*Journal of Applied Electrochemistry* **29**: 1339–1345, 1999.

# Investigation of copper corrosion inhibition by STM and EQCM techniques

E. SZŐCS[1], Gy. VASTAG[2], A. SHABAN[1], G. KONCZOS[3] and E. KÁLMÁN[3]
[1]*Chemical Research Center, HAS, Bp., H-1525, PO Box 17, Hungary;*
[2]*University of Novi Sad, Faculty of Natural Sciences and Mathematics, 21000 Novi Sad, Yugoslavia;*
[3]*Bay Zoltán Institute for Materials Science and Technology, H-1116 Budapest, Fehérvári út 130, Hungary*

Received 15 December 1998; accepted in revised form 9 June 1999

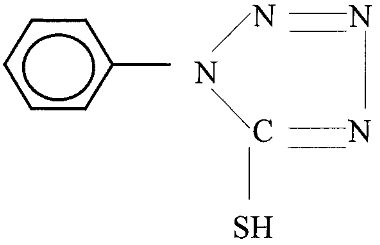
*Key words:* copper corrosion inhibition, EQCM, STM, 5-mercapto-1-phenyl-tetrazole

## Abstract

The mechanism of copper corrosion and its inhibition were studied using electrochemical techniques, *in situ* scanning tunneling microscopy (STM) and electrochemical quartz crystal microbalance (EQCM) methods. The morphological changes of Cu (111) were followed in 0.1 M $Na_2SO_4$ solution at pH 2.95. The adsorption of 5-mercapto-1-phenyl-tetrazole (5-McPhTT) at different concentrations was studied. The anodic dissolution of copper in 0.1 M $Na_2SO_4$ was clearly modified and hindered by the addition of 5-McPhTT. The anodic current density was reduced sharply due to the adsorption of the inhibitor on the metal surface thus providing protection. EQCM data revealed that the addition of the inhibitor to the aggressive solution did not cause a continuous increase in the electrode mass. This fact indicates that the inhibitor effect in hindering copper corrosion was due to the adsorption of a monolayer or even a submonolayer.

## 1. Introduction

It is well known that benzotriazole inhibits copper corrosion in neutral and alkaline solutions, but that it is less effective in acidic solutions [1,2]. The inhibition is due to the formation of thin layers of copper-inhibitor complexes and probably the formation of copper oxide layers protected by inhibitors. The search for environmentally friendly inhibitors has been the main task for researchers. Against copper corrosion in neutral chloride solutions, 5-mercapto-1-phenyl-tetrazole (5-McPhTT) showed an excellent inhibition efficiency [3]. The molecular structure of the 5-McPhTT is shown below:



The electron donation of nitrogen and the protonation properties of the –SH group play an important role in the adsorption process. The 5-McPhTT molecule adsorbs probably through the $-S^-$ or through coordination with nitrogen from the tetrazole ring [3]. It is well recognized that electrode properties depend on the structure of the electrode surface. Direct structural information on the surface changes due to its inhibition can be obtained by *in situ* structural sensitive techniques, such as scanning tunnelling microscopy (STM). Recently, the atomic and nanoscale, as well as morphological, changes during copper dissolution were observed by *ex situ* [4,5] and *in situ* [5–8] STM–AFM methods on well-defined surfaces.

The aim of this work is to investigate the behaviour of 5-McPhTT in acidic solution and to analyse the dependence of corrosion current density ($i_{corr}$) and mass change ($\Delta m$) at the copper surface on the inhibitor concentration ($c_i$). The electrochemical behaviour of copper and the inhibitor effect on copper corrosion were studied using electrochemical (polarization curves), electrogravimetrical (EQCM) and surface analytical analysis (STM and SEM–EDAX) measurements.

## 2. Experimental details

All measurements were performed in 0.1 M $Na_2SO_4$ as blank solution without and with the addition of different concentrations of 5-McPhTT. The pH was adjusted to 2.95 using diluted sulfuric acid.

A polycrystalline Cu (99.99%) electrode was used for electrochemical and SEM–EDAX investigations. Prior to each electrochemical or SEM measurement, the working electrode was polished with emery paper (1200 grit size) and diamond paste (down to 0.25 $\mu$m size), and rinsed with acetone and distilled water.

A single crystal electrode Cu (111) was used for STM experiments. The copper sample was electrochemically polished in 66% orthophosphoric acid for 10 min, at an anodic potential between 1.5 and 2 V [8]. The samples were then thoroughly rinsed with ultrapure water and immersed in the electrolyte. Electrochemical measurements were made using a Solartron electrochemical interface (ECI-1286). The experimental arrangement consisted of a standard three-electrode cell, Cu-working electrode, Pt-counter electrode and an SCE reference electrode. The measurements were performed at room temperature and with continuous agitation using a magnetic stirrer. The measurements were performed after the open circuit potential (OCP) was stabilized to 5 mV per 5 min. The potential was scanned between OCP and 600 mV in both anodic and cathodic directions. The potential scan rate was 15 mV min$^{-1}$.

