

Effects of Particle Conductivity on the Fe-Si co-deposition Process

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Composite iron deposits containing non-conductive Si particles and conductive Si-Fe alloy particles with an average size of 1 μm were prepared in circulating solution, the effects of particle conductivity on the co-deposition process of particles were investigated. The results show that high conductivity contributed to the co-deposition process of particles into the composite coatings, and in a mode of "cladding" for the co-deposition of conductive Si-Fe particles, while that for non-conductive Si particles was "embedding" mode. At the same time, with increasing the conductivity, the co-deposition process of particles was obviously deviate from the Guglielmi model. A possible mechanism on the forming process was discussed.

Keywords: Fe-Si coating; Electrodeposition; Particle; Conductivity; Co-deposition

1. INTRODUCTION

6.5wt% Si silicon steel exhibits superior soft magnetic properties, such as low iron core loss, high magnetic induction and near-zero magnetostriction, which has a wide application prospects in high frequency fields, including the electric relay, power generators and high performance transformers[1-2]. However, owing to the high brittleness of 6.5wt%Si silicon steel, the qualified silicon steel strip with high silicon content can not be prepared by the traditional cast-rolling process. At present, researchers worldwide have done a lot of research on the production process of 6.5wt% silicon steel strip, such as powder rolling method[3], laser cladding[4], chemical vapor deposition (CVD)[5] and molten salt electrodeposition[6] methods, but most of above methods still have high cost, environmental pollution and long production cycle, which seriously blocks its large-scale industrial production and application compared with cast-rolling process[7].

As a high efficient and green technology, composite electrodeposition has many advantages such as low temperature, low cost and little environmental pollution. In recent years, composite electrodeposition technology has been developing rapidly and widely applied in aerospace, transportation, repair, functional material and decoration etc.[8-12]. The content and distribution of inert particles in the coating often become the key factors affecting the composite coating[13-15]. Pan[16] proposed to prepare 6.5wt%Si silicon steel strip by composite electrodeposition with Si-Fe alloy particles or pure Si particle, and found that the silicon content of coatings can reach 6.45%, while that only 3.45% when applied pure silicon particles. Long[17] also found that increasing the silicon content of iron-silicon particles with an average size of 2.5 μm , the co-deposition process of particles was more difficult, and it can be attributed the conductivity of the particles decreased significantly, but the adsorption mechanism needs for further study. So far, electrodeposition containing particles in the composite coatings were main ceramic and nano-scale particle[18-19], there are few research to prepare composite coating with micro-scale and conductive particles.

Therefore, the Fe-Si coating with different conductive Si-Fe alloy particles and pure Si particles was prepared in this paper, and the influence of particle conductivity on the co-deposition process was investigated, and the possible mechanism of the effects was discussed in detail.

2. EXPERIMENTAL

Pure Si particles and Si-Fe powders with mass fraction of 30%, 50% and 70% were used to prepare composite coatings. Figure 1 gives the distribution range of particle diameter tested by particle diameter sizer(Mastersizer 2000). From Figure1, it can be found that the average particle diameter was about 1 μm , and the distributions were similar for these different types of particles. The basic plating solution was 250g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 50g/L $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 50g/L NH_4Cl , all the chemicals were analytical grade and the distilled water was used for preparing all kinds of solution. Meanwhile, using the hexadecyl trimethyl-ammonium bromide(HTAB) with the concentration of 0.2g/L as the dispersing agent to prevent the adopted particles from agglomeration in the plating bath.

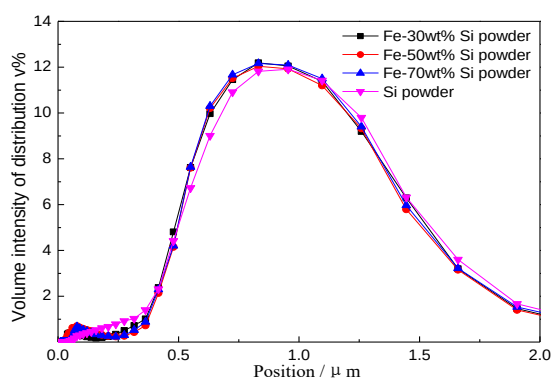


Figure 1. distributions of particles diameter

In electrodeposition, using pure iron sheets(20×30×0.5 mm, Fe 99.99%) as the cathode and anode, and the distance between them was 20 mm. Before electroplating, adjusting the solution pH

