Publication III


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Benzotriazole (BTAH) is a common corrosion inhibitor for copper. Its role is overwhelming, and consequently it has been studied in detail. It is known the copper forms a cuprous benzotriazole complex, [Cu(I)-BTA], which is responsible for the corrosion inhibition. Furthermore, the [Cu(I)-BTA] complex forms a chemisorbed layer at low coverage and a multilayer with a polymerized structure at high coverage. Scanning tunneling microscopy (STM) studies in vacuum have shown that BTA adsorbs on clean copper surfaces with a well-defined structure, while the adsorption was more random on surfaces shown that BTA adsorbs on clean copper surfaces. Chemisorption of BTA occurs in a similar way on both oxidized and electrochemical microscopy. Moreover, the [Cu(I)-BTA] complex forms a chemisorbed layer at low coverage and a multilayer with a polymerized structure at high coverage. Scanning tunneling microscopy (STM) studies in vacuum have shown that BTA adsorbs on clean copper surfaces with a well-defined structure, while the adsorption was more random on surfaces exposed to oxygen. Chemisorption of BTA occurs in a similar way on both oxidized and electrochemical microscopy. Moreover, the [Cu(I)-BTA] complex forms a chemisorbed layer at low coverage and a multilayer with a polymerized structure at high coverage. Scanning tunneling microscopy (STM) studies in vacuum have shown that BTA adsorbs on clean copper surfaces with a well-defined structure, while the adsorption was more random on surfaces exposed to oxygen. Chemisorption of BTA occurs in a similar way on both oxidized and electrochemical microscopy. Moreover, the [Cu(I)-BTA] complex forms a chemisorbed layer at low coverage and a multilayer with a polymerized structure at high coverage.

The inhibition of copper corrosion by benzotriazole (BTAH) has been studied by scanning electrochemical microscopy as a function of time and oxygen content. Under normal atmospheric conditions the inhibiting [Cu(I)-BTA] film was formed in approximately 1 h. When the oxygen content was lowered below 15 ppm, an insulating film could not be obtained in 4 h, clearly showing that the formation of the inhibiting [Cu(I)-BTA] requires oxygen.

**Experimental**

All measurements were performed in a nitrogen box where the atmospheric oxygen content can be controlled. Nitrogen gas (99.999%, AGA) was purged into the box and the oxygen content was measured from the gas outlet with an oxygen meter (model 912, System Instruments). The O2 content of the nitrogen box was in the first measurement series 0–15 ppm and in the second 25–75 ppm. All solutions (except the solutions of the electropolishing containing concentrated acids) were purged with nitrogen gas (99.9999%, AGA) several hours before the measurements. The oxygen contents of the solutions in every measurement were below 90 ppb, measured with a dissolved oxygen meter (MO128, Mettler-Toledo). All solutions were made in MQ water from solid substances (FeMeOH: Aldrich, Na2SO4 and BTAH: Merck, p.a.).

The measurements were performed with a CHI 900 scanning electrochemical microscope (CH Instruments, TX) using a three-electrode cell, with a saturated calomel electrode (SCE) as the reference electrode, a Pt wire as the counter electrode, and OF-HC copper (diameter 5 mm, O2 max 10 ppm, Outokumpu Copper) sealed in a Teflon holder as the substrate. The SECM tip consisted of a Pt wire (diameter 25 μm) sealed in a glass capillary, and functioned as the working electrode. The copper substrate was placed at the bottom of the cell. All measurements were performed at open-circuit potential (OCP).

Before every measurement the copper sample was polished mechanically outside the box, first using a sandpaper (grit 600), then polishing cloth and alumina powder (particle size 0.3 μm), and finally only polishing cloth and MQ water. The substrate was stored in ethanol in the nitrogen box between polishing and the measurements. The measurements were performed both in the presence and absence of BTAH. Before the measurements the copper substrate was held at a negative potential in a solution of 1 mM FeMeOH + 0.1 M Na2SO4 to reduce any residual copper oxide left on the surface (~0.35 V, 10 min; ~1.0 V, 6 min). The solution was changed to a clean solution immediately after the reduction. The SECM tip was characterized by measuring an approach curve to the insulating Teflon surface surrounding the copper sample in a solution of 1 mM FeMeOH and 0.1 M Na2SO4. Then, the approach curve to the clean copper surface was measured in the absence of BTAH. The solution was removed, the cell was rinsed twice with MQ water, and a fresh solution containing BTAH was added to the cell (0.333 mM BTAH + 0.667 mM FeMeOH).
+ 0.067 M Na$_2$SO$_4$ and the approach curves to the copper surface were measured after 3 s, 10, 30 min, 1, 2, 3, and 4 h exposure to the BTAH solution. The times correspond to the moments the approaches were commenced, and the measurement of an approach curve took approximately 2 min. During the whole procedure the position of the tip was kept constant in the horizontal plane so that the measurements were done exactly above the same spot on copper surface. This ensured that the same region of the copper substrate surface and the current measured at the tip. Furthermore, the electropolishing was also done in a normal atmosphere.