Important information about the processes occurring *in situ* at the electrode surface during corrosion can be obtained by the QCM. The quartz crystal blade operates with one of its faces exposed to the electrolyte and acting as working electrode [9–11]. An electrochemical nanobalance, model EQCN-701, and an AT-cut quartz crystal, with nominal frequency of 10 MHz, were used. The crystal was coated on both sides by vacuum deposited layers of chromium (thickness 15 nm), and gold (thickness 180 nm). The crystal was glued to a glass vessel that had a side circular opening. Copper layers (thickness 250 nm) were galvanostatically deposited onto one face of the crystal using a current density of 20 mA cm$^{-2}$. The deposition bath consisted of 1 M ethanol, 0.5 M $H_2SO_4$ and 0.5 M $CuSO_4$ in 1 dm$^3$ distilled water [12]. EQCM measurements were performed at OCP. The freshly deposited copper surface was immediately exposed to 0.1 M $Na_2SO_4$ for 3000 s. The solution was then changed to 0.1 M $Na_2SO_4$ containing 0.5 mM 5-McPhTT and the mass variation was monitored for 10 000 s. Finally, the solution without inhibitor was again applied for another 7000 s.

*In situ* scanning tunneling microscopy (STM) experiments were carried out using a Nanoscope III (Digital Instruments, Inc.). The tunneling tips were made of tungsten and covered with an epoxy layer up to the operational tip, to decrease the faradic current [13]. A three-electrode electrochemical cell was used. The electrochemical potentials of the electrode and tip were independently controlled by means of a potentiostat. The working electrode was Cu (111). The potential of the tip was held in the double layer region, where the faradaic current is minimal.

A scanning electron microscope (HITACHI S-570) with an EDAX-RÖNTEC analyser was used to study the surface morphology in the absence and presence of inhibitor. Measurements were performed after an immersion time of 18 days with the same pretreatment as in the electrochemical experiments.

## 3. Results and discussion

The polarization curves for polycrystalline copper in different electrolytes, 0.1 M $Na_2SO_4$ without and with the addition of 0.1, 0.5 and 1 mM of 5-McPhTT can be seen in Figure 1. In the inhibitor-free solution, oxygen reduction was noticed in the cathodic region and copper dissolution in the anodic region. Both cathodic and anodic current densities were reduced by the presence of 5-McPhTT. The corrosion potential was shifted to more positive values due to the inhibitor addition. Table 1 shows the values of corrosion potential ($E_{corr}$) and corrosion current densities ($i_{corr}$) obtained from Figure 1. The highest inhibition efficiency was obtained by 0.5 mM 5-McPhTT where $i_{corr}$ was reduced from 4 to 0.005 $\mu$A cm$^{-2}$ and $E_{corr}$ was shifted from −35 to 120 mV. The data for the $E_{corr}$ and $i_{corr}$ were calculated from Tafel slopes of the corresponding curves. The percentage inhibition efficiency ($\eta$) was also determined using the following formula:

$$\eta = \left(\frac{i_o - i_{corr}}{i_o}\right) \times 100 \tag{1}$$

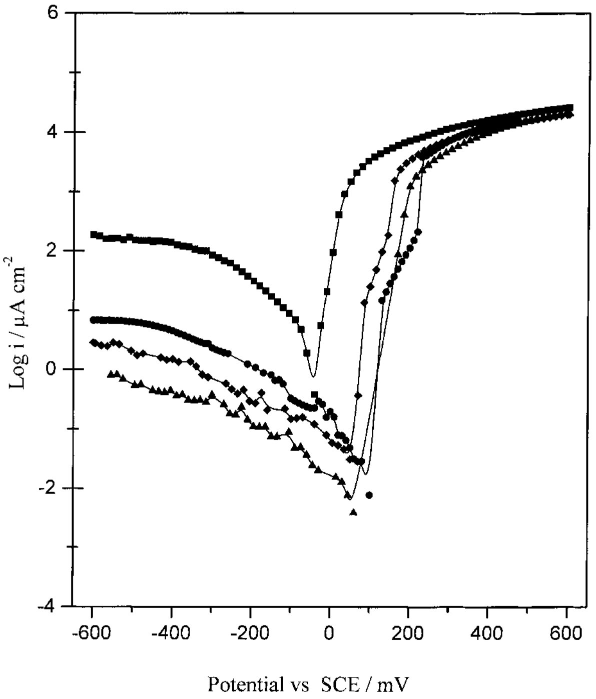


*Fig. 1.* Polarization curves of copper in acidic 0.1 M $Na_2SO_4$, Key: (■) in blank solution; (●) in 1 mM 5-McPhTT; (▲) in 0.5 mM 5-McPhTT; (◆) in 0.1 mM 5-McPhTT concentration.

