

Measurement of Metal-Film Removal Rate in a Microemulsion Using QCM

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Abstract

A set of Quartz Crystal Microbalances (QCM's) was used to observe the film removal characteristics of three different CO₂-nitric acid microemulsions. QCM's electroplated with nickel or copper were used as specimens. F-AOT, NP-4 and the newly synthesized Proline Surfactant-1 were used as surfactants to create microemulsions. While the F-AOT microemulsion yielded a relatively low removal rate, that of the Proline Surfactant-1 completely removed the Cu metal film within a short period of time. The NP-4 microemulsion removed the metal surface. However, removal rate measurements per QCM were not possible due to the instability of the microemulsion when Cu ions were present in the nitric solution. The reaction kinetics and metal removal capabilities of microemulsions formed by the different surfactants are explained along with the characteristics of reverse micelles.

Keywords: Supercritical, Carbon dioxide, CO₂, Microemulsion, Surfactant, Environment, QCM

1. Introduction

The 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. Also, because a drying process is required, the current method incurs more time and labor expenses. Stains are also produced as well. However, when supercritical carbon dioxide is used as a solvent, separating the solvent from the materials is much easier (but only with depressurization after stripping). Furthermore, the carbon dioxide can be recovered for reuse. Moreover, since a drying process is not required, surface defects, such as stains, can be reduced and energy expenses saved. Therefore, a process using carbon dioxide is far more environment-friendly and more economical.

Carbon dioxide has excellent properties. It is economical and can be used in a low critical condition. In its use with a surfactant, it is environment-friendly

and can be used efficiently to remove surface contaminants with the only requirement being the adjustment of pressure and temperature. Moreover, since supercritical carbon dioxide is very dense, like a liquid, it can effectively clean broad surfaces. But it also has a low viscosity and high diffusivity, like a gas, which enables it to penetrate and effectively clean deep into micro pores. Therefore it has advantages appropriate for surface treatment of precision parts.

However, carbon dioxide is a non-polar compound that is very poor at dissolving polarized materials. Many scientists are researching ways to increase the dissolving power of carbon dioxide against polar materials. To date, there are basically the surface chelating method and carbon-dioxide + microemulsion method. The former is widely utilized in the extraction of metal ions. In that technique, a surfactant is formulated or utilized to combine strongly with metal ions, as well as maintain high solubility within the carbon dioxide after combination. The latter method is used for dissolving polar contaminants within carbon dioxide by using polar solvent within a micelle core. Water is used mainly as the polar solvent in the micelle cores. Salt, metal nano-particles, metal ions,

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and proteins can be dissolved in water. Recently, acids, such as nitric acid, have been used instead of water. In this case, since all materials soluble in acid can be extracted from the carbon dioxide, nitric acid can be applied to various fields such as decontamination and surface treatment of radioactive contaminants in materials much the same as chemical stripping^{1, 5)}.

In this study, the characteristics of metal film removal by supercritical carbon-dioxide-micro emulsion, which utilizes nitric acid, was investigated using QCM.

2. Theory

2.1 Cleaning Method Using a Microemulsion

In an emulsion, the dispersed phase exhibits properties of an independent phase, which means a state of being dispersed into small particles. The size of the dispersed phase at such a time is 2~10 nm. An emulsion in a transparent state is known as a microemulsion. An opaque emulsion of 200 nm~10 μ m is known as a general emulsion. The thermodynamic stability of a microemulsion is different from other emulsions⁶⁾.

A variety of fluids can be used industrially in a supercritical state depending upon the peculiar characteristics of the fluid. Since carbon dioxide is cheap, non-toxic, non-combustible, and can reach a supercritical state comparatively easily, it is widely used as a supercritical fluid. But, since carbon dioxide is non-polar, it has the disadvantage of having a very low dissolving effectiveness against polar solvents. Two methods have been tried to improve the dissolving power of supercritical carbon dioxide against a polar solvent. One is a method by which surfactants are first applied to polar materials and then dissolved into carbon dioxide. Another method has polar materials be dissolved into a polar emulsion solvent and then treated with a carbon-dioxide emulsion combined with a polar solvent.

