



An electroplating technique using the post supercritical carbon dioxide mixed watts electrolyte

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ABSTRACT

The nickel films with nano-sized grains, high hardness and smooth surface have been prepared using a new electroplating technique involving the post supercritical mixed electrolyte. After mixing watts bath with Sc-CO₂, the pH value of exposed electrolyte got lower but then raised backward gradually. The released CO₂ concentration from this Sc-CO₂ mixture has also been evaluated within 3 h of agitation. As the plating result, average grain size of the 20 μm-thick coatings were 16, 34, and 210 nm for those plated from pure Sc-CO₂, post Sc-CO₂ and conventional method, respectively. Evaluated on the cross section, microhardness of a 100 μm-thick post Sc-CO₂ nickel coating has reached 650 Hv within the regions below 50 μm from the substrate interface then decreased to 350 Hv on further away regions. The high hardness region of nickel coating was found closely related to the electrodeposited duration when electrolyte still possessed high CO₂ concentration. Moreover, the incorporation of carbon in nickel electrodeposit was found not only at the pure Sc-CO₂ coating but also at the post Sc-CO₂ one. Therefore, this new plating technique not only confirms the roles of dissolved CO₂ bubbles in electrolyte but also provides a potential to overcome most issues associated with the cost in building high-pressure environment for large size products and continuous plating using supercritical method.

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1. Introduction

Recently, electrodeposition of pure metal through the supercritical carbon dioxide (Sc-CO₂) electrolyte mixture has been stated as a novel method for fabricating the nano-material products. The special characteristics of these Sc-CO₂ plated nickel films include uniformity and high hardness, nano-sized grains, bright appearance, smooth surface, and high corrosion resistance [1–5]. Furthermore, by adding copper particle suspension into the Sc-CO₂ electrolyte mixture, the copper was able to electrodeposit in high aspect ratio, nano-scaled gap (70 nm in diameter) without any significant defects [6]. Thereby, the excellent wettability of Sc-CO₂ electrolyte/solution promises itself a viable vehicle for plating/coating nano-sized scale electronic devices, which would be the inaccessible regions of the conventional methods.

Above the critical point at a pressure of 73 atm (~7.4 MPa) and a temperature of 31.1 °C, the supercritical state of CO₂ is formed. Under this condition, with proper agitation, the CO₂ bubbles are introduced into electrolyte forming a mixture possessing both gaseous and liquid phases. Practically, with an addition of surfactant, the supercritical CO₂ droplets have been observed in nano scale (~10 nm) and in some cases, the stability can exist over 24 h. [7]. Those nano-sized bubbles

in aqueous electrolyte are postulated as the key factors in transforming the direct current into the periodic one and assisting the desorption of generated hydrogen simultaneously in the electrodeposition process. Both the size reduction and population increase of CO₂ bubbles in Sc-CO₂ mixed electrolyte have been reported as the main reasons for refining grains and smoothening coating surface. Nonetheless, the circular marks observed on deposited surface was mentioned because of a formation of large size CO₂ bubbles [3].

Although the superior mechanical properties aforementioned in Sc-CO₂ electroplating, the nickel coating was found suffering higher tensile internal stress than that of the conventional one. The internal stress increased when the CO₂ fraction in the reaction chamber was raised, implying more soluble CO₂ in aqueous electrolyte. The charging of CO₂/H₂ in the cavities during film formation under such a high pressure of Sc-CO₂ state constitutes one of the causes [8,9]. In thin film applications, the internal stress of a deposition is crucial for its structural integrity. Furthermore, the electrodeposition under supercritical state of CO₂ demands a high-pressure chamber, which is high in equipment cost especially for large work piece and is difficult to implement for continuous plating. In this study, instead of doing electrodeposition inside the high-pressure chamber, the post Sc-CO₂ mixed electrolyte was introduced to a plating cell at atmospheric pressure and plating was performed therein as conventional practice. Thus, some of the shortcomings of the Sc-CO₂ plating may be overcome and the investigation

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on the feasibility of using the post Sc-CO₂ electrodeposition would have potential in industrial applications accordingly.

2. Experimental

2.1. Materials

In this work, the Watts bath electrolyte consisting of 300 g/l NiSO₄ · 6H₂O, 50 g/l NiCl₂ · 6H₂O, and 30 g/l H₃BO₃ was used. All the chemicals of the Watts bath were purchased from First Chemical Co. Ltd, Taiwan and employed in the electrodeposition without further refinement. Carbon dioxide with minimum purity of 99.9% was acquired from CC Gaseous Corp., Taiwan. The circular copper plate with an area approximately 2 cm² and thickness of 0.5 mm was used as the working substrate, which has a similar cross section size to that of the nickel anode.

2.2. Experimental apparatus and method

The schematic diagram of the post Sc-CO₂ electroplating system used in this work is depicted in Fig. 1. The Sc-CO₂ forming chamber, which had a volume of approximately 190 cc, was made of stainless steel with inner Teflon lining for chemical inertness. The underneath magnetic agitator and a surrounding temperature controlled water jacket were used for mixing and maintaining the constant temperature of the inner chamber, respectively.

The nickel electroplating solution was first put into the Sc-CO₂ forming chamber. With the chamber cap closed, liquid CO₂ was introduced into the chamber using a high-pressure air driven liquid pump, Haskel DSF-60, and the chamber was pressurized to a predetermined pressure. The Sc-CO₂ mixture was agitated with a magnetic stirrer at a speed of 500 rpm for at least 30 min then pressure was released and the solution was introduced into the plating chamber.

