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Quantitative Determination of the Amount of Copper(I) Oxide in the Corrosion Products Formed on Copper by the Potassium Permanganate Titration Method

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In the present work, an improved titration method, called the potassium permanganate titration, was developed to quantitatively measure the mass of copper(I) oxide in the corrosion products formed on copper. This method can accurately measure the mass of copper(I) oxide on the copper surface, and the error is within ±3%, which was calibrated by microgravimetry. The accuracy of this improved method is higher than other current commonly used methods for determining the amount of copper(I) oxide. The effect of oxygen on the accuracy of the measurements was studied, which determined whether the operating environment of each step was in an aerobic or anaerobic environment. It was verified that ammonia can act as the solvent to completely dissolve the corrosion products without damaging the copper matrix. The amount of the copper(I) oxide formed on copper surface was also measured using this method. The potassium permanganate titration is particularly applicable to determine the amount of copper(I) oxide on the copper exposed in atmospheric environments in the absence of chloride ions.

Keywords: copper(I) oxide, potassium permanganate titration, quantitative determination, copper, atmospheric corrosion products

1. INTRODUCTION

Copper has excellent electric and thermal conductivity, machinability and glossy appearance, and it has been extensively used in microelectronic devices, and in artistic, structural and architectural applications. The widespread applications of copper in the atmospheric environment has led to an increasing chance of copper being damaged by atmospheric corrosion[1-7]. The presence of salt particles and air pollutants in the ambient environments will dramatically increase the atmospheric corrosion rate of copper and cause the formation of a large amount of corrosion products on the surface of copper [8-17].

The atmospheric corrosion of copper is quite complex, and the atmospheric corrosion products are various, which mainly depends on the exposure environments. In marine environments, the atmospheric corrosion products of copper include copper hydroxyl chloride, copper hydroxyl carbonate and copper(I) oxide. In the marine atmosphere containing sulfur dioxide pollutant gas, copper hydroxyl sulfate is normally found on copper surface in addition to the above products. Although there are many kinds of atmospheric corrosion products of copper in different exposure conditions, copper(I) oxide is one of the main products formed on copper under any circumstances. Quantitative analysis of the mass of copper(I) oxide in the corrosion products of copper is beneficial to analyze the atmospheric corrosion process and corrosion mechanism of copper. Therefore, it is of great significance to quantitatively characterize the mass of copper(I) oxide in the atmospheric corrosion products.

Up to now, the methods for quantitatively analyzing the mass of copper(I) oxide in the copper corrosion products include the coulometric reduction[8,18-22], infrared spectroscopy[23-25] and the ratio of the mass loss to the mass gain[26,27]. In coulometric reduction, a fixed reduction current density is applied to the specimen immersed in a deaerated electrolyte and the resulting variations of the open circuit potential of the specimen versus time are measured. Typically, one or more horizontal potential steps, which correspond to the specific reduction potentials of different products, can be found in the obtained potential-time plot. The amount of each product can be calculated by analyzing the total reduction charge of its corresponding horizontal potential step. This method has been proved to be applicable particularly to analyze the oxides formed on the surface of copper and silver. However, the specimen, in general, will be sealed using epoxy resin and only a part of the surface, normally 1 cm^2, will be exposed for performing the coulometric reduction tests. As we may know, the corrosion products are often not evenly distributed on the specimen surface, which leads to the generation of a large error of the obtained results by this method. Meanwhile, when the corrosion product layer is relatively thick, well-defined horizontal reduction potential steps normally cannot be obtained due to the resistance polarization of the corrosion product layer. Thus, large errors cannot be avoided by the calculation of the reduction electric charge, resulting in large errors of the obtained mass of copper(I) oxide by the coulometric reduction.

The mass of the copper(I) oxide in the corrosion products can also be estimated by analyzing the FTIR transmission spectra. The mass of the copper(I) oxide in the corrosion products can be calculated based on the Beer-Lambert law, $A = \varepsilon bc$, where A is the absorbance and it can be obtained by the intensity of the characteristic absorption band of copper(I) oxide, ε is the extinction coefficient of the absorbent. The value of the extinction coefficient of the copper(I) oxide can be obtained from the transmission spectra of pure copper(I) oxide. b is the thickness of the layer of the absorbent, and c is the concentration of the absorbent. However, the Beer-Lambert law is only a semi-quantitative analysis method and a lot of factors can affect the accuracy of this method, such as the nonuniformity of the products and non-monochromatic incident light. Meanwhile, this method is suitable for analyzing the products with low amount. When the amount of the copper(I) oxide is high, the Beer-Lambert law will deviate from the linear relationship, resulting in a large error of the obtained results

Normally, the corrosion products of copper include copper(I) oxide and copper hydroxyl chloride, copper hydroxyl carbonate, copper hydroxyl sulfate and copper hydroxyl nitrate [1-3]. The ratio obtained by dividing the mass loss using the mass gain can provide information about the corrosion product composition of copper. The corresponding ratio is 7.94 if copper(I) oxide is the only corrosion product. If the corrosion is only due to the formation of copper hydroxyl chloride, copper hydroxyl carbonate, copper hydroxyl sulfate, and copper hydroxyl nitrate, the ratio of mass loss to mass gain will be <3. Therefore, the mass of the copper(I) oxide in the corrosion products can be roughly analyzed according to the value of the ratio of mass loss to mass gain. However, this method can only roughly estimate the mass of copper(I) oxide in the corrosion products, and it cannot accurately characterize the mass of copper(I) oxide in the corrosion products of copper.

