Corrosion Inhibition of Copper by 2-Mercaptobenzothiazole and Benzotriazole in Low-Conductivity Solutions

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(Received January 21, 1993)

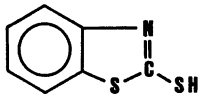
Corrosion inhibition of copper in a low-conductivity medium (<10 μS cm^{-1}) containing benzotriazole (BTA) and/or 2-mercatobenzothiazole (MBT) was studied by using the AC impedance technique, Auger electron spectroscopy and corrosion tests. As the MBT concentration increased, the corrosion rate of copper abruptly rose to a peak, rapidly fell, and then finally decreased steadily. The maximum corrosion rate appeared at a MBT concentration of about 0.5 ppm. However, a concentration of more than 1.5 ppm MBT could effectively inhibit copper corrosion. The results from AC impedance measurements agreed with those from corrosion tests. The film resistance could be observed only when the MBT concentration was in excess of 1.5 ppm. A combination of BTA and MBT proved to be more effective than either compound used alone.

Water cooled generators are widely used in power plants. Water of low-conductivity (<10 μS cm^{-1}) flows through copper conduit and functions as the cooling medium, but causes corrosion of the copper conduit. The temperature of the water generally ranges from 10 to 65 °C. In order to protect the conduit against corrosion, two measures are usually adopted: (1) the purging of oxygen and maintenance of pH within the range 8—8.6 and (2) the addition of corrosion inhibitors. As a cooled system with oxygen-free water is difficult to maintain, especially in the case of the generator rotor, the addition of inhibitors is found to be more suitable for practical applications in power plants in China.

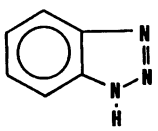
This paper studies the inhibition of copper corrosion with 2-mercaptobezothiazole (MBT) and benzotriazole (BTA) in low-conductivity solutions by using AC impedance measurements, Auger electron spectroscopy (AES), and corrosion tests.

Experimental

The chemical analysis of the low-conductivity solution is as follow: O_2 1.5—2 ppm, NH_3 less than 1 ppm and SiO_2 less than 20 ppb. Figure 1 shows the chemical structures of MBT and BTA. The copper electrodes (with surface area of 1 cm^2) for the AC impedance measurements and the copper specimens (with surface area of 36 cm^2) for corrosion tests were prepared from a 99.9% pure copper plate. Before every run the surface was polished with emery papers, then washed, degreased with acetone, rinsed with deionized water, and finally immersed in the solution. All reagents used in the study were of analytical grade. The pH of the solution was adjusted by using ammonia water and maintained at 7.4. After the pH adjustment, the NH_3 concentration in the solution was less than 1 ppm. This method of pH maintenance is a common practice in most power plants in China. The MBT powder was dissolved in NaOH solution and therefore the solution conductivity increased with MBT concentration. The condctivity of each solution was maintained at less than 10 μS cm^{-1}.



2—Mercaptobenzothiazole(MBT)



Benzotriazole(BTA)

Fig. 1. Chemical structure of the inhibitors.

Impedance measurements were carried out at the corrosion potential in a three-electrode electrochemical cell at 30±0.5°C after an immersion time of 30 min over a frequency range of 0.05 Hz—100 kHz by using a PARC M273 potentiostat, PARC 5208 EC lock-in analyzer, PARC M378 software system. A Pt electrode was used as a counter electrode and a saturated calomel electrode served as a reference electrode. Corrosion tests were performed on copper specimens after 24 h immersion in the solution described above at a temperature of 60±0.5°C. The concentrations of copper ions were analyzed to estimate the corrosion rate by means of a M751 spectrophotometer made by Shanghai Analytical Instruments Factory. A Perkin–Elmer PHI 550 ESCA/SAM was used to make Auger Electron Spectroscopy experiments.

