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Study on the inhibiting behavior of AMT on bronze in 5% citric acid solution

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The corrosion behavior of bronze in the presence of 2-amino-5-mercapto-1,3,4-thiadiazole (AMT) has been investigated in 5% citric acid by electrochemical measurements such as potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS). It has been revealed that AMT is a good inhibitor for bronze. Both cathodic process and anodic process on bronze treated with AMT were different from that on the bronze without AMT treatment. Fourier transform infrared (FTIR) analysis was carried out to characterize the protective film, which revealed that the composition of the protective film was polymeric Cu(I)-inhibitor complex. AMT acted as bidentate ligand through the aminic nitrogen atom and the closed ring nitrogen in the complex.

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1. Introduction

Corrosion of bronze artefacts is a serious problem for archaeologists, numismatists and archaeological chemists. Some corrosion products, such as CuO, $Cu(OH)_2 \cdot CuCO_3$, are useful for corrosion protection. But cuprous chloride, one of the corrosion products of artefacts, has no protection ability. For the bronze artefacts with this compound on their surfaces, the corrosion process is continued after excavation from early graves. Furthermore, this powdery corrosion product can be removed by wind. New corrosion processes will begin if this powdery product falls down on other un-corroded surfaces. This phenomenon is named bronze disease[1, 2]. Many attempts have been made to clean excavated bronze artefacts with different chemical compounds, such as formic acid, alkaline glycerol, sulphuric acid and citric acid.

However, these chemical compounds were unsatisfactory because they leached out some of the alloying metals during treatment. Moreover, corrosion products could not be removed completely. A few organic inhibitors such as benzotriazole (BTA) have also been used to arrest corrosion by the protective layer composed of Cu-BTA polymeric complex. However, this complex covers the details of coins and artifacts. On the other hand, BTA can neither remove the powdery rust effectively nor replace chloride ions.

Some researches showed that 2-amino-5-mercapto-1,3,4-thiadiazole is an excellent inhibitor for copper and its alloys [3–7]. Ganorkar [8] revealed that AMT acts as an excellent remover for cuprous chloride powder. Furthermore, the inscriptions and other details of bronze cultural relics were very clear and visible after the treatment.

Even though the scientists have found the promising use of AMT, the aspects of the inhibitive mechanism and characteristics of AMT towards the corrosion of bronze in the citric acid have not been studied efficiently and systematically yet. In this present work, the inhibiting ability, the inhibiting mechanism and the chemical component of the AMT protective film were investigated by the electrochemical method, FT-IR and STM.

2. Experimental method

2.1. Chemical and materials

The Aggressive environment was an aqueous solution containing 5% citric acid (pH 2). The concentration of AMT was 7.5 mmol/L. AMT was produced by Nanjing Museum. Citric acid was analytical grade. Solutions were prepared using double distilled water.

Bronze (Cu 87.4%, Sn 10.15%, Pb 2.36%, wt%) was employed as specimens. The specimens for potentiodynamic and EIS measurement were covered by epoxy resin with 10 mm × 10 mm of working surface left.

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The specimens for reflection FTIR was a Bronze plate of 10 mm × 10 mm × 2 mm size. All the specimens were ground with SiC paper down to 800 grit, polished to 0.5 μm, and then rinsed with distilled water and acetone with ultrasonically cleaning before experiment.

2.2. Equipment and methods

The corrosion rate of bronze was measured by CMB-1510 Portable Corrosion Rate Measurement Instrument. The corrosion rate was measured using the weak polarization method. Polarization potential was ±40 mV and the time of interval measurement was 20 mins

The potential dynamic measurement was conducted on an EG&G Model 273 potentiostat instrument with 0.167 mV/s scan rate. During measurement, the IR drop in the solution was deducted automatically by a current intermittent method. For all electrochemical measurements, a three-electrode system cell was employed with platinum auxiliary and saturated-calomel reference electrode (SCE) under aerated conditions. Data were collected by PC computer and analyzed by CorrView software with Corrosion rate (i_{corr}), corrosion potential (E_{corr}), Tafel slope of anodic and cathodic reaction (β a, β c) obtained after curve fitting.

