], the CRH for NaCl deliquescence is 75% ( $25^{\circ}$ C), however, an obvious corrosion process occurred while RH lies below the deliquescence point of NaCl. In order to ascertain this problem, the relationships of Cu  $\Delta m_{all}$  vs. t with different salts are tested in Figure 2. Figure 2 undoubtedly confirms that: (1) the electrochemical inert particles like  $SiO_2$  and  $Al_2O_3$  can only absorb water molecules but initiate Cu corrosion; (2) the synergistic effect of 70% RH and NaCl particles in our experiment leads to the onset of Cu corrosion, which also verifies the results of Stranberg and Johansson (their investigated RH is in the region from 30% to 70%) [37]. In fact, Chen and his coworkers pointed out that copper with NaCl deposited suffered from significant corrosion attack even at 55% RH [15], and other research groups also proved that plenty of water monolayer would adsorbed onto copper and lead to its significant atmospheric corrosion at the RH of 40% [7] or even 15% [9]. On the other hand, Rice and his coworkers [38] pointed out that the so-called "critical humidity" is not existed or meaningless in absolute sense, and they could measure the atmospheric corrosion rate of copper in the entirely studied RH range (from 30% to 80%). However, when compare the  $\Delta m_{\rm all}$  values of curve a, b and e (Figure 2) at the same time, the so-called "critical relative humidity" should exist for the onset of Cu atmospheric corrosion, but it's lower than the CRH of NaCl deliquescence (75%).



**Figure 2.** Relationship of  $\Delta m_{all}$  versus *t* after deposited different salts onto Cu surface (25°C). a - without salt at 70% RH; b - with  $60\mu g \cdot cm^{-2}$  NaCl at 30% RH; c - with  $60\mu g \cdot cm^{-2}$  Al<sub>2</sub>O<sub>3</sub> at 70% RH; d - with  $60\mu g \cdot cm^{-2}$  SiO<sub>2</sub> at 70% RH; e - with  $60\mu g \cdot cm^{-2}$  NaCl at 70% RH

The increase of  $\Delta m_{\text{corr}}$  ( $\Delta m_{\text{corr}}$  is obtained by using the method elucidated in Figure 1) with both *t* and C<sub>NaCl</sub> (Figure 3), which can also be intuitively verified by the weight loss of the corroded Cu (Table 1), indicate that the concentration augment of chloride accelerates the corrosion process.



**Figure 3.**  $\Delta m_{corr} \sim t$  curves at 25°C and 70% RH with different C<sub>NaCl</sub> (in the unit of  $\mu g \cdot cm^{-2}$ ). a - 15; b - 30; c - 37.5; d - 45; e - 52.5; f - 60.

**Table 1.** Weight loss of copper samples with different C<sub>NaCl</sub> (25°C, 70% RH)

$C_{NaCl}/\mu g \cdot cm^{-2}$	Weight loss /mg·cm <sup>-2</sup>	Average Corrosion rate obtained by weight loss / µg·cm <sup>-2</sup> ·h <sup>-1</sup>
15	$0.16 \pm 0.04$	2.03±0.51
30	$0.24 \pm 0.04$	3.39±0.56
37.5	$0.28 \pm 0.04$	$3.95 \pm 0.56$
45	$0.32 \pm 0.08$	$4.52 \pm 1.10$
52.5	$0.36 \pm 0.08$	$5.08{\pm}1.11$
60	$0.49 \pm 0.08$	6.78±1.12



**Figure 4.** XRD spectra of the copper surface at each  $C_{NaCl}$  (in the unit of  $\mu g \cdot cm^{-2}$ ) after 1h corrosion (25°C, 70% RH). a -15; b - 30; c - 37.5; d - 45; e - 52.5; f - 60.

According to the previous reports [1,6,39], in the presence of chloride ions, the main atmospheric corrosion product (composition) of Cu during initial stages is Cu<sub>2</sub>O. Then, the corroded copper surfaces of different  $C_{NaCl}$ , after atmospheric corrosion for 1h, are tested using XRD (Figure 4) after removing their residual NaCl particles (by simply rinsing the surface with double-distilled water several times slightly). As shown in Figure 4, the evident peaks at 43.3°, 50.5° and 74.2° refer to copper substrate, while the peaks at 36.7° and 61.8° are attribute to (1,1,1) and (2,2,0) diagnostic reflexions of Cu<sub>2</sub>O respectively, and no chloride containing compounds can be detected in all cases.