In the present paper, a potassium permanganate titration method was developed, and the principle of this method was described. This method can be used to quantitatively measure the mass of copper(I) oxide in the corrosion products formed on the copper surface, and it has very high accuracy of measurement (<±3%). This method can dissolve all of the corrosion products on the surface of the copper specimen, therefore, the uneven distribution of the corrosion products on the surface of copper specimen will not affect the accuracy of the measurement.

2. EXPERIMENTAL

2.1. Analysis of copper(I) oxide by the potassium permanganate titration

Figure 1 schematically illustrates the process for determining the mass of copper(I) oxide using the potassium permanganate titration, which mainly includes deaeration, dissolution of the corrosion products on the surface of the copper specimen, washing the specimen, oxidation and titration. Firstly, a high-purity nitrogen flow with the airflow rate of 100 $mL\cdot min^{-1}$ passed through the whole device to remove the oxygen, including passing through the aqueous ammonia solution, iron(III) sulfate solution, deionized water, as well as the empty bottles, for more than 1 h. Secondly, 50 mL deaerated aqueous ammonia solution ($V_{NH3\cdot H2O} : V_{H2O}$=1:3) was pressed into the empty bottle, where the copper specimen was put inside in advance. The bottle was ultrasonically vibrated for more than 30 minutes to make sure that the corrosion products on the copper specimen were completely dissolved in the deaerated aqueous ammonia solution. Thirdly, the copper specimen was pulled out of the aqueous ammonia solution and hung under the glass nozzle. A small amount of deionized water, which was deaerated in advance, was injected into and washed on the suspended copper specimen to remove the residual copper ammonia complex ions on its surface. Fourthly, 150 mL deaerated iron(III) sulfate solution (0.01 $mol\cdot L^{-1}$) acidified by sulfuric acid (1.8 $mol\cdot L^{-1}$) was pressed into the bottle containing the aqueous ammonia solution with the dissolved corrosion products. Of course, if the mass of copper(I) oxide in the corrosion product is relatively large, the amount of the added iron(III) sulfate solution must also be increased accordingly. Iron(III) sulfate reacts with cuprous ions and the ferric ions are reduced to ferrous ions. Finally, the ferrous ions obtained above was titrated at ambient atmosphere using the potassium permanganate solution (1.3425×10^{-3} $mol\cdot L^{-1}$). When the color of the solution changes from light green to light red, the titration ends. In addition to the titration step, the high-purity nitrogen flow was applied throughout the whole process to maintain the oxygen-free environment. The mass of the copper(I) oxide in the corrosion products formed on copper specimen can be calculated based on the volume and the concentration of the consumed potassium permanganate solution.

