



An adsorption strength model for the electrochemical codeposition of α -Al₂O₃ particles and a Fe–P alloy

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An adsorption strength model is developed to describe the mechanism of codeposition of α -alumina and Fe–P alloy. Based on hypotheses concerning the effective adsorption and the distribution of the adsorption strength of particles on the cathode, a general expression relating the content of embedded particles to the suspension concentration and the current density is deduced. This relationship is in good agreement with the experimental results. The variation of the content of particles in deposits with current density is an overall balance of two opposing effects which leads to a maximum in the particle content against current density curve.

Keywords: adsorption strength model, alumina particle, electrochemical codeposition mechanism, ferrophosphorus alloy

List of symbols

C_p	concentration of particles in plating bath (kg m ⁻³)	r_p	radius of a particle (m)
C_p^*	number of particles in plating bath (m ⁻³)	W_p	weight of one particle (kg)
F	Faraday constant (C mol ⁻¹)	<i>Greek symbols</i>	
i	current density (A m ⁻²)	α	particle content in deposit (kg m ⁻³)
j_p	flux of particles reaching the cathode per unit time and area (s ⁻¹ m ⁻²)	θ	amount of particles adsorbed per unit area of cathode (m ⁻²)
k	Boltzmann constant (J K ⁻¹)	v_a	adsorption rate of particles on cathode (s ⁻¹ m ⁻²)
k'_a	adsorption rate coefficient	v_d	detachment rate of particles from cathode (s ⁻¹ m ⁻²)
k'_d	detachment rate coefficient	v_p	deposition rate of particles on cathode (s ⁻¹ m ⁻²)
k_0	flow coefficient associated with fluid flow velocity and particle radius	ρ_m	density of electrodeposited metal (kg m ⁻³)
K	adsorption and detachment constant (m)	ρ_p	density of particles (kg m ⁻³)
n	valence of electrodeposited metal	σ	constant for the dispersion of particle adsorption strength
N	rate constant for particle deposition (s ⁻¹)	μ	adsorption strength of a particle on cathode
M	molecular weight of electrodeposited metal (kg mol ⁻¹)	μ_0	minimum adsorption strength for a particle to be incorporated in deposit
P	probability of particles being effectively adsorbed	$\bar{\mu}$	average adsorption strength of particles on cathode

1. Introduction

Inert particles suspended in an electrolytic bath can be codeposited during electrodeposition. Composite coatings produced by this technique possess many enhanced physical and mechanical properties such as wear and corrosion resistance as compared to pure metal coatings [1, 2]. These improved properties mainly derive from the presence of particles dispersed in the metallic matrix and thus depend on the content and nature of particles in the coatings. Extensive investigation into the codeposition process and mechanism of particle incorporation is, therefore, essential

to control and predict the degree of particle incorporation in the coatings. However, there are many plating parameters affecting particle incorporation, including particle concentration, particle structure, bath composition, current density, temperature, pH, agitation and surfactants [3–5]. It is difficult to build a precise model to elucidate the mechanism of codeposition, which takes into account the effects of all parameters [6].

In general, the interaction between the particles and the cathode surface plays an important role in the codeposition process. Upon arrival at the cathode a particle has to overcome unfavorable forces acting

on it such as gravity and hydrodynamic forces, in order to stick to the surface and be incorporated in the deposit. The nature of the adhesive force is a basic question treated in the present models [7]. In 1972, Guglielmi developed a mathematical model based on two successive adsorption processes [8]. In the first step, which is of a physical nature, the particles approaching the cathode become loosely adsorbed on the cathode surface. These loosely adsorbed particles are in equilibrium with the particles in suspension and still surrounded by a cloud of adsorbed ions. In the second step, which is thought to be electrochemical in nature, the particles lose this ionic cloud and become strongly adsorbed on the cathode. The strongly adsorbed particles are now permanently bound to the cathode and are embedded into the growing metal deposit. The formula deduced from this model has successfully predicted the volume fraction of particles in the deposit for different codeposition systems such as SiC and TiO₂ with nickel from sulfamate baths [8], as well as α - and γ -Al₂O₃ with copper from acidic copper sulfate baths [9]. However, Guglielmi's model cannot explain the maximum in the weight percent of particles in the deposit against current density curve for Cu–Al₂O₃ codeposition.

