

ELECTROPLATING PROCESS IN EMULSION WITH FLUORONATED ANALOGUES OF AOT IN SUPERCRITICAL STATE

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ABSTRACT

We synthesized the fluorocarbon-hydrocarbon hybrid surfactant for the emulsion of the aqueous solution/CO₂ and measured the cloud point of this surfactant and microemulsion. After that, the electroplating of Ni on Cu was carried out in macroemulsion composed of CO₂ and plating solution in supercritical state. The electrolyte solution was reduced by using this process, and the properties of plated ware was better than that by the existing process.

INTRODUCTION

As the supercritical fluid was mentioned in many research papers, it was used in various fields such as separation, extraction, reaction/synthesis, fractionation, and chromatography for its advantages, and the research about this has been developed because the usage of this fluid was effective. In recent years, the application fields of the supercritical fluids were changed to economy of energy, and clean technology from the existing research fields. It proves the fact that the supercritical fluid was used in fields such as nano formation of particle, removal of fat, wastewater treatment, organic or electro-synthesis without toxic solvent. In this paper, we introduced electroplating process by using emulsion in supercritical state as one of new researches used the characteristics of supercritical fluids. This process was reported for the first time in 'Chemistry Letter' by Hideo Yoshida (Japan, 2002)[1] and was presented by the present author and Jong Sung Lim in 'SuperGreen 2002' conference (KyungHee Univ., Korea)[2]. The electroplating suggested is a new environmental-friendly process by using the Ni-plating solution/scCO₂ emulsion. In this study, the fluorocarbon-hydrocarbon hybrid surfactant analogues of AOT such as the sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl)-2

sulfosuccinate(H(CF₂)₄CH₂OOCCH₂CH(SO₃Na)COOCH₂(CF₂)₄H)[3,4,5] was used for formation of emulsion between the aqueous solution and CO₂. This surfactant has both 'CO₂ philic' chain and 'hydrophilic' head group simultaneously, and research like formation of nano particle from metal was used synthesized[6]. Prior to the electroplating in emulsion, the cloud point of this surfactant was measured and the microemulsion was formed in supercritical state. In addition, 'microemulsion stability region' was measured by measuring the cloud point in microemulsion. After then, electroplating of Ni on the surface of Cu was carried out in macroemulsion solution composed of CO₂ and plating solution in supercritical state. The plating solution could be reduced to 1/3 times by this method. Qualities of plated ware can be evaluated by measuring thickness, uniformity, and corrosion resistance. Qualities such as corrosion resistance and uniformity of surface of plated ware obtained by this method were better than those by current method.

Part I : Water/CO₂ microemulsion in supercritical state

Chemicals Carbon dioxide (CO₂ = 99.99%, Duck Yang, Korea), 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (F₂CH(CF₂)₃CH₂OH = 98%, Aldrich), p-toluenesulfonic acid monohydrate (CH₃C₆H₄SO₃H·H₂O = 99%, Yakuri chem. co.), sodium metabisulfite (reagent, Aldrich), maleic anhydride (C₄H₂O₃ = 98%, Junsei chemical co.), toluene (C₆H₅CH₃ = 99.8%, J.T. Baker), water (Millipore water).

Procedure of synthesis The synthesis of fluorocarbon-hydrocarbon (F-H) hybrid surfactants, the sodium salt of bis (2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate (di-HCF₄) was reported by H. W. Kim [5] and prepared it by this method.