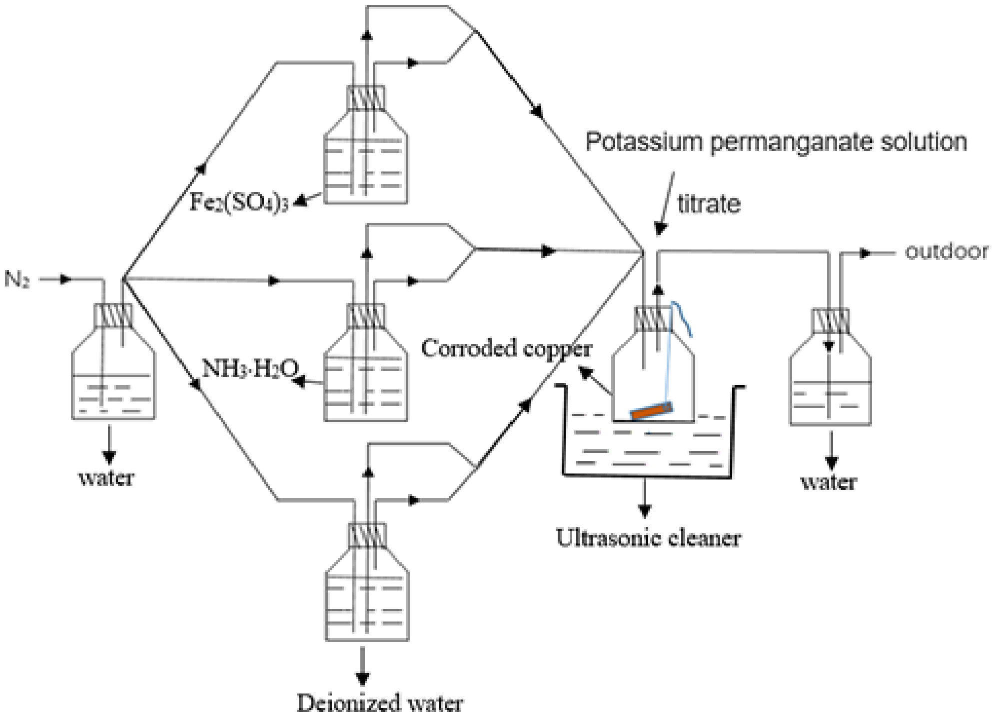

Figure 1. Schematic illustration of the processes for determining the mass of the copper(I) oxide formed on the copper specimen by the potassium permanganate titration.

2.2. Preparation and characterization of the copper(I) oxide layer on copper surface

The copper specimens were of 99.99% purity and 25×10×1 mm^3 in size. Each copper specimen was mechanically abraded and diamond polished down to 1 μm. All specimens were ultrasonically cleaned in acetone of analytical grade for approximately 10 min and then dried with a pure dry airflow. The copper specimens were subsequently immersed into a boiling saturated copper(II) sulfate solution for 20, 40 and 60 min, respectively, and then they were taken out, rinsed with deionized water, ultrasonically cleaned for 20 s, and finally rinsed with deionized water. A uniform copper(I) oxide layer was prepared on the copper surface.

The compositions of the products formed on the copper specimens were analyzed using X-ray diffraction (XRD, Ultima IV, Rigaku, Japan) and infrared spectroscopy (FT-IR, Nicolet IS10, Thermo

Fisher Scientific, USA). The microstructure of the products was characterized using scanning electron microscopy (SEM, TM3000, Hitachi, Japan).

2.3. Microgravimetry measurements

The amount of the copper(I) oxide formed on the copper surface was also quantified by measuring the mass difference after preparing copper(I) oxide layer on the copper surface and after removing all of the copper(I) oxide on the copper surface. Each copper specimen was weighed after preparing and removing all of the copper(I) oxide on the copper surface. A microbalance (Sartorius CPA 26P, Germany) with a ±4 μg-specified precision (±0.8 $\mu g \cdot cm^{-2}$ in this study) was used for the weight measurements. A reference stainless steel specimen was weighed to eliminate the system error of the microbalance during the weight measurement. The copper(I) oxide layer on the copper surface was ultrasonically removed using the deaerated aqueous ammonia solution ($V_{NH3 \cdot H2O}$: V_{H2O}=1:3). The limited removal of copper substrate during the dissolution of the copper(I) oxide in the deaerated aqueous ammonia solution was calibrated by a pure copper specimen without the copper(I) oxide layer on its surface. Triplicate specimens were taken for the measurements of the mass of the copper specimens after preparing and removing the copper(I) oxide products.

2.4. Coulometric reduction

A conventional three electrode cell was used to carry out the coulometric reduction testing[8,18-22]. The copper specimen was used as the working electrode. The exposed area of the working electrode is 1 cm^2, and the rest is sealed with epoxy resin. Ag/AgCl (saturated KCl) was used as the reference electrode and a platinum mesh was used as the counter electrode. The electrolyte for the coulometric reduction was 0.1 $mol \cdot L^{-1}$ Na_2SO_4 (pH=10) [18], which was purged with high-purity nitrogen gas prior to as well as during the coulometric reduction. The coulometric reduction was performed at a constant cathodic current density of -100 $\mu A \cdot cm^{-2}$. The electrode potentials mentioned in this paper are respect to a saturated KCl Ag/AgCl electrode.

3. RESULTS AND DISCUSSION

3.1. The principle for quantitatively determining the mass of copper(I) oxide by the potassium permanganate titration

As mentioned above, the method for quantitatively determining the mass of copper(I) oxide by potassium permanganate titration developed in this paper includes the following major steps, which are deaeration, dissolution of the corrosion products on copper surface, washing the specimen, oxidation of the cuprous ions, titration of the ferrous ions. In addition to the procedure of ferrous ion titration can be performed under aerobic conditions, the other steps must be strictly carried out under anaerobic conditions. Firstly, the corrosion products on the surface of copper reacted with the oxygen-free aqueous ammonia solution. The cuprous ions in the corrosion products were converted into monovalent copper ammonia complex ions, and the cupric ions in the corrosion products were converted into divalent copper ammonia complex ions. Secondly, the monovalent copper ammonia complex ions were oxidized into cupric ions by the iron(III) sulfate solution acidified by sulfuric acid. At the same time, iron(III) sulfate was reduced to iron(II) sulfate. Divalent copper ammonia complex ions are already at the highest valence of copper. Therefore, they will not participate in the oxidation reactions. Finally, the amount of the iron(II) sulfate in the solution was titrated with potassium permanganate. And the mass of copper(I) oxide in the corrosion products could be obtained based on the total volume (V_{KMnO4}) and the concentration (C_{KMnO4}) of potassium permanganate solution used in the titration process. The formula for calculating the mass of copper(I) oxide in the corrosion products is shown in Equation 1.

$$m_{Cu2O} = 2.5 \times 143 \times C_{KMnO4} \times V_{KMnO4} \quad (1)$$

where C_{KMnO4} is in mol·L^{-1}, V_{KMnO4} is in L, and m_{Cu2O} is in g.