In order to confirm the atmospheric corrosion product of Cu is Cu<sub>2</sub>O during initial stage, the  $\Delta m_{\text{corr}} \sim t$  curves are transferred into the relationship of electric quantity versus time ( $Q \sim t$ ) (Figure 5) based on the hypotheses that the parameters used in Faraday equation (eq. 4) are only related to the formation of Cu<sub>2</sub>O [6].

$$Q = \frac{\Delta m_{corr}}{M} nF \tag{4}$$

In eq. 4, *n* is the number of the electrons consumed in the electrochemical process (n=1 for the formation of Cu<sub>2</sub>O), *F* is the Faraday constant and *M* is the molar mass of the reactant [40].



**Figure 5.**  $Q \sim t$  curves at 25°C and 70% RH with different C<sub>NaCl</sub> (in the unit of  $\mu g \cdot cm^{-2}$ ). a -15; b - 30; c - 37.5; d - 45; e - 52.5; f - 60.

Figure 5 is the same as Figure 3 except their different vertical coordinate, which also undoubtedly indicates that, in our experimental conditions, the main corrosion product of Cu in its initial atmospheric corrosion stages ( $t \le 1$ h) is Cu<sub>2</sub>O. This result also supported by the results obtained by other authors [1,6,39]. Then, why  $\Delta m_{corr}$  increases with the concentration augment of chloride in Figure 3?

For the initial atmospheric corrosion of copper, which cathodic reaction with or without the existence of other aggressive particles (such as chlorides and sulfides) is always as follows [6,21]:

 $\frac{1}{2}O_2 + H_2O + 2e^{-\frac{k_1}{2}}2OH^-$ (5)

In the absence of any other aggressive particles except  $H_2O$  and  $O_2$ , the anodic reaction of Cu atmospheric corrosion process can be presented as [41],

$$\operatorname{Cu}(s) \xrightarrow{\kappa_2} \operatorname{Cu}^+ + e^- \tag{6}$$

where,  $k_1$  and  $k_2$  stand for the apparent rate constant of cathodic and anodic reactions, respectively. Then, the generated OH<sup>-</sup> and Cu<sup>+</sup> interreact to form Cu<sub>2</sub>O,

 $Cu^+ + 20H^- \to Cu_20 + H_20$  (7)

The corrosion rate of Cu without chloride is very low, which can be proved by the relationship of  $\Delta m_{all}$  versus *t* (curve a in Figure 2), and can be attributed to the slow formation rate of Cu<sup>+</sup> for that reaction 6 acts as the rate-determining step and progresses very slowly [12].

In the presence of NaCl particles, the anodic reaction mechanism will be changed. Nowadays, two possible anodic reaction mechanisms (Case 1 and Case 2) for copper atmospheric corrosion have been proposed [10,11,42,43]:

Case 1:  

$$Cu+2Cl^{-} \xrightarrow{k_{3}} CuCl_{2}^{-} + e^{-} \qquad (8)$$

$$r_{3} = k_{3}[Cl^{-}]^{2} \qquad (9)$$
Case 2:  

$$Cu+Cl^{-} \xrightarrow{k_{4}} CuCl+e^{-} \qquad (10)$$

$$r_{4} = k_{4}[Cl^{-}] \qquad (11)$$

$$CuCl+Cl^{-} \xleftarrow{k_{5}} CuCl_{2}^{-} \qquad (12)$$

$$r_{5} = k_{5}[Cl^{-}][CuCl] \qquad (13)$$

Then, the generated cuprous chloride  $CuCl_2^-$  (in Case 1 or Case 2) reacts with OH<sup>-</sup> to form Cu<sub>2</sub>O,

$$CuCl_{2}^{-}+OH^{-} \xrightarrow{k_{6}} \frac{1}{2}Cu_{2}O + \frac{1}{2}H_{2}O + 2Cl^{-}$$
(14)  
$$r_{6} = k_{6}[CuCl_{2}^{-}][OH^{-}]$$
(15)

where,  $k_i$  is rate constant and  $r_i$  is reaction rate. Therefore, the presence of Cl<sup>-</sup> in NaCl particles accelerates the formation of Cu<sup>+</sup>, which is the rate-determining step for copper corrosion [12]. On the other hand, reactions 8-15 also indicate that the corrosion product during the initial atmospheric corrosion process of copper is Cu<sub>2</sub>O regardless of the possibly followed anodic reaction mechanisms (Case 1 or Case 2).