Experimental apparatus and procedure The schematic diagram of the apparatus is shown in previous paper [2]. This apparatus was designed to carry out the microemulsion formation and the cloud point measurement in supercritical state at the temperature up to 373.15 K and pressure up to 100 MPa. The reactor was an internal variable-volume view cell that contained by a movable piston for change the cell volume and pressure. A pressure generator (High-Pressure Equipment Co. 376-30 model, pressure rating 15,000 psi) is used to pressurize contents in the cell. A change in the cell volume causes a change of the system pressure. A visual observation of the cell inside through the sapphire window is made by a bore scope (Olympus model R080-044-000-50) and a CCD camera (Watec, WAT-202B), which was connected, to a VCR/TV (Anam co.) monitor and a computer. An advantage of using the variable-volume cell is that the concentration of the system is kept constant during experiment. On the other side, using a constant-volume cell often requires venting off solution to decrease the pressure of the system, causing unknown changes in the concentration of contents in the cell. In the front part of the cell, sapphire glass windows of 19.2mm thickness and 19.2mm in diameter was placed to allow the observation for mixing and reaction phenomena. A stirrer, rotated at variable speeds by an external magnet, was used to mix the CO₂, water (with alcohol), and surfactant solution in the high-pressure reactor and to form microemulsion. A simple thermostatic air bath was used to maintain the system temperature constant within ±0.1 K. The temperature in the reactor was measured with a K-type thermocouple and a digital indicator (OMEGA Co.), which was calibrated by KRISS (Korea Institute of Standards and Science) with an uncertainty of ±0.1 K. The pressure in the reactor was measured with a pressure transducer (SENSOTEC Model TJE) and digital indicator (SENSOTEC Model L20000WM1), which were calibrated by a dead weight gauge (NAGANO KEIKI PD12) with the measuring accuracy of ±0.01bar. The experimental procedure to water/CO₂ micro-emulsion in supercritical state was as follows. The reactor cell was evacuated and a constant molar ratio ($W_o = [\text{water}]/[\text{surfactant}]$) of the water and surfactant solution was introduced into the cell. To remove any entrapped air present in the cell, the cell was purged at least three times with low-pressure CO₂ of less than 0.3 MPa at a very slow rate so that the water and surfactant in the cell was not disturbed and loss of them was avoided. A certain amount of liquid CO₂ was charged into the cell through the inlet line. The amount of CO₂ was determined by weighing the CO₂ sample cylinder before and after CO₂ was charged into the cell. The solution in the cell was continuously pressurized using the pressure generator. As the pressure increases, the solution in the cell finally becomes a single homogeneous phase. At the same time the solution was well agitated by a stirring bar to form microemulsion. As the pressure generator pressurizes water, the compressed water displaces the piston to the window side to decrease the cell volume and thus raise the pressure in the cell. The temperature of the entire system was maintained constant by controlling the temperature of the air bath. When an optically transparent single-phase solution was obtained, to raise pressure was stopped. The pressure was then slowly reduced until the solution become cloudy. The pressure was reduced at a rate of about 0.05 MPa/min when the cloud point pressure was approached. After completing the test at a given

temperature, the cell temperature was stabilized at a new value and the experimental procedure was repeated.

RESULTS

Cloud point of W/CO₂ microemulsion Prior to measurement of cloud point of water/CO₂ microemulsion, the cloud point of F-AOT surfactant synthesized for formation of micro-emulsion was measured in CO₂. Cloud point of surfactant was measured with three concentration (0.469wt%, 4.52wt%, 7.024wt%) of surfactant in CO₂. In every cases, surfactant was soluble in CO₂ completely. According to results, the cloud point became high as the quantities of surfactant were increased. In the temperature ranges of 310.15~ 405.15 K, the cloud points in concentration of 0.469 wt%, 4.52wt%, and 7.024wt% was 10.0~27.7 MPa, 16.8~35.0 MPa, and 20.0~42.0MPa. According to these results, as surfactant was more in CO₂, as the cloud point of surfactant was higher. This result was shown in **Fig.1**. And, the microemulsion of water and CO₂ was carried out by adding F-AOT surfactant. In this study, the quantities of surfactant were added to the solution composed of constant water and CO₂.

The values of W_o (molar ratio of water and surfactant) were 5, 10, 15, 25, and 30. The experimental condition was shown in **Table 1**. In the process of W/CO₂ microemulsion formation, W/CO₂ micro emulsion became the homogenous phase that is colorless, clear and transparent. (**Fig.2**).

After formation of microemulsion, the cloud point of microemulsion could be measured as the pressure was dropped slowly. At this moment, the water and surfactant, which were soluble in CO₂, were extracted and didn't form the microemulsion any more. The cloud points measured in every temperature were curves ? .

When the pressure of CO₂ was elevated from the region formed the microemulsion, the homogenous phase become two phases at specific pressure and this is the curve ? .

According to experimental results, the microemulsion was maintained stably in the region between the curve ? and ? , but,

it was unstable out of this region. So, we called this region

In case of the cloud point of microemulsion with W_o , as the value of W_o was smaller, as the curve ? was lower, and as the value of W_o was larger, as the curve ? was higher. In that, the values of W_o were smaller, 'the microemulsion stability region' becomes wider. As **Table 1** shows, this was related with the concentration of surfactant in CO₂ or water and not related with the concentration of water in CO₂. To be brief, when the constant water is soluble in the constant CO₂, the solubility was sustained for a long time.