The chemical reaction mechanism in the titration process is shown in Equations 2-5.

$$Cu_2O + 4NH_3 + H_2O = 2Cu(NH_3)_2^+ + 2OH^- \quad (2)$$

$$3H_2SO_4 + 2OH^- + 2Cu(NH_3)_2^+ = Cu_2SO_4 + 2(NH_4)_2SO_4 + 2H_2O \quad (3)$$

$$Fe_2(SO_4)_3 + Cu_2SO_4 = 2FeSO_4 + 2CuSO_4 \quad (4)$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O \quad (5)$$

3.2. Validation of the accuracy of the potassium permanganate titration

0.0112, 0.0312 and 0.0612 g of copper(I) oxide powder were weighed, and subsequently they were dissolved in the deaerated aqueous ammonia solution, respectively. The potassium permanganate titration was used to determine the amount of cuprous ions, thereby the mass of copper(I) oxide can be calculated by the amount of cuprous ions obtained by the potassium permanganate titration. The mass of the copper(I) oxide measured by the titration method were 0.0113, 0.0303 and 0.0606 g, respectively. The errors of the measurements are -0.89%, 2.88% and 0.98%, respectively, demonstrating that the potassium permanganate titration is feasible to accurately determine the mass of copper(I) oxide.

3.3. The effect of oxygen on the accuracy of the potassium permanganate titration

The conversion of Cu^+ to Cu^{2+} and Fe^{2+} to Fe^{3+} are involved in the potassium permanganate titration, and the presence of oxygen will probably affect these conversion processes, thus affecting the accuracy of the potassium permanganate titration. In the following, the effect of oxygen on the accuracy of the potassium permanganate titration would be studied.

0.0156, 0.0292 and 0.0375 g of copper(I) oxide powder were weighed, and they were placed in three different conical flasks in the ambient environment, respectively. 50 mL aqueous ammonia solution ($V_{NH3·H2O} : V_{H2O} = 1:3$) was added to each conical flask to dissolve the copper(I) oxide in it. And the steps of dissolution of the copper(I) oxide power and oxidation of cuprous ions to cupric ions were all operated in ambient environment. The mass of the copper(I) oxide measured by the potassium permanganate titration in the ambient environment were 0.0117, 0.0229 and 0.0291 g, respectively.

The masses of the copper(I) oxide obtained by the potassium permanganate titration in the ambient environment are much lower than those obtained by microbalance, demonstrating that oxygen was directly involved in the process of oxidizing Cu^+ to Cu^{2+}. The oxygen-driven oxidization process of Cu^+ to Cu^{2+} makes the consumption of the amount of the ferric ions be less, resulting in the decrease of the mass of the copper(I) oxide obtained by the potassium permanganate titration in the ambient environment. The errors of the potassium permanganate titration in the ambient environment are 25.0%, 21.6% and 22.4%, respectively. Therefore, the presence of Cu^+ in the solution need to avoid the interference of oxygen. That is to say, the steps of dissolution of the corrosion products on the surface of the copper specimen, washing the specimen and oxidation of cuprous ions to cupric ions must be carried out in an anaerobic environment.

Oxygen may also affect the oxidation of ferrous ions to ferric ions, thus affecting the accuracy of the potassium permanganate titration. The iron(II) sulfate solution with the concentrations of 0.001, 0.005 and 0.01 $mol \cdot L^{-1}$ was prepared and air was bubbled into the test solution (air flow rate is 60 $mL \cdot min^{-1}$) for 1, 3, 5 and 8 min. The concentration of the iron(II) sulfate in the solution was titrated by the potassium permanganate solution in the ambient atmosphere. The variation percentages of the concentration of the iron(II) sulfate solution versus time are measured, and the results are shown in Figure 2. As shown in Figure 2, the concentration variations of iron(II) sulfate are not significant within the time frame of this experiment, and they do not increase with the increase of the duration of air bubbling. The concentration variations of iron(II) sulfate only randomly change from -0.4% to 0.7%, which may be due to the accidental errors of the measurements. The results demonstrate that oxygen in the air has little effect on the oxidation of ferrous ions to ferric ions in the iron(II) sulfate solution within the time frame of the titration step in this work. Therefore, the titration step in the potassium permanganate titration can be directly performed in ambient environment.