To overcome this shortcoming in Guglielmi's model, Celis, Roos and Buelens proposed a model from a statistical approach, in which the codeposition of particles is considered to be a five-step process [10]. The basic hypothesis of the model is that the particles will be incorporated only if a certain amount of ions adsorbed on the particles are reduced on the cathode. This model has been demonstrated to be valid for Cu–Al₂O₃ and Au–Al₂O₃ codeposition. Nevertheless, some assumptions in this model lack reliability. A more general model has been developed by Hwang and Hwang [11]. Based on the model of Guglielmi, Hwang and Hwang proposed that the codeposition rate of particles is determined by the electrode reactions for adsorbed species on the particles at various current densities. They investigated Co–SiC codeposition and three different current density ranges are distinguished according to the reduction of adsorbed ions. At low current density, only H⁺ ions are reduced and the particle codeposition rate is determined mainly by the reduction of adsorbed H⁺ ions on the particles. At intermediate current density, the H⁺ reduction rate has reached its limiting value and Co²⁺ is also reduced. The codeposition rate of particles is determined by the reduction of both ions. At high current density, the reduction of both H⁺ ions and Co²⁺ ions adsorbed on the particles is at its limiting value. Experimental results were predicted well by the model simulation.

What these models have in common is that they emphasize the importance of the reduction of adsorbed ions on the particles in the codeposition process and involve the complex interrelationship between factors such as limiting current density, amount of adsorbed ions on the particles, and the

transition current density etc., especially in the Celis and Hwang models.

In 1992, Fransaer, Celis and Roos reported a trajectory model for the codeposition of spherical particles with metal on a rotating disc electrode (RDE) [7, 12]. Based on the knowledge of the flow field around an electrode and taking into account all the forces acting on a particle, the trajectory of that particle is determined from the equation of motion. Therefore, the particle volume flux colliding with RDE can be obtained by calculating the limiting particle trajectory, namely, the particle trajectory separating the trajectories of particles reaching the electrode from those passing by. By setting up a force balance on the particle in contact with the electrode, an equation for the probability that a particle on the electrode will be incorporated is given. The trajectory model successfully illustrates the influence of fluid flow velocity, particle concentration, surfactants and current density on the rate of particle deposition.

Based on aspects of the model of Fransaer, an adsorption strength model will be presented here to describe the mechanism of codeposition. Instead of the force balance on a particle at the electrode with a distribution of adhesion forces in the model of Fransaer, the average adsorption strength of particles on the electrode is employed to describe the intensity of the interaction between the particles and the electrode. In order to verify this model, we also investigate the Fe–P– α -Al₂O₃ composite plating system and discuss the relationship between the particle content in the deposit and the current density.

2. Description of adsorption strength theoretical model

Because not all particles reaching the cathode surface will necessarily be incorporated in a deposit, some of the particles that come into contact with the cathode detach. Based on this knowledge, three fundamental postulates are proposed:

- (a) The particles adsorbed on the cathode surface can detach again. A dynamic equilibrium is set up during electrodeposition, that is, the adsorption rate of particles should be equal to the sum of the detachment rate and the deposition rate of particles.
- (b) If the intensity with which a particle sticks to the cathode surface is described in terms of adsorption strength, the adsorption strength of particles is not identical and its distribution on the cathode conforms to the classical energy law, that is, a normal distribution.
- (c) A particle may be incorporated into the deposit when its adsorption strength is above a critical value. The adsorption of this particle is termed effective.

From these hypotheses, the particles must proceed through three stages: (i) movement by forced convection towards the hydrodynamic boundary layer at

the cathode, (ii) adsorption and (iii) some particles being incorporated irreversibly into the metal matrix, others detaching again.