EIS measurement was conducted on EG&G Par M378 measurement system consisting of Model 273 potentiostat instrument and 5208 two-phase lock-in analyzer. Frequency was in the range of 100 kHz–10 MHz and amplitude was 10 mV. EIS data were fitted with Z-View 2.1 software.

Magna-IR 560 infrared spectrometer (Nicolet Co.) was used for IR spectra analysis. Reflection spectra were obtained by using a Vee Max reflection accessory (Nicolet Co.) attached to the spectrometer.

RFS100 Raman Spectrometer (Bruker) was used for Raman spectra analysis. The scan range was changed from 4000 to 100 cm^{-1} and resolution was 4 cm^{-1}.

3. Results and discussion

3.1. The inhibiting ability of AMT for bronze in citric acid solution

Fig. 1 shows the corrosion rate of bronze in 5% citric acid with and without AMT at room temperature. It can be seen that the corrosion behavior of bronze changed as the AMT is added to the solution. In the solution without AMT, the corrosion rate of bronze decreases sharply in first hour, and oscillated around the lowest value for next 4 h of immersion, and then, increased again and kept at a stable value after 5 h immersion. Bastidas's group [5] found that a cuprous oxide film formed on the surface in citric acid solution and resulted in a decrease of i_{a}. However, this oxide film was not compact and grew with the increasing immersion time. Cracks appeared in the oxide film when the oxide film was thick enough. Aggressive ions can transport from solution to the surface of metal via those defects and result in an increase of i_{a}.

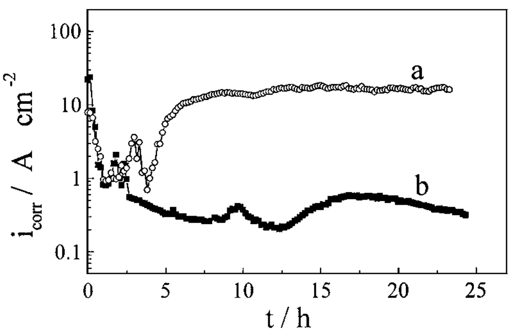


Figure 1 Corrosion rate and time curve of bronze in 5% citric acid with and without AMT: (a) without AMT and (b) with AMT.

The corrosion rate of bronze did not change in the initial 2 h immersion when AMT was added to the solution; after that, the corrosion rate slowed down. 4 hr later, the corrosion rate kept at a stable value. In this case, the corrosion rate is lower than that without AMT. This means the corrosion process of bronze has been inhibited by AMT. Inhibiting efficiency calculated by the formula IE% $= (1 - i_{\mathrm{b}}/i'_{\mathrm{a}}) \times 100\%$ was 97%, where i'_{a} and i'_{b} are the average corrosion current density after 5 h immersion without and with AMT respectively. Based on the results above, it can be known that AMT is a good inhibitor for bronze in citric acid solution.

3.2. Possible inhibiting mechanism of AMT

Fig. 2 shows the polarization curves of bronze in 5% citric acid solution at 60°C after 4 hr immersion. Obviously, the presence of AMT cause a remarkably decrease in corrosion rate. The anodic process also changed from a process controlled by electrochemical reaction to that controlled by a mass transportation process. This was attributed to the protective film formation on the bronze.

Corrosion potential (E_{corr}), corrosion current density (i_{corr}) and inhibition efficiency (IE%) of bronze with and without the presence of AMT in solution were listed in Table I. It reveals that the corrosion potential did not change, but the corrosion current density decreases considerably. From the polarization curve, It can be seen that the overpotential of both cathodic and anodic process on bronze treated by AMT were much higher than

TABLE I Electrochemical parameters of bronze in 5% citric acid (60°C)

Medium	E_{corr}/V	$i_{\mathrm{corr}}/\mu A \cdot \mathrm{cm}^{-2}$	IE(%)
Blank	−0.0308	13.9	–
With AMT	−0.0423	1.71	87.7

