INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title:
Mechanistic and Kinetic analysis of Anodic Dissolution of Metals (Carbon Steel and Molybdenum) in Solution of Interest by Electrochemical Methods

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Oil and gas industries experience failures due to corrosion due to the exposure of the most used material, carbon steel, being exposed to various components such as CO_2, H_2S, NaCl, and volatile fatty acids present in produced water. In spite of the corrosion failures, carbon steel is still used widely because of economic considerations and also a property of the material that the material inhibits corrosion up to some extent from the corrosion product layer. However, due to prolonged exposure and several other factors, loss due to corrosion failure happens. Hence understanding the corrosion mechanism will help to find ways to control and mitigate corrosion.

Semiconductor industries use slurries to planarize materials for microelectronics fabrication. Cu and Ta/TaN have been used conventionally since time, but in the present day, Mo is replacing Cu for interconnect materials due to its suitable properties for semiconductor applications. The

planarization process includes oxidizing the metal using a suitable oxidizer, and the oxidized layer is removed by abrasives or a polishing pad. Hence, to achieve the desired planarization designing of the slurry is most important with desired selectivity. To accomplish the desired oxidation, understanding the dissolution mechanism is most important. Several oxidizers are reported for the CMP process of metals, but the dissolution mechanism for Mo has not been explored in detail.

The initial part of the present study is to investigate the dissolution mechanism of Mo in H_2O_2 at alkaline pH. Various electrochemical techniques, such as potentiodynamic polarization and electrochemical impedance spectroscopy, were implemented to study the dissolution mechanism in detail. According to the polarization measurements data obtained, there was no passivation observed in the applied conditions, and active dissolution was observed throughout. Further, the impedance data was acquired at various DC overpotentials, and the EIS data was further analyzed using electrical equivalent circuit and reaction mechanism analysis. The surface characteristics were also studied using FESEM, and uniform corrosion behavior was observed. The mechanism with three intermediate adsorbates *(Mo^{2+}, Mo^{4+}, Mo^{6+})* and two dissolution paths, including electrochemical and chemical, is proposed to predict the metal surface behavior in an oxidizing medium in the alkaline region. XPS analysis of the corrosion product confirmed the formation of Mo oxides. RMA analysis suggests that the dissolution via the electrochemical reaction pathway is predominant compared to the chemical reaction pathway. Further, the surface coverage of all the intermediate adsorbates is estimated, revealing that oxides of Mo with a +6 oxidation state are mainly occupied on the metal surface. FESEM and XPS measurements substantiated the findings from the RMA analysis.

The second part of the study discusses the dissolution mechanism of Mo in $KMnO_4$ solution under alkaline conditions. If compared with the second part, the etch rate of Mo in $KMnO_4$ was observed

to be less than the etch rate of Mo in H_2O_2. However, the polish rate for Mo in $KMnO_4$ was observed to be significantly high. The dissolution mechanism proposed for the H_2O_2 system was used in the $KMnO_4$ system to compare the dissolution behavior of both systems. The potentiodynamic polarization measurements showed a higher rate of change in current density with respect to the potential at higher potential. Through RMA analysis, it was found that the surface coverage was mainly due to Mo (VI) and the surface coverage decreased with an increase in overpotential. FESEM and XPS analysis corroborated with the RMA analysis results.

The third part of the thesis is about comparing the corrosion behavior of various grades of carbon steel in CO_2-H_2S solution at various acetic acid concentrations. Electrochemical techniques and other complementary methods, such as FESEM, contact angle, and XPS measurements, were incorporated to investigate the corrosion behavior of API 5L X52 and X60. The results are evident to suggest that the carbon steel grade strongly influences corrosion rate as X60 corrodes more than X52 in the system being investigated. The possible mechanism behind the higher corrosion rate observed for X60 is elucidated via analyzing the impedance data acquired at various overpotentials by the reaction mechanism analysis approach. The kinetics of dissolution in the given environment for the carbon steels is also reported. It is observed that X52 possesses higher surface energy due to lower contact angle. This eventually increases the production of corrosion product $FeCO_3$ on the X52 surface. The $FeCO_3$ layer formed on X52 is fine in nature, acts as a protective layer, and decreases the corrosion rate. XPS study confirms a higher fraction of $FeCO_3$ formed on X52.