*Table 1.* D.C. results of Cu in 0.1 M $Na_2SO_4$ + inhibitor solution

| Solution | $E_{corr}$/mV | $i_{corr}$/$\mu$A cm$^{-2}$ |
|---|---|---|
| Blank solution | −35 | 4 |
| 1 mM 5-McPhTT | 100 | 0.187 |
| 0.5 mM 5-McPhTT | 120 | 0.005 |
| 0.1 mM 5-McPhTT | 90 | 0.08 |

*Table 2.* Thickness reduction rate of copper electrode

| Electrolyte | Thickness reduction rate, $\delta$ $/\mu m\ y^{-1}$ |
|---|---|
| Blank solution | 144 |
| 0.5 mM 5-McPhTT | 2 |

where $i_o$ and $i_{corr}$ represent the corrosion current density in the absence and presence of the inhibitor, respectively. The best inhibition efficiency ($\eta$ = 99%) was obtained using the solution containing 0.5 mM 5-McPhTT (Figure 1).

The EQCM measurement was carried out in 0.1 M $Na_2SO_4$ solution without and with the addition of 5-McPhTT and the results are depicted in Figure 2 (a) and (b). The electrode mass decreased sharply with time while in contact with the uninhibited solution. The slope of the curve represents the corrosion rate at any particular time. After changing to the solution containing inhibitor, the mass increased over a short time due to inhibitor adsorption on the electrode surface. The mass change for the inhibitor adsorbed on the surface was 0.1 $\mu$g which represents a coverage of less than a monolayer seen in Figure 2(b). The time dependence of the mass

*Table 3.* Diameter of pits on the copper surface after different immersion times in 0.1 M $Na_2SO_4$ solution at pH 2.95

| Time /s | Horizontal distance /nm | Vertical distance /nm |
|---|---|---|
| 60 | 13.5 | 0.7 |
| 120 | 21.5 | 1.0 |
| 180 | 23.0 | 1.0 |
| 240 | 25.0 | 1.0 |
| 300 | 31.0 | 1.0 |
| 360 | 32.0 | 1.0 |

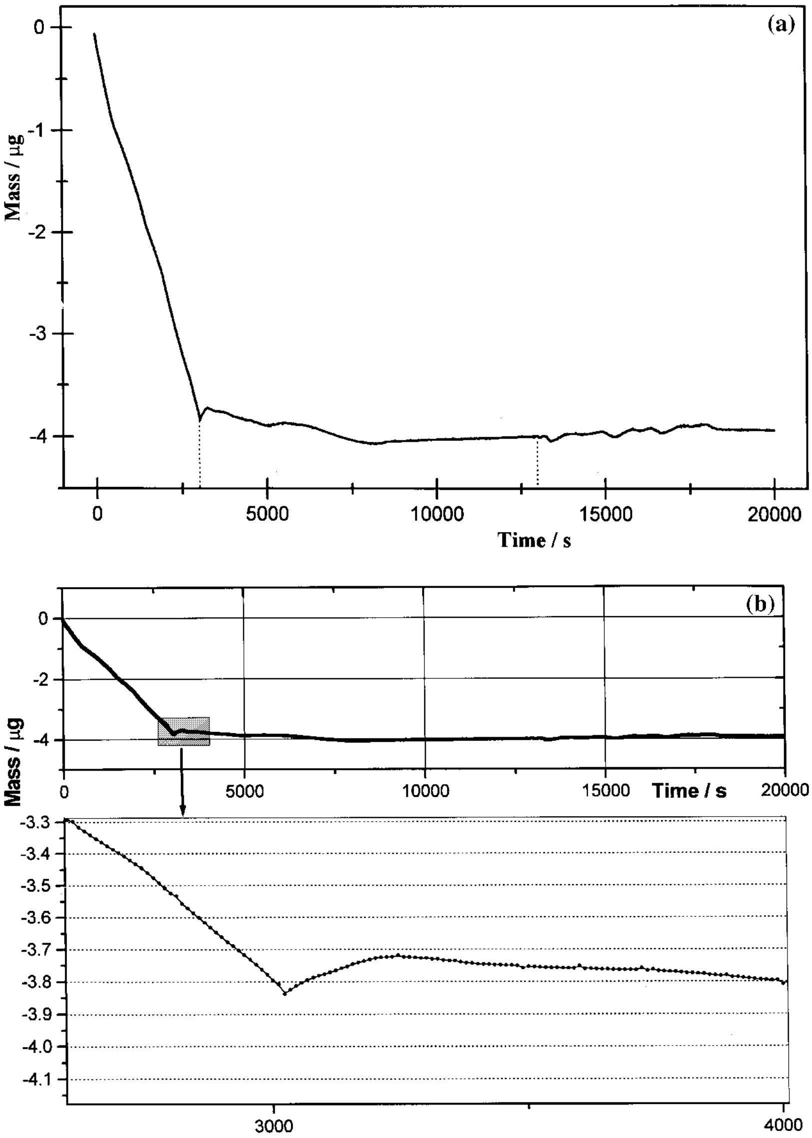


*Fig. 2.* (a) Mass change of Cu electrode in acidic 0.1 M $Na_2SO_4$ without and with the addition of 5-McPhTT in time. (b) Mass change of Cu electrode against time during inhibitor adsorption.