2.1. Calculation of amount of adsorbed particles per unit cathode surface area

The adsorption rate of particles on the cathode surface is determined by the number of particles reaching the cathode. With a fixed stirring process, the flux of particles colliding with the cathode per unit time is proportional to the concentration of suspended particles in the bath [7]:

$$j_p = k_0 C_p^* \quad (1)$$

where the symbols are as stated at the outset. Assuming the particles are all spherical, the weight of one particle is given by

$$W_p = \frac{4\pi}{3} r_p^3 \rho_p \quad (2)$$

Then C_p^* in Equation 1 can be replaced by the mass concentration

$$j_p = k_0 C_p^* = k_0 \frac{C_p}{W_p} = k_0 \frac{3C_p}{4\pi r_p^3 \rho_p} \quad (3)$$

Considering the adsorption coverage of the particles existing on the cathode, the adsorption rate of particles can be expressed as

$$v_a = k'_a (1 - \pi r_p^2 \theta) j_p = k_a (1 - \pi r_p^2 \theta) \frac{3C_p}{4\pi r_p^3 \rho_p} \quad (4)$$

where $k_a = k'_a \times k_0$. All other symbols are as stated in the list of symbols. The detachment rate of particles can be written as

$$v_d = k_d \theta \quad (5)$$

Now, according to hypothesis (a)

$$v_a = v_d + v_p \quad (6)$$

and v_p can be obtained as

$$v_p = N\theta P \quad (7)$$

Substituting Equations 4, 5 and 7 into Equation 6 and rearranging for the adsorption coverage, we obtain

$$\theta = \frac{K \frac{3C_p}{4\pi r_p^3 \rho_p}}{\left(1 + K \frac{3C_p}{4\pi r_p^3 \rho_p}\right)} = \frac{3KC_p}{(4\pi r_p^3 \rho_p + 3K\pi r_p^2 C_p)} \quad (8)$$

where $K = k_a / (k_d + NP)$ is the adsorption and detachment constant. Obviously, K depends essentially on the codeposition conditions such as stirring rate and current density.

2.2. Calculation of probability of particles being adsorbed effectively

If E_a is the adsorption energy between a particle and the cathode, we define the adsorption strength of this

particle, μ , and the average adsorption strength of particles on the cathode, $\bar{\mu}$, respectively as

$$\mu = -\frac{E_a}{kT} \quad (9)$$

$$\bar{\mu} = \frac{1}{n} \sum_{i=1}^n \mu_i \quad (10)$$

where k is the Boltzmann constant and T is the absolute temperature. Obviously μ and $\bar{\mu}$ are dimensionless parameters. The adsorption energy of a particle may be resolved into an electrical and a nonelectrical part. If the plating system and agitation rate is fixed, the nonelectrical adsorption energy is a constant. This means that the average adsorption strength is determined by the electrical adsorption energy. In other words, it is associated with overpotential and is a function of the current density. According to hypothesis (b): The adsorption strength of particles on the cathode has a normal distribution. Therefore, the probability density of the particles having an adsorption strength μ is

$$f(\mu) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(\mu - \bar{\mu})^2}{2\sigma^2}\right] \quad (11)$$

where $f(\mu)$ is the probability density and σ can be considered as a parameter describing the dispersion of the particle adsorption strength. As shown in Fig. 1, as σ becomes larger, $\int_{\bar{\mu}-\Delta\mu}^{\bar{\mu}+\Delta\mu} f(\mu) d\mu$ becomes smaller and the adsorption strength of the particles is more dispersed.

Assuming the critical value of the effective adsorption strength is μ_0 , the probability, P , of the particles being effectively adsorbed can be expressed as

$$\begin{aligned} P &= P(\mu_0, +\infty) = \int_{\mu_0}^{+\infty} f(\mu) d\mu = 1 - \int_{-\infty}^{\mu_0} f(\mu) d\mu \\ &= 1 - \int_{-\infty}^{\mu_0} \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{(\mu - \bar{\mu})^2}{2\sigma^2}\right] d\mu \end{aligned} \quad (12)$$

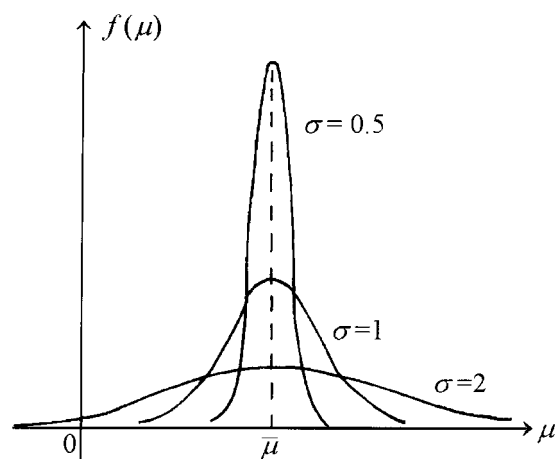


Fig. 1. Probability density of particle adsorption strength at various σ values.