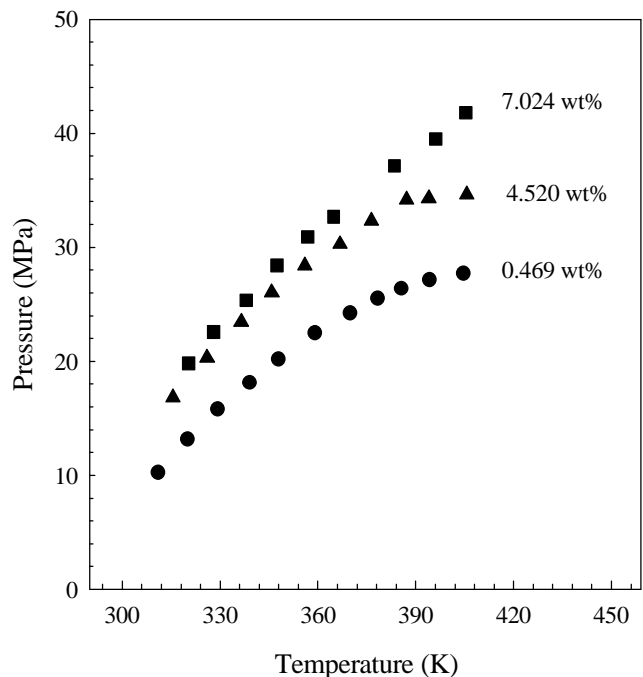


Fig. 1. The cloud point of F-AOT in CO₂

Table 1. Experimental condition for formation of microemulsion

| CO ₂ | | F-AOT | | H ₂ O | | W _o | Conc. of H ₂ O | | Conc. of F-AOT | |
|-----------------|-------|------------|--------|------------------|-------|----------------|---------------------------|-------|----------------|---------|
| (g) | (M) | (g) | (M) | (g) | (M) | | (wt%) | (M) | (wt%) | (M) |
| 10.360 | 0.235 | 0.00111047 | 0.7640 | 0.006 | 0.100 | 5 | 0.956 | 2.305 | 6.868 | 0.00469 |
| 10.600 | 0.241 | 0.00055552 | 0.3822 | 0.006 | 0.100 | 10 | 0.935 | 2.254 | 3.480 | 0.00230 |
| 10.600 | 0.241 | 0.00037035 | 0.2548 | 0.006 | 0.100 | 15 | 0.935 | 2.254 | 2.347 | 0.00153 |
| 10.29 | 0.234 | 0.00022224 | 0.1529 | 0.006 | 0.100 | 25 | 0.962 | 2.320 | 1.464 | 0.00095 |
| 10.49 | 0.238 | 0.00018517 | 0.1274 | 0.006 | 0.100 | 30 | 0.944 | 2.277 | 1.200 | 0.00078 |