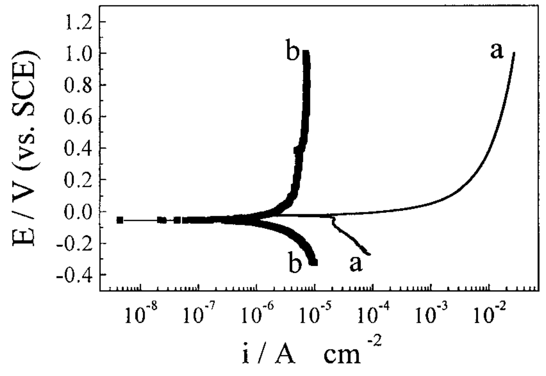


Figure 2 Polarization curves of bronze in 5% citric acid at 60°C: (a) blank and (b) with AMT.

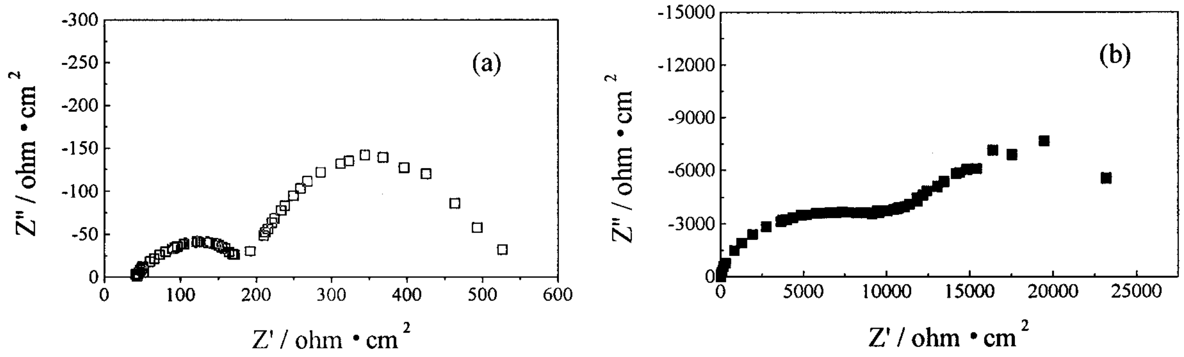


Figure 3 Nyquist plots of bronze in 5% citric acid (60°C): (a) blank and (b) with AMT.

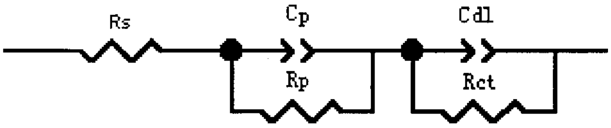


Figure 4 Electrical equivalent circuit for EIS in Fig. 3.

those without treatment. That indicates both anodic and cathodic reactions were restrained as AMT was added in solution.

EIS measurements have been conducted on the bronze in 5% citric acid with and without AMT at 60°C. The results are shown in Fig. 3. The equivalent circuit for those EIS is shown in Fig. 4. The shape of the Nyquist plots for the bronze in citric acid solution with and without AMT is similar, presenting two depressed semicircles at high and low frequency ranges. The semicircle in the high-frequency range represents the bulk properties of the organic film, and the semicircle at low-frequency represents the properties of film/substrate interface [9–11]. However, the diameters of those semicircles were different if AMT is present. The one with AMT present is larger.

EIS was analyzed by Zview software [?]. The results are listed in Table II. R_p is the pore resistance resulting from the existence of ionically conducting paths across the surface film, associated with the corrosion products in a blank test, and with the inhibitors complex film in the inhibition test. R_p, together with C_p, is a useful parameter to interpret the impedance spectra in the high frequency range. C_{dl} is the capacitance corresponding to the metal/protective layer interface at which corrosion occurred. The capacitance value is lower when organic inhibitor exists. R_{ct} is the polarization resistance. It is larger when inhibitor exists in the blank solution.