The formation rates of  $Cu_2O$  for Case 1 and 2 can be calculated as follows,

$$\begin{aligned} r_{Case \ 1} &= k_6 [CuCl_2^-][OH^-] = k_6 \cdot \frac{\kappa_8}{k_{-8}} \cdot [Cl^-]^2 [OH^-] \quad (16) \\ r_{Case \ 2} &= k_6 [CuCl_2^-][OH^-] = k_6 \cdot \frac{k_8}{k_{-5}} \cdot [CuCl][Cl][OH^-] = k_6 \cdot \frac{k_4}{k_{-4}} \cdot \frac{k_5}{k_{-5}} \cdot [Cl^-]^2 [OH^-] \quad (17) \end{aligned}$$

From eqns. 16-17, it can be seen that the corrosion product during the initial atmospheric corrosion process of copper is Cu<sub>2</sub>O, which formation rate is directly proportional to  $[CI^{-}]^{2}$  also regardless of the possibly followed anodic reaction mechanism (Case 1 or Case 2),

$$r_{corr} = k_{corr} \cdot [Cl^{-}]^{2}$$
(18)  
where,  $k_{corr} = k_{6} \cdot \frac{k_{5}}{k_{-5}} \cdot [OH^{-}]$  for Case 1 and  $k_{corr} = k_{6} \cdot \frac{k_{4}}{k_{-4}} \cdot \frac{k_{5}}{k_{-5}} \cdot [OH^{-}]$  for Case 2. Here,

it should be mentioned that, the relationship between the corrosion rate of Cu in bulk solutions and [Cl<sup>-</sup>] is similar to equation (18) except that the exponent "2" is replaced by "m" [44],

$$r_{corr} = k_{corr} \cdot [Cl^{-}]^{m}$$
(19)

where, *m* possesses different value in different conditions. However, the QCM data (Figure 3 or Figure 5) give no information about what corrosion mechanism (Case 1 or Case 2) is followed by the atmospheric corrosion process of copper at different [Cl<sup>-</sup>].

The atmospheric corrosion process is simultaneously coupled with the break of old chemical bonds and the generation of new chemical bonds, which undoubtedly results in the energy exchange between the corroding metal and its serving environment. Among these exchanged energies, the work obtained by the corroding metal is presented as its mass variation (or as the potential, current or charge fluctuations in the traditional electrochemical tests [24,26,30,45,46], which is in fact another kind of noises. Therefore, the  $\Delta m_{corr} \sim t$  curves shown in Figure 3 are analyzed by Fast wavelet technique (FWT) [47], which theoretical algorithm is depicted in details in Figure 6.



Figure 6. Theoretical algorithm scheme of the fast wavelet transform

Briefly, the real time signal sets  $S_n(t)$  (n=1,2,...N) is decomposed into two sets of coefficients: a smooth coefficient set,  $S=(S_1, S_2, ..., S_J)$ , which contains the information about the general trend of the signal; a detail coefficient set,  $D=(D_1, D_2, ..., D_J)$ , which contain the information about the local fluctuations in the signal [48]. In FWT analyzes,  $D_1$ ,  $D_2...D_J$  and  $S_J$  are designated as the so-called "crystals". Thus,  $S_n(t)$  can be reconstructed by adding together the contributing wavelets weighed by their corresponding coefficients [49]:

$$S_{n}(t) = \sum_{k} S_{J,k} \phi_{J,k}(t) + \sum_{k} D_{J,k} \varphi_{J,k}(t) + \sum_{k} D_{J-1,k} \varphi_{J-1,k}(t) + \dots + \sum_{k} D_{1,k} \varphi_{1,k}(t)$$
(20)  

$$S_{J,k} = \int S(t) \phi_{J,k}^{*}(t) dt$$
(21)  

$$D_{J,k} = \int S(t) \varphi_{J,k}^{*}(t) dt$$
(22)