Results and Discussion

From the corrosion test, the dependence of corrosion rate of copper on concentrations of BTA and MBT is shown in Fig. 2. The corrosion rate decreases with the increase of BTA concentration. This behavior coincides with AC impedance results previously reported.[1] With the increase of MBT concentration, the corrosion rate is seen to rise abruptly, falls rapidly, and finally decreases steadily. The maximum corrosion rate appears at the MBT concentration of about 0.5 ppm. It seems that at a MBT concentration of more than 1.5 ppm copper corrosion can be effectively inhibited, while at less than 1 ppm MBT copper corrosion is accelerated. Af-

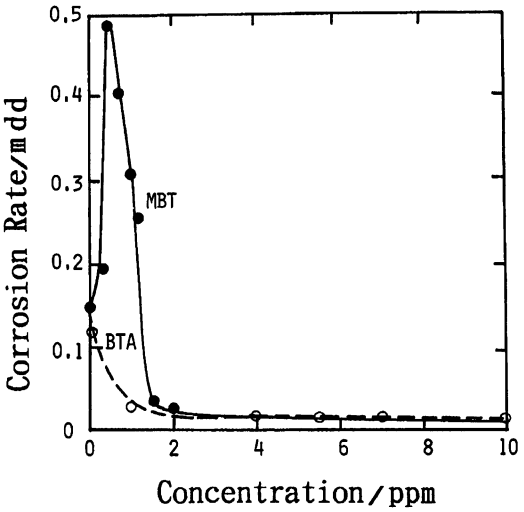


Fig. 2. Corrosion rate of copper vs. concentrations of BTA and MBT. The copper specimens were immersed in low conductivity solutions for 24 h under stagnant conditions at 60±0.5°C. BTA (-O-O-O-O-), MBT (-●-●-●-●-).

ter corrosion tests in the solution containing 0.5 ppm MBT some black spots were found to be present on the copper surface.

Figures 3a and 3b show the Auger electron spectra for the black spot ant the spot-free area, respectively, after 2.75 min sputtering. The elements of C, S, N, O and Cu appear on the spot, and only Cu is seen on the spot-free area. Figures 4a and 4b show the depth profile in Auger analysis of the spot and the spot-free areas, respectively. Note that during profiling of the spot, as shown in Fig. 4a, C and S fall together, O fluctuates and Cu rises during a sputter time of about 11 min. After this, C and S disappear, and after about 14 min, only Cu can be seen. Some disulfide might have deposited on the copper surface, as MBT in the solution reacted with dissolved oxygen, and some of MBT was oxidized to disulfide which had low solubility and no inhibiting properties. Therefore, the spot was mainly composed of disulfide, CuMBT and CuO (CuO was identified due to the black color of the spot). Because CuO existed as many small points dispersed on the spot, the back-

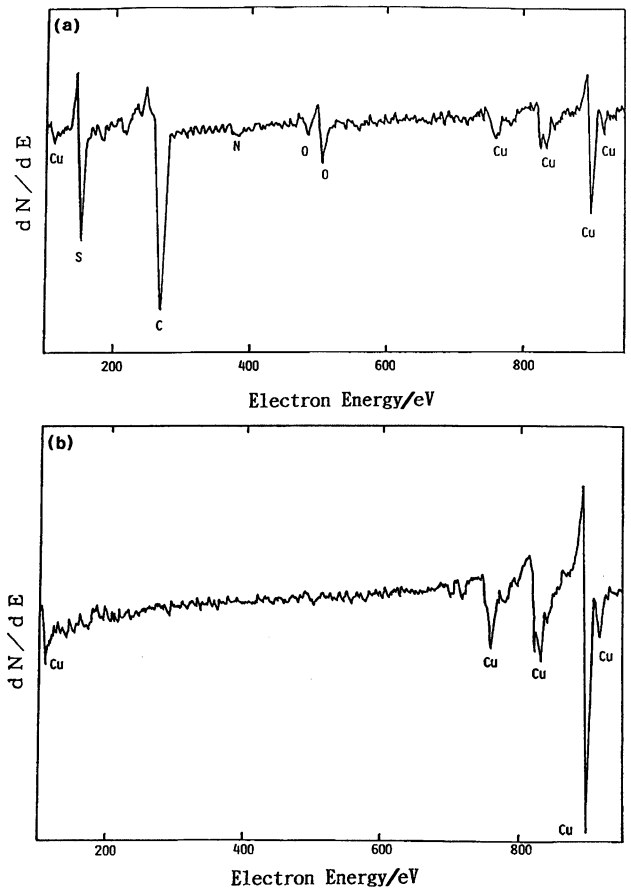


Fig. 3. Auger electron spectra for copper specimen after a corrosion test in the low conductivity solution containing 0.5 ppm MBT. Sputter time: 2.75 min. (a) on the black spot (b) on the spot-free area.

