The Dependency of Surfactants on the Metal Surface Removal Using CO₂-HNO₃ Microemulsion

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1. Introduction

Metal surface removal is one of important steps in decontamination of radioactive contaminated metal parts and components. The conventional chemical stripping method prevalently used today cleans materials by dipping them into a strong acidic or alkaline solution in order to remove metal film. Because so much more toxic solvent is used than needed, excessive expense is incurred in treating the waste by-products. Carbon dioxide (CO₂) has excellent properties; economical, environment-friendly, good in penetration and reasonable in critical conditions. However, CO₂ is a non-polar compound that is very poor at dissolving polarized materials. To increase the dissolving power of CO₂ against polar materials, our laboratory has developed a CO₂ micro-emulsion method. We use acid- CO2 microemulsion in metal surface or coating removal.

Formation of microemulsion in liquid or supercritical CO_2 essentially needs surfactants[1-4]. So far, we have developed 3 types of surfactants- fluorinated AOT, proline, and NP-4. This three surfactants help the formation of microemulsion of water (or acid) with CO_2 . In this paper, we compare the characteristics of microemulsion formed by each surfactant in metal coating removal. Quartz crystal microbalance (QCM) was used to measure the rate of metal coating removal[5].

2. Experiments

Three different surfactants were used for the formation of microemulsion in CO_2 . The molecular structures of the surfactants are shown in Fig. 1. F-AOT and proline surfactants are synthesized in the lab. and NP-4 was purchased.

The one side of QCM was electroplated with cupper or nickel, and used for the metal coating

removal rate measurements. A reference QCM, the surface of which is gold plated, was also inserted for reference frequency measurement. Fig.2 shows the reactor system (high pressure viewcell) and QCM arrangements in it. The experimental set of connections is shown in Fig.3



Fig.1. Surfactants used in this study. a) F-AOT, b) Proline, c) NP-4.



Fig.2. The high pressure viewcell (reactor) and QCM arrangements in the cell.



Fig.3 The experimental set of connections.

The surfactant and nitric acid were inserted into the viewcell before the measurement. After

insertion of CO_2 , microemulsion started to form with the agitation of a magnetic bar inside the cell. The frequencies of the coated and reference QCM's were recorded for the measurement of metal coating removal rates.

3. Results and discussion

Metal removal rates under F-AOT and proline surfactants are shown in Fig.4 and Fig.5, respectively. In the case of F-AOT, the metal removal rates are strongly depends on the amount of HNO₃ and W values. The removal rate increases with HNO₃ amount in the system. Metal dissolves faster at the lower W values. However, with proline surfactants, metal dissolves faster and fully. The rates are relatively independent to W values or HNO₃ amount.



Fig.4. Cu coating removal rates in microemulsion by F-AOT at different conditions.



Fig.5. Cu coating removal rates in microemulsion by proline at different conditions.

The forms of microemulsion seem quite different depending on the surfactants. F-AOT takes a form of sphere-core microemulsion, while proline and NP-4 may form very fine dispersion all across their chains. W value dependency under F-AOT also results from Na ions in F-AOT that can neutralize nitric acid. No meaningful data were obtained under NP-4 surfactant. The fine dispersion became very unstable if metal dissolves into it, which was conformed by variable volume viewcell experiments.

4. Conclusion

Three different surfactants take different forms of microemulsion with CO₂, which resulted in different metal dissolving kinetics. F-AOT makes spherical cores, and the kinetics of metal dissolution depends on acid amount and W-values. The fine dispersion by NP-4 becomes unstable if metal dissolves into the dispersion. Proline was very effective in metal dissolution, which is somewhat independent to acid amount and Wvalues. This behavior can be explained by fine dispersion form of microemulsion.

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