Electroplating of Nanostructured Nickel in Emulsion of Supercritical Carbon Dioxide in Electrolyte Solution

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We report electroplating in emulsion of supercritical carbon dioxide and electrolyte solution for the first time. Compared to conventional electroplating, this technology has advantages in covering, leveling and throwing effects on plating. Moreover the particle sizes of plated nickel are sub-100 nm.

Supercritical fluids are an attractive alternative to conventional solvents for a variety of applications.[1–8] Supercritical carbon dioxide (sc-CO_2), in particular, is generally viewed as replacement of harmful organic solvents for extractions, separations, reactions, and in many other fields. This is because the sc-CO_2 is nonflammable, virtually inert, essentially nontoxic, exhibits relatively low critical conditions, abundant and cheap. Electrochemical studies on sc-CO_2 were recently reviewed by Grinberg et al.[7] and there are no report on their practical applications.[8]

Herein, we describe a new nanoscale plating technology which is a hybrid of traditional direct current (dc) electroplating and sc-CO_2 techniques. It involves the electrochemical reaction in emulsions formed by sc-CO_2 and aqueous electrolyte with surfactants doping. The emulsion particle size ranges typically from several nanometers to several millimeters and can be controlled with surfactants to within a relatively narrow size distribution.[1,2,4] Therefore, in principle, nanometer order electrodeposition is possible. As a first example, we report nickel electroplating in emulsion that formed by surfactants, sc-CO_2, and the commonly used Watts bath. We demonstrate that films plated by this plating have significantly enhanced uniformity than that of conventional electroplating. Moreover, harmful organic solvents used for cleaning have also been eliminated.

Metal salts are generally soluble in water, but water and CO_2 are almost not miscible. It was believed that sc-CO_2 is not suitable for electrolysis.[9] This problem, however, can be solved by surfactants doping. Anionic, cationic, and nonionic surfactants have been found to form water in CO_2 (w/c) or CO_2 in water (c/w) emulsions.[1–5] C/w emulsion has a continuous water phase, and is conductive. Such emulsion can be used for electroplating. In our experiments, we employed nonionic block copolymer poly(ethylene oxide)-b-poly(propylene oxide) (PEO-PPO) as surfactants. At 306 K, under 10 MPa, and without stirring, a biphasic state was observed. In this case sc-CO_2 could be used for electrodes cleaning. Under the same temperature and pressure, but with agitation, we got a uniform c/w emulsion. Plating was carried out at this state. After decreasing the pressure to gaseous CO_2 of 6 MPa with the same agitation, an incomplete dispersion state was observed. The results indicate that the formation of c/w emulsion by the surfactant is not only affected by temperature and pressure over the critical point of CO_2, but also by agitation. Such dynamic emulsion made the sc-CO_2 is recyclable and can be used as cleaning and drying regent.

The use of supercritical fluid as a cleaning and drying agent is also a topic of increasing research interest, and has found industrial application in the removal of contaminants from high precision metal parts.[10] In our experiment, at first, we set the articles into sc-CO_2 phase for cleaning but not dipped into the electrolyte solution. The sc-CO_2 reaction apparatus was made by Japan Spectra Company (Jasco). The anode was a nickel plate (10 × 20 mm) and the cathode was a brass plate with the same size. The distance between the two electrodes was 20 mm. The cell was a closed system made of stainless steel that was set in a thermostat with magnetic stirring. Before plating, the temperature of the cell was increased to 323 K and the pressure was kept at 10 MPa for 25 min for cathode cleaning by sc-CO_2.

The electroplating bath consisted of nickel sulfate (372 g/L), nickel chloride (88 g/L), and boric acid (95 g/L). In the bath, a 6.0 wt% PEO–PPO surfactant to the aqueous electrolyte was doped. Without agitation, the biphasic state of sc-CO_2 and aqueous electrolyte was formed at 323 K, and 10 MPa. Under agitation, a uniform emulsion was formed. When a bias of 3.0 V, which corresponds electric current density of 2.0 A/dm^2, was applied to the electrodes, electroplating started. In 15 minutes plating, we got the thickness of 12.8 and 11.8 μm on the front and reverse side surfaces, respectively. This result shows higher throwing power of our method than conventional dc electroplating.