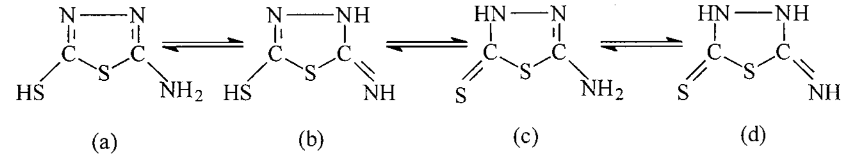
TABLE II Fitted results of bronze electrode in 5% citric acid with and without AMT

Fitted element	R_s ($\Omega \cdot cm^2$)	R_p ($\Omega \cdot cm^2$)	C_p ($F \cdot cm^{-2}$)	R_{ct} ($\Omega \cdot cm^2$)	C_{dl} ($F \cdot cm^{-2}$)
(a) blank	42.4	1.57E2	1.02E-3	3.28E2	3.17E-2
(b) with AMT	20.9	7.58E3	4.19E-6	1.94E4	8.11E-5

In the solution without AMT, the EIS of bronze presents low R_p, low R_{ct}, high C_p and high C_{dl}. This was attributed to cuprous oxide forming. Cuprous oxide film grew initially with a porous structure where corrosion ions are easy to pass through. Copper dissolution occurred at the bottom of the pores [5]. With AMT addition, the EIS presents high R_p, high R_{ct}, low C_p and low C_{dl}, which implies that a protective film formed.

3.3. The chemical characters of inhibition film

AMT exists in four tautomeric forms (a–d) in nature. They coexist in the solid state, but amino-thione (c) is the dominant one. The structures are plane, whose 1,3,4-thiadiazole is aromaticity [12, 13].



Previous papers [6, 7, 14] revealed that polymeric copper-AMT complex covered the bronze surface after treatment. In order to obtain some information on the vibration properties of copper complex with AMT and

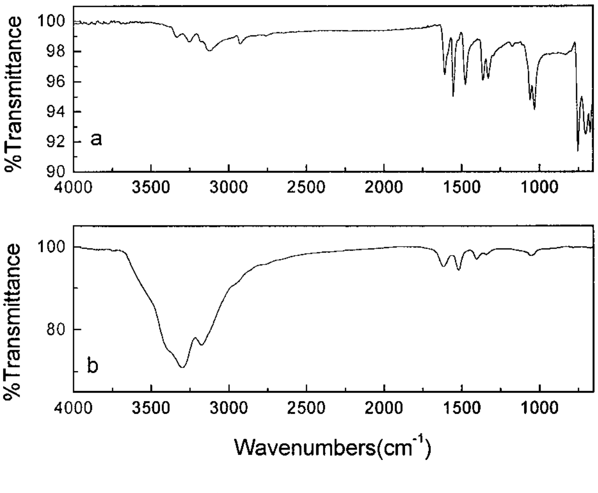


Figure 5 FT-IR spectra of AMT on (a) pure organic compound power and (b) the film on the bronze surface after immersion in the solution of AMT +5% citric acid.

TABLE III Assignment of vibration spectra of AMT and bronze surface film

	AMT		Surface film
Assignment	FTIR	Raman	FTIR
$\nu_{as}(NH_2)$	3332 (m)		3309(s)
$\nu_{s}(NH_2)$	3254 (m)	(3250 (w), 3175 (w)	3179(s)
ν (N_{ring}—H)	3121 (s), 2925 (m)	3138 (w), 2924(w)	
δ (N—H)$_{in-plane}$	1607(s)	1614(w)	1614(w)
Ring modes			
ν (C=N)	1553 (s), 1474 (s)	1541 (s), 1479 (s)	1519 (w), 1401 (w)
ν (C—N)	1361 (m), 1327 (m)	1365 (m), 1330(m), 1294 (m), 1201 (w)	1341 (w)
ν (C=S)	1169 (w)		
ν (N—N)	1059 (s), 1031 (s)	1042 (m)	1048 (m)
δ (N—H)$_{out-of-plane}$, Ring$_{in-plane}$ bending	752 (s), 704 (m)	755 (s)	
Ring torsion + ν (CS)	673 (m)	671 (m)	

s: strong; m: medium; w: weak.