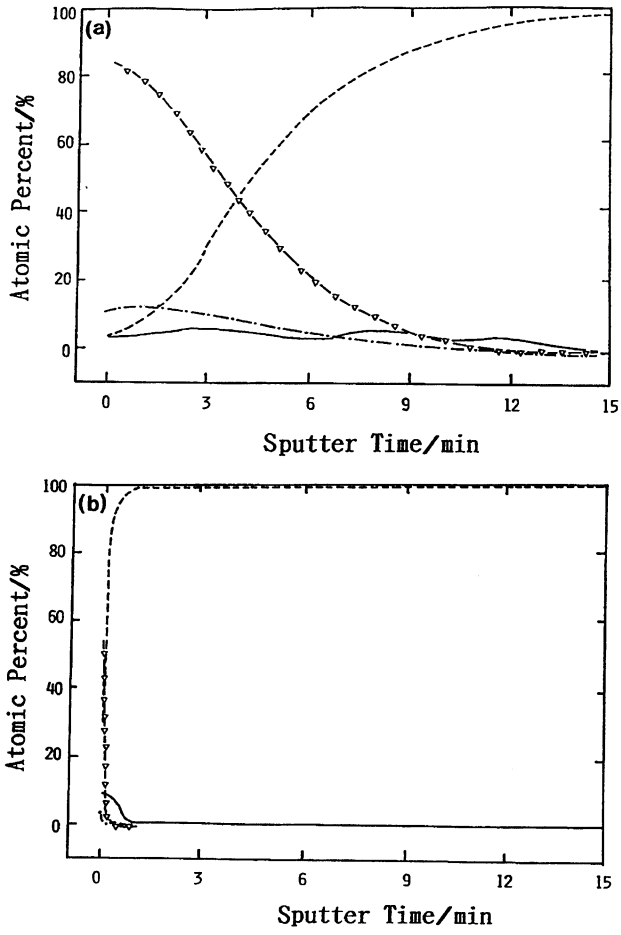


Fig. 4. Auger depth composition profile for copper specimen after corrosion test in the low conductivity solution containing 0.5 ppm MBT. C (-▽-▽-▽-), O (—), S (-·-), Cu (- - -). (a) on the black spot, (b) on the spot-free area.