decrease was very slow. The electrode mass was approximately constant during this period. In the final period, the mass loss rate was minimal and steady, which shows that the inhibitor remained adsorbed. The thickness reduction rate per year ($\mu$m y$^{-1}$) can be calculated as

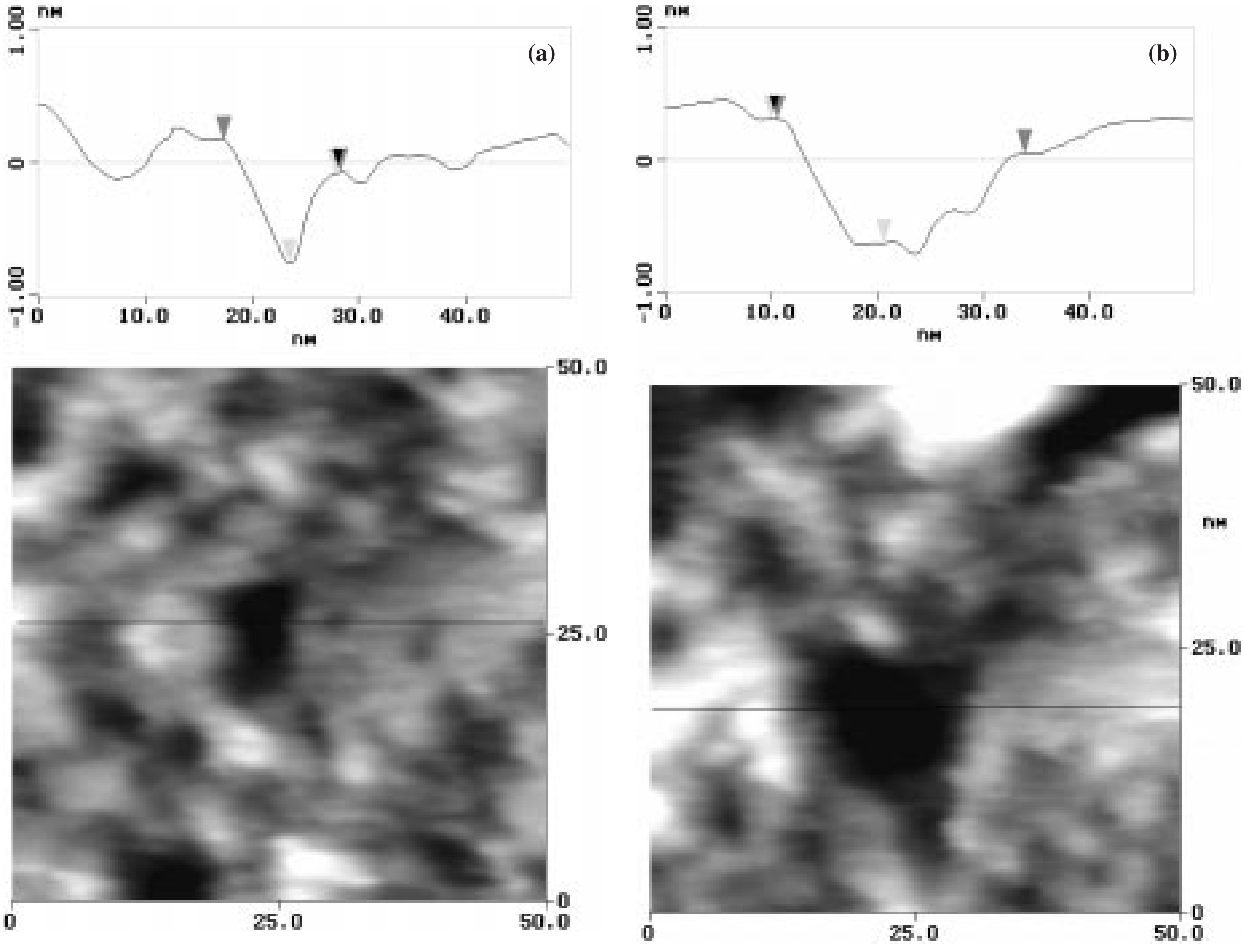
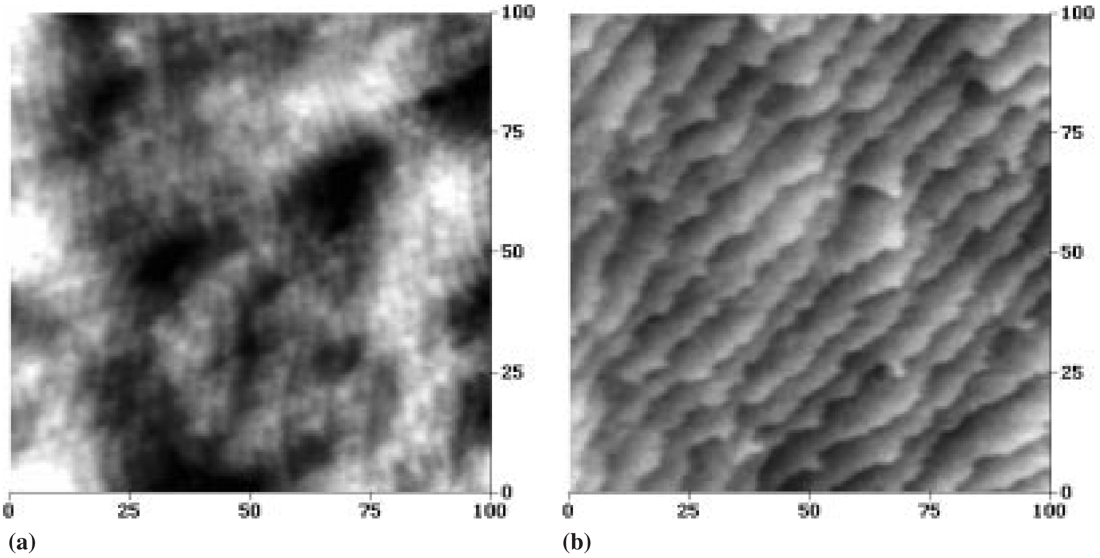


