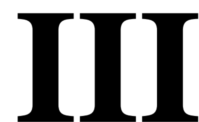

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The Effect of Oxygen on the Inhibition of Copper Corrosion with Benzotriazole

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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.
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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 that copper forms a cuprous benzotriazole complex, [Cu(I)-BTA], which is responsible for the corrosion inhibition.[1-5] Furthermore, the [Cu(I)-BTA] complex forms a chemisorbed layer at low coverage and a multilayer with a polymerized structure at high coverage.[1,3-10]

Scanning tunneling microscopy (STM) studies in vacuum[11] 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. Cho et al.[11] observed that when part of the copper surface is exposed to oxygen, BTAH preferentially adsorbs on the oxidized areas. Additionally, they reported that oxygen seems to enhance film growth. Fang et al.,[12] however, have observed that chemisorption of BTA occurs in a similar way on both oxidized and clean copper surfaces.

Theoretical calculations by Jiang and Adams[13] show that BTAH and BTA^- can either physisorb or weakly chemisorb on Cu(111) surfaces without oxygen. However, the hydrogen bonds between the C–H and N atoms cannot form and induce polymerization. Tromans et al.[14] suggested that adsorption of BTAH on oxygen-free surfaces depends both on time and potential. According to these studies, the [Cu(I)-BTA] complex is formed in the diffusion layer from $CuCl_2^-$ in chloride-containing solutions; then, the [Cu(I)-BTA] complex forms a polymeric film when it is adsorbed on the monolayer-covered copper surface. According to Ling et al.,[15] the formation of [Cu(I)-BTA] occurs on the Cu_2O surface and not in the solution. Additionally, they did not observe the inhibitive effect of BTAH when the copper surface was etched before immersing in BTAH solution.

Additionally, the difference between free oxygen (i.e., O_2) and oxygen bound in the metal oxide (i.e., Cu_2O) in the inhibition mechanism has been studied.[16] When the copper surface was etched before exposure to BTAH, adsorption of BTAH on metallic copper was observed. The Cu(0)-BTAH film was then proposed to form [Cu(I)-BTA] through reaction with O_2 and copper. We have previously studied inhibition of copper corrosion with scanning electrochemical microscopy (SECM) under ambient atmospheric conditions.[17,18]

The studies where oxygen has been removed simply by bubbling with nitrogen should be taken into account with caution. Copper oxide films start to grow in milliseconds if any oxygen is present in the atmosphere or in the solution, and bubbling the solution with nitrogen may not be enough to prepare oxygen-free solutions. In this communication the effect of oxygen on the formation of an inhibitive [Cu(I)-BTA] film on oxygen-free dehydrated copper (OF-HF) has been studied with SECM. The measurements were performed in oxygen-free conditions (O_2 in solution <90 ppb and in gas phase <75 ppm) and under ambient conditions. The importance of oxygen in the film formation is clearly shown.

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 O_2 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 (FcMeOH: Aldrich, Na_2SO_4 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, O_2 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. After this the sample was transferred into the nitrogen box and electropolished at 5 V for 2 min in a solution of concentrated phosphoric and sulphuric acid (77% H_3PO_4, 11.5% H_2SO_4, 11.5% H_2O by volume). The sample was rinsed carefully with ethanol and MQ water. The substrate was stored in ethanol in the nitrogen box between polishing and the measuring.

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 FcMeOH + 0.1 M Na_2SO_4 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 FcMeOH and 0.1 M Na_2SO_4. 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 FcMeOH

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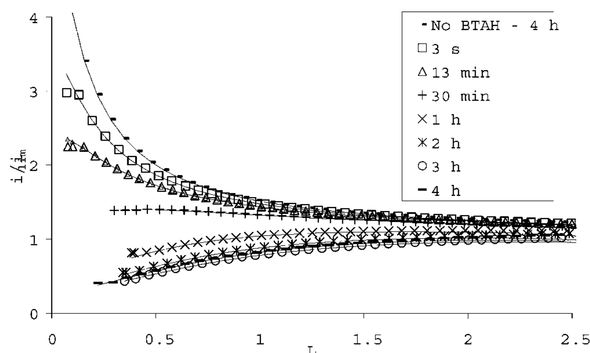

Figure 1. The approach curves measured in a normal atmosphere at OCP (−0.082 V vs SCE). i/i_{lim} is the dimensionless tip current, and $L = d/a$ is the dimensionless distance between the sample and the tip.