In this study, a microemulsion formed by combining carbon-dioxide with a polar solvent (nitric acid) was used to remove a metal film. Fig. 1 shows how the microemulsion was made. An aqueous solution containing ions or protein and carbon-dioxide is not mixed (1), but an emulsion is formed with the aid of a surfactant (2). Alternatively from the formation of an oil emulsion in an aqueous solution, the structure of a reverse micelle of an aqueous solution is seen in an oily fluid (carbon dioxide) by means of fluorinated-AOT (F-AOT) (3). A Na ion of F-AOT dissolves in an aqueous solution and then becomes a cation. The

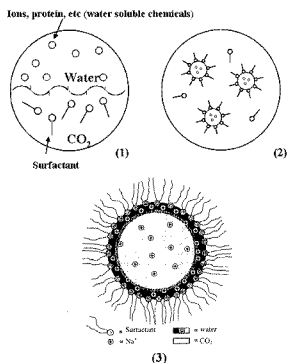


Fig. 1. sc-CO₂ Emulsion (1) Before emulsifying, (2) After emulsifying, (3) Reverse micelle composed of water, surfactant, and CO₂.

F-AOT exists as an anion, and together they stabilize a reverse micelle^{7, 10)}.

The cleaning method utilizing a microemulsion of carbon dioxide and an aqueous solution is shown in Fig. 2. This is a method that cleans (extracts) polar and ionic materials with a micelle of aqueous solution, and cleans (extracts) non-polar contaminants with CO₂. After creating a microemulsion within a micelle with an aqueous solution, polar and ionic contaminants are cleaned (extracted) after reacting for a while on the target surface. If the microemulsion containing contaminants is discharged together with CO₂ in the cleaning process, cleaned target materials will remain. When the temperature of the discharged microemulsion is adjusted, or the pressure lowered below its cloud point, the aqueous solution and carbon-dioxide naturally separate from each other due to the instability. The aqueous solution containing separate contaminants can be treated, and both the surfactant and CO₂ can be recovered and reused later on. This process is economical, and is environment-friendly because secondary waste is not generated.

2.2 Quartz Crystal Microbalance (QCM)

The QCM technique was first applied to measuring surface film laminations in a vacuum or within air, but its scope of application has since been expanded.

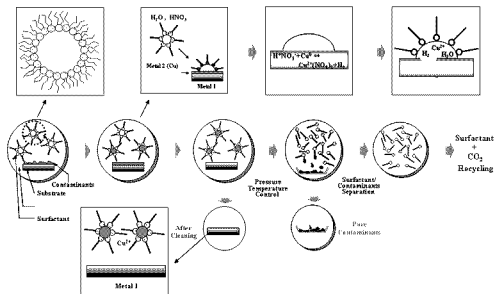


Fig. 2. Cleaning process using microemulsion.

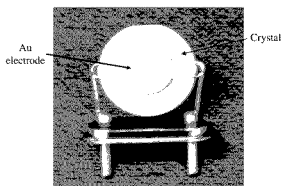


Fig. 3. QCM (Quartz Crystal Microbalance).

Recently the QCM technique has also been utilized in liquid phase (high-density fluid). When metal electrodes are plated on both end faces of a thin quartz plate, and an alternative current applied between these electrodes, the quartz oscillator oscillates naturally at a certain frequency by means of piezoelectricity (Fig. 3). At this time, the peculiar oscillating frequency of the quartz oscillator is affected by the thickness of the quartz plate and thickness of material forming on the electrodes. When a change of mass occurs by either adsorption or desorption on the electrode surface of the quartz oscillator, the oscillation frequency changes. By measuring this change, information for adsorption or desorption of material on the electrode surface can be obtained directly.

Factors affecting the peculiar oscillating frequency of the quartz oscillator vary widely. In particular, the change of frequency that follows a change of temperature is affected by the direction and angle of the cuts of the quartz oscillator. When an alternative current

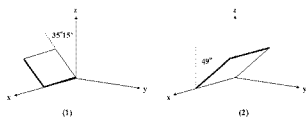


Fig. 4. Cutting angle of the crystal (1) AT-cut, (2) BT-cut.

is applied, the quartz plate oscillates. The oscillation frequency stabilizes when the thickness of the quartz plate becomes half of the sound wave length or a multiple of it. To make a sound wave move vertically against the face of the quartz plate, the quartz plate is cut at specific angles. The AT-cut and BT-cut are mainly used. Generally, an AT-cut (35.15° against the y-z face), which has a small change of oscillating frequency in relation to temperature change, is mainly used (Fig. 4)⁽¹¹⁾⁽¹³⁾.

