Initial Corrosion Behavior of Pure Copper in Atmospheric Environment

Fengjie Yan¹, Xingeng Li*, Bo Jiang¹, Deyuan Lin², Min Fu¹ and Wenjing Li¹

¹State Grid Corporation Joint Laboratory of advanced electrical engineering materials (Shandong), State Grid Shandong Electric Power Research Institute, Jinan, China
²State Grid Fujian Electric Power Research Institute, Fujian, China

*Corresponding author e-mail: 923990271@qq.com

Abstract. The corrosion behavior of pure copper with sodium chloride deposition and without sodium chloride deposition in atmospheric environment was studied by 500h environmental corrosion test and linear polarization test in laboratory, as well as characterization of corrosion products by SEM and XRD. The results showed that pure copper displayed good corrosion resistance in inland atmospheric environment without pollution. After depositing NaCl salt to the surface of pure copper, the corrosion current density increases sharply and plenty of corrosion products is formed on the surface of the sample, consisting of CuO, Cu₂O and CuSO₄·H₂O.

1. Introduction

Copper is the first metal to be discovered and used by human. In the production of non-ferrous metals of China, the output ranks second only to aluminum [1]. It is widely used in substation equipment as conductor material because of its good conductivity. Most of the equipment are exposed in atmospheric environment. Owing to its high self-corrosion potential and its stable thermodynamic property, copper generally displays good corrosion resistance. However, copper still suffers from serious damage when exposed to high temperature, high humidity and high salt content aggressive environments. Generally, the surface of copper adsorbs a layer of water molecules to form a thin liquid film in the atmospheric environment. Under the thin liquid film, copper interacts with the corrosion medium of the aggressive environment, and occurs electrochemical corrosion to form patina. Patina are consisting of all kinds of corrosion products. Copper as a kind of conductor material, corrosion will lead to poor contact, and low conduction performance, which will affect the normal operation of the equipment, and may lead to accidents or failures [2-5]. In order to eliminate the safety risks and ensure the safe operation of the equipment, it is necessary to identify the corrosion behavior of the copper.

The effect factors of copper atmospheric corrosion mainly include temperature, humidity, pollution and so on [6,7]. Relative humidity affects the formation of thin liquid film on metal surface and plays a major role in atmospheric corrosion [8]. Some studies show that the corrosion of copper in the atmosphere can occur only when the relative humidity reaches 70%. Sodium chloride is the main component in the marine atmospheric environment, which has a strong moisture absorption. The existence of sodium chloride increases the conductivity of the thin liquid film on the metal surface, and coupled with the erosion of chloride ion itself, which accelerating the corrosion of metals [9-11]. In this
paper, the initial corrosion behavior of pure copper in atmospheric environment were studied by environmental corrosion test and electrochemical test in laboratory.

2. Experimental

2.1. Preparation of Samples
The experimental materials were copper which contained (in mass %) $\geq 99.00\%$ copper (Cu), $\leq 0.12\%$ arsenic (As), $\leq 0.10\%$ antimony (Sb), $\leq 0.02\%$ bismuth (Bi), $\leq 0.12\%$ lead (Pb). In order to increase the samples area and study the effect of machining to the copper atmospheric corrosion, samples for environmental corrosion test were machined a lot of holes with a diameter of 3 mm. The sample size was $35\times35\times1$ mm. The sample area was $2357.9\,\text{mm}^2$. Samples for electrochemical experiment were cut to $100\times50\times1$ mm. The samples were cleaned ultrasonically in acetone before experiment. An exposure area of 1 cm$^2$ was prepared by sealing with insulating tape.

2.2. Linear Polarization Curve Test
Linear polarization curve measurements were performed through a VersaSTAT3 electrochemical workstation using three electrodes corrosion sensor at room temperature ($25\,\text{℃}$). The working electrode (WE) were copper electrodes with 18935 mg/m$^2$ sodium chloride deposition and without sodium chloride deposition. Gold-plated sheets were used as the reference electrode (RE) and the counter electrode (CE). Linear polarization curves were measured from $-10\,\text{mV}$ to $10\,\text{mV}$ vs. open-circuit potential (OCP) at a scan rate of $1\,\text{mV/s}$. The relative humidity of the test environment were 80%, 85%, and 90%.