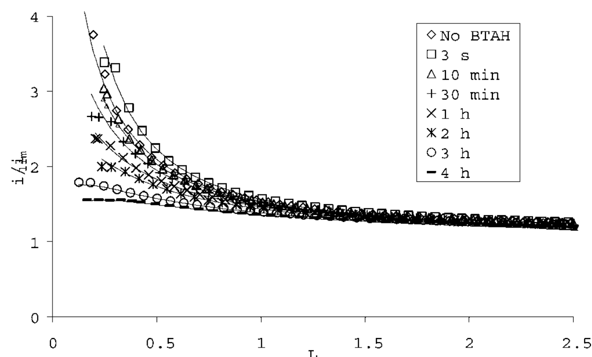

Figure 2. The approach curves measured in oxygen content 25–75 ppm at OCP (−0.027 V vs SCE). i/i_{lim} is the dimensionless tip current, and $L = d/a$ is the dimensionless distance between the sample and the tip.

+ 0.067 M Na_2SO_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 was studied, and consequently, artifacts due to a heterogeneous substrate surface were avoided. The measurements were modeled as previously described[17,18] using models reported.[19-21]

Additionally, a blank test was made in normal oxygen-containing conditions in the absence of BTAH (1 mM FcMeOH + 0.1 M Na_2SO_4) to ensure that the observed passivation of the copper surface was due to the [Cu(I)-BTA] film rather than copper oxide. The measurement setup was as described above; however, 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.[17,18]

Figures 2 and 3 show the approach curves of OF-HC copper at oxygen contents of 25–75 and 0–15 ppm, respectively. As shown in these figures, the formation of the insulating [Cu(I)TBA] 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.[17-21] 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 $4 \cdot 10^{-9}$ cm^2 s^{-1}.[5,22] 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,[15] 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.[15] have shown that it is likely that [Cu(I)-BTA] is formed on Cu_2O. We have previously found that the formation of [Cu(I)-

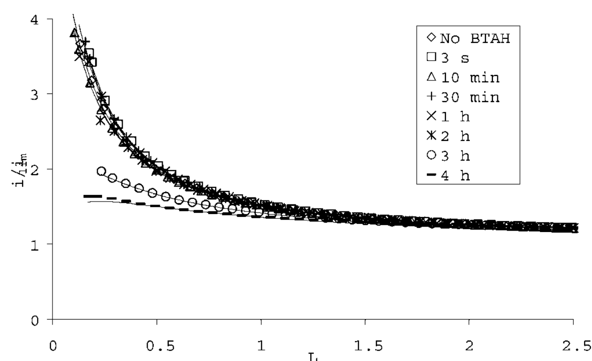

Figure 3. The approach curves measured in oxygen content 0–15 ppm at OCP (−0.040 V vs SCE). i/i_{lim} is the dimensionless tip current, and $L = d/a$ is the dimensionless distance between the sample and the tip.

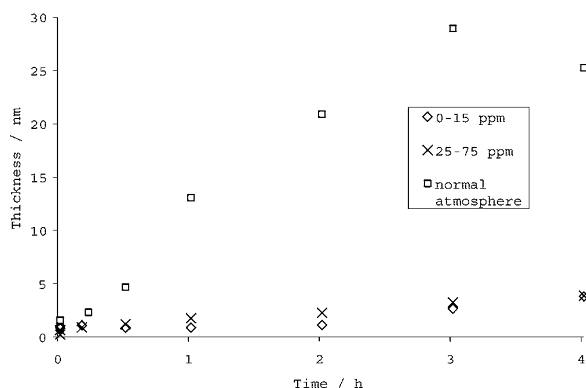

Figure 4. Thicknesses of the [Cu(I)-BTA] film as function of exposure time to the solution containing benzotriazole at OCP.

BTA] film is faster if the surface has not been reduced before the application of the BTAH solution.[18] Xue et al.[16] 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_2O 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 (Fig. 3). It is known that the formation rate of Cu_2O is strongly dependent on oxygen content.[23] 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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