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Hidetaka Hayashi
Okayama University

Shin-ya Izumi
Okayama University

Isao Tari
Okayama University

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Codeposition of α -Alumina Particles from Acid Copper Sulfate Bath

Hidetaka Hayashi,* Shin-ya Izumi, and Isao Tari*

Department of Applied Chemistry, Faculty of Engineering, Okayama University, Tsushima, Okayama, 700, Japan

ABSTRACT

The purpose of this work is to elucidate the factors affecting the codeposition of α -alumina particles with copper from an acid copper sulfate bath. The effect of current density and particle concentration in the bath on the amount of codeposited α -alumina were determined. In order to evaluate the surface-chemical properties of the particles, the zeta-potential of α -alumina particles in the plating bath was determined by means of the streaming potential method. The amounts of adsorbed Cu^{2+} and SO_4^{2-} from the plating bath were also determined. The amount of codeposited α -alumina particles was found to be greater than those reported in literature, in spite of the negative zeta-potential values of α -alumina. This indicates that the electrostatic interaction between the particles and the cathode is not the essential factor of the codeposition process. It is considered that the amount of adsorbed Cu^{2+} on the α -alumina particle plays an important role in the codeposition behavior.

Composite coatings consisting of a metal matrix with fine particles or fibers have been studied by many and have been used for a number of industrial applications.

The purpose of composite coating is to give various functional properties, such as wear resistance, self-lubricating, corrosion or oxidation resistance, etc. to the plated surface. Although the composite coatings are used in many industrial processes, the mechanism of codeposition of dispersoid is not fully elucidated.

The mechanism of the codeposition of particles into a metal matrix has been studied by many authors.¹⁻³ Three possible mechanisms are regarded as predominant: mechanical entrapment of the particles to the cathode, adsorption of the particles on the cathode, and electrostatic interaction of the particles with the cathode. It is well known that most of the particles used in the formation of composite coatings are charged. Their sign of charged state and charge densities seemed to depend not only on the characteristics of the particle itself but also on the composition of the plating bath, such as solution pH or metal ion concentration. Therefore, most of the previous works that are directed to the analysis of the mechanism of codeposition were based on the electrostatic interaction. Many authors stressed that the electrostatic interaction between the particles and the cathode dominated the codeposition behavior.

As pointed out by Tomaszewski *et al.*,⁴ it is well known that composite coating can be easily obtained from a nickel bath. In nickel plating bath, almost all kinds of particles can be incorporated into the metal matrix, while it is rather difficult to obtain appreciable codeposition from acid copper sulfate bath, regardless of the types of particles. Therefore, a number of studies on the composite coatings by using a nickel bath have been reported from technical point of view.

Concerning the codeposition behavior of aluminum oxide from a copper sulfate bath, Sautter *et al.* investigated the codeposition of aluminum oxide from acid copper sulfate bath and found that α -alumina particles were incorporated into the metal matrix but γ -alumina failed to codeposit with copper.⁵ They also found that the amounts of α -alumina incorporated in the metal matrix decreased with increasing bath aging and that γ -alumina particles calcined at high temperature codeposited under the same conditions. They claimed that the crystalline form of the incorporating particles seemed to control the codeposition behavior.

Roos and Celis found codeposition of γ -alumina as well as α -alumina with copper from an acid copper sulfate bath although much smaller amounts of γ -alumina were incorporated as compared with α -alumina,^{6,7} even though the content of α -alumina was pretty low (*ca.* 1 weight percent

(w/o)). They also indicated the enhanced effect of Ti^+ on the codeposition reaction. This effect has also been pointed out in the case of codeposition of BaSO_4 particles from the same bath.⁴

The amounts of adsorbed metal cations on the depositing particles or the zeta potential of the particles have been measured^{8,9,10} to elucidate the mechanism of codeposition. However, both of the measurements are usually carried out in the solution more than 10 times diluted from the actual plating bath, except in some cases.^{8,12} Therefore, it is equivocal whether the measured values reflect the actual state of the particles in the plating bath or not.