Prior to deposition, the polished copper substrate working as the cathode later on was treated sequentially in 10 wt.% NaOH solution for degreasing, 10 wt.% HCl solution for surface activating and then rinsed in de-ionized water.

Inside the reaction chamber, the cathode and anode were arranged in horizontal orientation with a working distance of 2 cm for allowing adequate fluid sweeping on both electrode surfaces. Both the cathode and anode were connected to the programmable power supply, NF BP 4610, Japan, through titanium rods to the lead wires outside the chamber. The plating started as soon as the post Sc-CO₂ solution was maintained at the desired temperature.

Each experiment was carried out in fresh solution and with parameters shown in Table 1. After plating, the copper cathode with nickel coating was rinsed in deionized water, and then dried with warm stream of air.

2.3. Microstructural examination

The surface morphology of the specimen was examined by a scanning electron microscope (SEM), the Carl Zeiss-SIGMA Essential, Germany. The chemical states of Ni and C in the electrodeposited film were examined by X-ray photoelectron spectroscopy (XPS), ULVAC-PHI, PHI 5000 VersaProbe, Japan. The average grain size of deposits was measured by the X-ray Diffraction (XRD), Philips 1830/Mac, Netherlands. The measurement was implemented at a sweeping rate of 2 deg/min and calculated by the Scherrer equation with taking the broadening effect of the XRD machine into account. The X-ray was generated by a Cu-K_α target operated at 30 kV and 20 mA with a wavelength of 0.15418 nm. The micro hardness measurement was performed at cross section plane of the coating using a diamond pyramid indenter, the Mitutoyo HM-113 microhardness tester, at a load of 10 g and duration of 15 s.

2.4. Carbon dioxide release and pH evaluations

The released CO₂ concentration from 135 cc solution, in the total exposed air volume of 340 cm³, was evaluated by using the portable gas analyzer, HORIBA MEXA-584 L, Japan while keep agitating for three hours. Measurements were carried out with a corresponding pure Watts bath electrolyte, just released post Sc-CO₂ solution, and post Sc-CO₂ solution after 30 min stillly exposed at the atmosphere, respectively. The corresponding pH values of previous solutions were evaluated by employing the Ezodo Digital Pocket PH Meter PH-5011, Taiwan. All measurements were carried out under the conditions of 500 rpm-stirring and 40 °C electrolytes. The released CO₂ concentration was evaluated up to 180 min while pH value was recorded within duration of 300 min.

3. Results

3.1. Surface morphology of coating

Fig. 2 depicts the SEM micrographs of nickel coatings electroplated in different methods. With 5 μm-thick coating, the surface of the conventional film was rough and with blisters (Fig. 2a) whereas the Sc-CO₂ and post Sc-CO₂ ones were smooth but a number of tiny pinholes were present (Fig. 2b–c). However, when the thicker film was obtained (15 μm), the post Sc-CO₂ deposit was pinhole-free with some blisters on surface, as seen in Fig. 2d.

On the nickel films plated in Sc-CO₂ electrolyte, without using surfactant, the micro-sized [5] and even the nano-sized [8] pinholes have been observed. Thus, these tiny pinholes, as observed in Fig. 6b-2 and c-2, on the nickel coating apparently show the presence of remained CO₂ bubbles in the post Sc-CO₂ electrolyte.

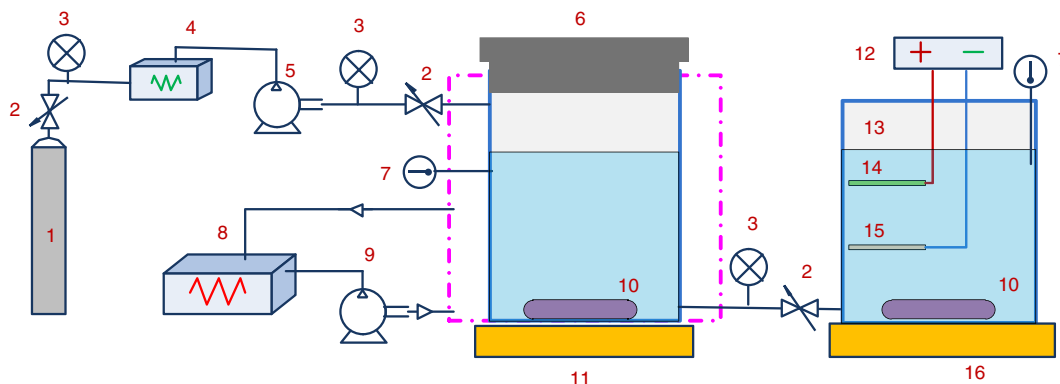


Fig. 1. The post Sc-CO₂ electroplating apparatus. It's labeled as follows: 1.CO₂ cylinder; 2.Valves; 3. Pressure indicators; 4.Cooler; 5.High pressure pump; 6.Sc-CO₂ forming chamber; 7.Thermometer; 8. Hot water reservoir; 9.Water pump; 10. Stir bars; 11.Agitator; 12. Power supply; 13.Post Sc-CO₂ plating chamber; 14.Anode; 15. Cathode; 16. Agitator and heater.

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