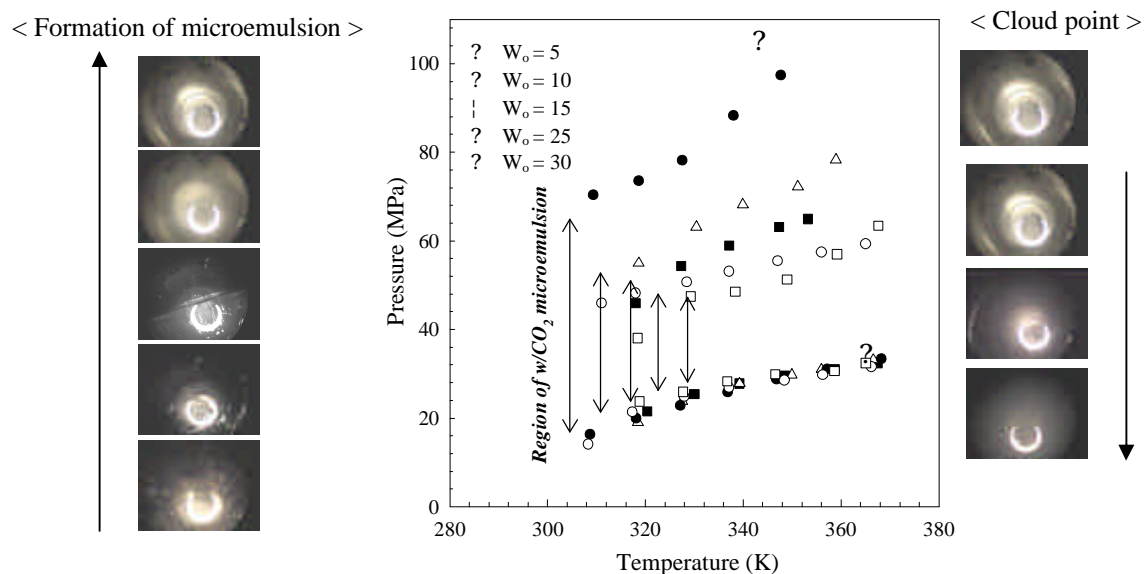


Figure 2. The cloud point of microemulsion and the microemulsion stability region of water/CO₂

PART II- Electroplating process by using emulsion in supercritical state

THEORY

Basic mechanism of Ni plating[7] Ni plating is electrolytic deposition of a layer of Ni in a substrate. The process involves the dissolution of the anode and the deposition of metallic Ni in the cathode. Direct current is applied between the anode and the cathode. Conductivity between the electrodes is provided by an aqueous solution of Ni salts. When Ni salts are dissolved in water, the Ni is present in solution as divalent, positively charged ions. When current flows, divalent Ni ions react with two electrons and are converted to metallic Ni at the cathode. The reverse occurs at the anode where metallic Ni dissolves to form divalent ions. The electrochemical reaction in its simplest form is $Ni^{2+} + 2e^- = Ni^0$. Because the Ni ions discharged at the cathode are replenished by the Ni ions formed at the anode, the Ni plating process can be operated for long of time interruption.

EXPERIMENTS

Composition of Ni-plating solution NiCl₂·6H₂O of 50g, NiSO₄·6H₂O is the principal source of Ni ions, Ni chloride improves anode dissolution and increases solution conductivity, and boric acid helps to produce smoother and more ductile deposits [7].

Experimental procedure of electroplating in scCO₂ The procedure of electroplating of Ni on Cu

substrates in sc CO₂ by using emulsion was represented as follows. The Cu plate was prepared after getting rid of impurities by using pretreatment agent (PC-732 10% aqueous solution). A newly designed high-pressure view-reactor equipped with a Ni anode and a Cu cathode was manufactured. CO₂ was introduced into the cell. The reactor cell was evacuated and the Ni-plating solution and surfactant was introduced into the reactor. To remove any entrapped air present in the cell, the cell was purged at least three times with low-pressure CO₂. A certain amount of liquid CO₂ was charged into the cell through the inlet line. The solution in the cell was continuously pressurized using the pressure generator. At the same time, the solution was well agitated by a stirring bar to form emulsion. As the pressure increases, the solution in the cell finally becomes the emulsion with a milky color. The temperature of the entire system was maintained constantly by controlling the temperature of the air bath. When the desired temperature was attained, plating solution was introduced by using the high-pressure pump. Plating solution in CO₂ emulsion was mixed by magnetic stirrer continuously. Electroplating temperature was 55°C and the pressure was 15.0, 18.0, and 20.0 MP, and constant current for 30 min. After electroplating, the Cu plate plated with Ni was taken out the cell and washed, and dried completely. Electroplating in atmospheric condition was omitted.

RESULTS

Quality evaluation of plated ware The quality of plated wares in scCO₂ and atmospheric condition as evaluated by using four items such as 1)brilliance (by Digital camera), 2) thickness measurement (SEICO instrument, SFT 720, X-Ray Fluorescence spectrometer, XRF), 3) uniform evaluation on Ni surface by SEM photo-graphing, 4) corrosion resistance by CASS method in accordance with the Korean Standard (KS D 8334).

Qualities of plated wares The qualities of plated wares in scCO₂ and atmospheric condition were evaluated by using three items such as 1) brightness, 2) thickness, 3) uniformity, and 4) corrosion resistance. These results were as follows.

1) Brightness; the brightness between two plated wares was compared. The plated ware plated in scCO₂ was as bright as that in scCO₂.

