MODELING OF THE PROCESS OF COMPOSITE ELECTRODEPOSITION [①]

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ABSTRACT A model of the codeposition process of particles and metal matrix was proposed in which the process was divided into three steps, that was, particles dispersing uniformly in the plating-liquid, particles transferring to the surface of electrode and being strapped on the surface of electrode. The thermodynamic criteria, the dynamic factors, the physical models and the mathematical models of these three steps were presented. The mathematical model for the whole process was also discussed.

Key words composite eletrodeposition mathematical model of codeposition process

1 INTRODUCTION

Composite coatings attracted more and more attention recently because of the excellent properties and the wide applications. Some theories and mathematical models were given to explain the process of codeposition, but none of them was very convinced. Most of them tried to establish the direct relationship between the processing parameters and the whole process and it was too simple to explain the complex process of codeposition[1-2].

The process of codeposition of particles and matrix is composed of a series of steps. Each processing parameter affects the whole process through one of these steps. The level of influence is decided by how important this step is in the whole process. To describe the mechanism of codeposition, the following three questions should be answered:

(1) How many steps can the process of codeposition be divided, and what are these steps?

(2) What are the thermodynamic criteria, dynamic factors, physical models and mathematical model of each step?

(3) Which step is the control one on the specific condition, and what is the dynamic model of the whole process decided by this step?

A new three-step model of composite eletrodeposition is proposed to answer these questions.

2 DIVISION OF COMPOSITE ELECTRODEPOSITION PROCESS AND MODEL OF EACH STEP

Three types of mass transfer in the liquid are convection, diffusion and electrotransfer. The transfer speed caused by convection is much larger than that by diffusion in the body baths. But, the effect of convection can be omitted in the thin liquid film near the electrode surface because of the friction of the electrode surface. So the particle transfer process can be divided into two steps according to the controlling transfer method and the bath can be divided into two regions, the body region and the diffusion layer (see Fig. 1).

The whole process of codeposition can be divided into the following three steps.

Step 1: Under the effect of stirring, particles enter the bath and disperse uniformly in the body region where the convection is the main transfer method.

Step 2: Particles move into the diffusion layer where both the diffusion and the electrotransfer are the important transfer methods.
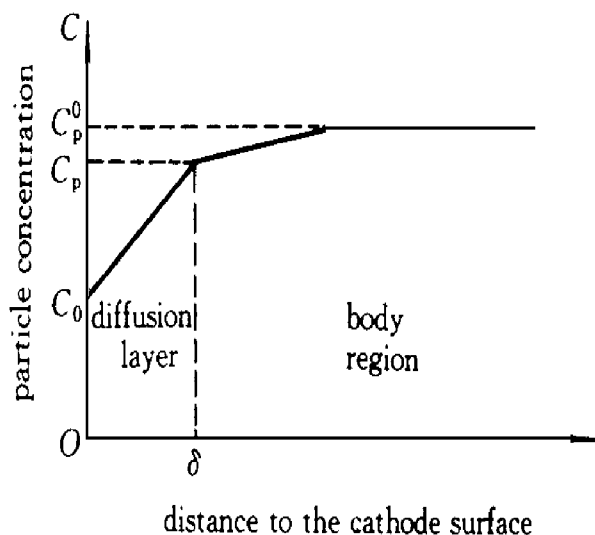
Fig. 1 Conceptual diagram of particle concentration distribution in the bath

C_P^0 —particle concentration in the center of body region; C_P —particle concentration in the edge of body region; C_0 —particle concentration in the surface of cathode

Step 3: Particles arrive and stay on the electrode surface, particles whose staying time is longer than the limiting time will be trapped.

2. 1 The model of Step 1

2. 1. 1 Physical description: The inert particles disperse in the low viscous liquid on the stirring condition.

2. 1. 2 Thermodynamic criterion: Particles can be wetted by the bath.

2. 1. 3 The main factors influencing this step are the method and strength of stirring. The particles are inert, and there will be not microblend caused by module diffusion between the particles and the bath, so the power of stirring must be large enough to form finely dispersed suspensoid[3]. When the power of stirring is small, the particles will be put together automatically because of the effect of surface energy, and it will decrease the effective concentration C_P^*. At the same time, the particles in the interface between the body region of the bath and the diffusion layer are consumed constantly, so the particle concentration C_P must be a little lower than the concentration in the body region C_P^0 (Fig. 1) . So the improvement of stirring increases the speed of

convection and C_P. The stirring condition is thus the main influence factor, while the size of particles, the viscosity of the bath, the wettability of the bath and the difference in density between the particles and the bath are also important factors.

2. 1. 4 The key to establish the mathematical model is how to calculate C_P, the concentration of the particles leaving the convection controlling region and moving to the electrode surface. But, the calculating equations were still absent. Most researchers omitted the difference between C_P^0 and C_P.

2. 2 Model of step 2

2. 2. 1 Physical description: Solid particles move to the electrode surface in the static and low viscous liquid on the effects of both a concentration gradient field and an electrical potential field.

