

Nanocrystalline Ni–C Electrodeposits Prepared in Electrolytes Containing Supercritical Carbon Dioxide

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Electrodeposition of Ni in a Watt's bath at different applied pressures and in the presence of supercritical CO_2 (sc- CO_2), either with or without surfactant addition, was investigated. The current efficiency was evaluated under constantly applied current density conditions. The crystal structure of the resulting Ni film was characterized by performing X-ray diffraction. The composition of the deposit was analyzed using X-ray photoelectron spectroscopy. Transmission electron microscopy was employed for microstructure analysis. Microhardness of the deposited film was measured to distinguish the role of bath composition. The experimental results showed that carbon-containing nanocrystalline Ni films could be obtained in the bath with the presence of sc- CO_2 . A significant increase in microhardness was found for the film electrodeposited in sc- CO_2 fluid, as compared with that formed in plain aqueous electrolyte. The fine grain size and solid solution strengthening caused by carbon were responsible for the increased hardness.

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Electroplating of nickel incorporating supercritical carbon dioxide (sc-CO₂) has been successfully developed.¹⁻⁴ Because sc-CO₂ has a low conductivity, electroplating in such a medium always involves an aqueous electrolyte. However, highly polar substances (such as water) and high molecular weight substances are less soluble in sc-CO₂, and thus a surfactant is needed. When an effective surfactant is added to the sc-CO₂/aqueous electrolyte, thermodynamically stable carbon dioxide-in-water (CO₂/W) microemulsions that contain polar microaqueous domains can be produced. Superior properties of a Ni film electroplated in such an emulsified fluid, compared with that electrodeposited at atmospheric pressure, have been reported.⁵ However, the same study has also shown that electroplating efficiency in this environmentally friendly sc-CO₂ fluid was less than that of the conventional process.

In the absence of any surfactant, the coexistence of sc-CO₂ and the aqueous electrolyte gives rise to a system with two separate phases. Without any surfactant, the roles of pressure and the presence of sc-CO₂ on the plating efficiency are of interest and are explored. Furthermore, CO₂ can be dissolved in water to form carbonic acid at ambient pressure. Under high pressure conditions, such as in a supercritical state, whether CO₂ participates in the film formation and modifies the composition of the deposited layer is also of interest. The incorporation of C into the Ni deposit is thus focused upon and highlighted in this investigation.

Experimental

For the electrodeposition, brass sheets of $1 \times 2.4\,$ cm were used as substrates. The brass substrates were successively ground with SiC paper to a grit of #2000, followed by polishing with Al_2O_3 slurry to 0.3 μ m, degreased in 0.1 M NaOH solution followed by water rinsing, etched in 0.1 M H_2SO_4 solution, rinsed with deionized water, and finally dried using a stream of hot air.

A high pressure cell made of stainless steel was fabricated for the electrodeposition in a bath containing sc-CO₂ fluid. The autoclave system and the apparatus used for the Ni electrodeposition have been described elsewhere.⁵ The composition of the sc-CO₂-based electrolyte and the operating conditions are listed in Table I. The bath was basically composed of NiCl₂ and NiSO₄, similar to that of a Watt's bath. As shown in this table, saccharin and C₇H₉NO₂S were added as brighteners, while octa(ethylene oxide)dodecyl ether (C₁₂EO₈) was added as a surfactant for the emulsified sc-CO₂ bath. Electrodeposition was performed on both sides of each specimen under constant current density conditions at 5 A/dm² for 36 min.

After electrodeposition, material characterization of the depos-

ited film was performed. A scanning electron microscope (SEM) was used to examine the surface morphologies, while the surface roughness of the electrodeposited nickel films was scanned and measured with an atomic force microscope (AFM). The chemical states of Ni and C in the electrodeposited film were detected by X-ray photoelectron spectroscopy (XPS) on a PHI 5000 system. The spectra were recorded with the Al K α line as the excitation source. The crystal structure of the as-plated film was analyzed by X-ray diffraction (XRD) using a monochromatic Cu K α (λ = 1.540562 nm) radiation. The microstructure of the nickel films was also examined with a field-emission transmission electron microscope (TEM) with an emission voltage of 200 kV. The Vickers microhardness measurements were carried out using a microhardness tester with a diamond pyramid indenter at a load of 50 g and a duration of 15 s. An average of ten readings was taken to obtain the hardness values of the nickel films.