value to 1.5 with dilute H_2SO_4 (0.5 mol/L), and the electroplating solution was agitated with high purity argon bubbles to reduce the oxygen content in the solution. In the electrodeposition process, circulating plating solution to prevent the settlement of particles. At the same time, electroplating solution was introduced into electrolytic bath using inverted funnel, and a couple of grid baffle with round holes of 3 mm diameter was installed at 10 mm in front of electrodes to avoid the scouring action of electrolyte on the electrode surface (Figure 2). The plating process was maintained at 298 K and the plating time was 30 min, and the surface morphologies, cross-sections and analyzing the concentration of silicon in the composite coatings were characterized by scanning electron microscopy (SEM) with energy dispersive X-ray spectrometer (EDS) and checking the distribution of particles. The conductivity of Fe-Si alloy powder was estimated by Fe-Si alloy bar with diameter of 8 mm and length of 10 mm. First of all, iron powder and silicon powder were mixed uniformly in the proportion of 30 wt%, 50 wt% and 70 wt%, and added in the induction furnace with high vacuum and high purity argon shielding gas respectively. After fully melting, the Fe-Si alloy ingots were casted into a bar with quartz tube by suction casting, and then the resistance (R) of the alloy bars was measured by a four-probe resistivity measurement setup composed of a Keithley 2400 digital source meter and a Keithley 2182A nanovoltmeter (America). The conductivity of the Fe-Si alloy bars was calculated via $\kappa = L / RS$, L and S in the formula were the length of alloy bar and the area of cross-section, respectively. The element distribution in the alloy bars obtained by suction casting was uniform, so the conductivity of the alloy bars can be used to characterize the conductivity of the particles.

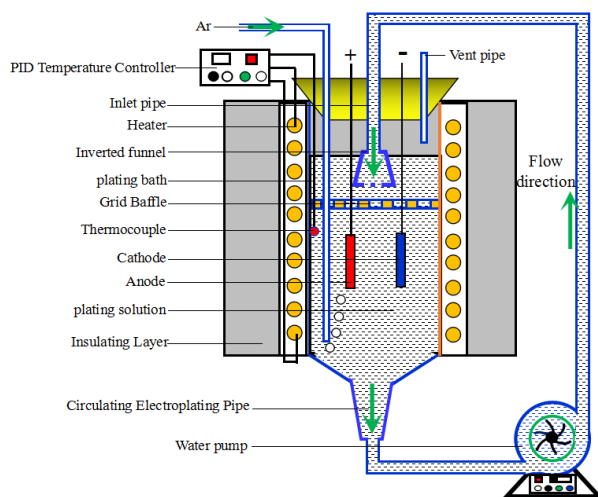


Figure 2. Schematic diagram of the experiment equipment

3. RESULTS AND DISCUSSION

Figure 3 shows the SEM micrographs of Fe-Si coatings obtained with different types of particles. From Figure 3, it shows a uniform distribution on the coating surface for all the different types of particles. At the same time, with increasing the silicon content in particles, the number of different types of particles distributed on the coating surface decreased significantly. As follows from the micrographs given in Figure 4, the cross-sections of the corresponding composite coatings were also noted that the particles were well entered into the composite coatings. Further more, the silicon content of coatings increased significantly with the increase of particle concentration (Figure 5), about

9.76wt% for 30wt%Si-Fe particle at the 50g/L of particle concentration and $2\text{A}/\text{dm}^2$ current density, whereas that for Si particles was only 4.48wt%. However, after the particle concentration was more than 50g/L, the silicon content of coatings increased relatively stable. Simultaneously, as the increase of the current density, the silicon content of coatings increased and reaching a maximum value at $2\text{A}/\text{dm}^2$, and then decreased as current density continuing increasing.