To use QCM in an environment other than a vacuum, the oscillation frequency variation factor of the QCM following the application environment should be considered. The oscillation frequency variation of QCM depends largely upon three factors - mass at the surface, pressure, and temperature. Considering these factors, the oscillation frequency variation of QCM can be expressed by the following equation (1)⁽¹⁴⁾.

$$f_{qc} = f_0 + \Delta f_m + \Delta f_p + \Delta f_T \quad (1)$$

Here, f_0 : resonance oscillation frequency of QCM

Δf_m : Variation of oscillation frequency following a change in mass

Δf_p : Variation of oscillation frequency following a change in pressure

Δf_v : Variation of oscillation frequency following a change in fluid density and viscosity

In the experiment, the quantity of materials that are adsorbed or desorbed on the QCM surface can be discerned with Δf_p . Therefore, it should be possible to distinguish the effect of pressure (Δf_p) and density/viscosity (Δf_v) of the fluid from the total frequency (Δf_t).

3. Experiment

3.1 Specimen Preparation and Surfactant

Liquefied carbon-dioxide (Air Tech.) of 99.98% purity was used as a solvent, and nitrogen having a purity of 99.98% was used to measure the natural oscillation frequency of the QCM within the pressurized container. A set of QCM's, upon which copper or nickel was electroplated, was used as specimens for surface decontamination. A smoothly polished QCM was dipped into a plating solution and electroplated for 30 seconds with either Cu or Ni. The current was 0.1 A (current density: 27 A/dm², plating thickness: about 40 μ m).

A microemulsion of supercritical carbon-dioxide

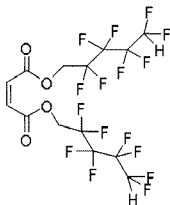


Fig. 5. Structure of F-AOT.

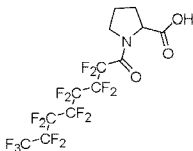


Fig. 6. Structure of Proline Surfactant-1.

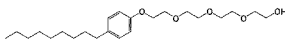


Fig. 7. Structure of NP-4.

and acid was then prepared using F-AOT, NP-4 and Proline Surfactant-1 (newly synthesized in our laboratory) as surfactants. The structures of the respective surfactants are shown in Fig. 5 to Fig. 7.

3.2 Experiment Method

A high-pressure reactor cell with sapphire windows installed on both sides was used to observe the microemulsion formation.

As shown in the formula (1), the natural oscillating frequency of the QCM is also affected by pressure and density/viscosity of nearby fluids as well as thickness of materials to be adsorbed and desorbed on the surface. To eliminate the effect of pressure and density/viscosity, a non-plated bare QCM was placed into the same environment, which was taken as a standard oscillating frequency. Two terminals were placed within the pressure vessel, which was fabricated so that two separate QCM's could be installed (Fig. 8). A bare QCM was installed in Ch1, and a plated QCM in Ch2 (33 ml, Hanul Engineering).

After a determined amount of surfactant and nitric acid (in accordance with the W value) was placed inside the high-pressure reactor cell, the door was closed and the pressure vessel subjected to a constant-temperature bath. Then the temperature was adjusted in accordance with the experiment procedures. The temperature was maintained constantly when it rose to the target of 40°C. The natural oscillating frequency of the QCM was measured by means of flowing nitrogen gas at 3 bar. Carbon dioxide was injected into the reactor cell with a pump (ISCO Model 260D, Lincoln, NB, USA). The pressure vessel was also filled with pure carbon-dioxide after discharging a mixed gas of nitrogen and carbon-dioxide. Carbon-dioxide was pressurized to 250 bar, and a microemulsion of nitric acid and carbon-dioxide was created while

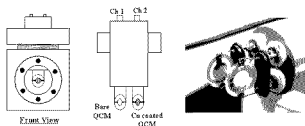


Fig. 8. QCM specimens installed in the reactor cell.

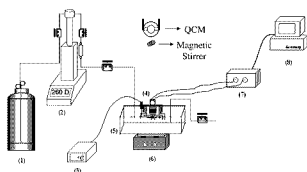


Fig. 9. Experiment apparatus (1) CO₂ cylinder, (2) Syringe pump, (3) Reaction cell, (4) Water bath, (5) Magnetic stirrer, (6) RQCM, (7) Monitor, (8) Temperature controller.

agitating continuously with an agitator. The oscillating frequencies of both the bare QCM and plated QCM were measured simultaneously for an hour, and thereby the metal film removal characteristics were observed. The oscillating frequency of the QCM was measured (RQCM, MAXTEK, INC. USA) and the data directly recorded by a PC (Fig. 9).