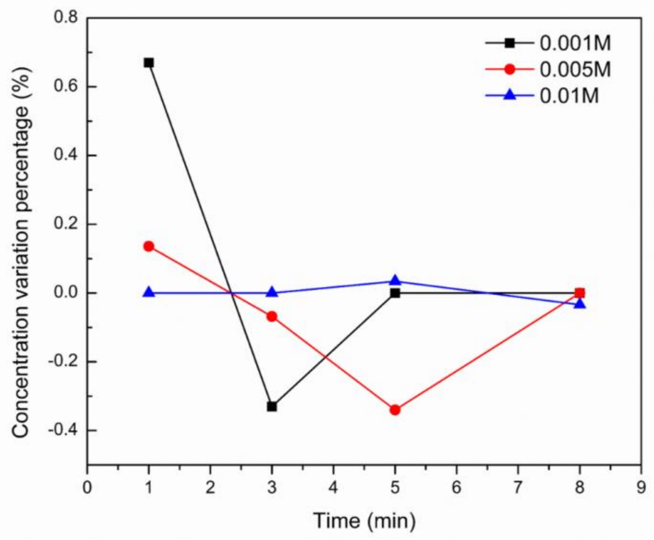

Figure 2. Variation percentages of the concentration of the iron(II) sulfate solution after 1, 3, 5 and 8 min of bubbling air into the iron(II) sulfate solution with the concentrations of 0.001, 0.005 and 0.01 $mol \cdot L^{-1}$. The bubbling air flow rate is 60 $mL \cdot min^{-1}$.

3.4. Quantitative study on the mass of copper(I) oxide produced on copper surface by the potassium permanganate titration

As mentioned above, the potassium permanganate titration developed in this paper can be used to accurately determine the mass of copper(I) oxide. In this section, the mass of copper(I) oxide produced on copper surface was measured using this method. In order to further verify the accuracy of the potassium permanganate titration, the results obtained by this method are compared with those obtained by the microgravimetry and the coulometric reduction.

A uniform and dense copper(I) oxide layer was produced on the surface of the pure copper specimen by immersing it into a boiling saturated copper(II) sulfate solution for 20, 40 or 60 min. Take 40 min as an example, the morphology and the composition of the products formed on the copper surface were characterized by SEM, XRD and FT-IR spectroscopy, and the results are shown in Figures 3-5. Figure 3 shows the SEM image of the products formed on the copper specimen after 40 min of immersion in the boiling saturated copper(II) sulfate solution. A relatively uniform and dense product layer was observed on the copper surface.

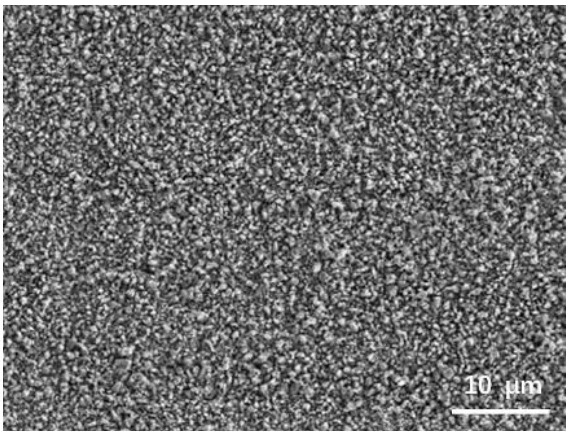

Figure 3. SEM image of the products formed on the surface of the copper specimen after 40 min of immersion in the boiling saturated copper(II) sulfate solution.

The crystal structures of the products formed on the copper specimen after 40 min of immersion in the boiling saturated copper(II) sulfate solution were characterized using XRD patterns and the results are shown in Curve a in Figure 4. The diffraction peaks at 2θ = 43.41°, 50.56° and 74.30° in Curve a were observed, which are assigned to the (111), (200) and (220) crystal planes of metallic copper (JCPDS Card No. 65-9743), respectively. In addition to the diffraction peaks from the copper substrate, the diffraction peaks at 2θ = 29.55°, 36.42° and 61.34° were observed, which are assigned to the (110), (111) and (220) crystal planes of copper(I) oxide (JCPDS Card No. 05-0667), respectively.

The products formed on the copper specimen after 40 min of immersion in the boiling saturated copper(II) sulfate solution were also characterized by FT-IR spectroscopy and the results are shown in Figure 5. The peaks at around 3448 cm^{-1} and 1627 cm^{-1} are the characteristic absorption peaks corresponding to the vibrations of OH^- and H_2O. The peak at around 620 cm^{-1} is due to the vibration of Cu-O bonds from Cu_2O[23-25].