2) The surface uniformity; The surface of Ni on Cu was observed by the analysis of SEM in detail (? 10,000). The minute particles were distributed uniformly on surface plated in scCO₂, and the thick particles were distributed on surface plated in atmospheric condition without CO₂ relatively. In case of surface plated uniformly, it is known that the properties such as ductility, hardness, and corrosion resistance is good. These results were shown in **Fig.3**. In plating process, the cleaning was carried out before plating. When we compare of two experiments in atmospheric and supercritical condition, scCO₂ was used as a cleaning media in plating and nothing acted for cleaning of electrode. Therefore, the surface of plated ware carried out in supercritical state was better than that in 1atm.

3) The surface thickness; The thickness of surface plated was measured by using X-Ray Fluorescence spectrometer (XRF) which didn't break the sample in accordance with the Korean Standard (KS D 0246). The surface plated in atmospheric condition was thicker than that in scCO₂ condition. This result was caused by the lack of Ni²⁺ ions attendant upon the reduction of Ni plating solution. In case of plated ware plated in scCO₂, As pressure is higher, as thickness is thinner. This result was shown in **Fig.4**. In **Fig.5**, shows the Ni weight plated and current passed in supercritical state

4) The corrosion resistance; The corrosion resistance was measured by using CASS method in accordance with the Korean Standard (KS D 8334). Both two Ni plated began to corrode after 24hrs. Although the thickness plated in supercritical condition was thinner than that in atmospheric condition, it was less corrosive than that. When we consider various things such as uniformity, hardness, ductility, and corrosion resistance, synthetically, the plating in scCO₂ is better than the plating in 1atm without CO₂.

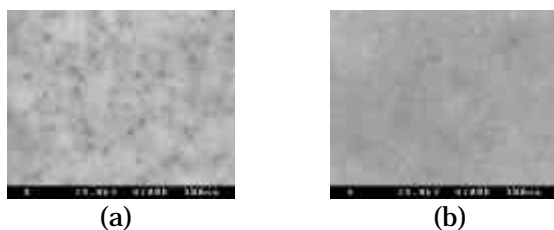


Fig. 3. SEM image of plating ware at T=55°C, (a) P=0.10MPa, (b) P=15.0MPa

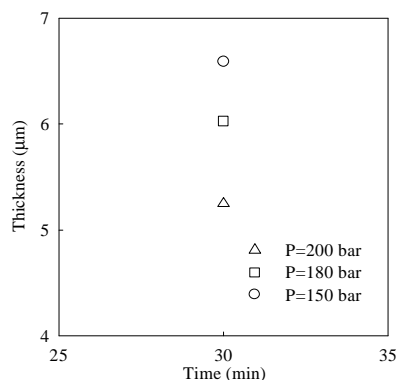


Fig. 4. Plating thickness of plated ware in supercritical state

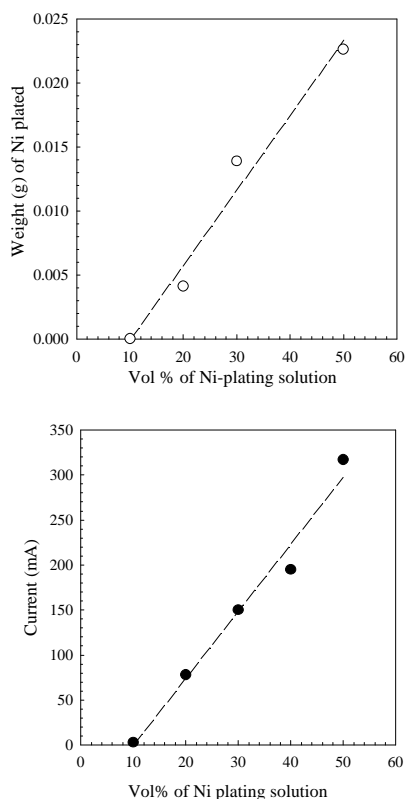


Fig.5.Ni weight plated and current passed in supercritical state

DISCUSSIONS

In this paper, the Ni-plating on Cu plate by using the new technology to reduce the plating solution was offered. The plating solution was reduced to one-fourth by this method. The plated ware plated in this condition has good quality in uniformity, hardness, ductility, and corrosion resistance.

CONCLUSION

We studied the water/CO₂ micro-emulsion and the electroplating by using macroemulsion in supercritical state. This research is expected as a great help for reducing the wastewater in plating process. Now, we are trying to develop the quality of plated ware and more detailed study is now in progress.

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