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ARTICLE

Simulation of Electrodepositing Process Based on Supercritical Fluid and Test Research

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Abstract: The coupling field of electrodepositing process under the supercritical fluid was simulated by COMSOL Multiphysics software to study the distribution of the current density and the growth of the electrodepositing coating which was verified by the experimental supercritical composite electrodepositing coating. Simultaneously the surface morphology and microhardness of the experimental supercritical nickel-diamond electrodepositing coating were studied. The results show that the current density on cathodic edge is much higher than that of the middle section and the predicted growth of the electrodepositing coating accords with current density distribution. The error between predicted and experimental thickness of the central supercritical electrodepositing coating is smaller. The biggest microhardness HV of the composite supercritical electrodepositing coating can reach 9540 MPa (200 g), 80% higher than that of ordinary composite electrodepositing coating. The supercritical composite electrodepositing coating has smooth surface and compact structure.

Key words: electrodepositing; supercritical fluid; coupling simulation; microhardness; thickness

The metal matrix composites and forming parts prepared by the composite electrodepositing technology have the characteristics such as excellent mechanical performance, flat surface and low cost, which has been widely used in aerospace, chemical engineering, shipbuilding and other industries[1,2]. In recent years, the scholars had a more detailed understanding of the composite electrodepositing process with the assistance of finite element analysis[3-5]. Ming[6] made the micro deep groove as the research object, and built the liquid phase mass transfer mathematic model. It can be found that the simulative change rules of the flow fields and the ion concentration space field including the affection on ions mass transfer under different boundary conditions are basically identical with the test results. Wu[7] set up the electromagnetic field and the flow field coupling model to study the influence law of magnetic field on the flow field, current density distribution, surface morphology, grain size and the SiC content, which are identical with the verification results.

The supercritical fluid technology (supercritical fluid, SCF) combined with the composite electroforming technology is a new study direction to prepare high performance micro/nano metal matrix composite materials and parts[8-13]. The supercritical CO_2 fluid (SCF-CO_2) has excellent diffusivity and mixed solubility for its physical and chemical properties fall in between gas and liquid. In SCF-CO_2 electrodepositing system, metal ions and micro/nano particles can be quickly transmitted to the cathode surface to realize high speed electrodeposition. Meanwhile H_2 can be dissolved rapidly due to good miscibility of SCF-CO_2 system in the cathode surface to avoid surface defects effectively. On the basis of previous researches[5,10,11], a mathematical model of SCF-CO_2 electrodepositing system was built using the COMSOL software to simulate coupling fields of electrodepositing system. The influence of process parameters on electrodepositing system was studied and the tests were carried out accordingly.

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1 Establishment of the Mathematical Model

To simplify the studies, a geometric model of the electrodepositing system with the dimension of 50 cm × 50 cm × 10 cm around the cathode was used. The distribution of the meshes divided in YZ section of electrolyte while X = 25 mm is shown in Fig.1. The local meshes on the cathode surface were refined to prevent distortion.

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; the applied voltage of the system was small enough to ignore ion transfer caused by electrophoresis; Ni^{2+} reduction precipitation was only considered on the cathode in the SCF-CO_2 environment; 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, On this basis, the coupling model of the SCF-CO_2 electrodepositing system was constructed [14-16].

1.1 Model of electric field

A model of the secondary current distribution was used. The electric field distribution of the electrodepositing system and the growth condition of the cathode plating were studied. According to the steady electric field theory and the electrodepositing theory, the electric field distribution is as follows:

$$\nabla^2\varphi=0,\ J=\sigma E,\ \nabla\cdot J=0,\ \nabla\cdot E=0 \tag{1}$$

In supercritical electrodepositing system, the diffusion coefficient of Ni^{2+} is great, which can supplement the ion concentration on the cathodic surface effectively in the electrodepositing process. So the occurrence that the cathodic potential deviated from the equilibrium value is caused mainly by slow electrochemical step. Then the cathodic rate accords with Butler-Volmer formula in electrodepositing process:

$$I=I_0[\exp(\alpha_A\eta F)]/(RT)-\exp((-\alpha_C\eta F/(RT))) \tag{2}$$

Where ∇^2 is Laplace operator, φ is potential, σ denotes conductivity, 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 conductivity of the nickel solution in supercritical condition was 20 S/m. 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, 700, 900 A/m^2 and the electrical potential was zero.