where  $\phi_{j,k}^*$  and  $\varphi_{j,k}^*$  are the complex conjugate of the basis functions  $\phi_{j,k}$  and  $\varphi_{j,k}$ , respectively. *J* is small natural number depended on  $\phi$ ,  $\varphi$  and *N*, (*N* is the number of specimen), *j*=1, 2... *J*, *k*=1, 2... *N*/2<sup>*j*</sup>. And  $\phi_{j,k}$  and  $\varphi_{j,k}$  are generated from a pair of functions through scaling and translation as follows:

$$\phi_{J,k}(t) = 2^{-J/2} \phi(2^{-J}t - k) = 2^{-J/2} \phi(\frac{t - 2^{J}k}{2^{J}})$$
(23)  
$$\phi_{j,k}(t) = 2^{-j/2} \phi(2^{-j}t - k) = 2^{-j/2} \phi(\frac{t - 2^{j}k}{2^{j}})$$
(24)

where  $2^{j}$  acts as the scale factor and  $2^{j}k$  as the translation parameter. The wavelet coefficient measures the correlation or the agreement between the wavelet (with its peaks and troughs) and the corresponding segment of the signal, and a low value of *l* corresponds to a small and fast scale.

Here, the orthogonal db4 Mallat wavelet [33,50] (J=8) is chosen for the FWT analysis of the data shown in Figure 3.



**Figure 7.** RP-EDPs according to the  $\Delta m_{\text{corr}} \sim t$  curves in Figure 3, a - 15µg·cm<sup>-2</sup>; b - 30µg·cm<sup>-2</sup>; c - 37.5µg·cm<sup>-2</sup>; d - 45µg·cm<sup>-2</sup>; e - 52.5µg·cm<sup>-2</sup>, f - 60µg·cm<sup>-2</sup>

Therefore, the ensemble noise energy (*E*) for Cu corrosion at each  $C_{NaCl}$  is calculated as following:

$$E = \sum_{n=1}^{N} S_n^2 (n = 1, 2, \dots, N)$$
(25)

where based on the constant  $\Delta t$ ,  $S_n^2$  is proportional to the square of  $\Delta m_{corr}$  ( $\Delta m_{corr}^2$ ) and represents the energy density of noise.

And the energy fraction associated with each crystal can be calculated as:

$$E_{j}^{D} = \sum_{k=1}^{N/2^{j}} D_{j,k}^{2}, (j = 1, 2, ..., J, J = 8)$$

$$E_{J}^{S} = \sum_{k=1}^{N/2^{j}} S_{j,k}^{2}, (j = 1, 2, ..., J)$$
(26)
(27)

where  $E_j^D$  stands for noise energy of  $D_j$  crystal and  $E_j^S$  for  $S_J$  crystal. Since the chosen wavelets are orthogonal, the following equation is satisfied [50,51]:

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$$E = \sum_{j=1}^{J} E_{j}^{D} + E_{J}^{S}, (J = 8)$$
(28)

The plots of the energy accumulated by each crystal versus the crystal name are referred to as the energy distribution plot (EDP). Usually, the EDP is re-plotted by discounting the contribution of  $E_J^s$  crystal from the ensemble signal energy to eliminate the energy contribution of the large smooth drift from the raw data, and thus obtained re-plotted EDP is designated as the RP-EDP [25,33]. Figure 7 shows the corresponding RP-EDPs obtained from the FWT analyzes of the data (shown in Figure 3).

Noise, including electrochemical noise is composed of distinct type of events, which can be distinguished by their different time constant. According to our previous studies [30,33], the RP-EDP can be divided into three segments (Figure 7): (1) region I between  $D_1$  and  $D_3$  mainly characterizes the nucleation process, (2) region II between  $D_4$  and  $D_6$  mainly characterizes the growth process, and (3) region III between  $D_7$  and  $D_8$  mainly reflects the information about the diffusion process, and it has also been verified by other literatures [52-54]. Therefore, the energy sum ( $E_c$ ) of  $D_1$ -  $D_6$ , which is defined hereinafter as the active energy of electrochemical reactions, should reflect the corrosion severity of copper,

 $E_c = E_1^D + E_2^D + E_3^D + E_4^D + E_5^D + E_6^D$ (29)