Results and Discussion

Current efficiency.— The current efficiencies of electrodeposition at various conditions under an applied current density of 5 A/dm² are depicted in Table II. The efficiencies were determined by comparing the weight gain with the theoretical value calculated from the applied charge using Faraday's law. In plain aqueous electrolyte and at ambient pressure, the current efficiency was 91.1%. The applied pressure, under Ar atmosphere at 10 MPa (about 100 atm), did not cause a noticeable change in the current efficiency. At the presence of sc-CO₂ at 10 MPa, either with or without surfactant addition, a decrease in the current efficiency (86.4 or 85.9%) was observed, as shown in Table II. The decrease in efficiency was mainly attributed to the lower conductivity of the electrolyte, as pointed out by Kim et al.⁶ CO₂ dissolved in water upon contact with it, causing the formation of carbonic acid according to the following reaction^{7,8}

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$$

A lower pH (about 3) of the aqueous solution was obtained.⁹ During electrodeposition, the amount of H^+ ions generated according to the above reaction was reduced. Consequently, the simultaneous reduction of Ni²⁺ and H⁺ caused a lower current efficiency.

The dependence of current efficiency on solution pH was confirmed by conducting the electrodeposition in a modified Watt's bath with various pH values, adjusted by the addition of ammonium water. As demonstrated in Fig. 1, the current efficiency decreased as the solution pH was lowered, which is consistent with previous studies.^{10,11} In the bath containing sc-CO₂, the lower current efficiency was also attributed to the relatively higher acidity of the electrolyte used. As shown in Table II, the current efficiency in the

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Table I. Bath composition and conditions used for Ni electrodeposition.

		Deposition conditions	
Electrolyte	Concentration	Parameters	Value
NiSO4·6H2O	300 g/L	Current density	5 A/dm^2
NiCl ₂ ·6H ₂ O	50 g/L	Bath temperature	50°C
H ₃ BO ₃	30 g/L	Deposition time	36 min
Saccharin	0.5 g/L	Solution pH	3.5
C ₇ H ₉ NO ₂ S	0.5 g/L	Aqueous electrolyte (exposed to air)	0.1 MPa
$C_{12}EO_8$	0.1 vol %	Electrolyte in Ar gas	10 MPa
12 0		Electrolyte in sc-CO ₂	10 MPa

Table II. Current efficiency for Ni electrodeposited at various conditions.

Conditions of coating	Current efficiency (%)
Aqueous electrolyte/0.1 MPa (air)	91.1
Aqueous electrolyte/10 MPa (Ar)	90.5
sc-CO ₂ /10 MPa (surfactant-free)	85.9
sc-CO ₂ /10 MPa (emulsion)	86.4







Figure 2. Surface morphologies of nickel films electrodeposited in (a) aqueous electrolyte at atmospheric pressure, (b) surfactant-free sc-CO₂ fluid, and (c) sc-CO₂ emulsion.

surfactant-free sc- CO_2 /aqueous electrolyte mixture was almost the same as that in the emulsified sc- CO_2 bath. This was probably because the acidity did not differ much between these two baths.

Surface morphology .--- The surface morphologies of the electrodeposited Ni films, produced in plain aqueous electrolytes at different pressures and in sc-CO₂-containing baths with and without surfactant addition, were examined by an SEM. Figure 2a shows the SEM image of the Ni film electrodeposited in plain aqueous electrolyte at atmospheric pressure, exhibiting a rather smooth surface appearance. Similar results were found for the Ni film deposited in a modified Watt's bath under an Ar atmosphere of 10 MPa. The results indicated that the surface appearance of the Ni film electrodeposited in an aqueous electrolyte was not affected by the pressure in which it was exposed. With the presence of sc-CO₂, but without surfactant addition, a large number of pinholes were found on the electrodeposited Ni film surface, as depicted in Fig. 2b. These pinholes could be as large as 150 nm, as shown in the micrograph. During electrodeposition, hydrogen reduction is commonly accompanied by metal ion reduction, resulting in the formation of pinholes. In the surfactant-free sc-CO₂ fluid, Ni was electrodeposited at the metal/ aqueous electrolyte interface. Under such high pressure conditions, the amount of CO₂ dissolved in the aqueous solution was increased. Once the Ni was reduced at the metal (substrate) surface, some of the dissolved CO₂ was trapped and encapsulated in the deposited Ni film. The pressure of the trapped CO₂ was so high that it erupted to form a pinhole (cavity) at the subsurface of the Ni film once the pressure was released when the autoclave was opened up. Whether the pinholes revealed in Fig. 2b mainly resulted from H₂ evolution or CO₂ encapsulation is worth further investigation.

