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The influences of monoethanolamine additive on the properties of nickel coating electroplated in post supercritical carbon dioxide mixed Watts bath

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ABSTRACT

Post supercritical (PSC) carbon dioxide electroplating process uses the fully mixed electrolyte with CO_2 in supercritical state and then performs conventional electroplating at atmospheric pressure. The oversaturated electrolyte provides the regenerated CO_2 micro bubbles and similar improvement on the prepared coating as in the supercritical electroplating is obtained. However, after being exposed to atmosphere, the electrolyte diminishes gradually the influence of oversaturated CO_2. In this study, monoethanolamine (MEA) was used as an additive for a Watts bath prepared for the PSC CO_2 electroplating. MEA had been employed in CO_2 capture for reducing carbon emission from power plants. The adoption of MEA in the electrolyte was intended to control the CO_2 regeneration from the post supercritical mixing and, subsequently, to assist the electroplating. The experimental results showed that the nickel coating prepared by adding 5 mL/L MEA in the electrolyte increased its hardness and corrosion potential both for conventional and PSC electroplating. Cross-sectional TEM micrograph revealed the columnar grain growth in the prepared nickel coating. Adding MEA in the electrolyte provided the PSC electroplated nickel coating with the emergence of crystalline defects such as dislocation and twin along with nano-grains. Therefore, the coating's hardness increased accordingly. Moreover, the collateral increase in internal tensile stress due to these defects produced cracking in the coating. More cracking and higher surface roughness of the coating should be responsible for the larger corrosion current measured in the polarization curves.

1. Introduction

Nickel electroplating has been a common practice for preparing functional coating on components for improving their corrosion and wear resistance besides better appearance. Among its industrial implementations, electroplating in Watts bath is widely regarded as an economical and efficient process [1]. By adding anionic surfactant into the Watts bath and mixing with the supercritical CO_2, Yoshida and coworkers [2] reported an improvement in reducing pinholes, enhancing uniformity, and increasing hardness of the nickel coating electroplated in the resulted electrolyte emulsion. The improvement was attributed to the periodic plating mechanism induced by the micro CO_2 bubbles sweeping through the cathodic surface and, consequently, disturbing the local electric field distribution [3, 4]. Moreover, the supercritical CO_2 emulsion was more capable of dissolving the hydrogen gas generated from side reaction in electroplating [3–5]. Although less pinhole was found in the coating, quick dissolution of hydrogen from cathode accelerated the side reaction and lowered the cathodic efficiency [6]. More nano gas pockets were found which, after depressurization, led to higher tensile internal stress of the coating [7]. Among the process parameters which influence the supercritical CO_2 plating results, pressure, temperature, surfactant, mixing and current density were considered to be more critical [8–12]. Chung and Tsai [13] showed that the increase in coating's hardness was due to both the grain refinement and carbon incorporation.

Although supercritical CO_2 emulsion showed several beneficial effects to electroplating and a semi-continuous process was demonstrated [14], the high pressure facility required for components with large dimensions still poses economic concerns. Therefore, a post supercritical (PSC) CO_2 electroplating was proposed by Nguyen and coworkers [15]. The PSC mixed electrolyte depressurized to atmospheric pressure was found to contain oversaturated CO_2 which returned to gaseous state and escaped from the electrolyte gradually. The degasing electrolyte generated micro gas bubbles and provided the periodic plating mechanism mentioned previously. Hence, part of the beneficial effects from supercritical CO_2 electroplating was retained in this PSC process. Although the PSC effect was a transient and decaying phenomenon, the electroplating at atmospheric pressure releases the constraint for

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having large high pressure chamber facility and the electrolyte can be remixed and replenished continuously with supercritical CO_2 in another chamber. On the other hand, the release of oversaturated CO_2 in the electrolyte could be controlled by the agitation and accordingly the characteristics of the coating through the thickness could be tailored [16, 17]. A similar manipulation on the electrolyte was also applied to an electroless Ni deposition in the blind holes of printed circuit board [18].

Apparently, the retention of CO_2 in the electrolyte such as in the PSC process is beneficial in improving coating's property. Thus, the reagent which is capable of capture CO_2 in the solution deserves attentions. In recent research about the carbon sequestration, the use of ethanolamines to capture the CO_2 from the emission of power plants is one of the promising techniques [19–22]. The CO_2 can be chemically absorbed by the molecules of monoethanolamine (MEA) and released again by process control. Therefore, in this study adding MEA in the Watts bath was attempted to control the absorption of CO_2 during supercritical mixing and the effect of MEA in the electrolyte was investigated for different electroplating processes.

2. Experimental

2.1. Electroplating

Table 1 presents the compositions of the Watts bath used in the electroplating of nickel coating on brass substrate in this study. The basic electrolyte contained 300 g/L nickel sulfate, 50 g/L nickel chloride and 30 g/L boric acid. Different amounts of MEA were added and mixed for controlling the MEA concentration in electrolyte. For the PSC assisted electroplating, the electrolyte was further mixed in a high pressure chamber with the process parameters described in Table 2. Fig. 1 shows the schematic diagram for the experimental setup used in the preparation of PSC CO_2 mixed electrolyte. The CO_2 from the storage bottle passed through a low-temperature bath to assure it was in liquid state. The high pressure pump (Haskel, max 670 atm), driven by an air compressor, pressurized the CO_2 to the required pressure described in Table 2. The mixing of CO_2 and electrolyte took place inside reaction chamber under controlled agitation and temperature.