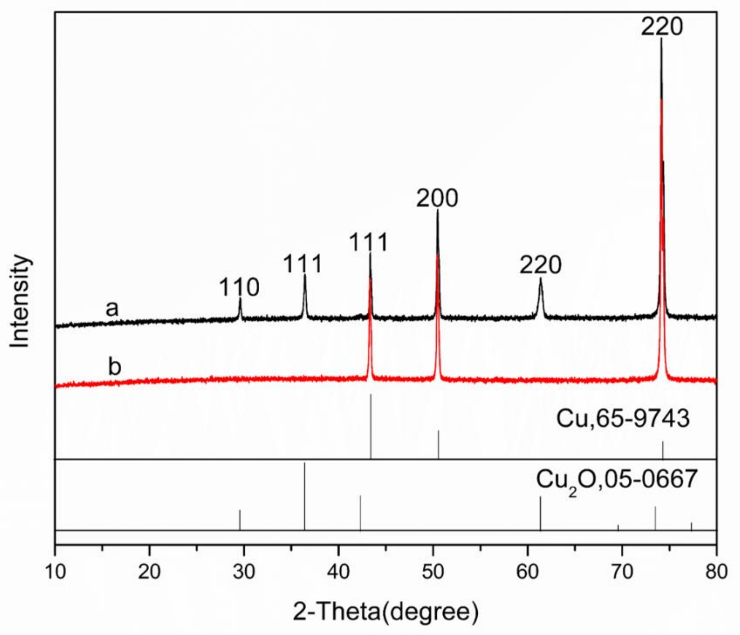

Figure 4. XRD patterns of the copper specimen after 40 min of immersion in the boiling saturated copper(II) sulfate solution (Curve a) and subsequently after 30 min of dissolution in the deaerated aqueous ammonia solution (Curve b).

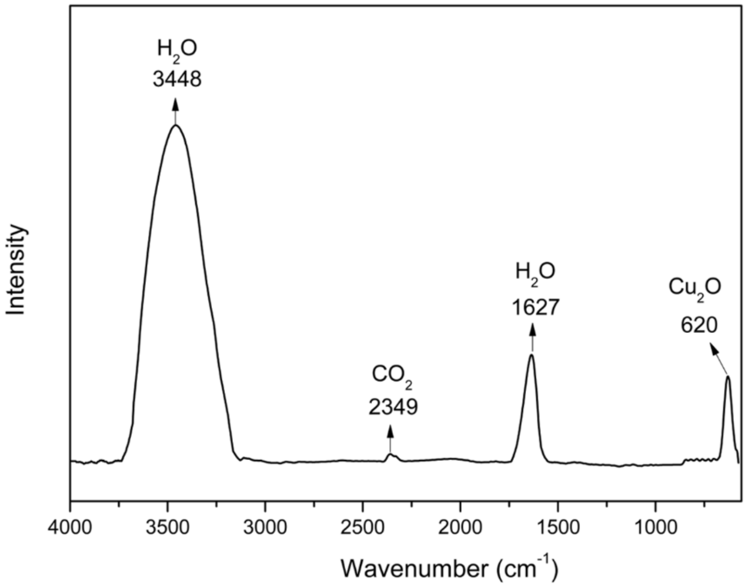

Figure 5. FT-IR spectrum of the products formed on the copper specimen after 40 min of immersion in the boiling saturated copper(II) sulfate solution.

Based on the results obtained from Figures 3-5, a relatively uniform and dense copper(I) oxide layer were prepared on the copper surface, and there were no other products except for copper(I) oxide formed on the copper surface.

The mass of the copper(I) oxide formed on the copper surface after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution was measured using the potassium permanganate titration. The experimental results show that the mass of the copper(I) oxide formed on the copper surface after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution was 200.8±6.5 $\mu g \cdot cm^{-2}$, 318.8±10 $\mu g \cdot cm^{-2}$ and 370.9±10 $\mu g \cdot cm^{-2}$, respectively.

In addition to the accuracy of the potassium permanganate titration itself, the accuracy for determining the mass of copper(I) oxide formed on the surface of the copper specimen by the potassium permanganate titration is also related to whether the products on the copper surface can be completely dissolved in the deaerated aqueous ammonia solution. If the products formed on the surface of the copper specimen cannot be completely dissolved in the deaerated aqueous ammonia solution, it is still impossible to accurately measure the mass of copper(I) oxide formed on the copper surface although the potassium permanganate titration itself possesses very high accuracy. Therefore, it is necessary to determine whether the products formed on the copper surface can be completely dissolved in the deaerated aqueous ammonia solution during the titration process. Curve b in Figure 4 shows the XRD patterns of the copper specimen after 40 min of immersion in the boiling saturated copper(II) sulfate solution and subsequently after 30 min of dissolution in the deaerated aqueous ammonia solution. As the results shown in Curve b in Figure 4, the diffraction peaks from the copper substrate were observed. While, those related to copper(I) oxide were disappeared after 30 min of dissolution in the deaerated aqueous ammonia solution, demonstrating that the copper(I) oxide formed on the copper surface was completely dissolved into the deaerated aqueous ammonia solution.