Results and Discussion

When a potential step is applied to a microelectrode, in this case the SECM tip, a steady-state current is quickly obtained. However, when an insulating surface is approached in an SECM measurement the diffusion field surrounding the tip is hindered and the tip current decreases. This is typical for an insulating surface. On the contrary, an increase in the current is observed when a conductor is approached, because the redox mediator is regenerated at the surface. The approach curves measured for the copper substrate in normal atmospheric conditions at open-circuit potential are shown in Fig. 1. The points are experimental results and the solid lines are the model fits (discussed later on). In the absence of BTAH the copper surface remains conductive, which is evidenced by an increase in current as the surface is approached. The copper surface stays conductive even after 4 h, showing that the passivation of the copper surface shown below is not due to the formation of copper oxide. When BTAH has been added to the solution (Fig. 1) a gradual transition from a conducting to an insulating surface is seen, i.e., at short exposure times the current increases as the surface is approached, but at longer exposure times the current decreases. The film is well insulating at exposure times exceeding 1 h. Similar observations were reported earlier in detail.

Figures 2 and 3 show the approach curves of OF-HC copper at oxygen contents of 25–75 ppm, respectively. As shown in these figures, the formation of the insulating [Cu(I)-BTA] film is significantly slower in the 25–75 ppm oxygen range than under normal atmosphere (Fig. 1). In the 0–15 ppm range the film formation is almost absent, and can be detected only after 3 h, probably as a consequence of the residual oxygen in the system. These results clearly show that oxygen is needed for the formation of the insulating film. The OCPs were similar in all three experiments varying between −0.082 and −0.027 V, and hence cannot explain the differences observed. Thus, it is evident that oxygen is needed for the formation of the inhibiting [Cu(I)-BTA] film.

The thickness of the [Cu(I)-BTA] films can be estimated using a model where the observed rate constant for the regeneration of the mediator is assumed to depend on the diffusion of electrons through the film. The model used and its application to passivation of copper by BTAH is described in detail in Ref. 17 and is based on a relation between the rate of regeneration of the mediator at the substrate surface and the current measured at the tip. Furthermore, the film thickness can be estimated from the observed rate constants. The diffusion coefficient of the electrons in the film was taken as 4·10$^{-9}$ cm$^2$ s$^{-1}$. The obtained film thicknesses are shown as a function of time in different oxygen contents in Fig. 4. In the low oxygen content the thickness is less than 5 nm, while in a normal atmosphere the thickness reaches approximately 25 nm after 4 h of exposure to the BTAH-containing solution. The thickness of the [Cu(I)-BTA] film has previously been reported to vary between 5 and 500 nm, which agrees with the results obtained in this study. However, it is pointed out here that the estimation of the film thickness includes many assumptions and cannot be considered exact, but it gives a means to compare results obtained here and in previous studies.

An interesting question is the role of oxygen and the source of cuprous ions in the formation mechanism of the [Cu(I)-BTA] film. Ling et al. have shown that it is likely that [Cu(I)-BTA] is formed on Cu$_2$O. We have previously found that the formation of [Cu(I)-

![Figure 1](image1.png)

Figure 1. The approach curves measured in a normal atmosphere at OCP (−0.082 V vs SCE). $i_{lim}$ is the dimensionless tip current, and $L = d/\alpha$ is the dimensionless distance between the sample and the tip.

![Figure 2](image2.png)

Figure 2. The approach curves measured in oxygen content 25–75 ppm at OCP (−0.027 V vs SCE). $i_{lim}$ is the dimensionless tip current, and $L = d/\alpha$ is the dimensionless distance between the sample and the tip.

![Figure 3](image3.png)

Figure 3. The approach curves measured in oxygen content 0–15 ppm at OCP (−0.040 V vs SCE). $i_{lim}$ is the dimensionless tip current, and $L = d/\alpha$ is the dimensionless distance between the sample and the tip.
BTA] film is faster if the surface has not been reduced before the application of the BTAH solution. Xue et al. have shown that dissolved oxygen also enables the formation of [Cu(I)-BTA]. Furthermore, if the copper surface is oxidized before the measurements, the rate of the film formation would be expected to be high until all Cu$_2$O has been consumed, and then decay to a rate determined by the dissolved O$_2$ available in the solution. However, the growth of the inhibitive film starts only after 2 h when oxygen level is 0–15 ppm, and even after 4 h the film is not insulating.

Thus, the slow formation of the [Cu(I)-BTA] film observed here is likely to result from residual oxygen in the solutions and not from a surface oxide.

Conclusions

In this study, the inhibition of copper by BTAH has been studied by scanning electrochemical microscopy. Oxygen was shown to be required for the formation of an inhibiting film. However, even in solutions where the O$_2$ content was <90 ppb, an inhibiting film gradually formed. The thickness of the film was estimated to reach approximately 30 nm in 4 h under normal atmospheric conditions, and only 5 nm in oxygen-free conditions.

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