INVESTIGATION OF COPPER CORROSION INHIBITION IN SULFATE-ION CONTAINING ACIDIC SOLUTIONS

Studies by electrochemical techniques and scanning tunneling microscopy

PhD thesis

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1. Summary

Different heterocyclic compounds were tested as copper corrosion inhibitors in sulfate-ion containing acidic (pH < 3) solutions. The investigated compounds are the following:

Thiazole derivatives:

- 5-(4'-isopropylbenzylidene)-2,4-dioxotetrahydro-1,3-thiazole (**5-IPBDT**)
- 5-benzylidene-2,4-dioxotetrahydro-1,3-thiazole (**5-BDT**)

Tetrazole derivative:

- 5-mercapto-1-phenyl-tetrazole (**5-MFT**)

The results can be summarized as follows:

1. In electrochemical measurements all tree inhibitors hindered the copper corrosion in sulfate-ion containing acidic solutions. These chemicals are cathodic type inhibitors, they effect the cathodic reactions. The results showed that 5-IPBDT is better inhibitor then 5-BDT. The concentration dependent anticorrosion efficiency of the 5-mercapto-1-phenyl-tetrazole in acidic solution has shown that the efficacy increased till the critical concentration value (C_{crit}) then the effect has decreased by increasing the 5-MFT concentration in the solution. The C_{crit} was $5 \cdot 10^{-4}$ mol·dm^{-3} 5-MFT where the corrosion current was minimum.

2. By electrogravimetrical measurements, it was obtained that the 5-mercapto-1-phenyl-tetrazole inhibitor forms an interface-type protective layer on the copper surface, while the thiazole derivatives cover the copper surface in a very thin, patchy layer. The XPS results showed that in presence of 5-MFT the copper surface was covered with Cu(I)-MFT layer.

3. In order to use the scanning tunneling microscopy effectively pre-experiments were done which result in the following:

- Atomic sharp tips were made from tungsten wire. A new tip etching procedure was developed.

- Clean, atomic smooth copper surfaces were prepared from bulk copper and thin layers. In case of bulk copper single crystal the mechanical polishing method was followed by electrochemical polishing procedure. A very smooth copper surface was obtained where the atomic steps on the surface were visible.

  Thin copper layers were deposited by vacuum evaporation method. Correlation was obtained between characteristics of the copper surface and the evaporation procedure. As the röntgen-diffraction measurements proved the thin layer of the copper showed (111) orientation.

4. Correlation was found between the inhibition efficiency of 5-mercato-1-phenyl-tetrazole and structure of the copper surface by using scanning tunneling microscopy. A relatively smoother surface structure was obtained in case of inhibitor with better corrosion inhibiting efficiency than in blank solution, where the dissolution of surface oxide layer was significant.

5. The adsorption property of 5-MFT inhibitor was studied by electrochemical scanning tunneling microscopy. The results have revealed that in the double-layer potential region an inhibitor layer formed, which was removed from the surface at a potential less then –400 mV vs. SCE.

6. Correlation was obtained between data got by STM and quantum chemical calculations. On the basis of the STM images the length of 5-MFT molecules

that covered the copper single crystal surface was 0.95 nm. According to the quantum chemical calculations the sizes of a 5-MFT molecule are the follows: length 0.96 nm and the diameter 0.6 nm.

7. A model showing the monolayer inhibitor film on copper surface was drawn for the observed superstructure of 5-MFT molecules on copper single crystal.

8. Significant difference was visualized on the copper single crystal dissolution in uninhibited and inhibited sulfuric acid solutions. The copper (Cu(111)) dissolution in sulfuric acid starts at the edges of the crystal steps and proceeds along the stairs, the dissolution in presence of 5-mercapto-1-phenyl-tetrazole inhibitor is initiated on terraces because the inhibitor molecules block the step edges.

2. Publications

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