Simulation and Test Analysis on Effect of Current Density on Electrodepositing Minuteness Structure under Supercritical Fluids

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This study simulates the electric field of the supercritical electrodepositing system using Comsol software. The effects of the current density on the Ni^{2+} concentration distribution and the electrodepositing film growth on the cathodic surface are analyzed. The surface morphology and micro-hardness were discussed first. The results show that the electric field is uniformly distributed inside the minuteness groove. The average Ni^{2+} concentration on the cathodic surface decreases at first, but then increases with the proceeding electrodepositing process; the growth of the electrodepositing films is similar to the distribution of the cathodic current density. The grain size and organization of the Ni-diamond composite electrodepositing minuteness films under supercritical fluid are fine and compact. Moreover, the micro-hardness of the sample reaches 900.75 HV (200 g), a figure that is 70 % higher than that of traditional electrodepositing when the current density is 700 A/m^2, the electrodepositing temperature is 323 K, the supercritical pressure is 12 MPa, and the nano-diamond particles content is 30 g/L.
Keywords: supercritical fluid, electrodepositing, minuteness groove, simulation, surface morphology.

1. INTRODUCTION

In order to adapt to the special requirements of materials in current medical biology, aerospace, micro-electro-mechanical systems (MEMS) and other fields, composite electrodepositing technology is often used for its unique ability to prepare high-performance precision metal matrix composites [1, 2]. Technical limitations existing in the traditional composite electrodepositing technology including low mass transfer efficiency, mixing solubility, and low dispersion ability of ions, were solved by this technology under a supercritical fluid (SCF) [3, 6]. The presence of supercritical composite electrodepositing technology has been reported [7, 8] but using supercritical composite electrodepositing technology to prepare micro films is reposted only on rare occasions.

For the basic research of this study [8, 9] in SCF condition, the metal ions and nano composite particles are given the high rate of diffusion and movement performance to supply the lack of metal ions and composite particles on the surface of cathode surface timely. At the same time the aggregation between composite particles is prevented due to the probability of collisions between composite particles reduced. The composite particles are better dispersed into the electroforming films. Then the electroforming film growth is more regular, the appearance of the supercritical electroforming film is smooth and the structure of the supercritical electroforming film is compact.

Comsol software was used to simulate the supercritical micro electrodepositing process to determine the influence of the current density on the micro film. The supercritical electrodepositing test was carried out accordingly. The influence of the current density on micro surface morphology and micro-hardness of the supercritical electrodepositing Ni-diamond films were analyzed.

2. SIMULATION OF SCF-CO₂ ELECTRODEPOSITES AND TEST CONDITIONS

Comsol Multiphysics software simulated the SCF-CO₂ electrodepositing system to research the influence of the electric current density on the electrodepositing system. Then, tests were carried out accordingly.

In these tests, the anode was a pure nickel plate with dimensions 2.5 cm × 3 cm and the cathode was a copper cone covering SU-8 photoresist microstructure with the size of 3 cm in diameter, 2 cm apart from the anode. Electrolyte composition and process conditions were as follows: nickel sulfate of 300 g/L, nickel chloride of 30 g/L, boric acid of 50 g/L, nano-diamond particles of 30 g/L, 6 drops of foaming agent per one hundred ml, a working pressure of 12 MPa, working temperature of 323 K, the current density of 500 ~ 900 A/m^2, pH 4, a magnetic stirring speed of 400 r min⁻¹, and a working time of 60 min. The reagents used followed the AR (Analytical Reagent). Test method: the surface of the microstructure was characterized by Hitachi S-3400 (SEM) and the micro-hardness was tested by an HXD – 1000 TMS Digital Micro-hardness tester. The supercritical composite electrodepositing device is shown in Fig. 1.