*Fig. 3. In situ* STM images of (a) Cu (111) surface in 0.1 M $Na_2SO_4$ solution at pH 2.95; (b) after 5 min. All images were recorded at open circuit potential (OCP) immediate after exposure to the electrolyte. (bias: 83.8 mV, setpoint: 1.39 nA, *z*-range: 1 nm), image size is 500 × 500 Å$^2$.



(a) (b)

*Fig. 4. In situ* STM images of 5-McPhTT- covered Cu (111) surfaces in 0.1 M $Na_2SO_4$ solution at pH 2.95, (a) in 1 mM 5-McPhTT inhibitor containing solution (*z*-range: 1nm, bias: 105 mV, setpoint: 1.09 nA), compact structure with defects; (b) in 0.5 mM McPhTT solution (*z*-range 1 nm, bias: 105 mV, setpoint: 1.04 nA), smooth, narrow terraces can be seen. Image size is 1000 × 1000 Å$^2$.

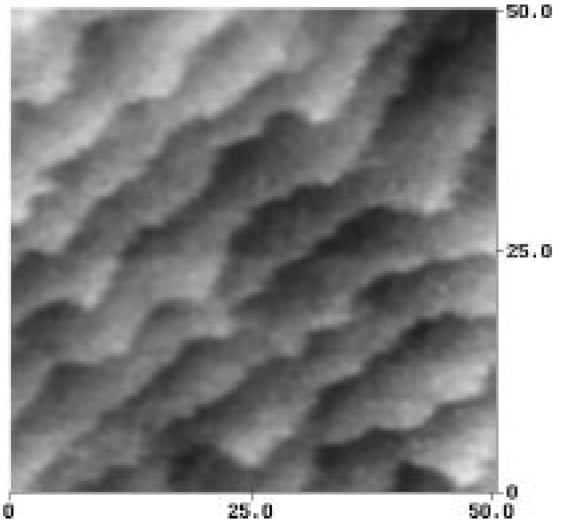


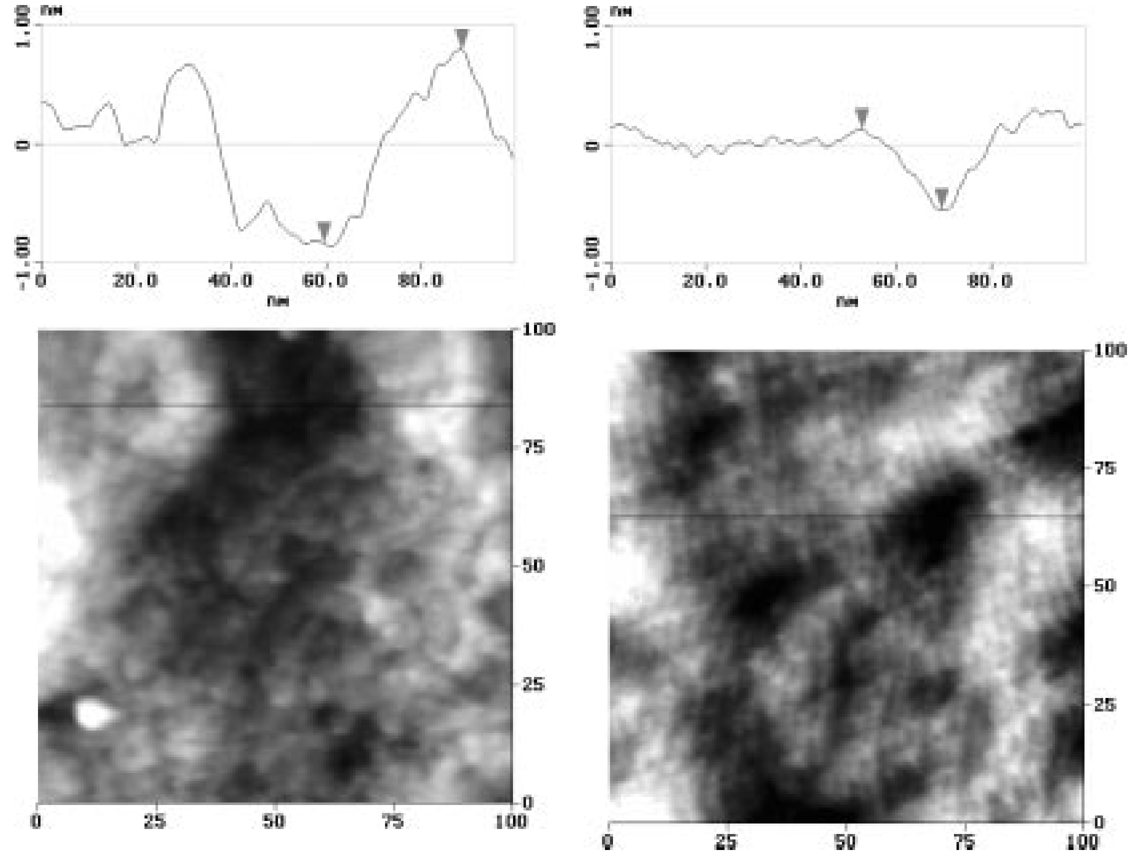
*Fig. 5.* *In situ* STM images of Cu (111) in 0.5 mM 5-McPhTT solution after 30 min exposure to the electrolyte (*z*-range: 1 nm, bias: 105 mV, setpoint: 1.04 nA). Image size is 500 × 500 Å$^2$.