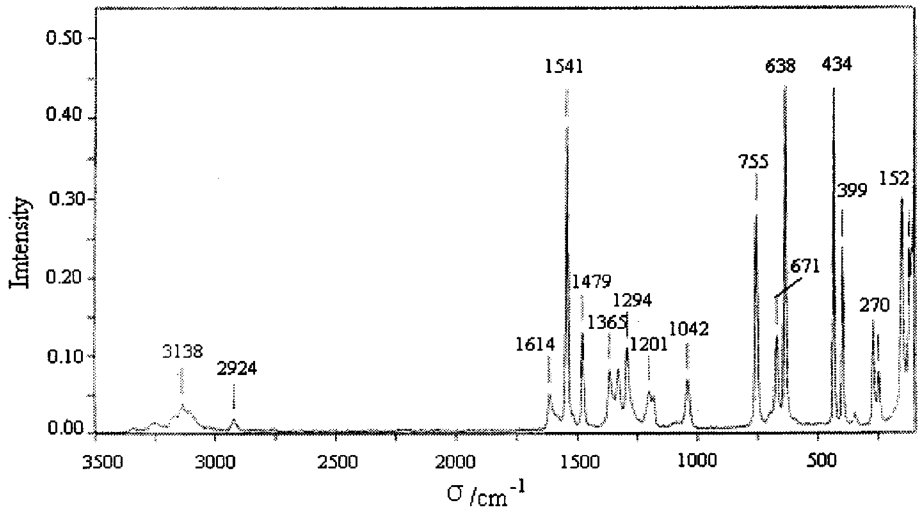


Figure 6 Raman spectra obtained for AMT on pure organic compound powder.

give some insights in the coordination mode of the ligand, the film on the bronze surface in 5% citric acid with AMT were investigated by FT-IR and surface enhanced raman spectra. The results are shown in Figs 5 and 6. The IR spectra of free AMT and its metallic complex were provided in references [15–17].

For the FT-IR spectrum of free AMT, the bands at 1607,1553,1361 cm^{-1} are assigned to 1,3,4-thiadiazole vibrations. For the FT-IR spectrum of bronze treatment by AMT, 1,3,4-thiadiazole vibrations shift to 1614,1519,1341 cm^{-1} for the rigidity of penta-atomic ring which contained three potentially coordinated atoms.

In the free AMT spectrum, the bands at 3332,3254 cm^{-1} (3250 cm^{-1} in Raman) are assigned to v $_{as}(NH_2)$ and v $_{s}(NH_2)$ modes, respectively. The band at 1614 and 755 cm^{-1} is assigned to in plane and out-of-plane bending of the amine group respectively. On the other hand, for the complexes' IR spectra, the band of the (NH_2) anti-symmetric stretching vibration shifted to low frequencies (3309 cm^{-1}). This suggests that amine group is involved in metal ion coordination. The ligand band at 1553 cm^{-1} assigned to an important v (C=N) contribution shifted significantly to 1519 cm^{-1} in the surface film. It indicated that the ring nitrogen atom closest to amine group is coordinated. Based on these results, we can come to the conclusion that AMT acts as bi-dentate ligand through aminic nitrogen atom and closest ring nitrogen in the complex.

Moreover, the chemical state of the copper atom can be analyzed by FT-IR spectrum. It is well known that two characteristic bands due to Cu(I)AMT are expected to appear in the IR zone 1600 ± 10 cm^{-1}, 1515 ± 5 cm^{-1}. [15] In our complex spectra (see Table III), these bands were observed at 1614,1519 cm^{-1}. This is a spectral evidence that confirms Cu(I)AMT covers the bronze surface.

4. Conclusion

AMT is an effectively inhibitor that decreases the corrosion of bronze in citric acid, which was attributed mainly to the protective film formed by an AMT complex. Both anodic and cathodic reactions on bronze have changed after treated by AMT. A polymeric Cu(I)-inhibitor complex that totally covered the bronze surface was identified. In the complex, AMT acts as a bidentate ligand through the aminic nitrogen atom and the closed ring nitrogen in the complex.

Acknowledgments

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