초임계 CO_2내에서 비이온 계면활성제에 의한 CO_2와 도금액의 에멀젼 형성 및 전해도금

박지영, 이윤우, 임종성
한국과학기술연구원 국가지정 초임계유체 연구실

Electroplating and formation of Ni-plating solution/scCO_2 emulsion by noninoic surfactant

Ji-Young Park, Youn Woo Lee, Jong Sung Lim
National Research Lab. for Supercritical Fluid, KIST

Introduction

Electroplating is employed in industry to improve the appearance of surfaces, to give the good corrosion protection on the substrate, to improve the wear resistance by hard facing of the relatively soft substrate, and sometimes to provide the good electrical and thermal contact. However, acid and alkali aqueous solutions, a cyanide, chromium, heavy metal, corrosive materials, and toxic substances used in plating process raised the pollution of working environment because of waste water. Since the latter half of 1990's, many researches on the effective method to treat the waste water began centering around industries and research organizations. By this tendency, the clean technologies are required in plating process of domestic plating industries. For this reason, the current process and equipment are in need of changing into the environmentally friendly-technical installations.

In this paper, we offer the new idea, the technology to reduce the plating solution by using sc CO_2. This is the method that the Ni-plating solution/sc-CO_2 emulsion is formed by using surfactant and then Ni in this emulsion is deposited to the surface of Cu substrate. For this study, the fluorocarbon-hydrocarbon(F-H) hybrid nonionic surfactants such as sodium salt of bis (2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate (di-HCF4) which has both 'CO_2 philic' chain and 'hydrophilic' chain was synthesized and was characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and DEPT NMR analysis. In addition, IFT of Ni-plating solution and CO_2 was measured for investigating the effects of surfactant ethanol as a co-solvent. and After then, electroplating of Ni on the surface of Cu plate was carried in emulsion solution composed of CO_2 and plating solution. The plating solution could be reduced to 1/4~1/7 times by this new electroplating technology. Quality value of plated ware can be evaluated by using the plating thickness, , and efficiency of plating. The quality values, such as corrosion resistance and uniformity of surface, of plated ware obtained by this new method was better than those by current method.

When we consider various things synthetically, this research is expected to begreat helpful for reducing the waste water in plating process. Now, we are trying to improve the quality of plated ware and more detailed study is now in progress.

Experimental

Synthesis of surfactant and measurement of solubility The synthesis of fluorocarbon-hydrocarbon hybrid nonionic surfactant such as sodium salt of bis(2,2,3,3,4,4,5,5-octafluoro-1-pentanol) sulfosuccinate (di-HCF4) was reported by Zhao-Tie Liu and Can Erkey[1] and the measurement of solubility was expressed in previous paper[2] in detail.

Interfacial tension measurement In formation of emulsion of immiscible phases like water or the aqueous plating solution and CO_2 emulsion, the interfacial tension (IFT) has an influence in formation of emulsion. Therefore these data are requisite as a basic information to understand the emulsion with CO_2. By this purpose, IFT was measured by using capillary rise method and it was calculated by following equation.

$$\gamma = \frac{1}{2} rg\left(h + \frac{r}{3}\right)\frac{\Delta\rho}{cos\theta}$$

γ(mN/m) is interfacial tension, r(m) is the radius of the capillary, h(m) is the height of the meniscus above a flat liquid surface (for which ΔP must be zero), (g/ml) is the difference between density of CO_2 and density of water (or nickel plating solution), g(m/sec^2) is the acceleration of gravity, θ is the contact angle (it is assumed as a 0^o). The procedure for IFT measurement is shown in Chun's paper in detail[3].