The purpose of this study is to clarify the factors affecting the codeposition of particles into a metal matrix. The effect of current density and concentration of particles in the bath on the codeposition of α -alumina with copper were determined. The streaming potential of α -alumina particle in an acid copper plating bath was measured to evaluate the surface-chemical properties of the particles. The amounts of adsorbed Cu^{2+} and SO_4^{2-} ions from the plating bath were also determined.

Experimental

Composite coatings.—The electrolyte used for the composite coatings was an acid copper sulfate bath ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 0.5M, H_2SO_4 0.5M). The plating baths were prepared from reagent grade chemicals (Ishizu Seiyaku Ltd.) and distilled water. The plating experiments were conducted in a 200 ml-capacity glass vessel using vertical copper cathode (Rare Metallic Co., Ltd., 2.0×3.5 cm). Two copper plates of the same source were used as an anode. The α -alumina particles (Sumitomo Chemical Co. Ltd., AKP-20; mean diameter 0.5 μm , specific surface 4.1 $\text{m}^2 \text{g}^{-1}$) were added to the plating bath in the concentration range of 6–50 g l^{-1} . To keep particles in suspension, agitation was provided by a magnetic stirrer, at about 1000 rpm. After the 15–20 min of stirring, the electrodeposition was carried out at various current densities. The current efficiency was measured by the amount of copper deposited during the electrolysis and the α -alumina content in the cathode deposit was determined gravimetrically. The copper-alumina composite coating obtained was dissolved in 5M HNO_3 solution. The remaining solution containing the α -alumina particles at the bottom of the vessel was centrifuged and the supernatant solution was sucked up. The resulting oxides were washed with distilled water, then centrifuged again. This procedure was repeated until the supernatant solution becomes colorless. Finally, the vessel containing oxides was dried in an electric oven at 120°C for 24 h and then weighed on a microbalance. The amount of the codeposited α -alumina particle was determined from the difference between the measured weight as shown above and the weight of the vessel alone. The amount of dissolved α -alu-

*Electrochemical Society Active Member.

mina during the dissolution process in 5M HNO₃ was below 10 ppm. Therefore, it seems that the dissolution process does not affect the determination of the amount of codeposited α -alumina particles.

Codeposition of alumina particles from a copper nitrate bath was also examined to compare with the results from the sulfate bath.

Streaming potential measurement.—Figure 1 shows the apparatus of the streaming potential measurements. Appropriate amounts of α -alumina particles were placed on a sheet of filter paper supported by a perforated PTFE disk. The α -alumina particles were suspended in a copper sulfate solution of various pH. Then the suspension was sucked through the plug A by using an aspirator. After packing, a sufficient quantity of the electrolyte was streamed through the plug. The streaming potential was measured as the potential difference between two silver-silver chloride electrode (D and D'), each of which was connected to the electrolyte through a salt bridge. The potential difference was recorded on a pen recorder (Nippon Denshi Kagaku Co. Ltd., Unicorder U228) through a micro voltmeter (Toa Electric Ltd., PM-16R). In order to measure the streaming potential, the electrolyte was forced to flow through the plug under a given pressure. Nitrogen gas from a cylinder was used to maintain the pressure necessary for the measurements.

Measurements of adsorbed Cu²⁺ and SO₄²⁻ on α -alumina.—Twenty grams of α -alumina particles were added to 50 ml of acid copper sulfate bath (0.5M CuSO₄ + 0.5M H₂SO₄). After 30 min agitation of the bath, the suspension was allowed to stand for 3 days with occasional shaking. Then the α -alumina particles were separated by centrifugation. The supernatant solution was sucked up and the concentration of remaining Cu²⁺ and SO₄²⁻ was analyzed, respectively.