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3. THE ESTABLISHMENT OF MATHEMATICAL MODEL

To simplify the studies, a geometrical model of the micro "cross" groove of the electro-deposition, shown in Fig. 2, was used. The cathode formed the bottom of the micro "cross" groove, and the electrolyte interface formed the top of the geometric model. These cross structures were fabricated using resist SU8.
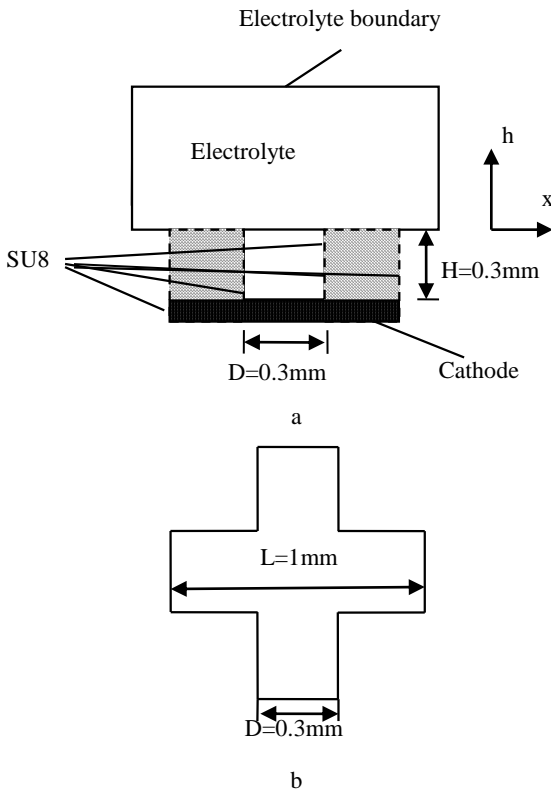

Fig. 2. Geometry model of minuteness electrodepositing groove: a – the micro electrodepositing unit; b – size of cross structure

In order to streamline the model and improve the rate of convergence, the following assumptions were made: the micro electrodepositing system with constant electric field and cathodic steady current was adopted [10]; the applied voltage of the system was small enough to ignore ion transfer caused by electrophoresis; in the SCF-CO$_2$ environment, Ni^{2+} reduction precipitation was only considered on the cathode; H$_2$ produced on the cathode quickly dissolved due to good solubility in the SCF-CO$_2$ electrodepositing environment; the influence of H$_2$ on the nickel ion concentration distribution was ignored; diamond particles had no influence on the nickel deposition; the pressure and the temperature of the system was kept at 10 MPa and 323 K, respectively. On this basis, the model of the SCF-CO$_2$ micro electrodepositing coupling field was constructed [11, 12].

3.1. Model of electric field

A model of the secondary current distribution was used. The cathodic potential deviated from the equilibrium value, an occurrence caused mainly by a slow electrochemical step because the diffusion coefficient of Ni^{2+} was great. Also, the ion concentration on the surface of the cathode could be supplemented effectively in the SCF-CO$_2$ system. The cathodic rate accorded with Butler-Volmer formula in electrodepositing process:

$$I = I_0[\exp(\frac{\alpha_A \eta F}{RT}) - \exp(\frac{-\alpha_c \eta F}{RT})], \tag{1}$$

where F denotes the Faraday constant, R is the ideal gas constant, I_0 represents the exchange current density, T is the absolute temperature, α_A, α_C and η are the charge transfer coefficient of the anode, the cathode, and the cathodic overpotential, respectively.

The electrolyte was of supercritical emulsified status. The boundary conditions of the electrode and the electrolyte interface are as follows: the electrolyte electric potential of the top boundary was 7 V; the cathodic current density imposed to the bottom of the groove was 500 A/m^2, 700 A/m^2, 900 A/m^2 and the electrical potential was zero.

3.2. Model of Ni^{2+} diffusion and transfer

Due to the fact that the Ni^{2+} reduction reaction was only considered on the cathode and that the mass transfer process was completed fully by diffusion, the following formula was obtained according to Fick's second law:

$$\frac{\partial C(x, y, h, t)}{\partial t} = D\nabla^2 C(x, y, h, t), \tag{2}$$

where D is the Ni^{2+} diffusion coefficient, $C (x, y, h, t)$ denotes the function of Ni^{2+} concentration.