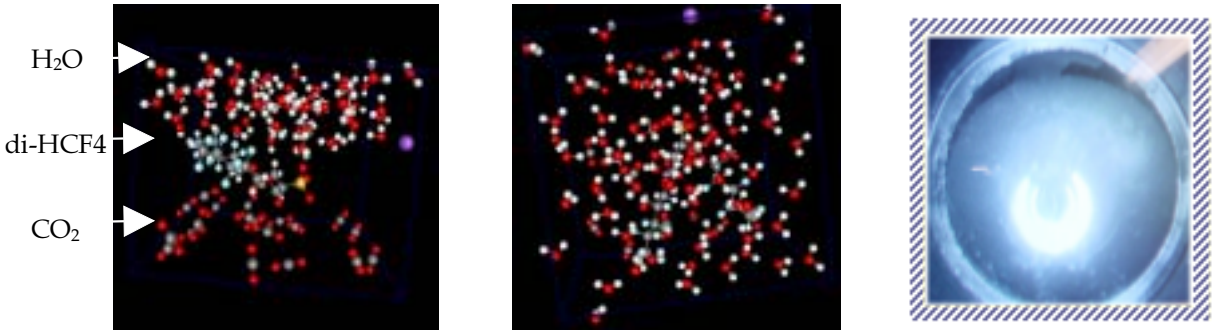


Fig. 1. W/CO_2 emulsion using di-HCF7 ; (a) interface of water-CO_2, (b) mixing, (c) emulsion

Cloud point of water/CO_2 emulsion The experimental procedure to water/scCO_2/di-HCF4 emulsion was as follows. The reactor cell was evacuated and a molar ratio (Wo=[water]/[surfactant]) of the water+di-HCF4 were introduced into the cell. A certain amount of liquid CO_2 was charged into the cell through the inlet line. The solution was continuously pressurized using the pressure generator. As the pressure increases, the solution in the cell finally becomes a single phase. At the same time the solution was well agitated to form emulsion. The temperature of the entire system was maintained constant by controlling the temperature of the air bath. When an optically transparent single phase was obtained, to raise pressure was stopped. The pressure was then slowly reduced until the solution become cloudy and when the cloud point pressure was approached. After completing the test at a given temperature, the experimental procedure was repeated at new temperature..

Electroplating of nickel by emulsion in sc CO_2 The experimental procedure of Ni electro-plating on Cu was represented in previous work[4]. The Cu plate was prepared after getting rid of impurities by using pretreatment agent. A newly designed high-press-ure view-reactor was manufactured. CO_2 was introduced into the cell. Temperature of the entire system was maintained constant. When the desired temper- ature was attained, plating solution was introduced by using the high pressure pump. Plating solution in CO_2 was mixed and plating was carried out. After electroplating, Cu plate plated with Ni was taken out the cell and washed, and dried.

Results and discussion

Cloud point and interfacial tension To look into effect of surfactant and ethanol, IFT of Ni plating solution+CO_2+di-HCF 4 (0.1, 0.3 wt %)+ethanol (10vol%) system were measured at 40°C, and 55°C. As the concentration of surfactant was higher, the IFT on between two fluids became lower. In case of ethanol addition, IFT of solution with both ethanol and di-HCF4 was increased. By this result, ethanol was not useful in emulsion formation. We measured cloud point of water/di-HCF4/CO_2. Solubility of this mixture was in range of 6.9MPa(T=10°C)~35.7MPa(T=70°C). Thesis results were shown in Figures 2 and 3.

Qualities of plated wares The quality of plated wares in supercritical CO_2 and atmospheric condition was evaluated by using three items such as 1) brightness, 2) thickness measurement by X-Ray Fluorescence spectrometer (XRF, SEICO instrument, SFT 720), 3) uniformity evaluation on nickel surface by SEM photographing, and 4) corrosion resistance by CASS method. These results were shown in Figures. 2~4.

1) Brightness

The brightness between two plated wares was compared. Unfortunately, the plated ware plated in 1atm was brighter than that in scCO_2. This result was caused by the lack of Ni^{2+} ions attendant upon the reduction of Ni plating solution. These results were shown in Figure 4 (a) .

2) 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 sc CO_2 condition.

3) The surface uniformity

The surface of nickel on copper was observed by the analysis of SEM in detail (× 10,000). The minute particles were distributed uniformly on surface plated in sc CO_2, and the thick particles were distributed on surface plated in atmospheric condition without CO_2 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 Figure 4 (b)-(c) .

4) The corrosion resistance

The corrosion resistance was measured by using CASS method in accordance with the Korean Standard (KS D 8334). Both two nickel plated began to corrode after 24hrs. Although the thickness plated in sc 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 sc CO_2 is better than the plating in 1atm without CO_2.

