

Investigation of the behavior of 5-mercapto-1-phenyl-tetrazole as an inhibitor against copper corrosion in sulfuric acid media

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The potential dependence of adsorption and kinetic properties of inhibitor film formation on copper surface was studied in acidic environment by using surface sensitive techniques (electrochemical quartz crystal microbalance (EQCM), electrochemical scanning tunneling microscopy (EC-STM). The investigated inhibitor was 5-mercapto-1-phenyl-tetrazole (5-MPhTT) in 1×10^{-3} M H_2SO_4 (blank) (see Fig. 1).

Results showed that 5-MPhTT was chemically adsorbed and remained effective on the surface even after changing back the electrolyte to sulfuric acid solution without any inhibitor. In this case results showed a protection efficiency of 99%.

QCM results provided some information that the inhibitor adsorption appears to be of a mono or even less than monolayer coverage.

ECQM results reflected that 5-MPhTT was chemically adsorbs onto copper electrode and was present on the surface during anodic dissolution.

The adsorption/desorption processes were investigated also by potentiodynamic STM. A well ordered sulfate layer showed a Moiré structure. The ordered superstructure depends on the scan rate, the chosen potential and also on the waiting time. The fast adsorption of sulfate resulted in a structureless surface. Cyclic voltammetry results showed that in pure sulfuric acid solution the sulfate adsorption-desorption peaks appeared. At a potential far enough from the sulfate adsorption peak, well defined straight monoatomic steps are visible. At positive potentials, where the sulfate should be adsorbed to the surface, the step edges are frizzy (Fig. 2). Stepping the potential to more positive direction, the step edges became rougher, which can be explaining by a mass transport on the copper surface, copper dissolution take place.

Due to the addition of 5-MPhTT to the solution, characteristic structural changes are observed on the Cu (111) single crystal surface in the double layer regime. Our previous measurement showed that, at open circuit potential, how inhibitors block the step edges and the copper dissolution could not take place [1-3].

In the presence work we analyzed the influence of adsorbed sulfate in the inhibition mechanism. When the inhibitor was added to the solution, where no adsorbed sulfate on copper, the surface morphology showed stepped structure. In some places an accumulation of the inhibitor, with height of 3-6 Å, was observed.

Measurements were done also in the presence of adsorbed sulfate layer on the surface. The inhibitor was added to the solution and the surface is now covered by a phase, which appears uniform in larger scale.

Stepping the potential slowly to more negative directions the same surface morphology was observed as in the pure H_2SO_4 solution, with smooth terraces separated by monoatomic steps.

Further investigations were done in more diluted solutions where the inhibitor concentration was 5×10^{-7} M 5-MPhTT.

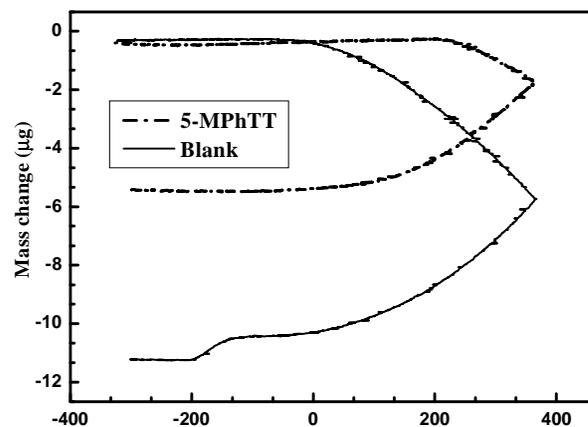


Fig. 1. Mass change vs. potential during anodic polarization from -300 mV to $+400$ mV and back to cathodic direction

EC-STM measurements in pure H_2SO_4 clarified the surface structure, atomic high steps with adsorbed sulfate layer, in the double layer potential range. The dissolution in pure sulfuric acid solution started at terrace edges and proceeds along the steps.

5-MPhTT adsorbate species are observed in the potential regime of adsorbed sulfate layer. At high inhibitor concentration (5×10^{-4} M), a thick uniform layers form on the surface. At more negative potentials where desorption of sulfate adlayer should occur, or the

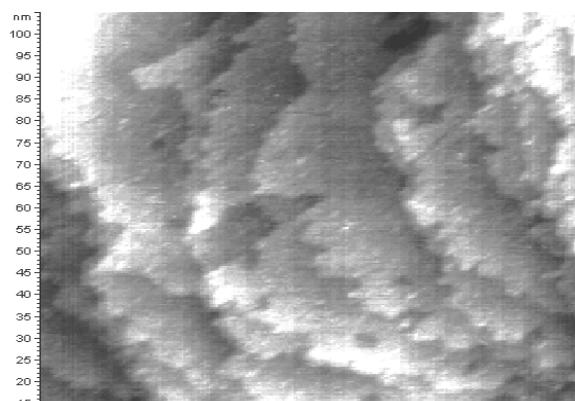


Fig. 2. Cu(111) morphology in pure H_2SO_4 solutions, frizzy steps in presence of sulfate layer

hydrogen evolution process took place, the inhibitor layer was partially removed and the stepped surface appear. When no sulfate adlayer was on the surface, stepped structure and inhibitor accumulations can be observed.

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