2.3. Environmental Corrosion Test
A 500h environmental corrosion test was performed in the laboratory environmental corrosion test system. The relative humidity of the environmental corrosion test system is kept at 80%. The temperature of the environmental corrosion test system is kept at $40\,\text{℃}$. The samples included two groups. One group is the samples with 18935 mg/m$^2$ sodium chloride deposition, the other group is the samples without sodium chloride deposition. Each group contains 3 parallel samples. After finishing the test, the samples were cleared with distilled water, and dehydrated using absolute ethyl alcohol.

2.4. Corrosion Product Analysis
For identification of the corrosion products formed on the laboratory environmental corrosion samples, an XPert Pro X-ray diffraction (XRD) was used. The surface morphology of the corrosion products were observed by Supra 55 field emission scanning electron microscope (SEM) and digital camera.

3. Results and discussion

3.1. Linear Polarization measurement
Fig. 1 shows the linear polarization curve of copper electrode without and with sodium chloride deposition in atmospheric environment with relative humidity of 80%. The linear polarization resistance and corrosion current density were obtained by fitting the linear polarization curve, as shown in Table 1. The results show that pure copper exhibits good stability, high linear polarization resistance, and low corrosion current density in inland pollution-free atmospheric environment. After depositing 18935 mg/m$^2$ sodium chloride, the linear polarization resistance of the copper electrode is reduced from the megohm to the ohmic level, the corrosion current density is increased by nearly 30,000 times. The copper electrode occurs rapid reaction.
Figure 1. Linear polarization curves of copper electrode without sodium chloride deposition and with sodium chloride deposition in atmospheric environment with RH 80%.

Table 1. Fitting results of linear polarization curves of copper electrode without sodium chloride deposition and with sodium chloride deposition in atmospheric environment with RH 80%.

| Electrochemical parameters | without sodium chloride deposition | with sodium chloride deposition |
|----------------------------|------------------------------------|---------------------------------|
| $R_p / \Omega$             | $4.146\times10^6$                 | $141.108$                       |
| $I_{corr} / (\mu A \cdot cm^{-2})$ | $5.242\times10^{-3}$ | $154.059$                       |

Fig. 2 shows the linear polarization curve of copper electrode with sodium chloride deposition in atmospheric environment with relative humidity of 80%, 85%, and 90%. The linear polarization resistance and corrosion current density were obtained by fitting the linear polarization curve, as shown in Table 2. The results show that the corrosion current density increases with the increase of the environment relative humidity. As known, a thin liquid film will be formed on the metal surface when the relative humidity of the atmosphere reaches a certain value. And the thickness of the thin liquid film increases with the relative humidity increasing. When the environment relative humidity is low, the cationic hydration of the metal is difficult due to the liquid film too thin. However, with the increasing of relative humidity, the thin liquid film becomes thicker and the oxygen content of the electrolyte solution increases, which leads to the reaction speed of the cathode increasing. So the corrosion rate of the copper increases [12, 13].
Figure 2. Linear polarization curves of copper electrode with sodium chloride deposition in atmospheric environment with different relativity humidity.

Table 2. Fitting results of linear polarization curves of copper electrode with sodium chloride deposition in atmospheric environment with different relativity humidity.

| Electrochemical parameters | Humidity / % |
|---------------------------|--------------|
|                           | 80           | 85           | 90           |
| \( R_p / \Omega \)        | 141.108      | 98.602       | 48.262       |
| \( I_{corr} / (\mu A \cdot cm^{-2}) \) | 154.059      | 220.472      | 450.437      |