In the SCF-CO$_2$ electrodepositing system, the Ni^{2+} diffusion coefficient was set at 3.11×10^{-8} m^2/s. According to the electrolyte formula, the initial Ni^{2+} concentration was 1200 mol/m^3 and the top boundary was fixed at the initial Ni^{2+} concentration.

4. SIMULATION ANALYSIS OF MICRO ELECTRODEPOSITING SYSTEM

4.1. Electric field analysis

Fig. 3 displays the electric field distribution. The distribution of current density corresponds with the distribution of the electric field line.
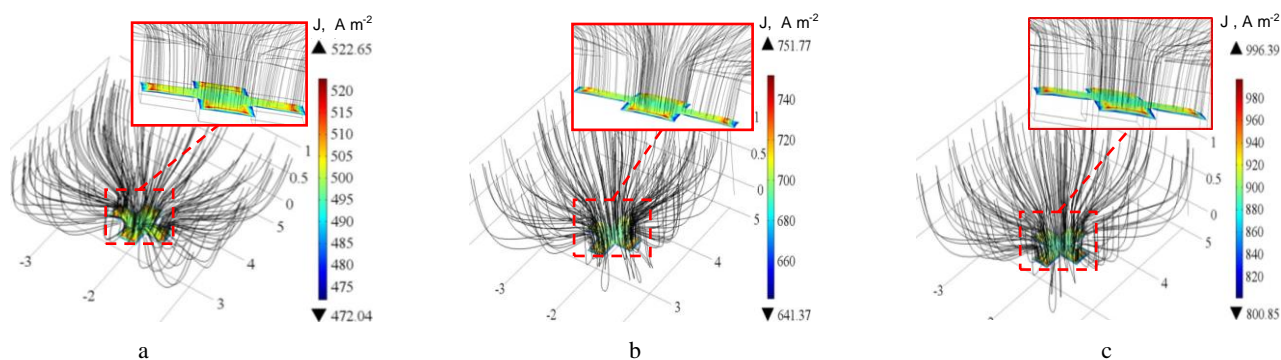
Fig. 3. Electric field distribution under different current density of SCF-CO$_2$ electrodepositing system: a – 500 A/m^2; b – 700 A/m^2; c – 900 A/m^2

From Fig. 3, it can be seen that the bending degree and consistency of the electric field line upon entering the micro groove increase gradually, the electric field intensity exhibits differences, and a potential gradient appears when the current density is 500 A/m^2, 700 A/m^2 and 900 A/m^2. The electric field line is uniform and orthokinetic in the micro groove, indicating the steadiness and uniformity of the electric field distribution. With the increase of the current density from 500 A/m^2 to 900 A/m^2, the uneven trend of its distribution in the interface of the cathode and the electrolyte is more obvious. This is because the Ni^{2+} electrodepositing rate is different on the cathode surface due to the current edge effect, the mass transfer rate, and other factors. Then, the flatness of the electrodepositing film declines, the electrical current concentrates in partial region, and with the increase of current density, the flatness of electrodepositing film is even less likely to be controlled.