1.2 Model of flow field

The electrolyte was the incompressible viscous fluid, which was conditioned to the mass and momentum conservation equation. At the same time the electrolyte accorded with the flow continuity equation and N-S equation:

$$\nabla\cdot u=0 \tag{3}$$

$$\rho(\mathrm{d}u/\mathrm{d}t)=\rho F\text{-grad}p+\mu\nabla^2 u \tag{4}$$

Where u is space velocity vector, ρ denotes the electrolyte density, p is the pressure, μ is the solution viscosity, and F is volume force.

According to the selection of experimental parameters and model assumptions, the electrolyte flowed from left to right, the velocity was minimum at the top of the electrolyte and increased downward.

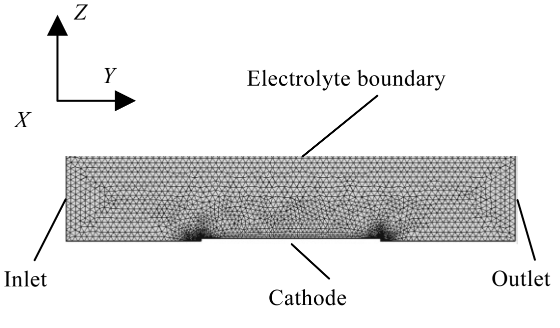


Fig.1 YZ section of electrodepositing physical model when X=25 mm

2 Simulation of Electrodepositing System

2.1 Simulation of electric field

The current density distributions on the cathode plate surface and in YZ section of electrolyte while X= 25 mm are shown in Fig.2. In Fig. 2 J_1 denotes the current density of the cathode surface and J_2 denotes the current density of the YZ section. It can be seen from Fig.2 that the cathode current density in the edge of the cathode is very high, the current density distribution of the middle part of the cathode is relatively uniform and the value is similar to external supplied current density. The result from YZ section also shows that the distribution of electric field lines in the middle of the cathode is uniform and the distribution of the electric field lines in the edge of electrolyte and cathode is relatively dense. The reason is that the electric field lines at the cathode edge easily gather due to current edge effect, in the corners current edge effect is more apparent which is caused by shape mutation and the distribution of electric field lines is more dense, and then intensity gradient of electric field is produced.

2.2 Electrodepositing coating thickness

Fig.3 shows the distribution of the simulative electrodepositing coating in the middle part of the cathode. Fig.3a shows the relationship between current density and electrodepositing coating thickness. Due to the current edge effect, the current density in the corners of cathode is higher than that of other parts at the beginning of the electrodepositing

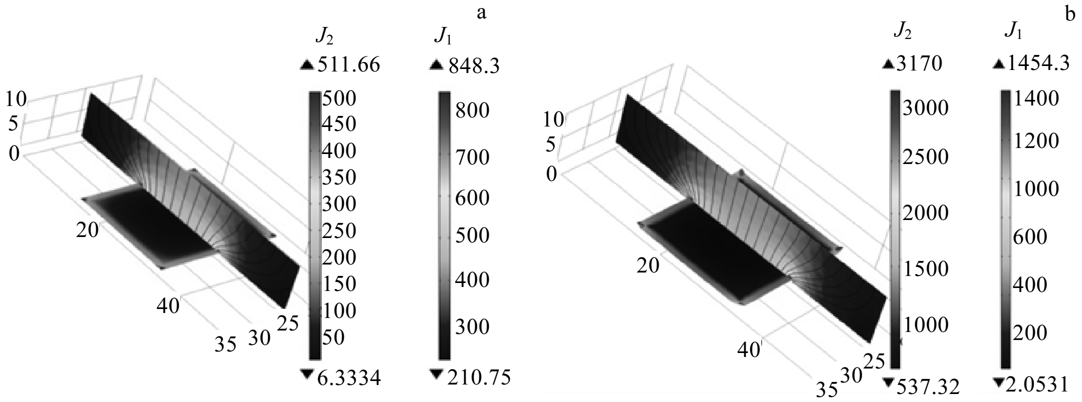


Fig.2 Current density distribution of electrodepositing system: (a) J = 300 A/m^2 and (b) J = 900 A/m^2