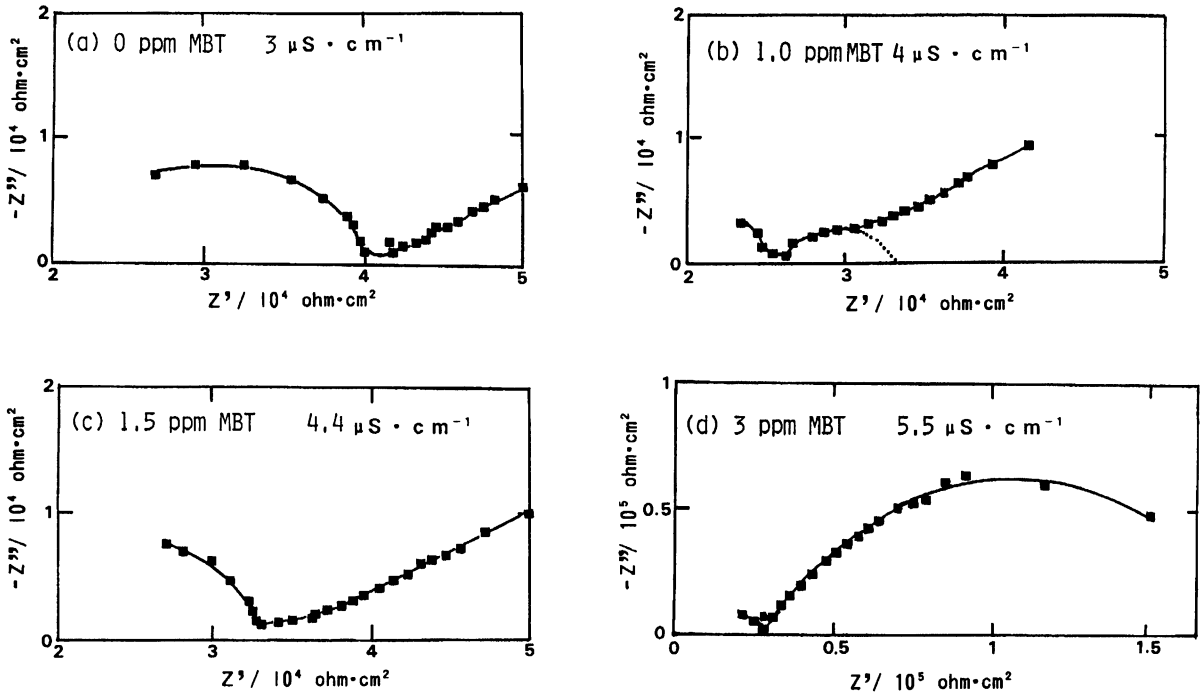


Fig. 6. Nyquist plots for copper electrodes after 30 min immersion in low conductivity solutions with (a) 0 ppm, (b) 1.0 ppm, (c) 1.5 ppm, and (d) 3.0 ppm MBT.

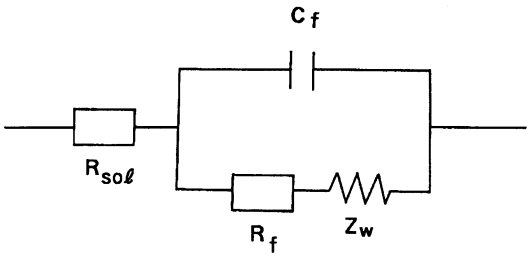


Fig. 5. Equivalent circuit for the copper electrode in the low conductivity solutions containing corrosion inhibitors.

ground on the spot was disulfide and CuMBT. Therefore the amount of disulfide and CuMBT was larger than that of CuO from AES results. However, during profiling of the spot-free area, as shown in Fig. 4b, Cu and O appear at a sputter time of 0.5 min and after 1 min only Cu can be observed. This indicates that almost no CuMBT or disulfide existed on the spot-free area. As the MBT concentration of 0.5 ppm was so low and some MBT was consumed by reacting with dissolved oxygen, only a small part of copper surface was covered with CuMBT. This CuMBT coating had many pores, in which copper corrosion occurred and then CuO was produced. This accounted for the coexistence of disulfide, CuMBT and CuO on the spot area. Therefore, the corrosion rate of copper in the solution containing less than 1 ppm MBT was greater than that in the absence of MBT.

The results from the AC impedance measurements agree with those from the corrosion tests. The equivalent circuit for the electrode system with corrosion inhibitors is shown in Fig. 5, where R_{sol} is the solution resistance, R_f the film resistance, C_f the film capacitance, and Z_w the Warburg impedance.[2] The value of R_f is obtained from the diameter or the chord of the semicircle on the Nyquist plot.[3]

Figures 6a, 6b, 6c, and 6d show Nyquist plots for Cu electrodes after 30 min immersion in solutions containing 0, 1, 1.5, and 3 ppm MBT, respectively. In the absence of MBT (Fig. 6a), a high-frequency semicircle and a straight line are observed. The straight line with a slope of about 45 degrees which appears at low frequencies represents a Warburg impedance due to the diffusion of oxygen or copper ions in the surface film. It implies that the corrosion reaction of copper in the absence of MBT is dominated by the diffusion process. The high-frequency semicircle can be attributed to the reference electrode system in the cell.[4—6]