4. Results and Review

4.1 Measurement of Metal Film Removal Rate

Surfactants used in this study for the formation of the microemulsion were F-AOT, NP-4, and Proline Surfactant-1. 1M of nitric acid was used as a polar fluid within the reverse micelle. The time-dependent removal quantity (variation of oscillating frequency) of Cu or Ni plating on the QCM surface electrode was compared. Fig. 10 shows the removal results of the Cu plating using the F-AOT surfactant and Fig. 11 shows the removal results of Ni plating using the

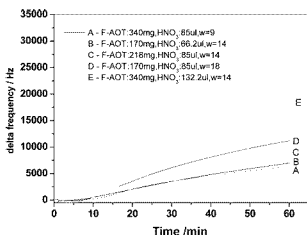


Fig. 10. Change of frequency during Cu removal (F-AOT).

Table 1. Cu removal rate (F-AOT)

Description	Surfactant (mg)	1 M nitric acid (μ l)	W value	Removal rate (μ g/cm ² -min)
A	340	85	9	0.8
B	170	66.2	14	0.7
C	218	85	14	0.9
D	170	85	18	1.2
E	340	132.2	14	1.6

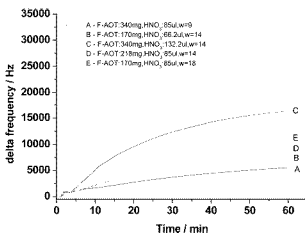


Fig. 11. Change of frequency during Ni removal (F-AOT).

Table 2. Ni removal rate (F-AOT)

Description	Surfactant (mg)	1 M nitric acid (μ l)	W value	Removal rate (μ g/cm ² -min)
A	340	85	9	0.5
B	170	66.2	14	0.8
C	340	132.2	14	1.7
D	218	85	14	1.3
E	170	85	18	1.5

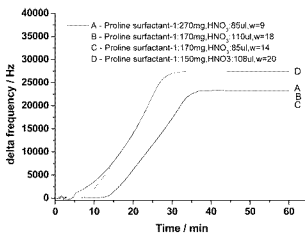


Fig. 12. Change of frequency during Cu removal (Proline Surfactant-1).

Table 3. Cu removal rate (Proline Surfactant-1)

Description	Surfactant (mg)	1 M nitric acid (μ l)	W value	Removal rate (μ g/cm ² ·min)
A	270	85	9	3.4
B	170	110	18	6.4
C	170	85	14	5.7
D	150	108	20	7.3

F-AOT surfactant. Fig. 12 shows the removal result of Cu plating using Proline Surfactant-1. The removal rate of the electroplatings in relation to the quantity of nitric acid within the reactor cell and the W value (mole ratio of aqueous solution against surfactant) is thus revealed.

When the nitric acid microemulsion was used with the NP-4 surfactant, a measurement could not be obtained with the QCM. When the electroplated surface was removed, the oscillating frequency of the QCM varied widely. For this reason, a meaningful result could not be obtained.

4.2 Specimen Surface

Fig. 13 shows the condition of the treated surface photographed through a microscope after cleaning the electroplated surfaces with a microemulsion of nitric acid (1 M concentration) in supercritical carbon-dioxide. F-AOT and Proline Surfactant-1 were used as the surfactants. As a result of the experiment, some plating still remained on the surface treated with F-AOT, but the entire electroplated surface treated with Proline

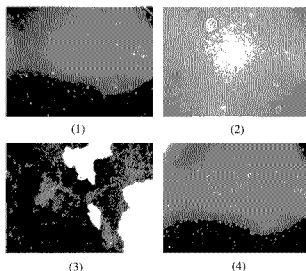


Fig. 13. OM images of the QCM surface (1) Bare (20), (2) Cu coated (\times 20), (3) metal removal using F-AOT(20), (4) metal removal using Proline Surfactant-1 (\times 20).

Surfactant-1 was removed, and furthermore, the surface of the QCM was very clean and smooth.

4.3 Discussion

When F-AOT was used, the metal removal rate was relatively higher as the quantity of nitric acid within the microemulsion increased. In nitric acid of the same quantity, the removal rate of the copper and nickel electroplating was higher as the W value became higher. The removal rate of nickel electroplating was higher at the beginning of the experiment compared with the copper electroplating. It seems that since some polishing agent is contained in the nickel plating, this polishing agent dissolved selectively in the nitric acid microemulsion at first.