With $z = (\mu - \bar{\mu})/\sigma$, Equation 12 can be transformed into

$$P = 1 - \int_{-\infty}^{(\mu_0 - \bar{\mu})/\sigma} \frac{1}{\sqrt{2\pi}} \exp[-z^2/2] dz$$

$$= 1 - \Phi\left(\frac{\mu_0 - \bar{\mu}}{\sigma}\right) = \Phi\left(\frac{\bar{\mu} - \mu_0}{\sigma}\right) \quad (13)$$

where $\Phi(x)$ is the standard normal distribution function. From this it can be easily seen that P is a function of the average adsorption strength (Fig. 2).

2.3. Calculation of particle content in a deposit

The volume increase per unit time and surface area due to particle incorporation is

$$\frac{dV_p}{dt} = \frac{4\pi}{3} r_p^3 v_p = \frac{4\pi}{3} r_p^3 N \theta P \quad (14)$$

The volume deposition rate of metal per unit surface area can be derived from Faraday's law assuming 100 current efficiency. That is,

$$\frac{dV_m}{dt} = \frac{Mi}{nF\rho_m} \quad (15)$$

with the symbols as explained at the outset. Then, the weight of embedded particles per unit volume in the deposit can be expressed as

$$\alpha = \frac{W_p v_p}{\left(\frac{dV_p}{dt} + \frac{dV_m}{dt}\right)} = \frac{\frac{4\pi}{3} r_p^3 \rho_p N \theta P}{\left(\frac{4\pi}{3} r_p^3 N \theta P + \frac{Mi}{nF\rho_m}\right)} \quad (16)$$

Inserting Equation 8 into Equation 16 and rearranging, we obtain

$$\frac{C_p}{\alpha} \left(1 - \frac{\alpha}{\rho_p}\right) = \frac{Mi}{nF\rho_m} \times \frac{1}{NP} \left(\frac{1}{K} + \frac{3C_p}{4r_p\rho_p}\right) \quad (17)$$

This equation is the final mathematical expression of the adsorption strength model for the codeposition of particles from a plating bath.

3. Experimental details

An electrolytic bath having the following composition was used to deposit Fe-P alloy: 400.0 kg m⁻³

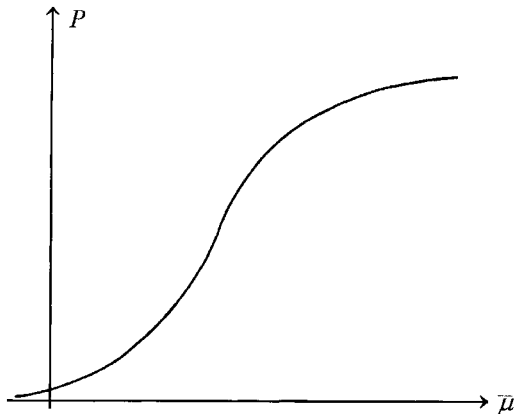


Fig. 2. Probability of the effective adsorption of particles against average adsorption strength.

ferrous chloride, 5.0 kg m⁻³ sodium hypophosphite and 1.0 kg m⁻³ butanedioic acid. α -Alumina particles with average size 7 μ m and density 4.0×10^3 kg m⁻³ were employed for the investigation. The particles were thoroughly cleaned in an acetone solution and treated with hot 5% HNO₃ to remove organic impurities; they were then washed thoroughly in distilled water and dried. The concentration of α -alumina particles in the bath was varied from 5 to 50 kg m⁻³. The bath was agitated with a magnetic stirrer to keep the particles suspended and the agitation rate was fixed at 500 rpm. The bath temperature was held at 50 °C, the current density employed ranged from 500 to 4000 A m⁻² and the pH was adjusted to 1.0 through HCl addition.