Figure 1 shows the current efficiency (a) and resistance (b) of the bath as a function of sc-CO_2 volume fraction in the electroplating cell. We observe that the current efficiency of electroplating depends on the volume fraction of sc-CO_2 in the cell. With an increase of sc-CO_2 volume fraction, the current efficiency decreases and the resistance increases slowly at first. When the volume fraction of sc-CO_2 is 22% in the cell, the current efficiency is 89%, which is comparable to the current efficiency of 94% in the conventional bright nickel-plating under normal atmosphere. When the volume fraction of sc-CO_2 reaches 60%,

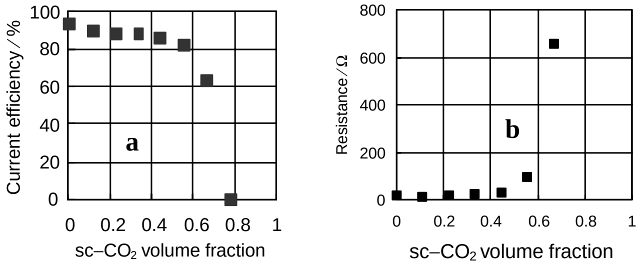

Figure 1. Current efficiency (a) and resistance (b) as a function of sc-CO_2 volume fraction in the plating bath.

the current efficiency is 75%, and electroplating can still be done smoothly. This result indicates that the plating electrolyte can be reduced at least 60% compared to that of currently industrially by used plating bath.

Figure 2 shows the cross section view of scanning electron spectroscopy image of plated nickel by our method. We see the particle sizes of plated nickel by our method are ~80 nm, which are significantly smaller than those of films plated by conventional dc electroplating. The surface of electroplated films by our method is also smoother than that of conventional electroplating. The reasons are as follows: in the experiment, the cathode used for plating was not polished, and there were a lot of defects on the plate. Moreover, in common electroplating in aqueous electrolyte, the cathode reactions include metal ion and H^+ reduction simultaneously. The formed hydrogen gases leave the bath, and induce voids defects in the plated films. With rare exception, electroplating processes will not conceal preexisting and newly produced surface blemishes such as scratches, dents, or pit. In fact, the plating process has a tendency to make most surface imperfections even more noticeable. This is because that in conventional electroplating, metal ions move from anode to cathode, and deposite on the front side surface of cathode by electrolysis. The current flows more densely around the outer edges of an object than the less accessible recessed areas. The plated film surface is rough. In our experiment, the generated hydrogen gas is solved in sc-CO_2, the hydrogen gas induced effect is eliminated. Moreover, the emulsion has lower viscosity than that of electrolyte, adopted metal atoms can move easily to the kink place on the cathode. The other possible reason is due to the emulsion which contains electrolyte and sc-CO_2, when the electrolyte contacts with cathode, electroplating takes place, but when sc-CO_2 part contacts with the electrode, electroplating will not occur. Therefore, electroplating in the emulsion is just like pulse plating. This technique can be used for plating of many other metals and for the fabrication of nanometer scale materials. The details on the physical chemical processes of electroplating in sc-CO_2/electrolyte emulsion also need further studies.

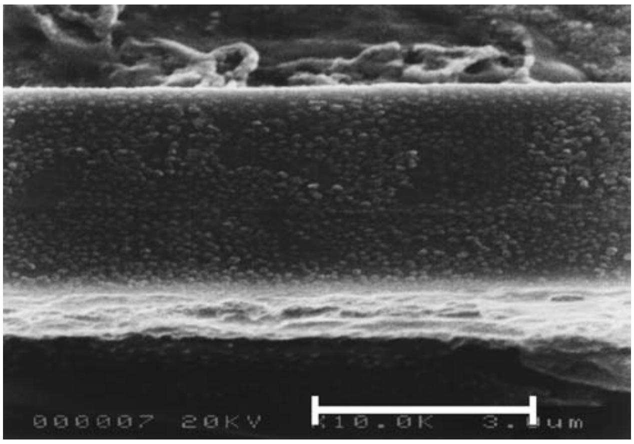

Figure 2. Scanning electron microscopy photograph of nickel cross-sections by our method. The scale bar is 3 μm.

In summary, we have developed a new technology that combines the merits of traditional electroplating and sc-CO_2 techniques. Sc-CO_2 is unique in cleaning cathode, forming emulsion with water under surfactants doping just as liquid, dissolves hydrogen just as gas, and gives rise to drying the cathode. All these factors made the technology an exciting method for high quality and rapid electroplating. The particle sizes of nickel by our method are about 80 nm, indicating that it is adaptable for uniform coating of very complex topographies.

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