When electrodeposition was performed in the emulsified sc- CO_2 electrolyte, a flat and almost pinhole-free surface was observed, as shown in Fig. 2c. In the emulsified bath, Ni²⁺ reduction occurred when the W/CO₂ microemulsion was in contact with the electrode surface. It has been reported that H₂ gas has a high solubility in sc- CO_2 fluid.^{12,13} When simultaneous reductions of Ni²⁺ and H⁺ occur in the W/CO₂ microemulsion, the evolved H₂ would be miscible in the sc- CO_2 phase. As a result, the pinhole formation could be minimized and even avoided, as demonstrated in Fig. 2c.

The surface roughness of the electrodeposited films was further examined using an AFM. Figure 3 shows surface images of nickel films deposited at various conditions. The surface roughness of the Ni film electrodeposited in aqueous electrolyte in air at ambient pressure (0.1 MPa) was about 9.8 nm. At a pressure of 10 MPa under Ar atmosphere, the surface roughness of Ni film was almost the same as that electrodeposited in air at ambient pressure. However, the surface of the Ni film became much rougher when it was electrodeposited in the surfactant-free sc-CO₂ fluid, and the presence of pinholes on the surface was responsible for this. For the Ni film deposited in the emulsified sc-CO₂ fluid, a significant reduction of surface roughness (about 5.7 nm) was seen, indicating the advantage of electrodeposition in such an environment. The average surface roughness (R_a) values of the nickel films deposited at various conditions are listed in Table III.



Figure 3. (Color online) AFM images showing the surface roughness of nickel films electrodeposited in (a) aqueous electrolyte at atmospheric pressure, (b) Ar atmosphere at 10 MPa, (c) surfactant-free sc-CO₂ fluid, and (d) sc-CO₂ emulsion.

Table III. Surface roughness of Ni electrodeposited at various conditions.

Conditions of coating	Surface roughness ^a (±2.4) (nm)
Aqueous electrolyte/0.1 MPa (air)	9.8
Aqueous electrolyte/10 MPa (Ar)	11.2
sc-CO ₂ /10 MPa (surfactant-free)	15.0
sc-CO ₂ /10 MPa (emulsion)	5.7

^a Average of five measurements.



Figure 4. XRD spectra of nickel films electrodeposited in aqueous electrolyte at atmospheric pressure, in Ar atmosphere at 10 MPa, in surfactant-free $sc-CO_2$ fluid at 10 MPa, and in $sc-CO_2$ emulsion at 10 MPa.

Table IV.	2θ ₍₁₁₁₎ , d ₍₁₁₁₎ ,	and lattice	constant	of Ni elect	rodeposited
at variou	s conditions.				

Conditions of coating	2θ ₍₁₁₁₎	d ₍₁₁₁₎	Lattice constant (Å)
Aqueous electrolyte/0.1 MPa (air)	44.390	2.039	3.531
Aqueous electrolyte/10 MPa (Ar)	44.410	2.038	3.530
sc-CO ₂ /10 MPa (surfactant-free)	44.320	2.042	3.537
$sc-CO_2/10$ MPa (emulsion)	44.310	2.043	3.538