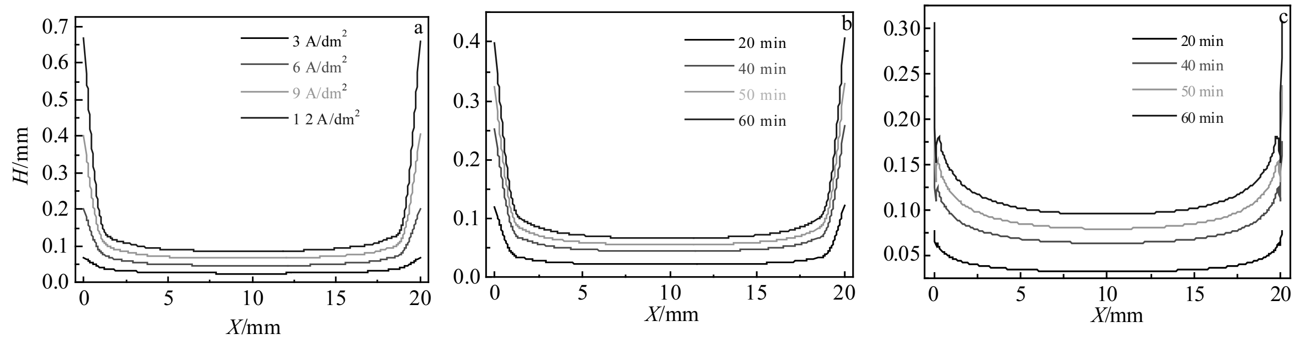


Fig.3 Simulative thickness in the center of the cathode plate: (a) SCF-CO$_2$, t = 60 min; (b) SCF-CO$_2$, J = 9 A/dm^2; (c) general environment, J = 9 A/dm^2

process, and then electrodepositing rate of nickel ions correspondingly increases. The nickel ions can be quickly replenished in corners of cathode for the excellent diffusion environment in supercritical electrodepositing system. With the electrodepositing process, the thickness of electrodepositing coating in the corners is greater, and the uneven trend is more obvious. Then the distribution of the current density is more uneven, which promotes electrodepositing rate of nickel ions in the corners of the cathode in return.

Fig.3b and Fig.3c show the thickness of electrodepositing coating under different time in the supercritical and normal environment respectively when current density J = 9 A/dm^2. It can be seen that the edges of the supercritical electrodepositing coating is smoother and the flat area of the supercritical electrodepositing coating is far larger in the middle area. The reason is that the current density is the decisive element to affect the electrodepositing rate of nickel ions for good mass transfer of supercritical electrodepositing environment. The nickel ions can be dispersed evenly in the cathode surface for the good dispersibility of the supercritical environment.

3 Experiment

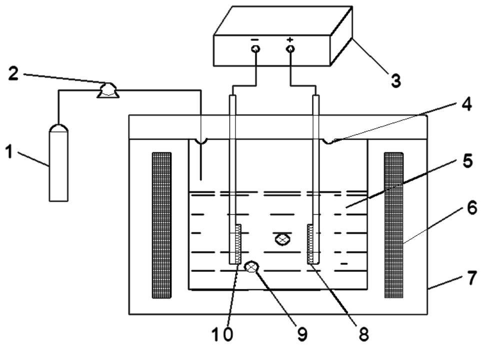
The experimental anode with dimensions of 2.5 cm × 2.5 cm was pure nickel plate and the cathode with dimensions of 2 cm × 2 cm was pure copper plate. The distance between anode and cathode was 2 cm. The electrolyte composition and process conditions were as follows: nickel sulfate of 300 g/L, nickel chloride of 30 g/L, boric acid of 50 g/L, nano-diamond particles of 20~60 g/L, 6 drops of foaming agent per one hundred ml, work pressure of 10 MPa, working temperature of 323 K, the current density of 3~12 A/dm^2, pH=4, magnetic stirring speed of 400 r/min and electrodepositing time of 45~60 min. The reagents used followed the AR.

The experimental device is shown in Fig.4. The working pressure was provided by high-pressure pump and working temperature was set by thermostat. First the nano-particles would be pre-dispersed in the electrodepositing solution in the ultrasonic reactor and the copper cathode would be polished and cleaned. Then the experiments were carried out under the predetermined parameters.

4 Results and Discussion

4.1 Surface morphology of electrodepositing coating

The surface morphology of the Ni-diamond electrodepositing coating under the common condition is shown in Fig.5a; that of the supercritical Ni-diamond electrodepositing coatings are shown in Fig.5b, 5c and 5d. Based on the comparison in Fig. 5, the crystal formation of the common electrodepositing coating which has more holes is not obvious and nano-diamond particles is not prominent. The reason is that the nickel ions and nano-diamond particles cannot be timely transferred to the cathode surface due to the low diffusion and mixing solubility of the common electrodepositing environment and H_2 that is generated on the cathode cannot be dissolved in time which causes a pinhole defects on the composite electrodepositing coating surface. Compared with the traditional electrodepositing system, the nano-diamond particles can be dispersed effectively to prevent reunion due to good mass transfer performance and mixing solubility in supercritical electrodepositing system. Therefore the structure of Ni-diamond electrodepositing coating prepared in supercritical condition is close and flat. The nano-diamond particles are dispersed evenly in composite electrodepositing coating.