$$\delta = (\Delta M \times 3600 \times 24 \times 365 \times 10\,000)/ADt \tag{2}$$

where $\delta$ is the thickness reduction rate, $\Delta M$ is the mass loss (g), $A$ is the electrode active surface area (cm$^2$), $t$ is the contact time (s), $D$ is copper density (g cm$^{-3}$). Table 2 shows the thickness reduction rate of the electrode during the different measurement periods.

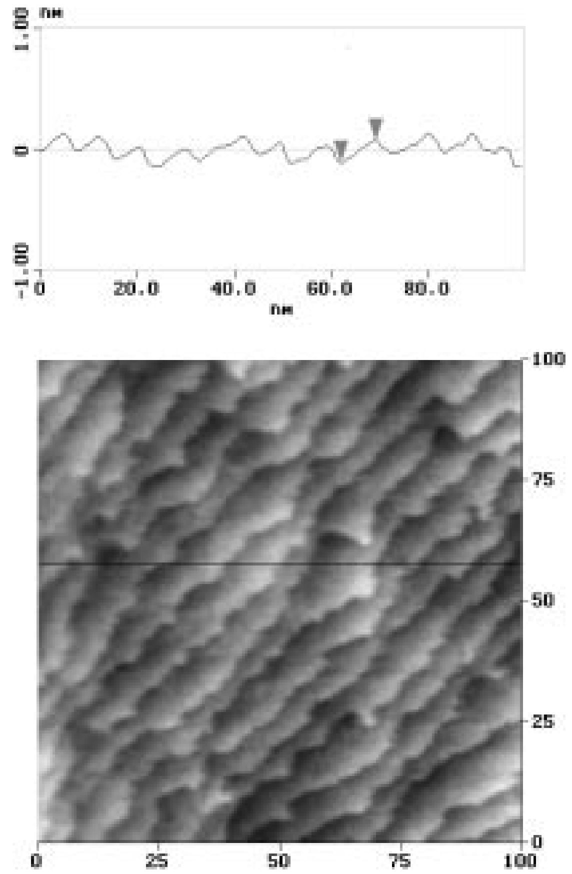
Copper dissolution was inhibited by 5-McPhTT, which was indicated by the decrease in slope of the curve and confirmed by the determined thickness reduction rate (Table 2). Addition of inhibitor resulted in a slight mass increase of the Cu electrode. This is an indication that the inhibitor film was very thin and the inhibitor adsorption was 2D type, where a mono- or submonolayer was formed. In the final period, where the uninhibited solution was applied again, the approximately constant mass of the copper electrode showed that the inhibitor has a long-term protective effect in hindering copper dissolution.

