Characterization of Films Developed on Copper in Presence of Different Triazole Derivative Inhibitors

W. Qafsaoui, C. Blanc, N. Pébère,
H. Takenouti* and G. Mankowski

CIRIMAT, UMR CNRS 5085,
ENSIACET, 118 route de Narbonne
31 077 Toulouse Cedex 4, France
*UPR 15 du CNRS, 4 place Jussieu
75252 Paris Cedex 05, France

In previous works, the inhibitive efficiency of different triazole derivative compounds - benzotriazole (BTAH), 1-hydroxybenzotriazole (BTAOH) and 3-amino 1,2,4-triazole (ATA) - to protect copper against pitting corrosion by chloride ions (1) and sulfate ions (2) has been investigated in a borate-buffered solution (pH 9). The inhibitive efficiencies of BTAH and BTAOH were found to be greater towards pitting induced by sulfate than towards pitting induced by chloride. For ATA, an opposite behavior was observed.

This work is devoted to the characterization of the films developed on copper by polarization at 400 mV/SCE for one hour in borate-buffered solution in presence of 10^{-4} M or 10^{-2} M BTAH, BTAOH or ATA. The results obtained from coulometric experiments were compared to those obtained from an electrochemical quartz crystal microbalance (EQCM).

Figure 1 shows the potential-time curves plotted during the reduction of the films. The applied cathodic current density was 50 µA cm^{-2}. For films formed in absence of inhibitor, the two first plateaus at -250 and –540 mV/SCE correspond respectively to the reduction of CuO into Cu_2O and to the reduction of Cu_2O into Cu. For films developed in presence of an inhibitor, no further plateau was observed. So, it can be assumed that the copper ions involved in bonds with the organic molecules are simultaneously reduced with the copper ions of oxides. From the duration of the plateaus, the amounts of Cu^+ and Cu^{2+} ions in the layers were calculated. By comparison with the oxide film developed in the only borate-containing solution, BTAOH did not produce a significant variation of the amounts of these ions. ATA induced a slight decrease of these amounts but only for the higher concentration. In presence of BTAH, the amount of Cu^+ greatly increased and that of Cu^{2+} was very low.

The potential of the Cu^{2+} into Cu^+ reduction plateau did not vary on addition of BTAOH and ATA. For BTAH, the variation observed only results from the low area surface fraction covered by CuO. The potential of the second plateau varied on addition of BTAH or ATA suggesting the existence of bonds between Cu^+ ions and the organic molecules. With BTAOH, this potential did not vary suggesting that this molecule only is adsorbed on the oxide surface.

Table 1 compares the mass increasing measured by EQCM and the mass increasing calculated from coulometric experiments and corresponding to the formation of Cu_2O and CuO (assuming all the copper ions are bonded with oxygen). These values very well agree in absence of inhibitor. In presence of an inhibitor, the difference between these values represents the mass increasing due to the organic part. It can be noticed that the organic part is very low for BTAOH by comparison to ATA and BTAH. Once more, BTAOH seems only adsorbed on the copper surface. Moreover, since BTAH and ATA are probably bonded to Cu^+ ions, the organic parts are, in these cases, underestimated.

References :
[1]. W. Qafsaoui, C. Blanc, N. Pébère, A. Srhiri and G. Mankowski, J. Appl. Electrochem. **30**, 959 (2000)
[2]. W. Qafsaoui, C. Blanc, J. Roques, N. Pébère, A. Srhiri, C. Mijoule and G. Mankowski, J. Appl. Electrochem. **31**, 223 (2001)

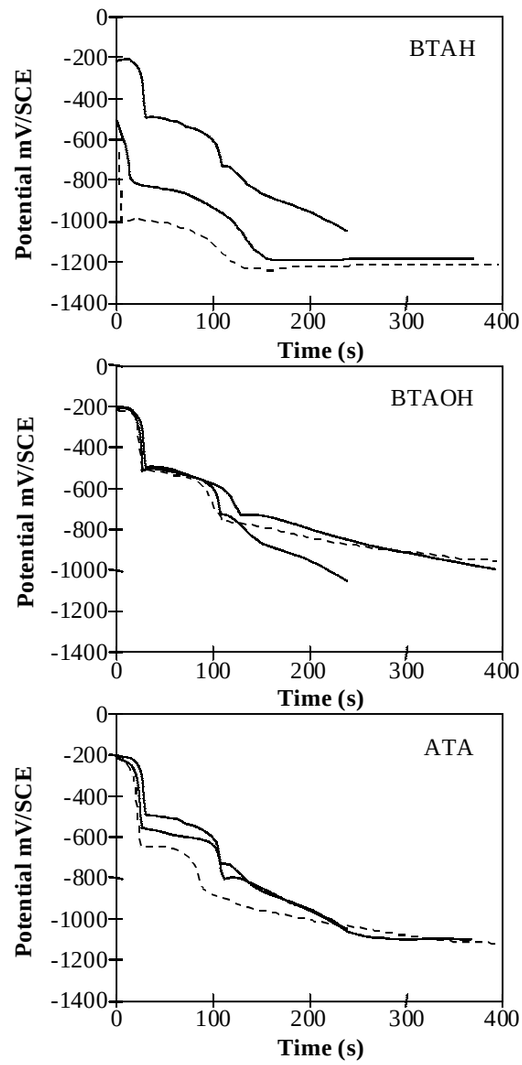

Figure 1 : Reduction curves of films developed on copper in solution without inhibitor (—) or with 10^{-4} M (·····) or 10^{-2} M (----) BTAH, BTAOH or ATA.
Applied cathodic current density : 50 µA cm^{-2}

Table 1: Comparison of mass increasing (µg cm^{-2}) measured by using an electrochemical quartz crystal microbalance and mass increasing calculated from coulometric experiments.

	Δm (EQCM)	Δm (coulometry)	Organic part
Without inhibitor	43.9 10^{-2}	44.0 10^{-2}	
ATA 10 mM	153.3 10^{-2}	35.7 10^{-2}	117.6 10^{-2}
BTAH 10 mM	92.8 10^{-2}	46.8 10^{-2}	46.0 10^{-2}
BTAOH 10 mM	57.2 10^{-2}	43.1 10^{-2}	14.1 10^{-2}