1-CO_2 cylinder; 2-high-preaaure pump; 3-power supply; 4-vent; 5-electrolyte solution; 6-thermostatic bath; 7-reactor; 8-anode; 9-mechanical agitator; 10-cathode

Fig.4 Schematic diagram of SCF-CO_2electroplating experimental apparatus

4.2 Electrodepositing coating thickness

In the middle of the uniform electrodepositing coating 5 points were selected to measure the average thickness (*D*). The measurement direction is shown in Fig. 6. The edge/corner growth condition is similar with the simulated result.

In Table 1, the electrodepositing time is 1 h and nano-diamond content is 30 g/L; in Table 2 the current density is 9 A/dm^2. When contrasting the two tables, it can be found that with the change of the current density, the measured values and predicted values of the composite

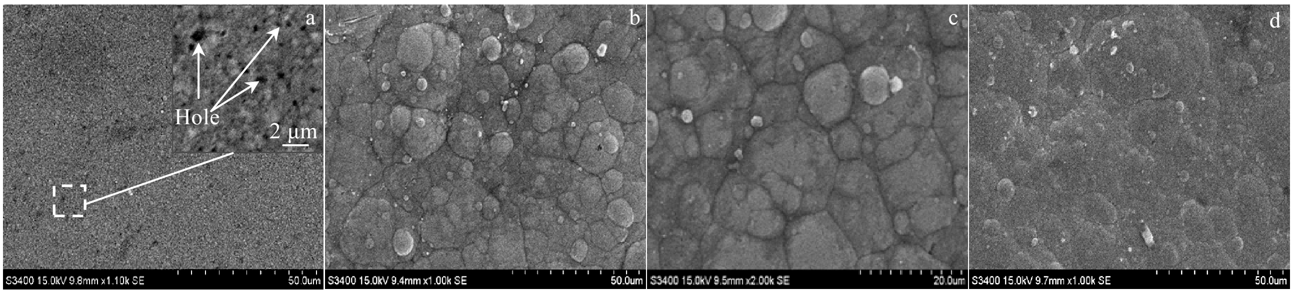


Fig.5 Ni-diamond electrodepositing coating morphologies under different conditions: (a) general conditions; SCF-CO_2 conditions: (b) 0.24 A, 3 g; (c, d) 0.36 A, 3 g

Table 1 Electrodepositing coating thickness in the middle part of the cathode under different current densities

Current density/ A·dm^{-2}	Predicted value/μm	Test value/ μm	Relative error/%
3	27.74	30.39	8.60
6	48.49	50.28	3.56
9	68.46	66.71	2.63
12	88.33	88.13	0.227

Table 2 Electrodepositing coating thickness in the middle part of the cathode under different nano-diamond contents

Diamond content/g·L^{-1}	Predicted value/ μm	Test value/ μm	Relative error/ %
20	68.46	67.27	1.77
30	68.46	66.71	2.63
40	68.46	60.96	12.3
60	68.46	58.92	16.19

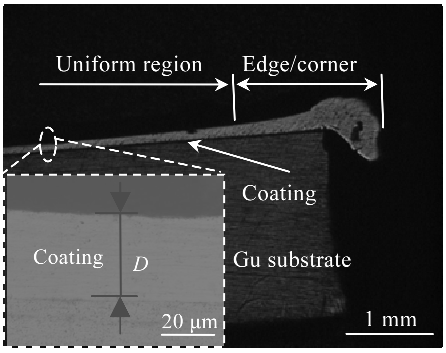


Fig.6 Measurement direction of electrodepositing coating thickness

electrodepositing coating thickness in the middle part are similar, the maximum error is 8.60% and the minimum error is only 0.227%. The simulation model can accurately reflect the trend of the electrodepositing coating thickness when changing current density. With the increase of nano-diamond, the error between the measured values and predicted values of the coating thickness expands, because when the nano-diamond particles gather a great at the cathode surface, the electrical contact area between the cathode and electrolyte will be reduced. Then the electrodepositing rate of nickel ions is restrained and the error between them is bigger. When the nano-diamond content reaches to 60 g/L, the error value is 16.19%.