3.2. Environmental Corrosion analysis

Fig. 3 shows the macro corrosion morphologies of copper exposed in atmosphere for 500 h in the environmental corrosion test system. The image shows that the surface of the copper without sodium chloride deposition is still bright and no obvious corrosion products are observed after 500 h environmental corrosion test. The corrosion of the samples with sodium chloride deposition is serious. The surface of the sample is covered with black and blue-green corrosion products. The black corrosion products are uniform, dense, and full of the matrix surface. The blue-green corrosion products are loose and nonuniform, mostly located at the edge of the hole. In the process of sample processing, the crystal defects around the hole increase and the surface activity increases. It is known that the crystal nucleuses of the electrode reaction products are formed firstly in the surface defects. The increase of surface defects leads to the increase of nucleation density [14]. So the corrosion around holes is more serious.
Figure 3. Macro morphologies of copper exposed in atmosphere for 500 h in the environmental corrosion test system: (a) without sodium chloride deposition (b) with sodium chloride deposition

Fig. 4 shows the micro morphologies of copper with sodium chloride deposition exposed in atmosphere for 500 h in the environmental corrosion test system. Fig. 4a shows the micromorphology of the blue-green corrosion products near the through hole of the sample, which appears granular. The surface of the corrosion products is uneven and has shedding phenomenon. Fig. 4b shows the microscopic morphology of the black corrosion products in the form of cotton wool. The surface of the corrosion products is flat and relatively dense, which has a certain protective effect to the matrix metal.

Figure 4. Micro morphologies of copper with sodium chloride deposition exposed in atmosphere for 500 h in the environmental corrosion test system: (a) Region one, (b) Region two

The corrosion products of copper with sodium chloride deposition exposed in atmosphere for 500 h in the environmental corrosion test system were characterized by means of X-ray diffraction (XRD). The result revealed that corrosion products consisted of Cu$_2$O, Cu$_2$(OH)$_3$Cl and CuCl$_2$$\cdot$3Cu(OH)$_2$. The corrosion of copper in atmospheric environment is electrochemical corrosion under thin liquid film. The anodic reaction is the electron loss process, which is also called the dissolution process of copper. The cathodic reaction is the depolarization reaction of oxygen. So the corrosion product is mainly copper oxide. When the salt containing chloride ion is dissolved into the thin liquid film, the chloride ion is adsorbed on the surface of the metal or the passivated film to form a strong electric field, which destroying the surface oxide film and accelerating the dissolution of the metal. And the chloride ions can penetrate the passivation film into the matrix and then react with the copper element to form the soluble CuCl$^2$. In addition, CuCl$^2$ then react with the oxygen to generate Cu$_2$O, Cu$_2$(OH)$_3$Cl and CuCl$_2$$\cdot$3Cu(OH)$_2$ [15,16] Cu$_2$O are dense black corrosion products, which show good protective effect to the copper [17-20]. Cu$_2$(OH)$_3$Cl and CuCl$_2$$\cdot$3Cu(OH)$_2$ are loose blue-green corrosion products, which have no protective effect to the matrix.
4. Conclusion
The results of environmental corrosion test and linear polarization measurement indicated that copper has very low corrosion current density and good corrosion resistance in inland pollution-free atmosphere. After depositing 18935mg/m² sodium chloride on the copper surface, linear polarization measurement shows that the corrosion current density increased sharply, which are obtained in the environment with 25℃ and relative humidity 80%. The corrosion current density increased with the increase of the environment relative humidity. And the corrosion current density of the copper with sodium chloride deposition was almost 30000 times higher than that of the copper without sodium chloride deposition. The copper with sodium chloride deposition occurs obviously corrosion in the 40℃ and relative humidity 80% environmental corrosion test system for 500h. The corrosion products is consisted of Cu₂O, Cu₂(OH)₃Cl and CuCl₂·3Cu(OH)₂.

Acknowledgments
This work was financially supported by State Grid Corporation of China (No.5206001601XQ; No.5206001601XL).