Either stainless steel or carbon steel specimens were used as the cathodes and a pure iron plate with an anode bag served as the anode. The electrodes were pretreated in the usual way. During plating, a cathode was vertically placed between two anodes so that good uniformity of the deposits could be obtained. The thickness of the deposits ranged from 30 to 50 μ m and the alloy composition was determined using an electron probe microanalyser. The quantitative determination of α -alumina particles incorporated in the deposits was performed by chemical analysis and checked by scanning electron microscopy. In this study the alloy contained 1.5 ~ 2.0 weight percent phosphorus in the composite coatings. The Fe-P alloy can therefore be treated as single metal.

4. Results and discussion

4.1. Effects of particle concentration on content of embedded particles at different current densities

The results of codeposition of α -alumina and Fe-P alloy from plating baths containing different particle concentrations are plotted in Fig. 3. It can be seen that the particle content in the deposits is greater by one order of magnitude than the corresponding particle concentration in the bath, which shows the existence of a particle adsorption process on the cathode. The higher particle concentration in the bath, the higher the particle content in the deposits. The particle content in the deposits shows a maximum with increase in current density.

From the results of Fig. 3, $(C_p/\alpha)(1 - \alpha/\rho_p)$ against $3C_p/4r_p\rho_p$ for different current densities are plotted in Fig. 4 according to Equation 17. Straight lines are obtained, indicating that the experimental results are consistent with Equation 17. The slope of these lines is then given by

$$\text{tg}\beta = \frac{Mi}{nF\rho_m} \times \frac{1}{NP} \quad (18)$$

The adsorption and detachment constant, K , at various current densities can be obtained from the intercept on the abscissa. The results are listed in Table 1.

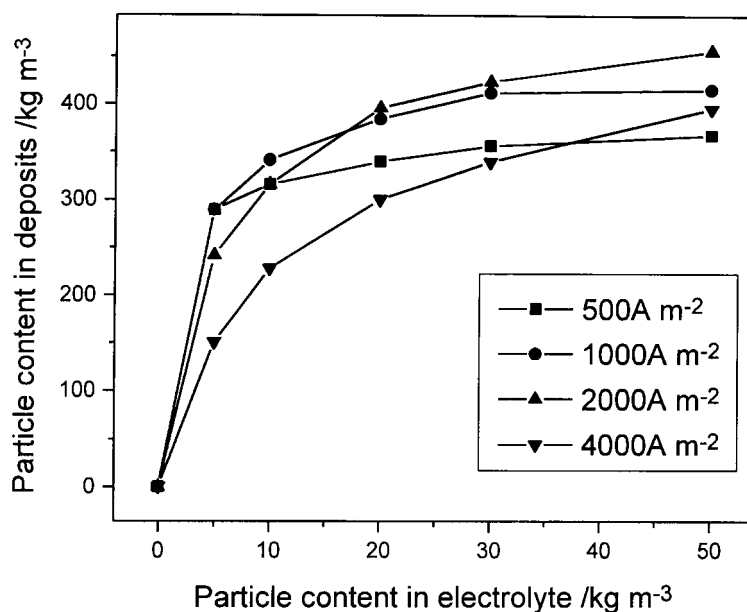


Fig. 3. Codeposition of α -alumina from plating bath containing various particle concentrations. Current densities: (■) 500, (●) 1000, (▲) 2000 and (▼) 4000 A m^{-2} .