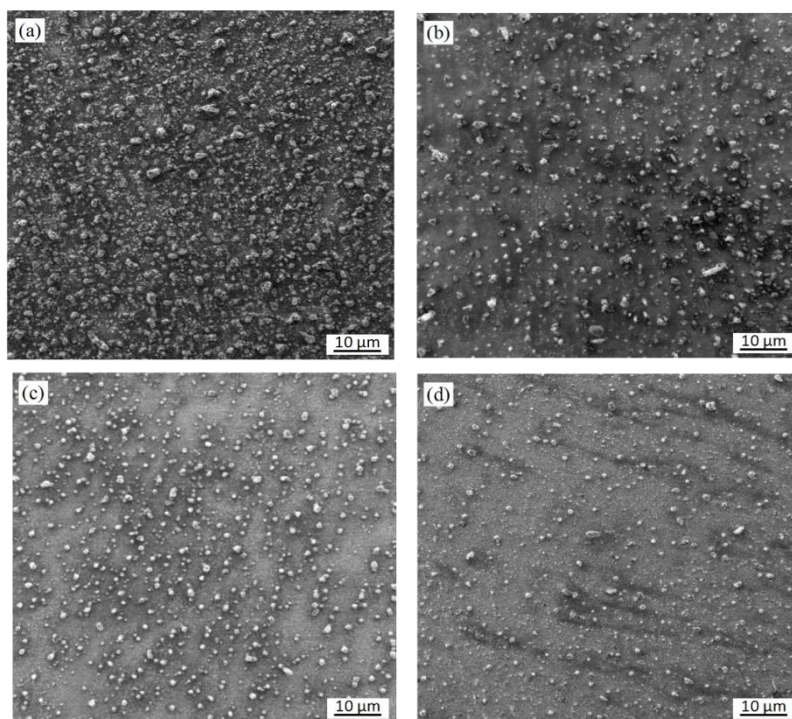


Figure 3. SEM micrographs of Fe-Si coatings for 30wt%Si-Fe powder(a), 50wt%Si-Fe powder(b), 70wt%Si-Fe powder(c) and pure Si powder(d) at $2\text{A}\cdot\text{dm}^{-2}$ with the particle concentration of $50\text{g}\cdot\text{L}^{-1}$

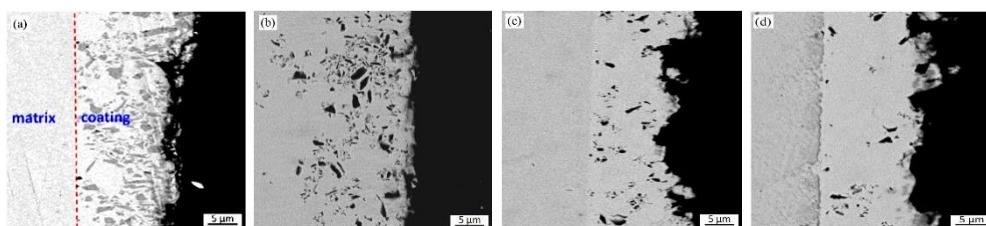
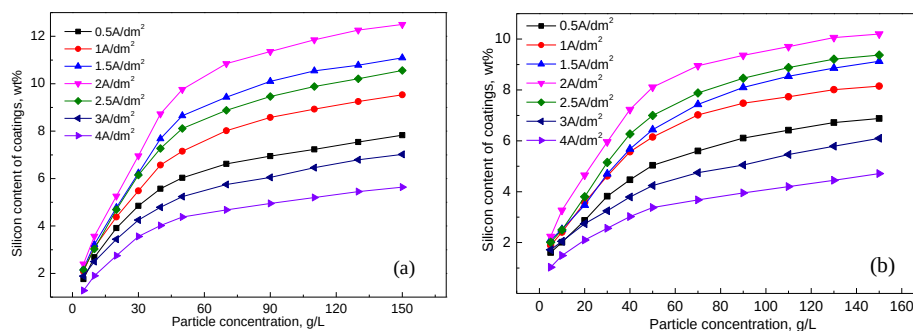


Figure 4. Cross-section morphologies of Fe-Si coatings at $2\text{A}\cdot\text{dm}^{-2}$ (a)30wt%Si-Fe powder (b) 50wt%Si-Fe powder (c)70wt%Si-Fe powder (d) Si powder