The Cu²⁺ concentration was determined by the EDTA chelatometric titration method. The SO₄²⁻ concentration was determined gravimetrically. The SO₄²⁻ was precipitated by the addition of excess amounts of BaCl₂ solution, and the BaSO₄ particles were separated by filtration, washed with distilled water, followed by ignition in the crucible, and then weighed on a microbalance.

The concentration of both Cu²⁺ and SO₄²⁻ in the particle-free solution was also determined by the same methods described above. The amounts of each ion adsorbed on the particles were calculated from the difference between the concentration after particle addition and that before particle addition, with errors of about 1% for SO₄²⁻, about 5% for Cu²⁺, respectively.

Measurement of pH shift in the solution due to the successive addition of particles.—Adjustment of pH in the bath (50 ml 0.5M CuSO₄) was carried out by adding sulfuric acid or copper hydroxide. The procedures of measuring solution pH shift were as follows. At first, 1 g of α -alumina

was added to the solution. After 2 min vigorous agitation by using a magnetic stirrer, the solution was allowed to stand for 1 min and the pH was measured by a pH meter (Toa Electric Ltd., HM-26S). Then, the next 1 g of α -alumina was added to the same solution and the pH was measured by the same method mentioned above. These procedures were repeated up to a total amount of α -alumina of 32 g.

When the initial pH of the bath was adjusted to the value where α -alumina acts as Brønsted acid, the solution pH decreased with the addition of particles. This tendency of pH shift due to the particle addition was reversed when the initial pH was adjusted to the value where α -alumina acts as Brønsted base. When the solution pH does not change at all by the addition of any amounts of α -alumina particles, the pH value of the solution corresponds to the EABP¹³ (equi-acid-base point) of α -alumina in this system. EABP value can be determined by solution pH change according to the reaction between the oxide surface and the species dissolved in the solution. EABP is in accordance with pzc under the condition that only H⁺ and OH⁻ interact with the oxide surface.

Results

Amounts of incorporated α -alumina.—Figure 2 shows the relation between the amount of incorporated α -alumina particles and the concentration of the particles in an acid copper sulfate bath. The amount of incorporated particles increased with an increase of the concentration of the particles approaching a plateau value at high particle concentration regardless of the current density. The shape of the curve was similar to the well-known Langmuir adsorption isotherm. The tendency of the codeposition behavior to lead off at high particle concentration apparently led Guglielmi to use the Langmuir adsorption isotherm.¹ It should be emphasized that the amounts of incorporated α -alumina of 0.5 μ m go up to about 5 w/o and are much larger than those reported in the literature for 0.3 μ m α -alumina.⁶

The results obtained from a copper nitrate bath were also shown in Fig. 3. The amounts of incorporated α -alumina particles were found to be comparable with those obtained from a copper sulfate bath.

Streaming potential of α -alumina.—Figure 4 shows typical examples of the relationship between streaming potential and the pressure difference between the plug. Each set of the data follows a straight line. Therefore, it is clear that the measurements are so successful even when used in concentrated solution. The values of zeta potentials (ζ) are calculated from Helmholtz-Smoluchowski equation

$$\zeta = \frac{4\pi\eta\kappa E}{DP} \quad [1]$$

Here, η , κ , D , E , and P are the viscosity of the solution, the specific conductance of the electrolyte, dielectric constant of the solution, streaming potential, and applied pressure, respectively. The value D is taken as 79, which is dielectric

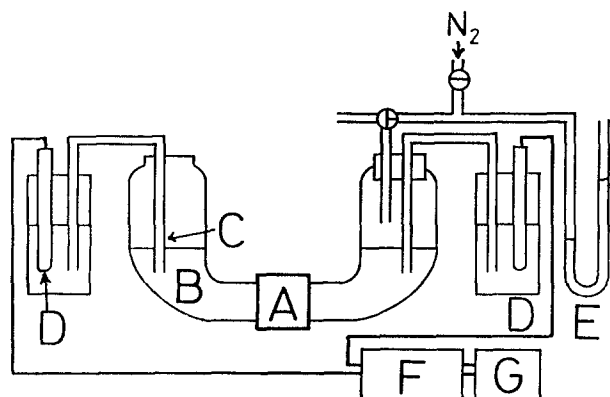


Fig. 1. Schematic diagram of streaming potential apparatus A: Plug B: Electrolyte solution C: Salt bridge D: Ag/AgCl electrode E: High manometer F: Microvolt meter G: Pen recorder.