2. 2. 2 Thermodynamic criterion: The addition of the concentration gradient field and the electrical potential field is favorable to the particle motion toward electrode surface. Because the particles near the electrode surface are consumed constantly, C_0 must be lower than C_P, and the concentration gradient field is always beneficial to the particle motion toward the electrode surface. When the particles carry positive charge, the effects of the concentration gradient field and the electrical potential field are the same. But, if the particles carry the negative charge, especially when both the carried electrical charge and the cathode over potential η(outer electric field) are large, the effects of them are opposite, and the addition of them is possibly unfavorable to the particle motion toward the surface of cathode. So carrying positive charge is favorable to form the composite coatings, but composite coatings can be also formed successfully when the particles carried negative charge or no charge. For example, when WC particles carry little charge, and SiC particles carry negative charge in citrate gold plating bath, the composite coatings can be easily formed[4].

2. 2. 3 The dynamic influence factor is mainly the concentration gradient field. Because large amount of electrolyte exists in the bath and the

charge carried by particles is small, the electro-transfer speed of particles is usually much smaller than the diffusion rate of the particles and could be omitted. That is to say, although the effect of carried charge of particles and over potential η are important on the view of thermodynamics, they are not important on the view of dynamics. The dynamic factors of this step are mainly those which affect the diffusion rate of the particles, such as the concentration gradient field of the particles in the diffusion layer, the diffusion co-efficient and the thickness of the diffusion layer.

2. 2. 4　The key to establish the mathematical model is to find the mathematical relationships between the particle concentration C_P and the number of particles arriving on the cathode sur-face in unit time and unit area, N_p.

Deriving from Fick's first law

$$N_P = D_P \frac{C_P - C_0}{\delta} \qquad (1)$$

where D_P is diffusion coefficient of particles in the bath, C_0 is the concentration of the particles near the cathode surface, δ is the thickness of diffusion layer. According to the theories of Levich[5], on the condition of rotating disk elec-trode, we have:

$$\delta = 1.61 D_{ion}^{1/3} \nu^{1/6} \omega^{-1/2} \qquad (2)$$

where D_{ion} is the diffusion coefficient of matrix cation, ν is the viscous of the bath, ω is the rota-tion speed of the rotating disk electrode. when this step is the lowest step (controlling step), the particles near the cathode will be consumed quickly and C_0 is very small, so equation 1 can be revised as

$$N_P = D_P \frac{C_P}{\delta} \qquad (3)$$

2. 3　Model of step 3

2. 3. 1　Physical description: The particles stay on the surface of electrode for a period of time then leave or are trapped under the act of all kinds of forces.

2. 3. 2　Thermodynamic criterion: the attractive force acting on the particles is not smaller than the repel force.

2. 3. 3　The dynamic influence factors include two aspects: One includes the factors related to the limiting time, such as the size of the parti-cles, the cathode current density and the cathode current efficiency; the other includes the factors related to the staying time of the particles on the electrode surface, such as the surface state of the particles, the surface state of the electrode and the plating conditions.

2. 3. 4　The key to establish the mathematical model is how to calculate the possibility of the trapped particles that arrived on the electrode surface, P. The state of the particles can be de-scribed as staying on for a period of time —leav-ing or being trapped in the surface of electrode, so the staying time must obey some possibility distribution. Since the particles staying shortly were more than those staying long, we can sup-pose it obeys the exponential distribution, so we have

$$f(t) = (1/t_a)\exp(-t/t_a) \qquad (4)$$

and

$$P = 1 - \int_0^{t_1} f(t)\,dt \qquad (5)$$

so

$$P = \exp(-t_1/t_a) \qquad (6)$$

where t_a is the average staying time of parti-cles on the electrode surface, t_1 is the limiting time. Supposing that the particles are considered as being trapped when half of their bodies are al-ready buried in the metal matrix, we have

$$t_1 = (nF\rho d)/(2iM) \qquad (7)$$

where ρ is the density of the metal matrix, d is the diameter of particles, M is the atomic weight of the metal matrix, n is the value of va-lence of the metal matrix, F is Faraday con-stant, i is the current density of cathode.

3　DYNAMICS OF THE WHOLE PROCESS

3. 1　Step 1 being the controlling step

The controlling step is the step 1 in the bad stirring and wetting systems. In this condition, improving the wettability and strengthening the stirring increase obviously the density of the par-ticles in the composite coatings. For example, when the hydrophobic PTFE particles codeposit-ed with Ni, the addition of the cationic surfac-tants improved the wettability and increased the particle content in the coatings[6]. When the flowing speed of bath was low, strengthening

