

Measurement of the Removal Rate of Metal Film in $\text{scCO}_2\text{-HNO}_3$ Microemulsion by QCM

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1. Introduction

As all components and materials in a nuclear power plant environment are exposed to radioactivity, regular cleaning is an absolute necessity. The chemical decontamination method currently used removes metal films by washing after soaking in a strong acid bath or strong alkali solution. This method uses highly toxic solvents that become problematic to dispose of while incurring excessive expense. Therefore, we require a new surface decontamination method. If CO_2 is used as a solvent for decontamination of radioactive contaminants, the wastes can be effectively reduced by CO_2 . CO_2 is an inexpensive, renewable and environment friendly solvent that has excellent properties at low critical conditions, and can separate and extract contaminants by controlling pressure and temperature. scCO_2 is an optimal solvent particularly for surface treatment of precision parts because it has the properties of being both highly-dense, almost liquid-like, to provide effective solvating capability, while also being gaseous enough to aggressively penetrate into micropores. However, carbon dioxide is a non-polar substance that has a very weak solvating effectiveness against polar materials. There have been many studies done to find ways to increase the solvating effectiveness of CO_2 against polar materials. [1-3]

This study used a QCM electrode to characterize the removal reaction of the metal film in $\text{scCO}_2\text{-HNO}_3$ microemulsion that has wide applications.[4-5]

2. Experiment

2.1 Material and surfactant

CO_2 and nitrogen with a minimum purity of 99.98% were purchased from Air Tech, Korea. Cyan-cooper plating solution was purchased from Aldrich. The surfactant used F-AOT and Proline surfactant-1, which were synthesized newly by our laboratory. QCM(AT-cut, 5MHz in inherent resonance frequency, and 0.268 inch in electrode diameter) was obtained from International Crystal Mfg, USA. Then we plated the Cu coating on QCM surface with 0.1A, 30sec.

2.2 Experimental procedures

Surfactant and HNO_3 were loaded in the high-pressure vessel, and it was put into the water-bath to

control temperature. When the QCM frequency was stable at 3bar N_2 gas and constant temperature, CO_2 was introduced into the high-pressure vessel by syringe pump (ISCO Model 260D, Lincoln, NB, USA). We continuously stirred and waited for the formation of microemulsion at 250bar CO_2 to observe removal of the metal film of QCM which is Cu-plated.

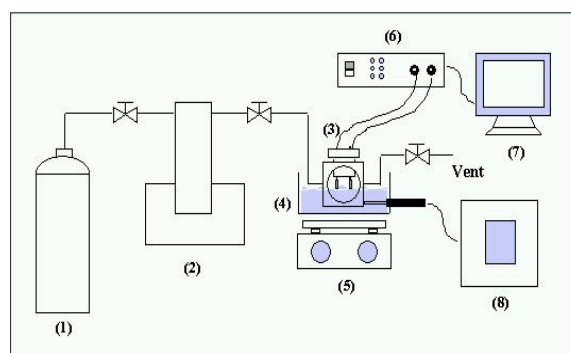


Figure 1. Experimental apparatus ; (1) CO_2 cylinder (2) Syringe pump (3) Reaction cell (4) Water bath (5) Magnetic stirrer (6) RQCM (7) Monitor (8) Temperature controller

3. Results and Conclusion

The real-time removal characteristics induced by both a $\text{scCO}_2\text{-HNO}_3$ microemulsion applied to a copper electroplated QCM were analyzed and compared.

The surfactants F-AOT and proline surfactant-1 were used for the microemulsion. For this experiment, Cu was selected as the metal and 1M HNO_3 as the polar substance in the reverse micelle. The removal characteristics of the Cu electroplated surface of the QCM electrode were analyzed and compared. The removal rate of the electroplated surface of the QCM electrode varied depending on the type of surfactant and experimental condition. For the F-AOT, the removal rate ranged from $0.8 \mu\text{g}/\text{cm}^2\text{min}$ to $1.6 \mu\text{g}/\text{cm}^2\text{min}$. The proline surfactant-1 displayed a far higher the removal rate of $7.3 \mu\text{g}/\text{cm}^2\text{min}$. It was concluded that the removal rate was determined by the diffusivity of the HNO_3 in the microemulsion, and the thickness of the surfactant, that is, the thicker the surfactant became relative to the size of the micelle, the more inhibited the reaction became. The proline surfactant-1 removed the metal film at a far higher rate than the F-AOT. In about

thirty minutes, the copper electroplate was completely removed from the surface of the QCM electrode after which the QCM operated at its original frequency. This study suggests basic data for the optimal decontamination conditions for cleaning metal surfaces.

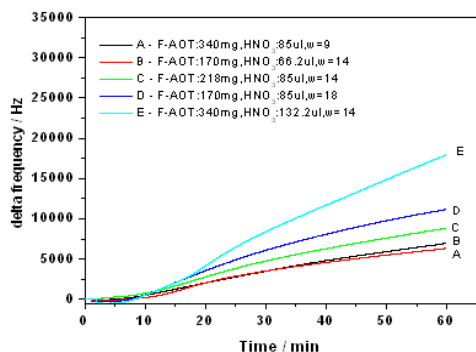


Figure 2. The results of the measurement removal rate by F-AOT

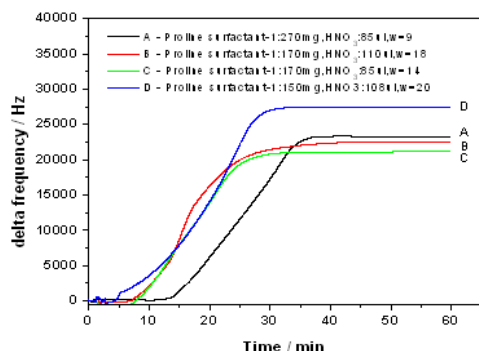


Figure 3. The results of the measurement removal rate by Proline surfactant-1

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