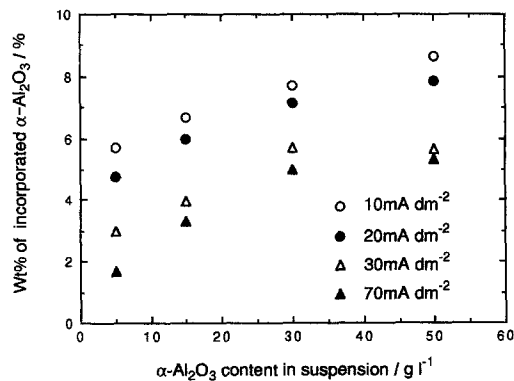


Fig. 2. The amounts of codeposited α -Al₂O₃ vs. α -Al₂O₃ content in 0.5M CuSO₄ + 0.5M H₂SO₄.

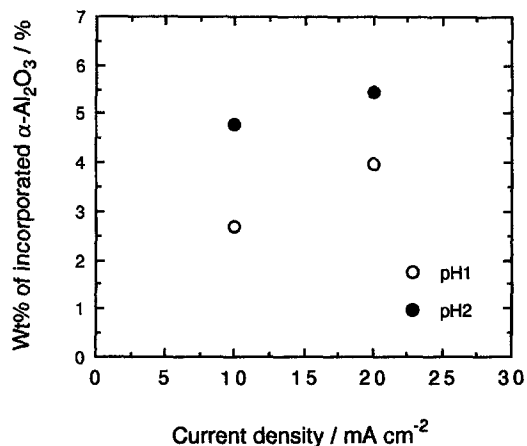


Fig. 3. The amounts of codeposited α -Al₂O₃ vs. α -Al₂O₃ content in 0.5M Cu(NO₃)₂ with 20 g/l of α -Al₂O₃.

constant for water at 25°C. Figure 5 shows the values of zeta potential of α -alumina as a function of solution pH. In the copper sulfate solution, all the zeta potentials were negative, decreasing with a decrease of solution pH. However, in the copper nitrate solution, the zeta potential was positive in the whole pH range studied. Therefore, it is confirmed that zeta potential of α -alumina is influenced by anions as well as H⁺ ions in the plating bath.

Adsorption analysis.—The amounts of adsorbed Cu²⁺ and SO₄²⁻ from an acid copper sulfate bath (CuSO₄ 5H₂O 0.5M, H₂SO₄ 0.5M) were determined to be $(2.2 \pm 0.1) \times 10^{-6}$ mol/g-alumina and $(1.5 \pm 0.1) \times 10^{-5}$ mol/g-alumina, respectively. The α -alumina particle used has a specific surface area of 4.1 m² g⁻¹, which was determined by BET method, so the numbers of adsorbed Cu²⁺ and SO₄²⁻ ions per nm² of the oxide surface are 0.3 and 2.2, respectively, provided that the surface of the particle is homogeneous. The ratio of the adsorbed SO₄²⁻ to Cu²⁺ ions corresponds to 6.8. Therefore, it is believed that the negative sign of zeta potential of α -alumina in a copper sulfate solution is brought about by the excess of adsorbed SO₄²⁻ on the surface. Adsorbed SO₄²⁻ compensates for the positive charge from adsorbed H⁺ and Cu²⁺, and gives excess negative charge to the particle.