Crystal structure.- The XRD patterns of Ni coatings prepared at different conditions are illustrated in Fig. 4. As shown in this figure, the nickel films electrodeposited in plain aqueous electrolyte, at 0.1 or 10 MPa, are crystalline and exhibits a face-centered cubic structure. The pressure applied did not cause any transformation in the crystal structure of the Ni films, except the change in the relative intensities between the (111) and (200) planes. The results indicate that (200) planes are favored to form in high pressure conditions. When electrodeposition was performed in the presence of sc-CO₂ at 10 MPa, but without any surfactant addition, the diffraction peaks broadened, revealing the nanocrystalline characteristics of the deposited film. An XRD pattern with broad, even peaks and much lower intensities (Fig. 4) was obtained when electrodeposition was performed in the sc-CO₂ emulsion. The loss of crystallinity of the Ni films electrodeposited in the electrolyte in the presence of sc-CO₂ was further confirmed by TEM analysis, as described below. The values of the d-spacing and lattice constant of the various Ni deposits are summarized in Table IV. The larger lattice constant for the Ni films deposited in the electrolyte containing sc-CO₂ indicates that lattice distortion occurred in these deposits. As shown later, the dissolution of carbon into the Ni lattice was the main reason for the modification of the crystal structure.

Chemical composition analysis.— XPS was employed for the chemical composition analysis of the surface layer of the deposit. A short Ar^+ ion etching was performed to clean the surface of the deposited film before XPS analysis. Figure 5 shows the survey scan of the Ni film electrodeposited in the plain aqueous electrolyte exposed in air at ambient pressure. The absence of C 1s in Fig. 5 indicates that Ar^+ ion etching is adequate for the surface cleaning to eliminate C contamination. A similar procedure was applied to other specimens in which XPS was performed. The XPS spectra of C 1s for the Ni films electrodeposited in the plain aqueous electrolyte at atmospheric pressure and in the sc-CO₂ emulsion are compared in



Figure 5. XPS survey spectrum of Ni film electrodeposited in aqueous electrolyte at atmospheric pressure after Ar⁺ sputtering.



Figure 6. (Color online) X-ray photoelectron spectra of the C 1s region of nickel films electrodeposited in aqueous electrolyte at atmospheric pressure and in sc-CO₂ emulsion at 10 MPa, both etched by Ar^+ ion for 1 min.

Fig. 6. In each case, Ar^+ ion etching was carried out for 1 min. A distinct C 1s peak was observed in the spectrum of the Ni film deposited in the sc-CO₂ emulsion. When Ar^+ ion etching was extended to 3 min, the C peak could still be observed, confirming the existence of C in the deposit layer. The C 1s binding energy for graphitic carbon is 284.6 eV.¹⁴ As shown in Fig. 6, the C 1s binding energy obtained in this investigation was 282.8 eV. The decrease in the C 1s binding energy due to the formation of metal–carbon bonds has been reported.^{15,16} Thus, the result shown in Fig. 6 indicate the dissolution of carbon into the Ni film deposited in the sc-CO₂ emulsion.

The formation of Ni–C deposits via sputtering or chemical synthesis has been reported. $^{17-19}$ However, to the best of our kowledge, it has not been reported an electrodeposition process. In the system containing sc-CO₂, as described in this investigation, the formation of Ni–C deposit might be associated with the following reduction reactions

and

$$\mathrm{HCO}_{3}^{-} + 5\mathrm{H}^{+} + 4\mathrm{e}^{-} \rightarrow \mathrm{C} + 3\mathrm{H}_{2}\mathrm{O}$$

 $Ni^{2+} + 2e^- \rightarrow Ni$

The reduction reaction of bicarbonate ion (HCO $_3^-$) might become favorable at high pressure, as found in the system incorporating sc-CO $_2$.

The XRD analysis shows that a higher lattice constant was observed when the Ni film was deposited in the electrolyte with the presence of sc-CO₂. This expansion of the lattice constant can be attributed to the solid solution of C in the Ni lattice.

Cross-section micrograph.— The cross-sectional micrographs of the various deposits are shown in Fig. 7. The results show that with a deposition time of 36 min, the thickness of the deposit varies with deposition conditions. In sc-CO₂-containing electrolytes, with or without surfactant addition, the film was thinner than those electrodeposited in plain aqueous electrolytes. These results are consistent with those of the weight change measurements.



Figure 7. Cross-sectional micrographs of nickel films electrodeposited in (a) aqueous electrolyte at atmospheric pressure, (b) Ar atmosphere at 10 MPa, (c) surfactant-free sc-CO₂ fluid, and (d) sc-CO₂ emulsion.