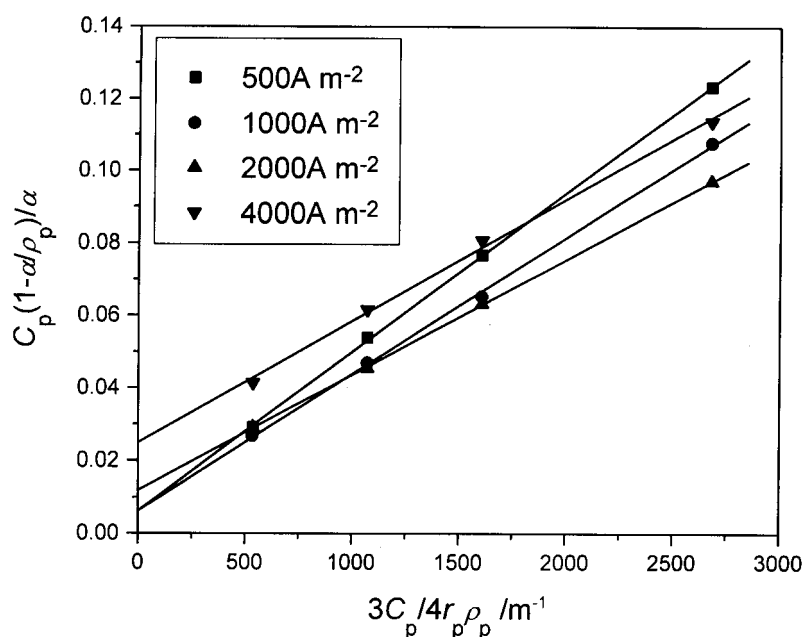


Fig. 4. Codeposition of α -alumina particles according to Equation 17. Current densities: (■) 500, (●) 1000, (▲) 2000 and (▼) 4000 A m^{-2} .

4.2. Effects of the current density on the adsorption and detachment constant K

If $\ln K$ is plotted against $\ln i$ as shown in Fig. 5, a straight line with a negative slope is obtained; this means that the adsorption and detachment constant K decreases with increase in the current density. Putting

$$\ln K = a + b \ln i \quad (19)$$

the values of the intercept on the $\ln K$ axis and the slope of this straight line are given by $a = 0.4$ and $b = -0.8$, respectively.

To understand the significance of the dependence of K on i , differentiation of Equation 8 with respect to i gives

Table 1. Effects of current density on K and NP from Fig. 4

i / A m^{-2}	$\ln i$ / A m^{-2}	$K \times 10^{-3}$ / m	$\ln K$ / m	$tg\beta \times 10^{-5}$ / m	$NP \times 10^{-4}$ / s^{-1}
500	6.22	7.07	-4.95	4.38	4.20
1000	6.91	6.10	-5.10	3.77	9.77
2000	7.60	2.69	-5.92	3.18	23.14
3000	8.01	1.96	-6.24	2.85	38.75
4000	8.29	1.35	-6.61	3.36	43.83

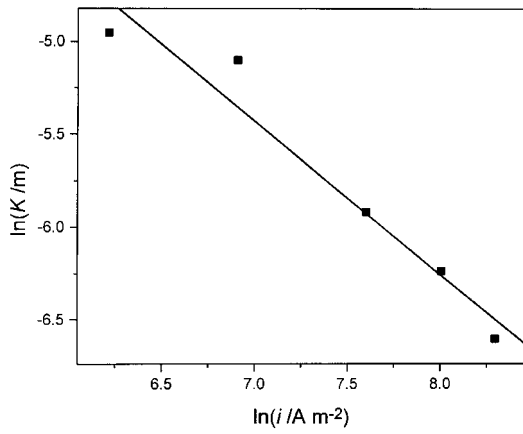


Fig. 5. Effect of current density on adsorption and detachment constant.

$$\begin{aligned} \frac{d\theta}{di} &= \frac{K \frac{3C_p}{4\pi r_p \rho_p}}{\left(1 + K \frac{3C_p}{4r_p \rho_p}\right)^2} \times \frac{b}{i} \\ &= \frac{12KC_p \rho_p b}{\pi r_p i (4r_p \rho_p + 3KC_p)^2} \end{aligned} \quad (20)$$

Obviously, $d\theta/di < 0$, so it can be concluded that the amount of adsorbed particles on the cathode decreases with increasing current density in the Fe-P- α -Al₂O₃ plating bath. The behavior of the adsorption coverage of particles may be due to the increasing rate of metal ion reduction with increasing current density. The rapidly growing metal layer continuously influences the geometry of the cathode and is unfavorable to the adsorption of particles, thus reduces the particle coverage.