Figure 7 shows that the energy fraction for nucleation and growth processes always take the most part of the energy (more than 90%) regardless of their different  $C_{NaCl}$ , indicating the main atmospheric corrosion type of Cu is pitting [52]. Based on the energy values list in Figure 7, the dependence of  $E_c$  with  $C_{NaCl}$  has been calculated and plotted in Figure 8, which undoubtedly indicates that the initial atmospheric corrosion rate ( $r_{corr}$ ) of Cu is directly proportional to square of  $C_{NaCl}$ , and verifies the correctness of the above deduced equation (18). This result also reveals that  $E_c$  can not only characterize the corrosion severity correctly (Figure 3, Table 1 and Figures 9-11) [52-56], but also benefit for the deducing of the corrosion mechanism appropriately.



Figure 8. Relationship between  $E_c$  and  $C_{NaCl}$ 

Figures 9-10 show that the diameter or/and the depth of pits dubiously increases with  $C_{\text{NaCl}}$ , but the relationship of  $R_q$  (the mean square roughness,  $R_q = \sqrt{\frac{1}{l} \int_0^l \{y(x)\}^2 dx}$ ) with  $C_{\text{NaCl}}$  (Figure 11), which represents the standard deviation of the distribution of surface heights, undoubtedly indicates that  $R_q$  increases with both  $C_{\text{NaCl}}$  and corrosion time.



**Figure 9.** Corroded morphologies of copper under different  $C_{NaCl}$  (in the unit of  $\mu g \cdot cm^{-2}$ ) deposited on its surface. a - 15, b - 30, c - 37.5, d - 45, e - 52.5, f - 60 (25°C, 70%RH)







**Figure 10.** The 3D AFM images of Copper surface after 1 hour's corrosion with corresponding  $C_{NaCl}$  (in the unit of  $\mu g \cdot cm^{-2}$ ): a - without NaCl; b - 15, c - 30, d - 37.5, e - 45, f - 52.5, g - 60 (25°C, 70%RH)



Figure 11. R<sub>q</sub> at different C<sub>NaCl</sub> vs corrosion time

In order to obtain the relationship between  $E_c$  and corrosion time at each  $C_{NaCl}$ , the EN data shown in Figure 3 are also analyzed by using FWT technique though the following procedures: (1) each set of  $\Delta m_{corr} \sim t$  data in Figure 3 is previously divided into 7 segments in sequence and each of them contains 5120 points (according to the theoretical algorithm scheme of FWT analysis shown in Figure 6, the analyzed data number should be an integral multiple of 2, so N=5120 is chosen in these procedures); (2) then, the EN data of each segment is analyzed by using FWT technique to obtain  $E_c$ . Figure 12 shows the dependence of  $E_c$  on corrosion time, which indicates that the atmospheric corrosion rate of copper increases with both corrosion time and  $C_{NaCl}$ . Because the tested standard molar Gibbs Free Energies ( $\Delta_r G^{\theta}$ ) of eq. 8 and eq. 10 are 18.89 KJ·mol<sup>-1</sup> and 26.39 KJ·mol<sup>-1</sup> respectively [57], and the rate-determining step for copper corrosion is the formation of Cu<sup>+</sup> [12], therefore the different rising rate of  $E_c$  with time (Figure 12) at different  $C_{NaCl}$  may also indicate that, the atmospheric corrosion of Cu at lower  $C_{NaCl}$  may follow the so-called "Case 2" anodic reaction mechanism, whereas the so-called "Case 1" anodic reaction mechanism at higher  $C_{NaCl}$ .



Figure 12. Relationships of  $E_c$  with  $C_{NaCl}$  and the atmospheric corrosion time (25°C, 70% RH)

## 4. CONCLUSIONS

Copper with NaCl deposited suffers from significant atmospheric corrosion even at the RH (70%, 25°C) lower than the deliquescence point of NaCl (75%, 25°C), which corrosion severity (such as weight loss) and surface roughness increase with both corrosion time and  $C_{NaCl}$ . The corrosion product of copper during its initial atmospheric corrosion process ( $\leq$  1h) is Cu<sub>2</sub>O, which is independent of  $C_{NaCl}$  (15-60µg·cm<sup>-2</sup>).

