Dissolution kinetics of metal coating in HNO_3-scCO_2 micro-emulsion using QCM

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1. Introduction

Radioactive contamination is rising because of an increasing number of nuclear facilities. Among the decontamination methods, the surface decontamination method is especially important. Conventional chemical decontamination methods for surface decontamination cause not only secondary radioactive wastes, but also corrosion and defects on the surface of equipment. 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 recycling the CO_2.

Supercritical fluid has many good points as a process solvent, including low viscosity, negligible surface tension, and variable selectivity. And supercritical fluids have physical properties of both liquid and gas, such as good penetration with a high dissolution capability. A number of workers applied supercritical CO_2 solvent for cleaning precision devices and waste treatments [1-2]. Since supercritical CO_2 has its mild critical point at 31℃ and 73.8bar as well as low surface tension, it is a potentially suitable cleaning substance. The operational costs of CO_2 cleaning were estimated to be lower than other cleaning processes [3]. However supercritical CO_2 has limited solubility about contaminated material. To tackle these problem, we researched various aspects of surfactants.

Quartz Crystal Microbalance (QCM) is a thickness-shear mode resonator in which the acoustic wave propagates in a direction perpendicular to the crystal surface [4]. The use of QCM as a chemical sensor has its origins in the work of Sauerbrey and King [5-6] who carried out micro-gravimetric measurements in the gas phase. It was assumed in their work that a thin film applied to a thickness-shear-mode device could be treated in sensor measurements, and a shift in the resonance frequency of an oscillating AT-cut crystal could be correlated quantitatively with a change in mass added to or removed from the surface of the device [7]. Now, the QCM technique expands its application area to pressurized fluids such as liquids and supercritical CO_2.

In this study, we made a HNO_3-scCO_2 micro-emulsion to remove a film from a contaminated metal surface. F-AOT and Proline surfactant-1 were used as a surfactant. HNO_3 was used as a acid solution for dissolution Cu coating. As a setting for experimental conditions, we analyzed the film removal characteristics of Cu and Ni coated QCM.

2. Experiment

2.1 Material and surfactant

Carbon dioxide 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 on the QCM surface with 0.1A, 30sec.

2.2 Experimental apparatus and procedures

We made a high-pressure system for removal characteristic of metal coating films in a HNO_3-scCO_2 micro-emulsion using QCM.(Fig 1). We had a sapphire window installed on both sides of the reactor vessel for in-situ observation of micro-emulsion formation.

<u>Experimental procedures</u> - 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 micro-emulsion at 250bar CO_2 to observe removal of the metal film of QCM which is Cu-plated.

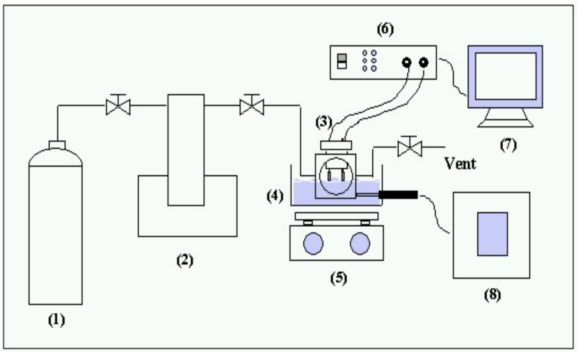

Figure 1. Experimental apparatus ; (1) CO_2 cylinder (2) Syringe pump (3) Reaction cell (4) Water bath (5) Magnetic stirrer (6) RQCM (7) Monitor (8) Temperature controller

3. Results and conclusion

3.1 Micro-emulsion formation in the supercritical CO_2

We performed the check micro-emulsion formation by installed sapphire windows in the high-pressure vessel. In case of F-AOT, we put the surfactant and 1M HNO_3 in the reactor vessel according to experimental conditions (temperature 55℃, pressure 250bar). Initially, the state in the cell appears in two phase without agitation. If it began after 5 minutes of agitation, a partial micro-emulsion formed. After more than 10 minutes, we observed that micro-emulsion formed on the whole uniformly. However, this experiment showed that, Proline surfactant-1 took less time than F-AOT to form a HNO_3-$scCO_2$ micro-emulsion.

3.2 Dissolution characteristics of Cu and Ni film in HNO_3–$scCO_2$ micro-emulsion

We compared the removal characteristics of Cu-coated QCM with the removal characteristics of Ni-coated. The results of the dissolution of the metal films can be seen in Fig 2 and 3, along with the quantity of HNO_3 and the w-value. The reason the different slope in the initial states of Cu and Ni, is that the composition of brightener contained in the film was removed with Ni. We found that the larger the volume of HNO_3, the faster the removal rate. Also, with an equal quantity of HNO_3, a large W-value, also correlated with a faster removal rate. We determined that the film removal rate depended on the HNO_3 diffusion in the micro-emulsion. The reaction was reduced as the thickness of surfactant increased in the micelle size. When using Proline surfactant of new synthesis surfactant, the plated film was completely removed much faster than when using F-AOT. After 30 minutes, QCM recovered the original frequency, because the Cu film was removed completely. When we used Proline surfactant-1, the coating film was removed completely. The reason may be that the micro-emulsion form is different with F-AOT. So we are still studying it.

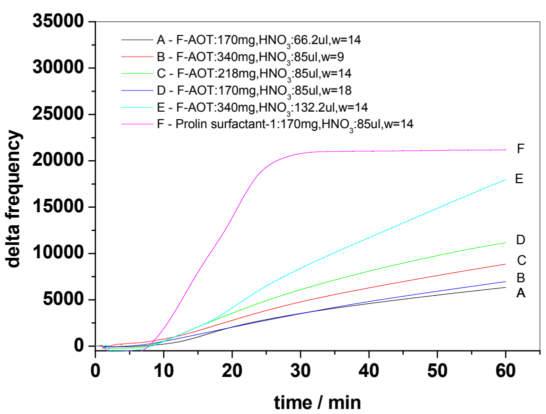

Figure 2. The results of the measurement Cu removal rate of the delta frequency

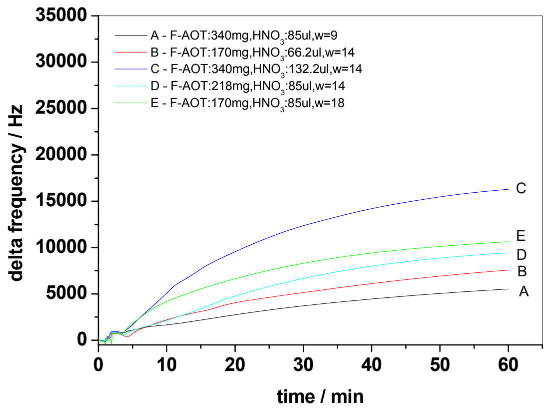

Figure 3. The results of the measurement Ni removal rate of the delta frequency

Acknowledgment

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