Both the conventional and PSC electroplating was conducted at atmospheric pressure and 50 °C. The nominal thickness of the coating was controlled at 10 μm while the 50 μm thick coating was exclusively employed to study the hardness variation through extended plating duration, especially at lower current densities with lower deposition rate. In accordance with the current density used in electroplating, the deposition time for a nominal 10 μm coating ranged from 48 min 49 s at 1 ASD to 3 min 15 s at 15 ASD.

The cathode used was a circular brass substrate with exposed area of 2.8 cm^2. The brass substrate was first ground and polished, then degreased and pickled to prepare a clean surface for electroplating. At the anode, a nickel plate with 99.9% purity in composition was employed. Similar grinding treatment as the cathode was used to ensure the removal of oxide on its surface.

2.2. Measurement of CO_2 release from the electrolyte

The gradual release of CO_2 from the supercritical mixing phase during electroplating was believed to contribute to the process improvement in PSC electroplating process. Therefore, understanding the release of regenerated CO_2 from different electrolytes was essential in this study. Fig. 2 presents the schematic diagram for measuring the CO_2 release from the PSC mixed electrolyte. The electrolyte was put in a container covered with a cap which had two opening holes. A vinyl tube passing through one of the opening holes connected the upper space of the electrolyte container to a buffer container. The other opening hole provided the inlet of air from outside to balance the pressure difference caused by the outflow of the mixed gas through the vinyl tube. At the other end of the buffer container, an exit connected to an air pump was to continuously ventilate the mixed gas out to atmosphere. A CO_2 concentration detector (Paspont CO_2 Sensor PS-2100) was mounted on the wall of the buffer container and was used to monitor the temporal variation of the CO_2 concentration. The processing module (Paspont SPARKlink PS-2009) relayed the measured

Table 1
Compositions of modified Watts bath.

Ingredient	Concentration
Nickel sulfate ($NiSO_4 \cdot 6H_2O$)	300 g/L
Nickel chloride ($NiCl_2 \cdot 6H_2O$)	50 g/L
Boric acid (H_3BO_3)	30 g/L
Monoethanolamine(C_2H_7NO)	0, 1, 5, 10, 15, 20 mL/L

Table 2
Process parameters in electroplating.

Parameters	Post supercritical CO_2 electroplating		Conventional electroplating
	Sc-CO_2 mixing	Electroplating	
Temperature, °C	50	50	50
Pressure, atm	82.6	1.0	1.0
Agitation speed, rpm	500	400	400
Current density, A/dm^2	–	1–15	1–15
Nominal coating thickness, μm	–	10, 50	10, 50

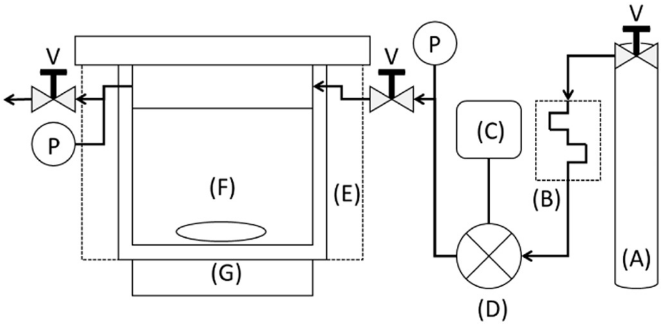

Fig. 1. Schematic diagram for the experimental setup used in the preparation of post-supercritical CO_2 mixed electrolyte: (A) CO_2 bottle, (B) low temperature water bath, (C) air compressor, (D) high pressure pump, (E) water jacket for reaction chamber, (F) reaction chamber, (G) magnetic stirrer, (P) pressure gauge, (V) control valve.

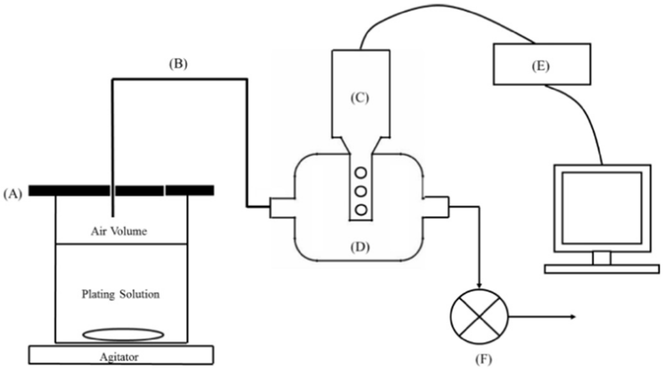

Fig. 2. Schematic diagram of the experimental setup for measuring CO_2 release from the electrolyte: (A) acrylic cap, (B) vinyl tube, (C) CO_2 concentration detector, (D) buffer container, (E) processing module of CO_2 detector, (F) air pump.