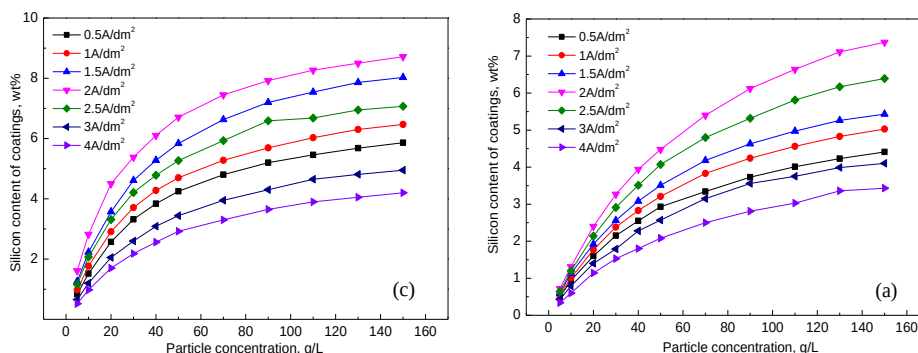


Figure 5. Silicon content of coatings under different particle concentrations and current densities for (a) 30wt%Si-Fe powder; (b) 50wt%Si-Fe powder; (c) 70wt%Si-Fe powder; (d) Si powder

4. DISCUSSION

Relatively larger particles with about 2.5 μm diameter were used to prepare Fe-Si composite coatings in our previous work[17]. To ensure that particles are uniformly suspended in solution by means of downward mechanical stirring owing to the great gravity effect. However, a strong scouring effect will be induced by the strong stirring effect on the electrode surface, which was undesirable to the adsorption process of particles into the composite coating. Under the optimum electroplating condition, approximately 6wt% silicon content of coatings can be obtained for the 30%Si-Fe powder with the particle concentration of 50g/L, whereas for Si powder was only about 2wt%. Therefore, in order to reduce these adverse effects, the small-size particles with the 1 μm of average particle size were used to prepare Fe-Si coating in this paper, and the final settling velocity of particles in the electroplating solution is relatively small according to the Stokes Formula, which will be addressed later. At the same time, cycle stirring solution in a downward direction, inverted funnel and a pair of baffles above the electrodes were applied(Figure 2), which can further reduce the scour effect of solution flow on the electrode surface. As a result, it should be helpful for the adsorption process of particle, and the co-deposition process of particles entering the Fe-Si composite coating was investigated.

According to Guglielmi N[20], the particle inclusion in metal matrix from electroplating solution occurs in two consecutive steps of adsorption, including the "loose adsorption" and "strong adsorption". The inert particle on its way from the bulk of the solution to the site of incorporation at the active cathode surface will proceed through the flowing stages(Figure 6)[21]: Firstly, particle surface adsorbs some cations and moves towards the hydrodynamic boundary layer(δ_0) by forced convection, and diffuses through the diffusion double layer(δ) and then which is absorbed at the cathode surface, then yield a high degree of coverage on the cathode surface, this process is reversible and so called the "loose adsorption". lastly, the reduction of metal ions adsorbed on the particles produces the circumstance of irreversible strong adsorption, which was "strong adsorption". Then, these particles were engulfed by the growing metal matrix. For the construction of the model, it is assumed that a homogeneous suspension of particles in the electroplating solution is maintained, and that steady-state conditions always exist, so that neither pressure, temperature, concentration, nor overpotential variations occur during the composite electrodeposition process, and finally that the

cathode surface is uniformly accessible for the inert particles and the plating solution.