4.3. Effects of current density on probability of effective adsorption of particles and average adsorption strength

The relationship between NP and the logarithms of current density is depicted in Fig. 6 from results of Table 1. Since N is a constant, this indicates that the probability of effective adsorption of particles increases with increase in current density. Fig. 6 compares well with Fig. 2. This implies that hypothesis (b) is reasonable and there should be a linear dependence of the average adsorption strength $\bar{\mu}$ on $\ln i$. According to probability theory, the value of probability is 0.50 at the inflection point in Fig. 6, where $\bar{\mu} = \mu_0$, and the standard normal distribution function $\Phi(\bar{\mu} - \mu_0)/\sigma = \Phi(0) = 0.50$.

Thus the value of N can be calculated to be 0.0075 and values of $(\bar{\mu} - \mu_0)/\sigma$ can be obtained by calculating P at various current densities. The results are listed in Table 2.

The quantity $(\bar{\mu} - \mu_0)/\sigma$ is plotted against $\ln i$ in Fig. 7. It can be seen that the values are almost grouped on a straight line, that is, the average adsorption strength of particles is proportional to the logarithms of the current density:

$$\frac{\bar{\mu} - \mu_0}{\sigma} = A + B \ln i \quad (21)$$

Table 2. Effects of current density on P and $\bar{\mu}$ from Fig. 6

$\ln i$	$p = \Phi\left(\frac{\bar{\mu} - \mu_0}{\sigma}\right)$	$\frac{\bar{\mu} - \mu_0}{\sigma}$
6.22	0.06	-1.59
6.91	0.13	-1.13
7.60	0.31	-0.50
8.01	0.52	0.04
8.29	0.58	0.21

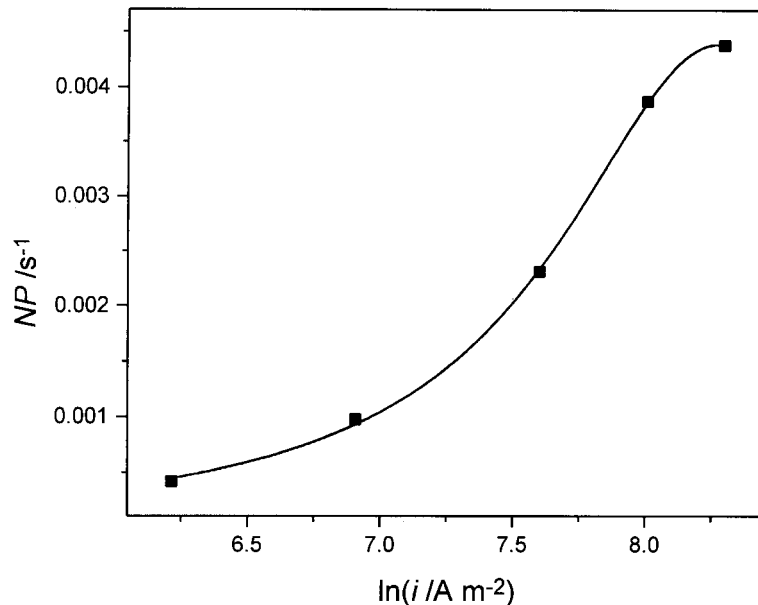


Fig. 6. Effects of current density on probability of effective adsorption of particles.