The increased removal rate in relation to the increased W value is caused by two factors. At first, the droplet size of nitric acid within the reverse micelle became larger as the W value became larger. In this case, the thickness of the F-AOT surrounding the droplets of nitric acid became relatively thinner as the droplets of nitric acid became larger. As a consequence, as the F-AOT layer became thinner (namely, as the W value became larger), the reaction between the metal surface and droplet of nitric acid occurred more rapidly. Another reason is because the Na ions existing in the hydrophilic radical of F-AOT neutralized the nitric acid. In case of 1M nitric acid, a nitric acid ion of about 1.8% as a mole ratio is contained in the aqueous solution. When the W value is 9, the mole ratio between the Na ion of F-AOT, and nitric acid ion within the droplet of nitric acid became approximately 6 to 1. It is difficult to know the neutralization reaction between the Na ion and nitric acid ion, but it seems that many Na ions will neutralize ions of nitric acid. But as the W value becomes larger, the relative quantity of nitric acid ions based on Na ions becomes larger, and thereby the capacity to dissolve metal becomes larger.

Proline Surfactant-1 proved to be a much more effective at metal removal than F-AOT. Since hydrogen ions are stuck to the hydrophilic radical in Proline Surfactant-1, they do not neutralize nitric acid ions in droplets of nitric acid within reverse micelle. Namely, the concentration of nitric acid ions is higher than in F-AOT. Therefore, metal removal efficiency becomes higher than in F-AOT. Moreover, since the quantity of metal film existing is not high, the nitric acid solution is not neutralized and so the metal removal rate is continuously high. Finally, as shown in Fig. 12, copper film plated on the QCM is completely removed.

The form of the reverse micelle in the microemulsion produced by Proline Surfactant-1 appears to be very different from that of F-AOT. The quantity of the aqueous solution droplets of the reverse micelle formed with F-AOT (approximately 10 nm) is visible to the extent that light caused by a luminous agent is observed, but the light of the luminous agent is not observed in the reverse micelle produced by Proline Surfactant-1. In this case, the quantity of nitric acid droplets in the reverse micelle is very small. Maybe there is a possibility that it is evenly dispersed within fluid of a smaller quantity, not the shape of nitric acid droplet surrounded by Proline Surfactant-1. Therefore, the plating removal rate did not vary consistently with the W value differently from F-AOT. Namely, since the form of the nitric acid droplets in the reverse micelle is much smaller than in F-AOT, it appears that the surface metal removal rate was very high.

Also, when NP-4 was used, the copper plating was only partly removed on the QCM surface, and the peculiar oscillating frequency of QCM became unstable. After observing with a volume-changing view cell, in case of NP-4, when the metal ions were contained in an aqueous solution, it was observed that the microemulsion of the aqueous solution and carbon-dioxide became unstable. Namely, at the moment that the microemulsion of nitric-acid + supercritical carbon-dioxide contacted the Cu surface and then Cu ions dissolved within the nitric-acid droplets, the microemulsion became unstable. Then the highly viscous NP-4 became stuck to the QCM electrode surface. At that time, the resonance oscillating frequency of the QCM underwent a drastic change, and then the movement of the QCM destabilized.

5. Conclusion

Removal characteristics within a microemulsion of nitric acid + supercritical carbon-dioxide were measured and analyzed in real time by using a set of QCMs. Cu and Ni were selected as target metals. After electroplating the QCM surfaces, the removal rate of the electroplated surfaces was obtained. With F-AOT, as the quantity of nitric-acid contained in the microemulsion increases and the W value increases, the metal removal rate appeared to be high. It seems that this is phenomenon exhibited by the thickness of the surfactant in the reverse micelle, and neutralization reaction of nitric-acid ions by Na ions being stuck to the hydrophilic radicals of F-AOT. In Proline Surfactant-1, it is judged that the quantity of nitric-acid

droplets is very small as compared with F-AOT in the shape of the reverse micelle. As the nitric-acid droplets reduce in number, the relative surface area becomes larger and thereby removal reaction becomes higher. Moreover, since there is no metal ion in the hydrophilic radical, the neutralization reaction of a nitric-acid radical also does not exist, and thereby metal can be dissolved and removed to the maximum. When NP-4 was used, the metal layer on the QCM surface is removed. But, when Cu ions are contained in an aqueous solution, the microemulsion destabilizes and NP-4 is stuck to the QCM surface. As a result of this, quantitative measurement becomes impossible. In conclusion, it was found that a microemulsion using nitric-acid can be created with a surfactant within supercritical carbon-dioxide, and that this microemulsion can remove metal film rapidly and effectively. In this experiment, it was confirmed that an economical and environment-friendly cleaning process that does not generate secondary wastes is available.

Acknowledgments

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