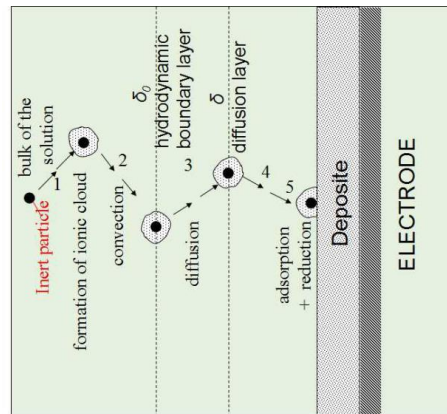


Figure 6. The stages in the co-deposition of a particle

The Guglielmi model may be expressed as follows:

$$\frac{(1-a_v)c_v}{a_v} = \frac{Mi_0}{nF\rho_m\nu_0} e^{(A-B)\eta} \left(\frac{1}{k} + c_v \right) \quad (1)$$

Where c_v and a_v are the volume fraction and volume fraction of the particle in the electroplating solution and composite coatings respectively, F is the Faraday constant, the ρ_m , M and n are the density, atomic weight and the valence of electro-deposited metal respectively, η is the cathodic overpotential, A is the constant in the kinetic equation of electrochemical reaction $i = i_0 e^{A\eta}$, i_0 is the exchange current density, k is the Langmuir isotherm constant, B and ν_0 are the constants related to the co-deposition process of particle. From the equation(1), when current density at the same value, $(1-a_v)c_v/a_v$ has a linear relationship with c_v , and the slope of each line can be expressed as follows:

$$\tan\varphi = \frac{Mi_0}{nF\rho_m\nu_0} e^{(A-B)\eta} \quad (2)$$

When $(1-a_v)c_v/a_v$ equal to 0, the intercept of each line can be calculated and therefore the value of $\left(-\frac{1}{k}\right)$ also can be derived. Figure 7 gives the relationship between $(1-a_v)c_v/a_v$ and c_v at different current density and particle concentration for Si and 70wt%Si-Fe particles. It can be found that the $(1-a_v)c_v/a_v$ was linear with the c_v for the Si particle. When the current density is less than 2A/dm^2 , the slope of the fitting straight line for $(1-a_v)c_v/a_v$ and c_v under different current density will extend to the A_0 on the X axis(Figure 7a), indicating that the adsorption of particles basically obeys Guglielmi model. When the current density was higher than 2.5A/dm^2 , the intersection on the X axis deviates from the A_0 , so the adsorption process of the particles deviates from the Guglielmi model, which was not consistent with Celis and Suzuki's similar research[22-23]. When using 70wt%Si-Fe particles, although showed a linear relationship between $(1-a_v)c_v/a_v$ and c_v in the current density of no more than 1.5A/dm^2 , and the intersection on the X axis at the same point B_0 , after higher than 1.5A/dm^2 , the intersection of straight line and X axis away from the B_0 (Figure 7b). However, when adopting 30wt%Si-Fe particles or 50wt%Si-Fe particles, $(1-a_v)c_v/a_v$ and c_v were no longer showing a linear

relationship, especially when the concentration of plating particles was less than 0.01(Figure 8). Therefore, the co-deposition process for 30wt%Si-Fe and 50wt%Si-Fe particles obviously disobeyed the Guglielmi's model under different current density.

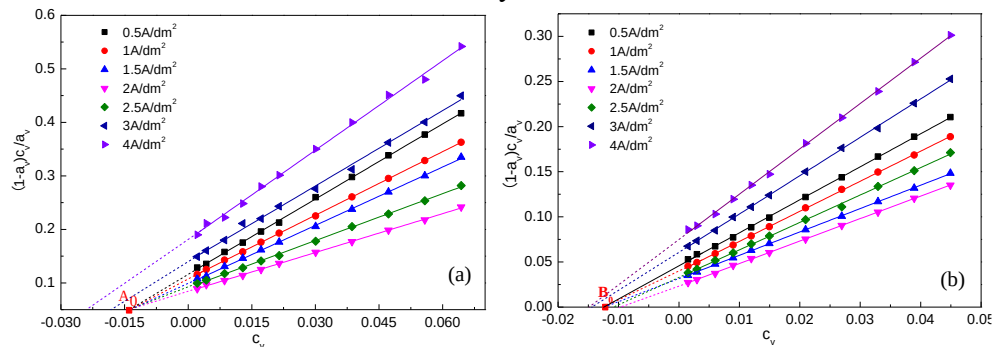


Figure 7. The relationship between $(1-a_v)c_v/a_v$ and c_v of (a) pure Si and (b) 70wt%Si-Fe powders