4.2. Ni^{2+} concentration on the surface of electrodepositig film

In the electrodepositing process, the Ni^{2+} concentration distribution on the surface is an important factor that affects the electrodepositing rate and the electrodepositing quality [13]. The average Ni^{2+} concentration under normal conditions and supercritical conditions can be seen respectively in Fig. 4. It can be seen that the Ni^{2+} concentration on the surface decreases dramatically in the beginning phase, but the decrease degree in the supercritical condition is much smaller. With the increase of the current density, the decrease degree of Ni^{2+} concentration enhances, causing the Ni^{2+} concentration to increase linearly. The higher current density is, the greater the slope is. The reasons are that the Ni^{2+} depositing rate on the cathode surface is great in the beginning phase, the internal Ni^{2+} concentration gradient forms newly, and the nickel ions precipitated on the cathode surface cannot be effectively supplied under ordinary conditions. But under supercritical conditions, the scarce Ni^{2+} on the surface of the electrodepositing film can be effectively supplied due to better diffusivity [8]. As the electrodepositing process continues, the thickness of the electrodepositing film increases, while inside, the height of micro groove decreases, and the Ni^{2+} can spread more easily to the surface of electrodepositing film because of the shorter diffusion distance.
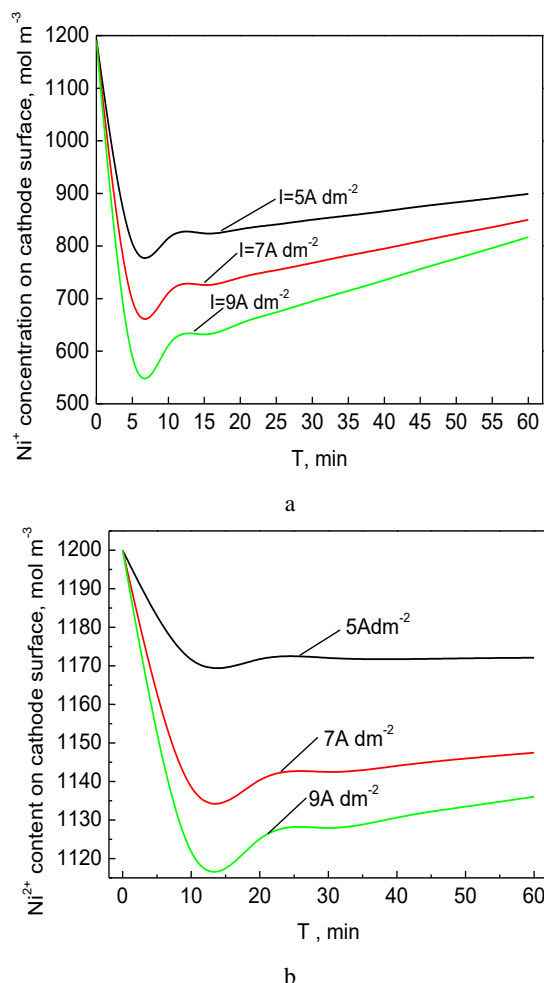

Fig. 4. Average Ni^{2+} concentration on cathode surface under different current density: a – ordinary condition; b – SCF-CO$_2$ condition

4.3. Electroforming layer thickness

The simulating thickness of the electrodepositing film is shown in Fig. 5 a when the working time is 60 min and the current density is 900 A/m^2. It can be seen that the thickness distribution of the electrodepositing film is relatively stable in the middle, but peaks at the edges, similar to that of the current density distribution shown in Fig. 5 b. It can be seen from Fig. 5 c that with the increase of current density, the average thickness of the electrodepositing film is greater, and thickness of the electrodepositing film grows linearly at the same current