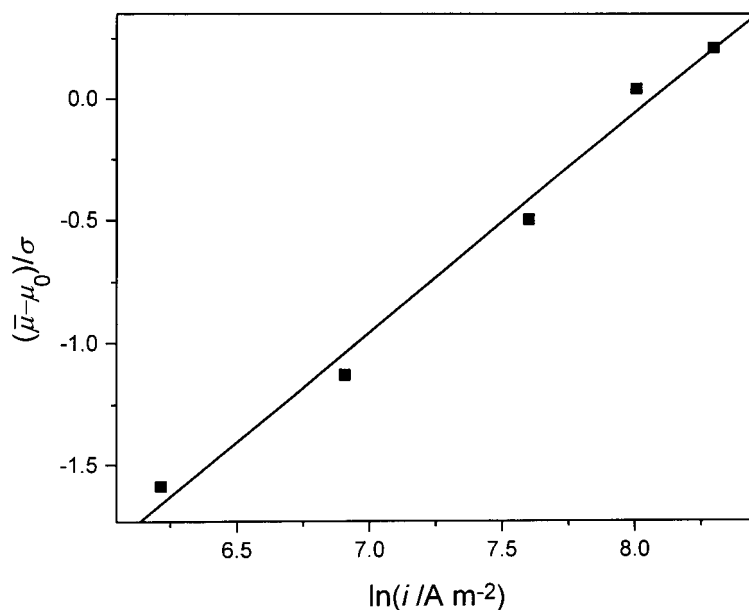


Fig. 7. Effects of current density on average adsorption strength of particles.

where $A = -7.3$ is the intercept of this line on the $(\bar{\mu} - \mu_0)/\sigma$ axis and $B=0.9$ is the slope.

This indicates that the increase in P with increasing current density is caused by the increase in average adsorption strength with increasing current density. Because the particle coverage on the cathode decreases with increasing current density, the content of particles in the deposit is an overall balance of two effects.

4.4. Effects of current density on deposit particle content

From Equations 12, 19 and 21, we obtain

$$\frac{dP}{di} = f(\bar{\mu}) \frac{d\bar{\mu}}{di}, \quad \frac{dK}{di} = \frac{b}{i} K \quad \text{and} \quad \frac{d\bar{\mu}}{di} = \frac{B}{i} \sigma$$

Then the derivative of α with respect to i can be calculated from Equations 8 and 17:

$$\begin{aligned} \frac{d\alpha}{di} &= \frac{3\alpha^2}{4\pi r_p^3 \rho_p N \theta P} \times \frac{Mi}{nF\rho_m} \\ &\times \left[\frac{f(\bar{\mu})}{P} \times \frac{d\bar{\mu}}{di} + \frac{4r_p \rho_p}{K(4r_p \rho_p + 3KC_p)} \times \frac{dK}{di} - \frac{1}{i} \right] \\ &= \frac{3\alpha^2}{4\pi r_p^3 \rho_p N \theta P} \\ &\times \frac{M}{nF\rho_m} \left(B\sigma \frac{f(\bar{\mu})}{P} + b \frac{4r_p \rho_p}{4r_p \rho_p + 3KC_p} - 1 \right) \quad (22) \end{aligned}$$

When the value of $(B\sigma \frac{f(\bar{\mu})}{P} + b \frac{4r_p \rho_p}{4r_p \rho_p + 3KC_p} - 1)$ is positive, the content of particles in the deposits increases monotonically with increase in current density. When the value of $(B\sigma \frac{f(\bar{\mu})}{P} + b \frac{4r_p \rho_p}{4r_p \rho_p + 3KC_p} - 1)$ is negative, the content of particles decreases monotonically with increase in current density. Because P increases and

K decreases with increasing current density, the value of $(B\sigma \frac{f(\bar{\mu})}{P} + b \frac{4r_p \rho_p}{4r_p \rho_p + 3KC_p} - 1)$ may change from positive to negative. Thus, the particle content may show a maximum at the point where

$$\left(B\sigma \frac{f(\bar{\mu})}{P} + b \frac{4r_p \rho_p}{4r_p \rho_p + 3KC_p} - 1 \right) = 0$$

with increasing current density.

5. Conclusions

An adsorption strength model has been developed to describe the mechanism of codeposition of inert particles and metals based on the intensity of adsorption between the particles and the cathode. In this model, the distribution of the adsorption strength of particles on the cathode is assumed to conform to the law of normal distribution and a particle may be incorporated in the deposit only when its adsorption strength is sufficiently high.

The model is found to be valid for the electrochemical codeposition Fe-P- α -Al₂O₃ composite coatings. Some model parameters can be determined by comparing theory and experimental data. In the Fe-P- α -Al₂O₃ plating system, the amount of adsorbed particles on the cathode decreases and the average adsorption strength increases with increasing current density. The variation of the particle content in deposits with current density is an overall balance of the two effects.

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