The proposed new parameter, i.e., the electrochemical active energy ( $E_c$ ) is both directly proportional to the corrosion severity and [Cl<sup>-</sup>]<sup>2</sup>, and the rising rate of  $E_c$  with corrosion time at different NaCl concentration may be used to deduce the corrosion mechanism.

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## References

- 1. A. R. Mendoza, F. Corvo, A. Gómez, J. Gómez, Corros. Sci., 46 (2004) 1189.
- 2. L. Nunez, E. Reguera, F. Corvo, E. Gonzalez, C. Vazquez, Corros. Sci., 47 (2005) 461.
- 3. J. Sandberg, I.O. Wallinder, C. Leygraf, N.Le. Bozec, Corros. Sci., 48 (2006) 4316.
- 4. R.B. Faltermeier, Stud. Conserv., 44 (1998) 121.
- 5. Z.Y. Chen, D. Persson, F. Samie, S. Zakipour, C. Leygraf, J. Electrochem. Soc., 152 (2005) 502.
- 6. X. Liao, F. Cao, L. Zheng, W. Liu, A. Chen, J. Zhang, C. Cao, Corros. Sci., 53 (2011) 3289.

- 7. T. Aastrup, M. Wadsak, M. Schreiner, C. Leygraf, Corros. Sci., 42 (2000) 957.
- 8. T. Aastrup, M. Wadsak, C. Leygraf, M. Schreiner, J. Electrochem. Soc., 147 (2000) 2543.
- 9. J.F. Dante, R.G. Kelly, J. Electrochem. Soc., 140 (1993) 1890.
- 10. H.P. Lee, K. Nobe, J. Electrochem. Soc., 133 (1986) 2035.
- 11. A. El Warraky, H.A. El Shayeb, E.M. Sherif, Anti-Corros. Method. M., 51 (2004) 52.
- 12. C. Leygraf, I.O. Wallinder, J. Tidblad, T. Graedel, Atmospheric corrosion. John Wiley & Sons, Inc. (2016), Hoboken. USA.
- 13. Z. Y. Chen, D. Persson, F. Samie, S. Zakipour, C. Leygraf, J. Electrochem. Soc., 152 (2005) B502.
- 14. Z. Y. Chen, D. Persson, A. Nazarov, S. Zakipour, D. Thierry, C. Leygraf, J. Electrochem. Soc., 152 (2005) B342.
- 15. Z. Y. Chen, S. Zakipour, D. Persson, C. Leygraf, Corrosion, 60 (2004) 479.
- 16. J.A. Gonzalez, E. Otero, C. Cabanas, J. M. Bastidas, Brit. Corros. J., 19 (1984) 89.
- 17. Z. Lu, P. Wang, D. Zhang, Corros. Sci., 91 (2015) 287.
- 18. M. Wadsak, M. Schreiner, T. Aastrup, C. Leygraf, Surf. Sci., 454-456 (2000) 246.
- 19. K.P. FitzGerald, J. Nairn, G. Skennerton, A. Atrens, Corros. Sci., 48 (2006) 2480.
- 20. T. Aastrup, C. Leygraf, J. Electrochem. Soc., 144 (1997) 2986.
- 21. Y. Chen, D.M. Qi, H.P. Wang, Z. Xu, C.X. Yi, Z. Zhang, Int. J. Electrochem. Sci., 10 (2015) 9056.
- 22. H. Huang, Z. Dong, Z. Chen, X. Guo, Corros. Sci., 53 (2011) 1230.
- 23. Y. Xia, F. Cao, W. Liu, L. Chang, J. Zhang, Int. J. Electrochem. Sci., 8 (2013) 3057.
- 24. Z. Yang, Z. Zhang, W. Leng, K. Ling, J. Zhang, T. Nonferr. Metal. Soc., 16 (2006) 209.
- 25. Y. Shi, Z. Zhang, J. Su, F. Cao, J. Zhang, *Electrochim. Acta*, 51 (2006) 4977.
- 26. A.M. Homborg, E.P.M. van Westing, T. Tinga, X. Zhang, P.J. Oonincx, G.M. Ferrari, J.H.W. de Wit, J.M.C. Mol, *Corros. Sci.*, 66 (2013) 97.