Microstructure.— The microstructure of each electrodeposited Ni film was examined by a TEM. Figure 8 shows the TEM micrographs and the selected area diffraction (SAD) patterns of four different as-deposited Ni films. As demonstrated in Fig. 8a, the average grain size of the Ni film electrodeposited in plain aqueous electrolyte in air at ambient pressure was about 43 nm, not too different from that deposited in Ar atmosphere at a pressure of 10 MPa (Fig. 8b). As shown in Fig. 8c and d, a much finer microstructure was found for the Ni film electrodeposited in the electrolyte containing sc-CO₂, either with or without surfactant. The average grain sizes determined from the TEM micrographs were 17 and 14 nm, respectively, for both cases, which are much finer than those deposited in the electrolyte without the presence of sc-CO₂ fluid. These results



Figure 8. TEM micrographs and SAD patterns of as-plated Ni coating produced at i = 5 A/dm² and in (a) aqueous electrolyte at atmospheric pressure, (b) Ar atmosphere at 10 MPa, (c) surfactant-free sc-CO₂ fluid, and (d) sc-CO₂ emulsion.

Table V. Grain size and microhardness of Ni electrodeposited at various conditions.

Conditions of coating	Grain size (nm)	Microhardness (Hv)
Aqueous electrolyte/0.1 MPa (air)	43	446 ± 21
Aqueous electrolyte/10 MPa (Ar)	45	412 ± 16
sc-CO ₂ /10 MPa (surfactant-free)	17	701 ± 14
sc-CO ₂ /10 MPa (emulsion)	14	736 ± 23

agree with the broadened XRD patterns shown in Fig. 4. da Rocha et al.²⁰ have reported that the emulsion of a saline solution with sc-CO₂ contains numerous micelles with radii in the range of several micrometers. Yoshida et al.² have also indicated that plating in the emulsion is similar to pulse plating. With the characteristic nature of the electrolyte and the unique electrodeposition mechanism, a much finer microstructure could thus be obtained, especially with the presence of a sc-CO₂ emulsion, as revealed in the TEM micrographs of Fig. 8d. The four diffraction rings shown in Fig. 8 are identified as the (111), (200), (220), and (311) reflections of the face-centered cubic Ni. The well-defined electron diffraction patterns indicated that the Ni films were crystalline in nature but with a nanoscale grain size.

Microhardness.- The microhardness of the electrodeposited nickel was also measured. For each sample 10 impressions were made, and an average hardness value was then calculated. The results obtained for various deposits are listed in Table V.

According to the Hall–Petch equation,^{21,22} the strength of a solid increases linearly and inversely with the square root of grain size (d), namely

$$\sigma_{\rm v} = \sigma_{\rm o} + k_{\rm v} d^{-1/2}$$

where σ_v is the tensile yield strength, σ_o is the intrinsic stress resisting dislocation motion, and k_v is the proportional constant. Because hardness is generally proportional to yield strength, the hardness also obeys the Hall-Petch equation, which increases with decreasing grain size. Table V shows that a substantial increase in microhardness occurs if the Ni film is electrodeposited in the electrolyte with the presence of sc-CO₂. As mentioned above, C could be dissolved in the Ni lattice if sc-CO₂ was present. The significant increase in microhardness was also attributed to solid solution strengthening due to the presence of C in the Ni lattice.

Conclusion

Electrodeposition of Ni was performed in a modified Watt's bath in the presence of sc-CO₂, either with or without surfactant addition. However, the current efficiency was lower in the bath containing

sc-CO₂ due to the increased participation of proton reduction. Pinholes were found in the Ni film electrodeposited in the surfactantfree sc-CO₂ bath, but these were eliminated when the deposition took place in an emulsified sc-CO₂ bath. Consequently, the surface roughness of the latter film was much lower than that of the former. A nanocrystalline Ni film was obtained, and the grain size became much finer when the sc-CO₂ bath was used. XPS analysis showed that the solution of carbon occurred to form Ni-C electrodeposits in the sc-CO₂ bath. The fine grain size and the solid solution of C in Ni gave rise to a substantial increase in the microhardness of the electrodeposited Ni-C film.

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