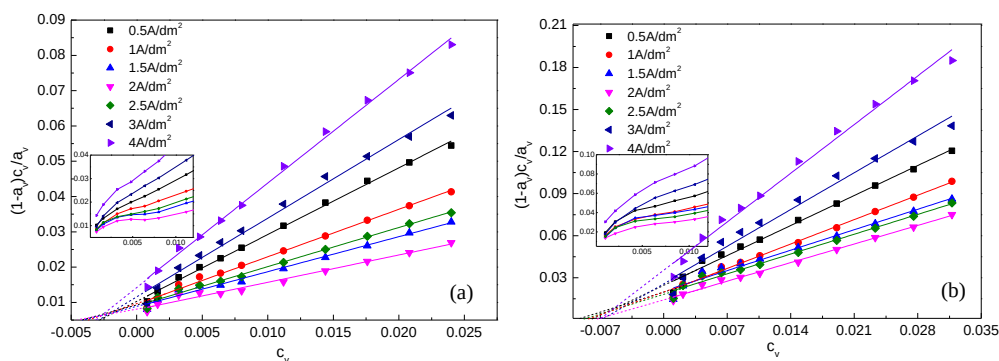


Figure 8. The relationship between $(1-a_v)c_v/a_v$ and c_v of (a)30wt%Si-Fe and (b)50wt%Si-Fe powders

During the co-deposition process of particles on cathode surface, the reaction constant(κ) can be expressed as:

$$k = \frac{k_a}{k_d} \quad (3)$$

Where k_a and k_d respectively are the adsorption and desorption coefficient of particles on the electrode surface. Thus, if $k > 1$, it can be deduced that the adsorption rate of particles is faster than the desorption rate. The Guglielmi's model implies the Langmuir adsorption isotherm can be modified simultaneously as follows[20]:

$$\sigma = \frac{\kappa c_v}{1 + \kappa c_v} (1 - \theta) \quad (4)$$

Where σ and θ are the loose adsorption coverage and the strong adsorption coverage respectively. From Eq.(4), we can estimate the loose adsorption coverage on the assumption of the surface coverage for strong adsorption is close to the volume fraction of the particles. However, just only a little fraction of the particles adsorbed loosely on cathode surface can be co-deposited by the reduction of Fe^{2+} . Thus, the transfer from the loose adsorption to the strong adsorption should be the determining step for the co-deposition process of particles. Above experimental results revealed that the co-deposition of 30wt%Si-Fe particle was apparently easier than that of Si particle, the silicon content of coatings about 9.76wt% for 30wt%Si-Fe particle at the 50g/L of particle concentration and 2A/dm^2 , whereas that for Si particles was only 4.48wt%. Moreover, the total silicon content in the

plating solution with 30wt%Si-Fe powder was only 30wt% of the Si powder when the concentration of particles in electrolyte at the same value, which further indicated that the co-deposition of 30wt%Si-Fe particles were more easily compared with Si particles. Thus, it is essential to discuss the effects of properties of applied particles on the co-deposition process.

During the composite electro-deposition process, the final settling velocity of particles in the electroplating solution by Stokes formula can be given as follows:

$$v = \frac{g(\rho_s - \rho)}{18\mu} d^2 \quad (5)$$

Where v is the settling velocity, d is the diameter of particles, ρ_s and ρ is the density of particle and electrolyte solution, g is the acceleration of gravity; and μ is solution viscosity. According to formula(5), it indicates that a greater density of particles will lead to the greater final settling velocity of particles, which is not conducive to being captured by the reduced metal ion. The effects of silicon content on the particle density and ration of final settling velocity were showed in Figure 9. However, above results show that the Si-Fe particles are easier to enter the coatings then Si particles, which indicates that the density of the particles is not the key factor affecting the co-deposition process of particles.