Conclusion

In this paper, the nickel electroplating on copper plate by using the new idea, the 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. This research is will be up to the expectation of a great help for reducing the waste water in plating process. Now, we are trying to develop the quality of plated ware and more detailed study is now in progress.

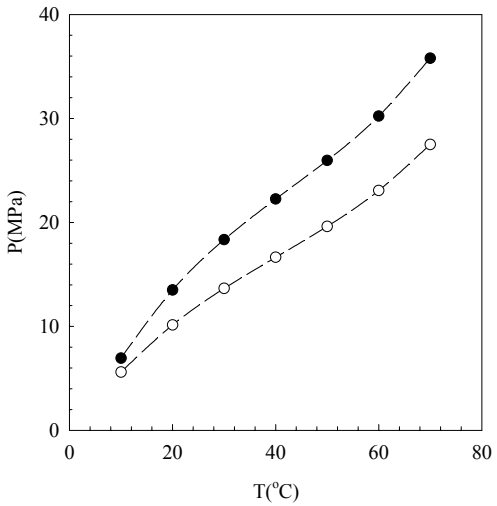


Fig. 2. Cloud point of Water/CO_2 emulsion using di-HCF7

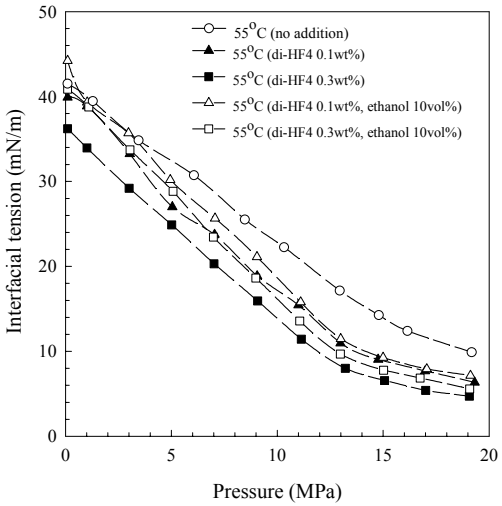
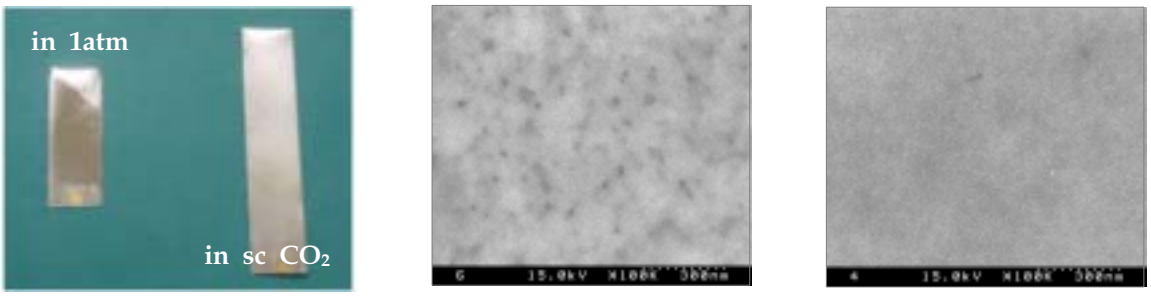


Fig. 3. IFT of CO_2 + Nickel plating solution + di-HCF 4 + ethanol at 55°C



(a) Ni surface plated

(b) Ni surface plated in1atm (×10,000)

(c) Ni surface plated in scCO_2 (×10,000)

Fig. 4. Results of Ni surface plated on Cu.

Acknowledgement

This work has been supported by the National Research Laboratory Program for Supercritical Fluid and the authors would like to thank to the Ministry of Science and Technology, Korea.

Literature Cited

1. Z. T. Liu and C. Erkey, Langmuir 2001, 17, 274.
2. J. Y. Park, J. S. Lim, Y. W. Lee, J. D. Kim, C. H. Lee, Theories and applications of chemical engineering, 2002, 8 (1), 145.
3. B. S. Chun, G. T. Wilkinson, Ind. Eng. Chem. Res., 1995, 34, 4371-4377.
4. J. Y. Park, J. S. Lim, Y. W. Lee, Theories and applications of chem. eng. 2002, 8 (1), 149.