4.3 Electrodepositing coating micro-hardness

The influence of current density is shown in Fig.7a. It can be found that the maximum microhardness HV of the supercritical composite electrodepositing coating reaches to 9540 MPa (200 g), 80% higher than that of the traditional electrodepositing. With the increase of current density, the cathode overpotential rises, and the adsorption quantity of diamond particles increases, a reason that results in diamond content increase gradually in the composite electrodepositing coating. Then the growth of nickel ion grain is inhibited and the nucleation rate is promoted, which lead to the composite electrodepositing coating micro-hardness improves when diamond particles are evenly distributed in composite coating. If the current density increases further, the nickel electrodepositing rate increases linearly, as shown in Fig.7a, and the errors between the predicted values and the measured values are small. Then the nickel electrodepositing rate is gradually faster than the co-depositing rate of diamond particles, holes increase gradually in composite coating, the grain size becomes bulky and the micro-hardness of the composite electrodepositing coating goes down.

In SCF-CO_2 electrodepositing system, a lot of nucleation points are produced to prevent and refine the nickel grains because the nano-diamond particles are well dispersed in the electrodepositing coating. At the same time the dispersion effect caused by the grains slippage is prevented greatly and then the values of the supercritical composite electrodepositing microhardness is higher than that of the traditional condition. If the diamond content continues to be increased, the nano-diamond particles will reunite around the cathode. The nickel electrodepositing rate is prevented since a lot of the diamond particles cover on the surface of cathode, the crystal lattice defects of the electrodepositing coating increase gradually and then the composite electrodepositing coating micro-hardness will decline relatively, shown in Fig. 7b.

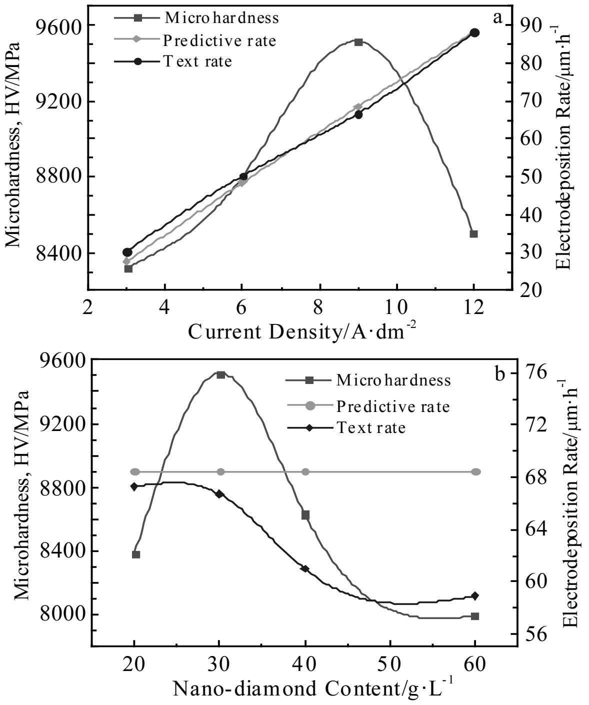


Fig.7 Effects of current density (a) and nano-diamond content (b) on micro-hardness, electrodeposition rate, and text rate

5 Conclusions

1) Through simulation of electrodepositing system, it can be found that the electric field distributes uniformly in the middle of the cathode plate.

2) The structure of the Ni-diamond electrodepositing coating prepared in SCF-CO_2 environment is close and flat; the nano-diamond particles are dispersed in the electrodepositing coating evenly.

3) The text influence of the current density on the electrodepositing coating thickness is similar to the predicted values; with the increase of nano-diamond content, the error value of the electrodepositing coating thickness increases gradually and the maximum value is 16.19% when the diamond content is 60 g/L.

4) With the increase of the current density and nano-diamond content, the electrodepositing coating micro-hardness increases first and then decreases. When the

current density is 9 A/dm^2 and diamond content is 30 g/L, the maximum microhardness HV is 9540 MPa, 80% higher than that of traditional electrodepositing.

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基于超临界流体电铸耦合场分析及试验研究

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摘 要：利用COMSOL Multiphysics对超临界流体电铸耦合场进行数值模拟，研究分析电流密度分布和电铸层生长规律，并且试验测试与验证；同时对超临界流体镍纳米金刚石复合镀层的表面形貌和显微硬度进行研究和探讨。结果表明，阴极边缘处电流密度远高于阴极中间部分，电铸层生长情况与电流密度分布较为吻合，电铸层中部厚度预测值的误差较小；电铸层显微硬度HV最大可达9540 MPa，比普通情况下复合铸层提高80%；制备的复合电铸层表面平整，组织致密。

关键词：电铸；超临界流体；耦合模拟；硬度；厚度

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