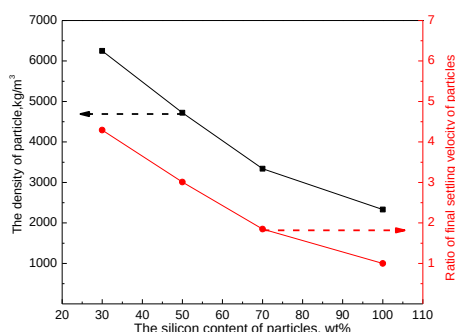


Figure 9. Effects of silicon content on the density and ration of final settling velocity of particles

Our preliminary work[24] shows that the conductivity of particles significantly affects the adsorption process of particles. Table 1 gives the conductivity of different types of particles, the conductivity of particle decreases with increasing the silicon content of particles, and Si particle displays poor conductivity compared to that of electroplating solution, which even much lower than the conductivity of solution (approximately $4.35 \text{ S} \cdot \text{m}^{-1}$). In order to investigate the discharge behavior of Fe^{2+} in the electro-deposition process, co-deposition of particles and the growth process of Fe-Si coatings, the composite coatings were prepared by Si particles and 30wt%Si-Fe particles with diameter of approximately $50 \mu\text{m}$ under the electrodeposition of horizontal electrode[25], and then observing the surface morphologies and cross-sections of Fe-Si coatings. Owing to the non-conductivity of Si particles, an uneven distribution of current was induced in the vicinity of particles after some Si particles reached on the cathode surface (Figure 10a), which would induce the effective current density significantly increased. Reduction of Fe^{2+} occurred at the surrounding area of Si particles on iron cathode surface(Figure 10b). When using the conductive 30wt%Si-Fe particles, the current distribution will be also affected, but tends to focus on the surface of the conductive particles, which equivalent to increasing the effective discharge area of cathode surface(Figure 10c-d). Fe^{2+} will be reduced easily on

the particle surface after the 30wt%Si-Fe particle contacted to the cathode surface, owing to it was conducive to the co-deposition process of conductive 30wt%Si-Fe particles. In other words, the conductive Si-Fe particles into the composite coating in the mode of "cladding", and the Si particles with poor conductivity into the coating in "embedding" mode. Meanwhile, it is obvious that was in accordance with the surface morphologies and cross-sections of corresponding Fe-Si composite coatings(Figure 11).

Table 1. Conductivities of different types of particles and electrolyte

Particulate silicon content (wt%)	30	50	70	100
Conductivity ($\text{S}\cdot\text{m}^{-1}$)	4.79×10^5	2.63×10^5	6.52×10^3	2.52×10^{-4}

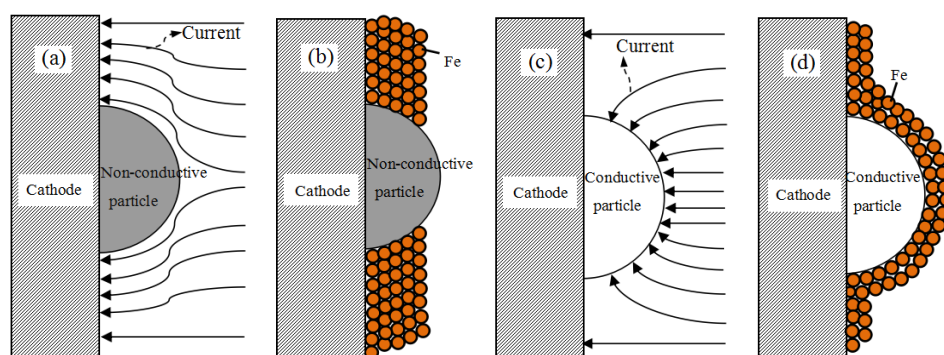


Figure 10. Electrolytic current distributions in the vicinity of applied particles and schematic views of composite electrodeposition for nonconductive particles(a-b) and conductive particles(c-d)