References
[1] D.M. Qi, R.Y. Cheng, X.Q. Du, et al, Review on atmospheric corrosion of copper and copper alloys, J. Chin. Soc. Corros. Prot., 2014, 34(5): 389-398.
[2] W. Liu, Y.K. Jiang, H.H. Ge, Comparison of electrochemical corrosion behavior of copper in Liquid Film in atmospheric containing SO2 or H2S, Corros. & Prot., 2015, 36(10): 934-937.
[3] Z.C. Liu, W. Su, S.M. Lu, et al, Atmospheric Corrosion of carbon steel, galvanized steel and copper for power grid equipments reserve, Guangdong Electric Power, 2016, 29(2): 104-108.
[4] X. Li, J.K. Guo, Cause and protection of corrosion of copper materials in a 35kV indoor transformer substation, Corros. & Prot., 2004, 25(3):133-134.
[5] Z.Q. Zhang, X.Q. Li, Z. Tu, et al, Corrosion Mechanism and protection methods of copper clad aluminum shielding cables in substation terminal boxes, J. Mater. Prot., 2015, 48(9): 63-65.
[6] J. Chen, Q.F. Zheng, J.G. Wen, Gray Correlation Analyses of influence factors on atmospheric corrosion of copper and copper alloys, Corros. & Prot., 2010, 31(12):917-922.
[7] X.T. Wang, L.Y. Wang, H.F. Sun, et al, Effects of SO2 and NaCl on atmospheric corrosion
behavior of copper, J. Mater. Prot., 2011, 44(9): 28-31.

[8] S. Oesch, M. Faller, Environment effects on materials the effect of the air pollutants SO2, NO2, NO and O on the corrosion of copper, zinc and aluminum, a short literature survey and results of laboratory exposures, Corros. Sci., 1997, 39(9):1505-1530.

[9] Q. Qu, C.W. Yan, L. Zhang, Influence of NaCl deposition on atmospheric corrosion of A3 steel, J. Mater. Sci. Technol., 2002, 18(6):552-556.

[10] S.Syed*, Outdoor atmospheric corrosion of copper in Saudi Arabia, Corrosion Engineering, Sci. & Technol., 2008, 43(3):267-272.

[11] R. Vera, D. Delgado, B.M. Rosaled, Effect of atmospheric pollutants on the corrosion of high power electrical conductors-patr2, pure copper, Corros. Sci., 2007, 49(5):2329-2350.

[12] T.E. Graedel, Copper patinas formed in the atmosphere-II. A qualitative assessment of mechanisms, Corros. Sci., 1987, 27(7):721-740.

[13] T. Aastrup, M. Wadsak, M. Schreiner, et al, Experimental in situ studies of copper exposed to humidified air, Corros. Sci., 2000, 42(6):957-967.

[14] F.J Yan, X.G. Wang, X.M. Wang, et al, Effect of shot peening and Pre-Oxidation duplex treatment on electrochemical corrosion behavior of Al alloy in alkaline soil, Int. J. Electrochem. Sci., 12 (2017) 11212-11223.

[15] X.Y. Xie, Research on the testing technology of atmospheric corrosion of metallic materials, Tianjin: Tianjin University, 2003.

[16] X.N. Liao, F.H. Cao, L.Y. Zhang, et al, Corrosion behavior of copper under chloride-containing thin electrolyte layer, Corros. Sci., 2011, 53(10):3289-3298.

[17] K. Li, X.C. Liu, Z.Y. Chen, Initial atmospheric corrosion behavior of copper in the presence of ammonium chloride particles, Equip. Environ. Eng., 2018, 15(10):15-20.

[18] M. Yang, Z.Y. Wang, Atmospheric corrosion of copper under wet/dry cyclic conditions, Equip. Environ. Eng., 2007, 4(4):6-9.

[19] C.W. Yan, Y.F. He, H.C. Lin, et al, Atmospheric corrosion of copper at initial stage in air containing sulfur dioxide, Trans. Nonferrous Met. Soc. China, 2000, 10(5): 645-648.

[20] M. Yang, Z.Y. Wang, Review of atmospheric corrosion of copper, Equip. Environ. Eng., 2006, 3(4):38-44.