the stirring was beneficial to increase the particle content in the composite coatings(Fig. 2)[1- 3]. When this step is not the controlling step, we
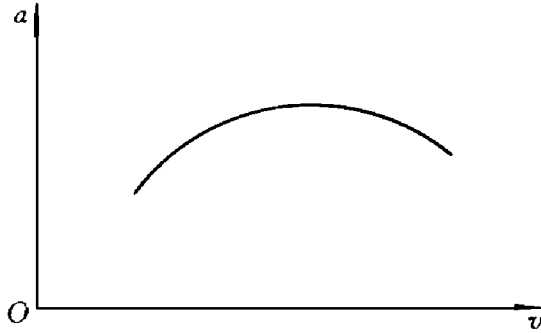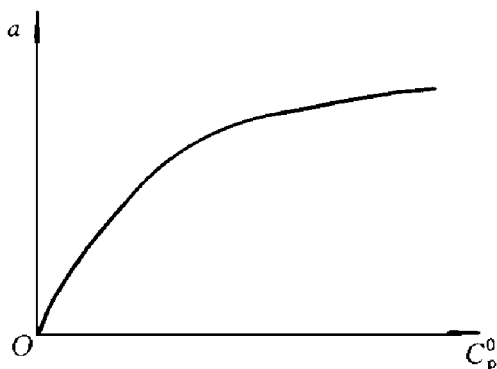

Fig. 2   The relationship between particle content in the coatings (a) and flow speed of the bath (v)

can think the particles form finely dispersed suspensoid in the bath, and the speed of the convection is infinitely great. So we have

$$C_P = C_P^0 \qquad (8)$$

3. 2   Step 2 being the controlling step

Because the dynamic properties are controlled by diffusion speed and the diffusion speed is small when the particle concentration in the bath C_P is low, step 2 becomes the controlling step in this situation. The increment of the particle concentration in the bath improves the particle content in the composite coatings greatly (Fig. 3)[1, 4- 5, 7- 9].

Fig. 3   The relationship between particle content in the coatings (a) and particle concentration in the baths (C_P^0)

Because C_P was low, the weight ratio of particles in the coatings, $a \ll 1$, so we have

$$a = W_P N_P P / \Delta W_m \qquad (9)$$

where W_P is the average weight of a particle, N_P is given by equation 3, P is given by equation 6, ΔW_m is the mass increment caused by the deposition of metal in unit time and unit area. According to the law of Faraday, we have

$$\Delta W_m = (iM)/(nF) \qquad (10)$$

when other parameters are constant, from this mathematical model we can obtain that a is proportional to C_P. This conclusion is the same as that of other two researchers[2, 5], and is also consistent with the experiment result (Fig. 3)[1, 4- 5, 7- 9].

3. 3   Step 3 being the controlling step

When the cathode current density is small, step 3 is the controlling step. In this condition, the limiting time is large, trapping a particle consumes long time and often make the step 3 the controlling step. So the increment of the cathode current density improves the particle content in the composite coatings greatly (Fig. 4)[2, 4, 5, 8, 10].
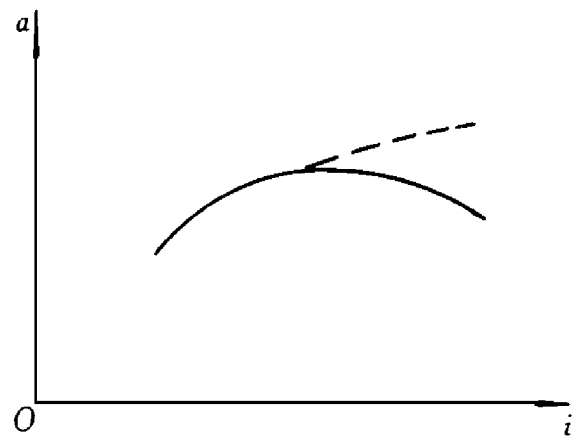
Fig. 4   The relationship between particle content in the coatings (a) and cathode current density (i)

Since the particles move very fast, and consumed particles are replenished easily on the cathode surface, all the particles on the cathode surface could be trapped, and the particle concentration C_0 is constant. So we have

$$\Delta W_P = W_P P C_0 d / t_1 \qquad (11)$$

where δW_p is the mass increment caused by the trapped particles in unit time and unit area.

So $a = \Delta W_P /(\Delta W_m + \Delta W_P) \qquad (12)$

where ΔW_P is given by equation (11), ΔW_m

is given by equation (10). It should be mentioned that C_0 is not equal to 0 here, since step 2 is not the controlling step. Assuming that step 2 is in a state of thermodynamic equilibrium condition, the quantity of particle flow caused by electrotransfer J_e is equal to that caused by diffusion J_d, but the directions are opposite

$$J_e + J_d = 0 \qquad (13)$$

Deriving from the related theories of electrochemistry

$$J_e = - D_P[(ZF)/(RT)] C_P E \qquad (14)$$

Deriving from Fick's first law

$$J_d = - D_P(C_P - C_0)/\delta \qquad (15)$$

Substitute equation (14) and equation (15) into equation (13), we have

$$C_0 = C_P[1 + (ZF\delta E)/(RT)] \qquad (16)$$

where Z is the charge quantity per particle, E is the strength of electrical field.

4　CONCLUSIONS

The advantages of the model are:

(1) The whole process is analyzed through three steps. The effects of parameters on the process dynamics are considered in separate steps which can describe the affecting mechanisms more profoundly.

(2) Only a few and concise assumptions are used in the analysis, the conclusion could be used more extensively.

(3) Based on physical models, the physical meaning of all the equations and parameters is clear.

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