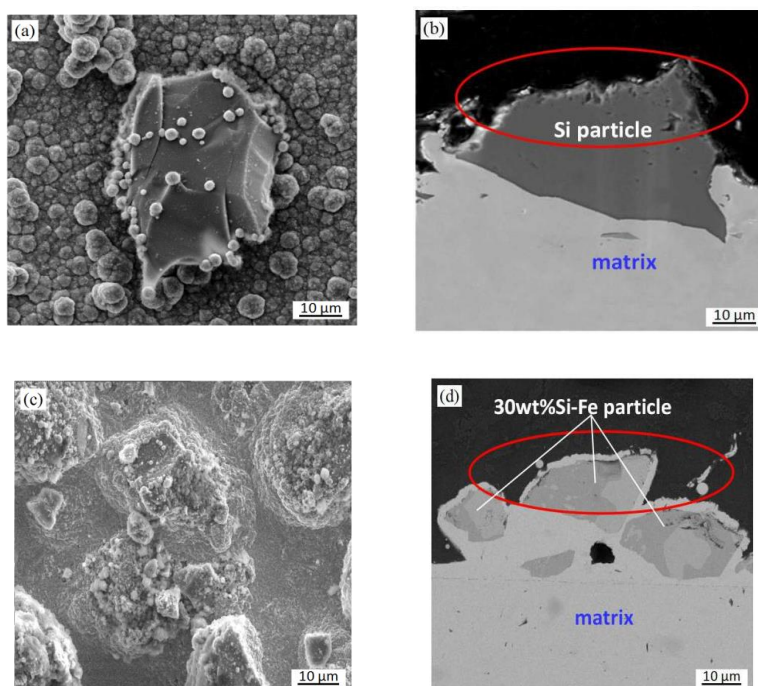
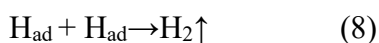
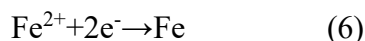


Figure 11. Surface morphologies and cross-sections of coatings for Si powder(a-b) and 30wt%Si-Fe powder(c-d)

Further more, the current density also had a great influence on the co-deposition process of particles. Above results revealed the silicon content of coatings increased for all the different types of particles with increasing the current density, and reaching a maximum value at $2 \text{ A} \cdot \text{dm}^{-2}$, and then decreased if continuing to increase the current density. During the electro-deposition process, the particles adsorbed ions migrated to cathode surface from solution under the effects of different forces, including electric force, natural convection and gravitational force, and some of them could be captured by the growing metal, then entered the coatings completely. Therefore, it can be deduced that the transfer rate of particles was faster than the growth rate of iron metal when the current density is less than $2 \text{ A} \cdot \text{dm}^{-2}$, and reversed while above $2 \text{ A} \cdot \text{dm}^{-2}$. Meanwhile, the standard electrode potential of Fe^{2+} is -0.44V , the polarization would significantly increased with the increase of current density. Therefore, an intensive hydrogen evolution reaction will always accompany the electro-deposition process, which provide additional agitation in the cathode surface, and it can be expressed in formulas (7) and (8):



A proper agitation can strengthen mass transfer of solution and may boost the incorporation of particles. However, too strong agitation will significantly reduce the co-deposition of particles, owing to the particles can be taken away by the turbulent flow induced by hydrogen evolution from the cathode surface before being incorporated completely. The current efficiency in the process of iron plating is approximately 65% [26-27], which indicated that the reaction of hydrogen evolution was very strong. Too large electroplating fluid disturbance affect the adsorption process of particles, reducing the rate of particles entering the composite coating. Thus, when the current density exceeds 2.5 A/dm^2 , the co-deposition process of Si particles was obviously deviated from the Guglielmi's model.

5. CONCLUSIONS

The Fe-Si composite electrodeposition have been conducted in the condition of circulating electroplating solution at a temperature of 298 K in a sulfate-chloride plating bath. The effects of particle conductivity on co-deposition process and coating surface morphology were investigated. The main conclusions were:

(1) High particle conductivity contributed to the co-deposition of particles, about 9.76wt% silicon content of coatings can be obtained for the 30%Si-Fe powder with the particle concentration of 50g/L, whereas that for Si powder was only 4.48wt%.

(2) The co-deposition of conductive Si-Fe powders into composite coatings in the mode of "cladding", while that for non-conductive Si powder was an "embedding" mode.

(3) When the current density was lower than 2 A/dm^2 , the co-deposition process of Si particles basically followed the Guglielmi's model, with increasing the particle conductivity, the co-deposition process of particles deviated the Guglielmi's model.

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