The copper substrate itself may react with ammonia to produce monovalent copper ammonia complex ions, thus affecting the accuracy of the titration method. For this purpose, blank copper specimens without any products on their surfaces were titrated according to the titration procedure, and the variations of the mass of the copper specimens and the mass of the cuprous ions in the solution after titration were measured. The results indicated that no significant mass changes of the blank copper specimens before and after titration were observed and the cuprous ions were not found in the aqueous ammonia solution after titration, demonstrating that metallic copper would not dissolve in the deaerated aqueous ammonia solution during the titration process.

Since the corrosion products formed on the copper surface can be complexed with ammonia to form monovalent and divalent copper ammonia complex ions, and no disproportionation reactions occur during this process. Therefore, this method makes it be possible to more completely remove the corrosion products formed on the copper surface and get very accurate data concerning about the amount of the corrosion products formed on the copper surface. Thus, this method can be used to measure the mass loss of the copper specimen after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution, and the mass of the copper(I) oxide formed on the copper specimen after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution can be calculated based on the mass loss data. The results indicated that the mass of the copper(I) oxide formed on the copper specimen after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution was 206.6±3.97, 326.3±4.08 and 363.6±4 μg·cm^{-2}, respectively.

As discussed above, a uniform copper(I) oxide layer was formed on the copper surface after 20 min, 40 min or 60 min of immersion in the boiling saturated copper(II) sulfate solution. Therefore, it is very convenient to quantitatively analyze the mass of the copper(I) oxide using the coulometric reduction. Figure 6 shows typical potential vs. time curves during the coulometric reduction of the copper(I) oxide layer formed on the copper surface after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution at a constant current density of ic = -100 μA·cm^{-2} in a deaerated 0.1 mol·L^{-1} Na_2SO_4 (pH=10) solution. Two distinct voltage plateau regions are observed. The first plateau is located in the potential range of -0.65 V to -0.75 V (vs. Ag/AgCl), which corresponds to the reduction of copper(I) oxide. The second plateau is located in the vicinity of -1.05 V (vs. Ag/AgCl), which is due to the hydrogen evolution on the bare copper surface. The amount of the copper(I) oxide can be calculated from the reduction charge based on Faraday's law, and the results indicated that the mass of the copper(I) oxide formed on the copper surface after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution was 187.8±20, 354.7±38.7 and 386.7±39 μg·cm^{-2}, respectively.

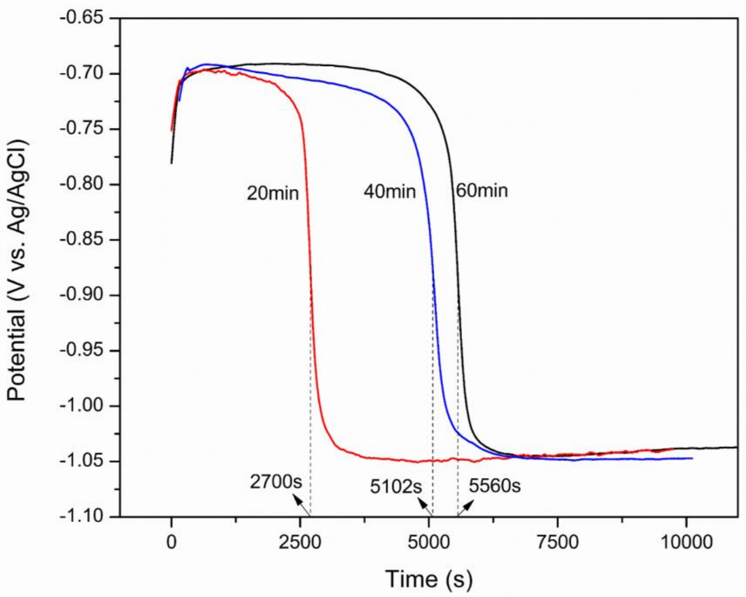

Figure 6. Potential vs. time curves during the coulometric reduction of the copper(I) oxide layer formed on the copper surface after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution at a constant current density of ic = -100 μA·cm^{-2} in a deaerated 0.1 mol·L^{-1} Na_2SO_4 (pH=10) solution.

In general, the microgravimetry method is often used to accurately determine the mass of the formed corrosion products if the chemical solvents can dissolve all of the corrosion products without damaging the metal substrate[31-33]. In this paper, copper(I) oxide is the only corrosion product and the aqueous ammonia solution can dissolve all of the copper(I) oxide without damaging the copper substrate. Thus, the amount of copper(I) oxide measured by the microgravimetry method is considered to be the most reliable data. Coulometric reduction is often used to determine the mass of the corrosion products formed on copper surface. However, the reduction platform is easy to procrastinate and results in the formation of a slope, as described in the literatures[22-24], leading to generation of errors in determining the reduction time. Therefore, the mass of copper(I) oxide obtained from the microgravimetry measurements is regarded as the standard value. And, the data obtained by the titration and coulometric reduction was compared with those obtained by microgravimetry. Figure 7 shows the histogram of the mass of copper(I) oxide, formed on the copper surface after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulphate solution, measured by the potassium permanganate titration, microgravimetry and the coulometric reduction, respectively. Obviously, the deviation of the mass of the copper(I) oxide obtained by the potassium permanganate titration is much smaller than that of the mass of the copper(I) oxide measured by the coulometric reduction. The error of the potassium permanganate titration was calculated and it is still lower than 3% on the premise that the data obtained from the microgravimetry measurements are accurate ones. While, the error of the coulometric reduction was in the range of 4% to 11%, which are much larger than that of the potassium permanganate titration.