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density. This is because the Ni^{2+} concentration on the surface of the electrodepositing film can be replenished quickly, and the middle part of the micro film is flat due to the excellent diffusion environment in the supercritical condition. Nickel ions deposit substantially on the edge of microgroove due to the current edge effect and the ion mass transfer limitations of the microgroove, resulting in the lack of nickel ions between the edge and central area of electrodepositing film.
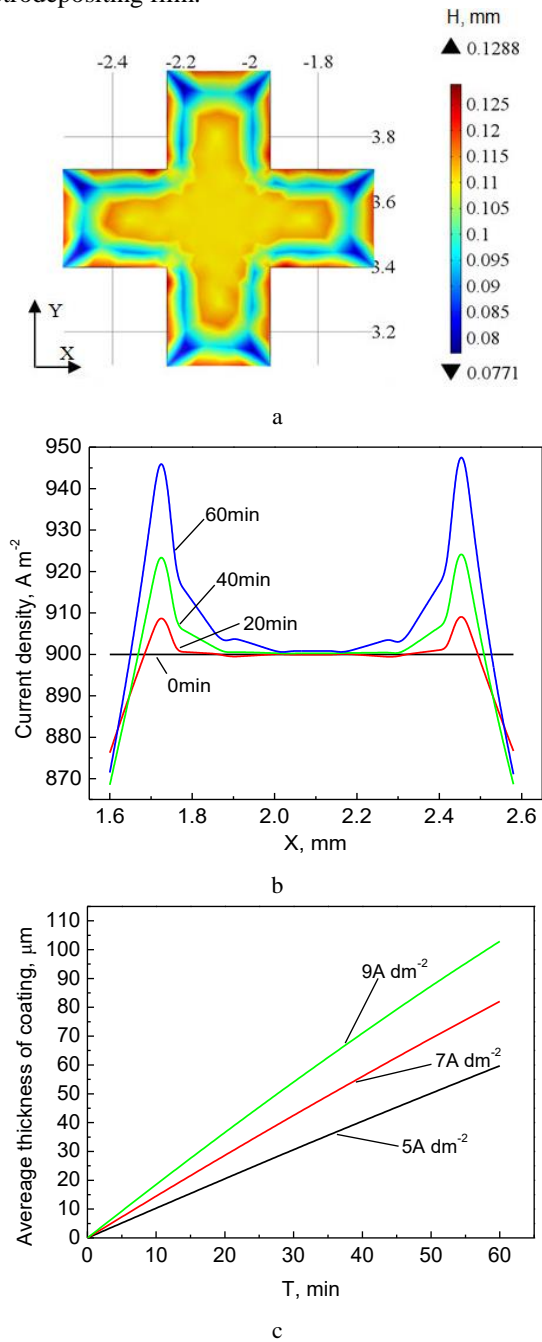

a

b

c

Fig. 5. Thickness changes of electrodepositing films under different current densities: a – I = 900 A/m², T = 60 min, thickness distribution of electrodepositing film; b – current density distribution in the middle of electrodepositing film; c – average thickness of electrodepositing films under different current densities

This means that wrinkles form easily. As time goes on, the Ni^{2+} on wrinkles cannot be supplied effectively, and the electrodepositing rate slows, causing the electrodepositing

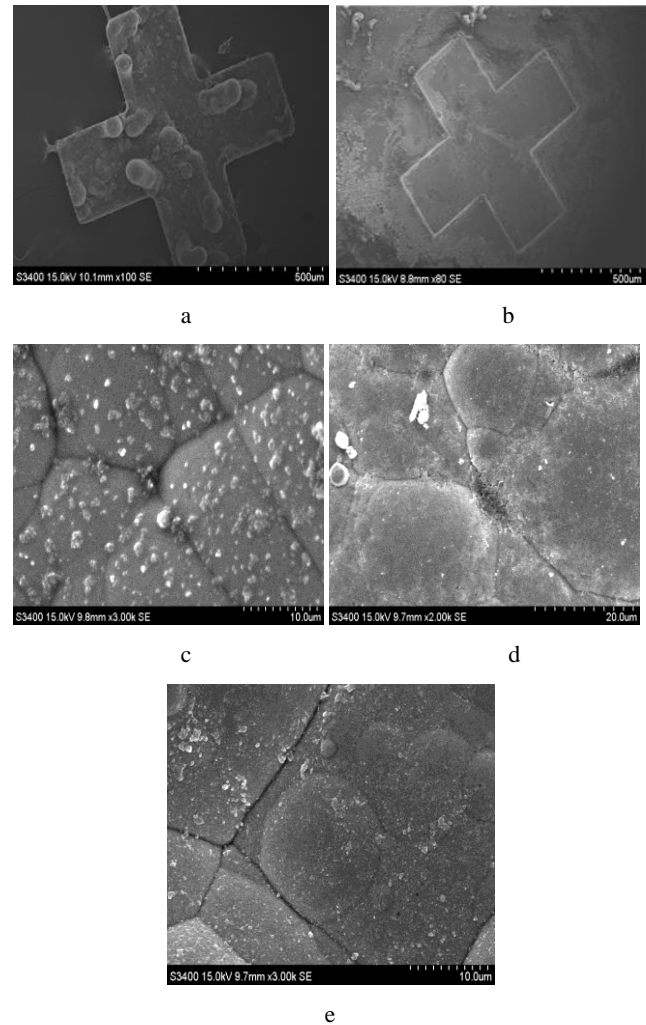film becoming uneven at the edges like the current density distribution.