Figures 3(a) and (b) show *in situ* information at nanometer resolution on the inhibition mechanism. The structure of the electrode surface can be visualized using STM. The morphology of a Cu (111) electrode was investigated in 0.1 M $Na_2SO_4$ solution at a pH 2.95. The copper corrosion process was followed at OCP. The copper electrode surface was covered with an oxide layer. This layer was not continuous, which caused the dissolution of copper. Pits, whose diameter increased with time, were formed as shown in Table 3. During the immersion time, the depth of the pits did not change from 1 nm deep, but their diameters increased by approximately 20 nm. Figure 3(a) shows the surface



**(a)** **(b)**

*Fig. 6.* a,b



**(c)**

*Fig. 6.* Section analyses images of Cu (111), (a) in 0.1 M $Na_2SO_4$ solution, showing the increase in surface roughness after longer exposure to the electrolyte solution; (b) in 1 mM 5-McPhTT (c) in 0.5 mM 5-McPhTT containing solutions (*z*-range: 1 nm, bias: 105 mV, setpoint: 1.39 nA), where the surface coverage depend of the inhibitor concentration. Image size is 1000 × 1000 Å$^2$.

morphology and cross section analysis after 1 min of immersion. After 5 min, the pit diameter increased and corrosion products were visible, as seen in Figure 3(b). When the electrolyte was replaced by solutions containing different inhibitor concentrations (1 and 0.5 mM 5-McPhTT), the surface morphology on the nanometer scale was changed.

A compact structure was visible in the case of 1 mM 5-McPhTT (Figure 4(a)). Atomically smooth, narrow terraces were obtained in the case of 0.5 mM 5-McPhTT containing solution (Figure 4(b)). The shape and position of the terraces did not change significantly with time, indicating a low surface mobility in 0.5 mM 5-McPhTT solution (Figure 5). This differs distinctly from the observations in 0.1 M $Na_2SO_4$ solution where a very high copper surface mobility was observed. Deep pits were found on the surface at OCP, while in 0.1 M $Na_2SO_4$ solution, the copper dissolution and corrosion product growth processes were followed. An ordered superstructure was visible in the presence of 5-McPhTT, which is attributable to a chemisorbed inhibitor layer. STM images of copper in 0.1 M $Na_2SO_4$ solution confirmed the dynamics of the copper electrode surface, which shows a general attack on the active part of the surface. Copper corrosion started at active sites and surface roughness increased as corrosion proceeded (Figure 6(a)). The surface was much smoother in 5-McPhTT containing solutions as confirmed by the section analysis images (Figure 6(b) and (c)). In the presence of 0.5 mM 5-McPhTT, steps were only 7–10 nm, and the vertical distance was 0.2 nm, as seen in Figure 6(c).

Figure 7 shows SEM morphological images of the copper surface after 18 days immersion in blank 0.1 M $Na_2SO_4$ solution. Copper corrosion began along grains or subgrain boundaries. Pits and corrosion products were observed. When copper was immersed for 18 days in solution containing 0.5 mM 5-McPhTT, an inhibitor layer was observed on the surface (Figure 8). SEM–EDAX analyses of the copper surface layer after 0.5 h immersion time showed that the protective films of the adsorbed inhibitors were very thin because only traces

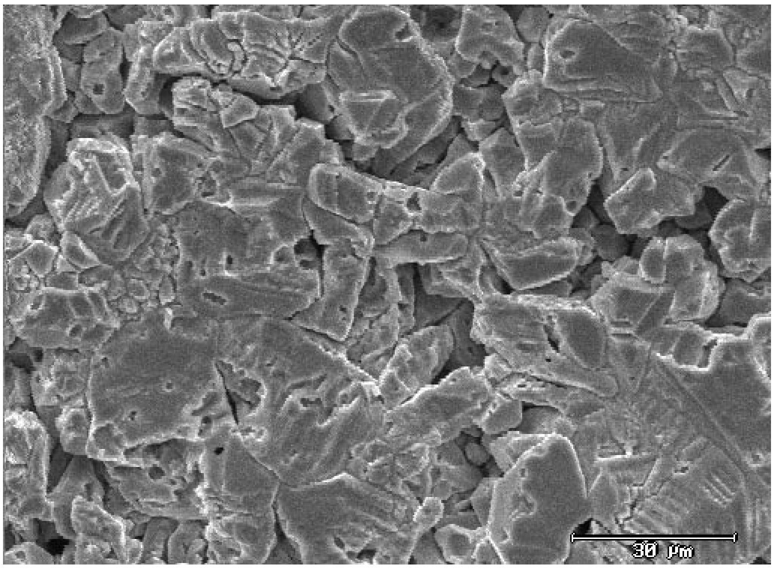


*Fig. 7.* SEM image of copper immersed 18 days in 0.1 M $Na_2SO_4$ solution.