Although the coulometric reduction curves obtained from this work are good, the potassium permanganate titration is still more accurate than the coulometric reduction. And in the natural environment, the corrosion products formed on copper surface are very complicate and are not uniformly distributed on the surface of copper. Therefore, in the determination of the amount of copper(I) oxide in the corrosion products, the potassium permanganate titration is much better than the coulometric reduction.

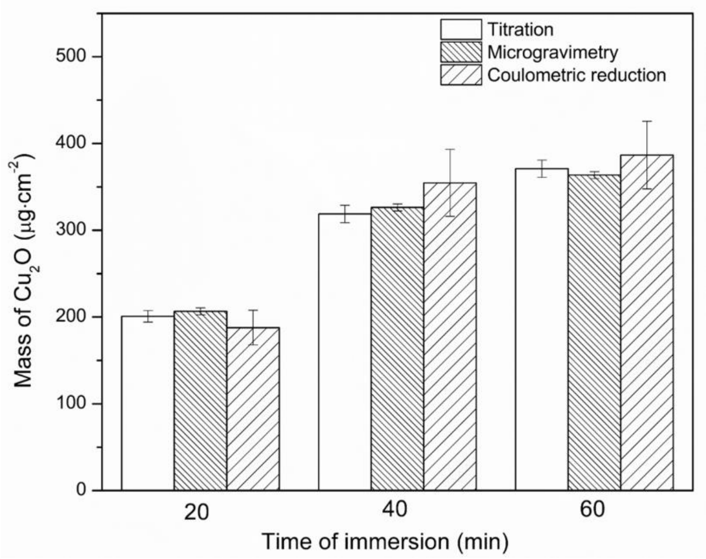

Figure 7. Mass of copper(I) oxide, formed on the copper surface after 20, 40 and 60 min of immersion in the boiling saturated copper(II) sulfate solution, measured by the potassium permanganate titration, microgravimetry and coulometric reduction, respectively.

3.5. Limitations

The potassium permanganate titration developed in this work has important limitations although it can accurately measure and analyze the amount of cuprous ions in the corrosion products formed on copper. This method is only applicable to the analysis of the case where the copper(I) oxide is the only cuprous ion corrosion product. Therefore, this method is particularly suitable for the analysis of the $(NH_4)_2SO_4$ particles induced atmospheric corrosion of copper because the only corrosion products produced are copper(I) oxide and copper hydroxyl sulfate in this case. However, for chloride ion-induced atmospheric corrosion of copper, the cuprous ion corrosion products contain a small amount of cuprous chloride in addition to copper(I) oxide. In this case, the mass of the copper(I) oxide obtained by the potassium permanganate titration developed in this paper will tend to be larger than the real value. Because the amount of cuprous chloride is relatively small, the cuprous chloride is unstable and it does not respond to the infrared light, the existing literature rarely reports the observation of cuprous chloride in the corrosion products of copper [28-30]. Therefore, by combining the potassium permanganate titration developed in this work with the coulometric reduction, the mass of the cuprous chloride in the corrosion products can be quantitatively calculated.

4. CONCLUSIONS

The potassium permanganate titration developed in the present work can accurately measure the mass of the copper(I) oxide formed on copper. And, the accuracy of the mass of the copper(I) oxide obtained by the potassium permanganate titration is much higher than that of the mass of the copper(I) oxide obtained by the coulometric reduction. Meanwhile, it was found that the aqueous ammonia solution can completely dissolve the corrosion products of copper, and the dissolution process of the corrosion products do not undergo disproportionation reactions, thus the mass loss of copper can be much accurately measured by the microgravimetry.

The potassium permanganate titration is very useful for studying the $(NH_4)_2SO_4$ particles induced atmospheric corrosion of copper since the copper(I) oxide is the only cuprous ion corrosion products formed in this environment. However, for the atmospheric corrosion of copper caused by the chloride ions, the cuprous ion corrosion products contain not only copper(I) oxide but also a small amount of cuprous chloride. The amount of copper(I) oxide obtained by the potassium permanganate titration herein will be the sum of the total mass of the copper(I) oxide and cuprous chloride formed on copper surface, resulting in obtaining a higher amount of copper(I) oxide. However, by combining the potassium permanganate titration developed in this work with the coulometric reduction, the mass of the copper(I) oxide and cuprous chloride in the corrosion products can be quantitatively calculated, respectively. The method for quantitative calculating of the mass of cuprous chloride has never been reported in the current literature.

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