a

b

c

d

e

Fig. 6. SEM images of Nickel-diamond electrodepositing composite minuteness films: a – ordinary condition; b – SCF-CO2 condition; c – SCF-CO₂, 500 A/m²; d – SCF-CO₂, 700 A/m²; e – SCF-CO², 900 A/m²

5. TEST ANALYSIS

5.1. Morphology of micro electrodepositing film

A self-developed supercritical electrodepositing device was used. Before the test, pre-dispersion treatment of electrodepositing solution must be carried out to make the nano-particles wetted sufficiently and dispersed uniformly in the bath. A nickel-diamond micro composite was prepared by electrodepositing technology under different current densities. Its surface is shown in Fig. 6.

The ordinary condition and the SCF-CO₂ condition are shown in Fig. 6 a and b respectively. The different current densities of 500 A/m², 700 A/m², and 900 A/m² in the SCF-CO₂ condition are shown in Fig. 6 c, d and e. When contrasting Fig. 6 a and b, it can be seen that the surface of the micro electrodepositing film prepared in the SCF-CO₂ is level, but the samples prepared in ordinary condition have uneven surfaces. It can be seen from Fig. 6 c – e that the micro electrodepositing film is flat, unit cells clearly appear, and the nano-diamond particles are dispersed evenly on the microscopic surface. The reason is that

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particle mass transfer relies mainly on the diffusion in micro grooves. Also, the SCF-CO_2 electrodepositing system was provided with very high diffusivity and wettability to restrain the reunion of nano-diamond particles. Nickel ions can co-deposit well with diamond particles and the simulated thickness values are similar to the measured thickness values. It means that the micro composite prepared by the electrodepositing method in the SCF-CO_2 has the advantages of surface morphology, grain size, and compact structure.

5.2. Microhardness of micro electrodepositing film

The samples were tested for their micro-hardness values. It can be found that when the current density is 700 A/m^2, the electrodepositing temperature is 323 K, the supercritical pressure is 12 MPa, the nano-diamond particle is 30 g/L, and the micro-hardness of micro electrodepositing composite reaches 900.75 HV (200 g). When the current density is 900 A m^{-2}, the micro-hardness decreases to 868.3 HV (200 g), which is greater than that of the ordinary condition of 530 HV (200 g) measured from contrast test sample. It shows that the Ni-diamond micro composite has a better micro-hardness. At the same time, the influence of the current density on the micro-hardness of the composite and the internal essence also need to be explored further.

6. CONCLUSIONS

Comsol software was used to simulate an electric field and the ion mass transfer of a micro electrodepositing system in SCF-CO_2. The results show that the electric field inside the micro groove distributes evenly. The average Ni^{2+} concentration on the surface of the electrodepositing film is more stable than that of the ordinary condition due to excellent mass transfer performance in SCF-CO_2. The thickness of the electrodepositing film is directly proportionate to the current density. The middle part of the micro sample is generally flat, but peaks occur on the edges of the sample distribution, which is similar to the distribution of the current density.

Compared with the ordinary electrodepositing method, the surface morphology of the Ni-diamond micro electrodepositing composite prepared in the SCF-CO_2 is smooth and compact. When supercritical pressure is 12 MPa, the temperature is 323 K, and the current density is 700 A/m^2, the micro-hardness of the Ni-diamond micro composite can reach up to 900.75 HV (200 g)

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