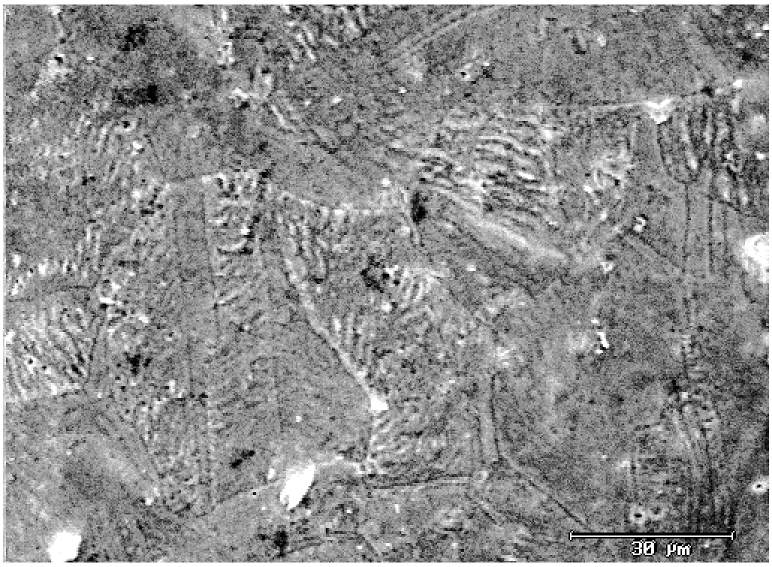


*Fig. 8.* SEM image of copper immersed 18 days in 0.1 M $Na_2SO_4$ solution containing 0.5 mM 5-McPhTT.

of inhibitor were detected. The thickness of the protective layer increased with time.

## 4. Conclusions

Copper corrosion in acidic 0.1 M $Na_2SO_4$ solution was studied using electrochemical measurements, EQCM, *in situ* STM and SEM–EDAX.

The dissolution of copper in 0.1 M $Na_2SO_4$ was clearly modified and hindered by the addition of 5-McPhTT inhibitor whose optimum concentration was 0.5 mM. The EQCM measurements showed that the presence of inhibitor decreased the copper dissolution rate and a 2D type mono- or submonolayer was formed on the copper surface.

The inhibition of copper corrosion was shown to be due to the partial adsorption of a thin layer or even a partial monolayer based on STM and SEM analyses, which were in agreement with EQCM results. STM results indicated a strong, irreversible inhibitor adsorption and a protective layer formed on the copper surface. From the combined previous results, 5-mercapto-1-phenyl-tetrazol can be considered as an excellent inhibitor for copper in acidic sulphate containing solutions.

## Acknowledgement

The authors wish to express thanks for the support given by Domus Hungarica Scientiarum et Artium, and National Science Foundation (OTKA F025492, T019785, F029709).

## References

1. J.B. Cotton and I.R. Scholes, *Br. Corros. J.* **2** (1967) 1.
2. G.W. Poling, *Corros. Sci.* **10** (1970) 359.
3. F. Zucchi, M. Fonsati and G. Trabanelli, Giornate Nationali Sulla Corrosione e Protezione, 3rd edn, (AIM, Milano, 1996), p. 115.
4. A. Shaban, E. Kálmán, J. Telegdi, G. Pálinkás and Gy. Dóra, *Appl. Phys.* **A66** (1998) 545–549.
5. C.B. Ehlers and J.L. Stickney, *Surf. Sci.* **239** (1990) 85.
6. C. Ehlers, I. Villegas and J. Stickney, *J. Electroanal. Chem.* **284** (1990) 403.
7. M.R. Vogt, W. Polewska, O.M. Magnussen and R.J. Behm, *J. Electrochem. Soc.* **144** (1997) 113.
8. O.M. Magnussen, M.R. Vogt, J. Scherer and R.J. Behm, *Appl. Phys.* **A66** (1998) 447.
9. S. Bruckenstein and M. Shay, *Electrochim. Acta.* **30** (1985) 1295.
10. M. Benje, M. Eiermann, U. Pittermann and K. Weil, *Ber. Bunnsenges. Phys. Chem.* **90** (1986) 435.
11. K. Kanazawa and J. Gordon II, *Anal. Chem.* **57** (1985) 1770.
12. E. Müller, 'Praktikum der Electrochemie' (Steinkopf-Verlag, 1953).
13. R. Kazinczi, E. Szőcs, E. Kálmán and P. Nagy, *Appl. Phys.* **A66** (1998) 535–538.