As previously described,[5,6] the high-frequency semicircle decreases in size with the increase of solution conductivity, and the R_{sol} value is determined by the low frequency intercept of the high-frequency semicircle with the real axis, Z axis. Though Fig. 6b is similar to Fig. 6a in shape, the high-frequency semicircle in Fig. 6b contracts and the R_{sol} value decreases from 4×10^4 ohm cm^2 (Fig. 6a) to 3.3×10^4 ohm cm^2 (Fig. 6b). This is attributed to the increase in solution conductivity from 3 μS cm^{-1} to 4 μS cm^{-1}, caused by the increase of MBT concentration. In Fig. 6c, the second semicircle appears in the middle frequency range, corresponding to the charge transfer process at the CuMBT/solution

interface. The R_{sol} value further decreases to 2.7×10^4 ohm cm^2 because of the increase in solution conductivity to 4.4 μS cm^{-1}. Figure 6d shows a much larger semicircle for 3 ppm MBT. Here, the film resistance R increases from about 7×10^3 ohm cm^2 (Fig. 6c) to about 1.7×10^5 ohm cm^2 (Fig. 6d) as MBT concentration increases from 1.5 to 3 ppm. Therefore, the corrosion reaction of copper in the presence of 3 ppm MBT is controlled by the CuMBT film resistance. AC impedance results (Figs. 6a, 6b, and 6c) indicate that almost no film resistance R appears on Nyquist plots at MBT concentration of less than 1 ppm, which results from the concentration of the MBT which reacts dissolved oxygen.

Unlike MBT, even small amounts of BTA, e.g. 0.05 ppm, show a considerable value of R_f on the Nyquist plot.[5] It is believed that there is a difference in the mechanism of inhibitive action between BTA and MBT. The adsorption of even a small amount of BTA on the "active" sites of a copper surface exhibits marked inhibitive action, while the formation of a CuMBT film of a certain thickness and sufficient compactness on the copper surface is required to effectively inhibit copper corrosion.

Accordingly, experiments were performed with a combination of BTA and MBT at a total concentration of 5 ppm, suitable for practical application in water cooled generators. Figure 7 shows both the corrosion rate from corrosion tests and R_f from AC impedance measurements vs. the ratio of BTA to MBT. The combination of BTA and MBT is more efficient than the use of either compound alone, which shows a synergistic effect. The optimum formation may be in the region between the ratios of 2 ppm BTA to 3 ppm MBT and 3 ppm BTA to 2 ppm MBT. BTA may spread out over the surface of copper and form a protective film consisting of a CuBTA polymeric network,[1,7] MBT may then fill up defects in the network of Cu/Cu_2O by forming a CuMBT film.

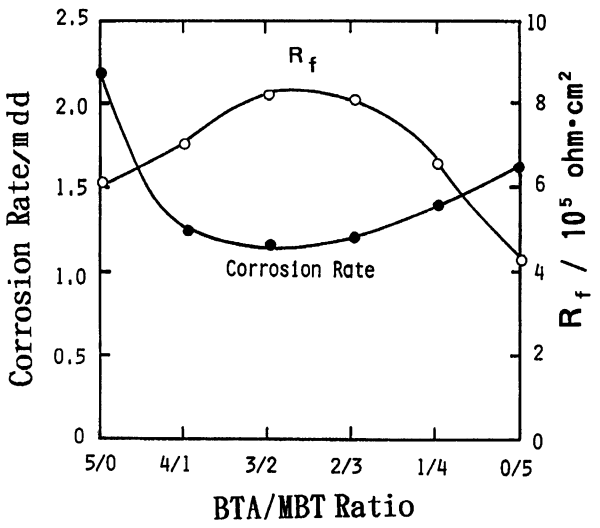


Fig. 7. Corrosion rate of copper vs. BTA/MBT ratio. The copper specimens were immersed in low conductivity solutions for a 24 h period under stagnant conditions at 60±0.5°C. R vs. BTA/MBT ratio for copper electrodes after 30 min immersion in low conductivity solutions at 30±0.5°C.

Summary

As the MBT concentration increased, the corrosion rate of copper rapidly rose to a peak, abruptly fell, and finally decreased steadily. The maximum corrosion rate was observed at 0.5 ppm MBT concentration. Impedance spectroscopy shows that the film resistance appears on the Nyquist plots only when the MBT concentration exceeds 1.5 ppm, which is consistent with the corrosion tests. A combination of BTA and MBT proved to be more effective than the use of either compound alone.

The project was supported by the National Natural Science Foundation of China.

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