- 27. L. Nie, Y. Xia, Y. Zhou, J. Zhang, F Cao, J. Zhang, Int. J. Electrochem. Sci., 11 (2016) 259.
- 28. J. Itoh, T. Sasaki, M. Seo, T. Ishikawa, Corros. Sci., 39 (1997) 193.
- 29. Y.Y. Shi, Z. Zhang, F.H. Cao, J.Q. Zhang, Electrochim. Acta, 53 (2008) 2688.
- 30. X. Huang, Y. Chen, T. Fu, Z. Zhang, J. Zhang, J. Electrochem. Soc., 160 (2013) D530.
- 31. R.A. Cottis, A.M. Homborg, J.M.C. Mol, Electrochim. Acta, 202 (2016) 277.
- 32. F.H. Cao, Z. Zhang, J.X. Su, Y.Y. Shi, J.Q. Zhang, Electrochim. Acta, 51 (2006) 1359.
- 33. Z. Zhang, W.H. Leng, Q.Y. Cai, F.H. Cao, J.Q. J. Electroanal. Chem., 578 (2005) 357.
- 34. G.Z. Sauerbrey, Z. phys., 155 (1959) 206.
- 35. J.F. Young, J. Chem. Technol. Biot., 17 (1967) 241.
- 36. E. Teunou, J.J. Fitzpatrick, J. Food. Eng., 42 (1999) 109.
- 37. H. Strandberg, L.G. Johansson, J. Electrochem. Soc., 145 (1998) 1093.
- 38. D.W. Rice, P. Peterson, E.B. Rigby, P.B.P. Phipps, R.J. Cappell, R. Tremoureux, J. Electrochem. Soc., 128 (1981) 275.
- 39. A.L. Bacarella, J.C. Griess, J. Electrochem. Soc., 120 (1973) 459.
- 40. A.N. Correia, M.C. Dos Santos, S.A.S. Machado, L. A. Avaca, J. Electroanal. Chem., 547 (2003) 53.
- 41. G. Faita, G. Fiori, D. Salvadore, Corros. Sci., 15 (1975) 383.
- 42. J.P. Ferreira, J.A. Rodrigues, I.T.E. da Fonseca, J. Solid State Electr., 8 (2004) 260.
- 43. L. Brossard, J. Electrochem. Soc., 130 (1983) 403.
- 44. G. Kear, B.D. Barker, F.C. Walsh, Corros. Sci., 46 (2004) 109.
- 45. F. Safizadeh, E. Ghali, T. Nonferr. Metal. Soc., 23 (2013) 1854.
- 46. A. Chen, F. Cao, X. Liao, W. Liu, L. Zheng, J. Zhang, C. Cao, Corros. Sci., 66 (2013) 183.
- 47. Y.J. Wei, D.H. Xia, S.Z. Song, Russ. J. Electrochem., 52 (2016) 560.
- 48. A. Aballe, M. Bethencourt, F.J. Botana, M. Marcos, Electrochem. Commun., 1 (1999) 266.
- 49. J. Smulko, K. Darowicki, A. Zieliński, Electrochem. Commun., 4 (2002) 388.

- 50. Z. Dong, X. Guo, J. Zheng, L. Xu, Electrochem. Commun., 3 (2001) 561.
- 51. Z. Zhang, Q.D. Zhong, J.Q. Zhang, Y.L. Cheng, F.H. Cao, J.M. Wang, C.N. Cao, *Acta Metall Sin.-Engl.*, 15 (2002) 272.
- 52. X. Liu, T. Zhang, Y. Shao, G. Meng, F. Wang, Corros. Sci., 52 (2010) 892.
- 53. A. Aballe, M. Bethencourt, F.J. Botana, M. Marcos, J.M. Sanchez-Amaya, *Electrochim. Acta*, 46 (2001) 2353.
- 54. L. Jian, Z. Huanjun, W. Ke, W. Xuejun, Int. J. Electrochem. Sci., 10 (2015) 931.
- 55. A. Aballe, M. Bethencourt, F.J. Botana, M. Marcos, *Electrochim. Acta*, 44 (1999) 4805.
- 56. L. Liu, Y. Li, F. Wang, Electrochim. Acta, 54 (2008) 768.
- 57. W. Liu, D.C. McPhail, Chem. Geol., 221 (2005) 21.

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