It was confirmed that α -alumina particle adsorbs Cu²⁺ ion from copper nitrate bath (Cu(NO₃)₂, 0.5M, pH = 1). However, the adsorption of NO₃⁻ on the particle from copper nitrate bath could not be determined.

pH shift in the solution due to the successive addition of α -alumina particle.—Figure 6 shows the relation between the added amounts of α -alumina and solution pH observed

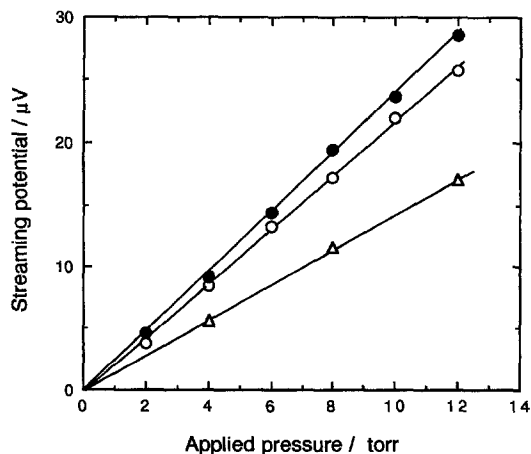


Fig. 4. The relationship between observed streaming potential and applied pressure for α -Al₂O₃ particles in 0.5M CuSO₄. ○: pH = 0.6, ●: pH = 1.0, △: pH = 2.7.

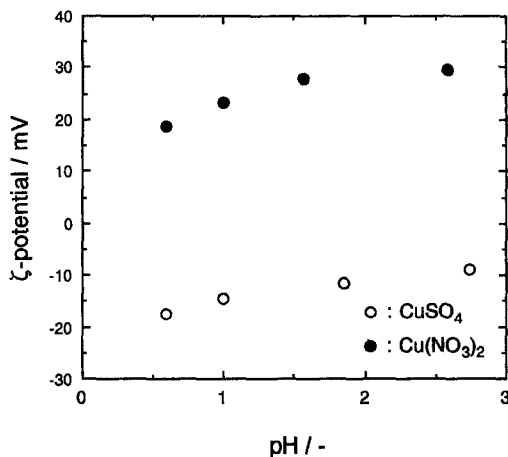


Fig. 5. Relation between ζ -potential of α -Al₂O₃ particle and solution pH for 0.5M CuSO₄ and 0.5M Cu(NO₃)₂.

after 2 min agitation and 1 min standing, when the initial pH was adjusted to 3.5 by using sulfuric acid or copper hydroxide. In the case of 0.5M K₂SO₄, the solution pH increased with an addition of α -alumina particles, then approached a pH of 8, which is close to the IEPs (Iso Electric Point of Solid) of α -alumina reported by Parks.¹⁴ In 0.5M CuSO₄, the solution pH also increased with an addition of α -alumina, but approached a pH value of 4.1. When the initial pH of the copper sulfate solution was adjusted below 2.0, the tendency of pH shift remained unchanged and the observed pH also converged to about 4.1. This pH value of 4.1 corresponds to the EABP of α -alumina particles in this bath. By titrating CuSO₄ solution with 0.5M KOH, the pH value at which copper hydroxide starts to precipitate was determined. The observed pH value for 0.5M CuSO₄ was 4.1 that is close to the observed EABP.

Discussion

In a number of articles concerning the codeposition behavior, it has been stated that the particles become positively charged when metal cations adsorb on the surface of the particle. It should be emphasized that the charged state reported in the literature was determined simply by electrokinetic potential measurements in diluted solutions. Assuming that the cathode during the electrolysis is negatively charged, an electrostatic attractive force prevails between the cathode and the particle, as far as the particle has a positive charge. Therefore, the positively charged particles may become incorporated into the metal matrix. On the other hand, negatively charged particles cannot be incorporated into metal matrix, because the repulsive force is acting between the particles and the cathode.

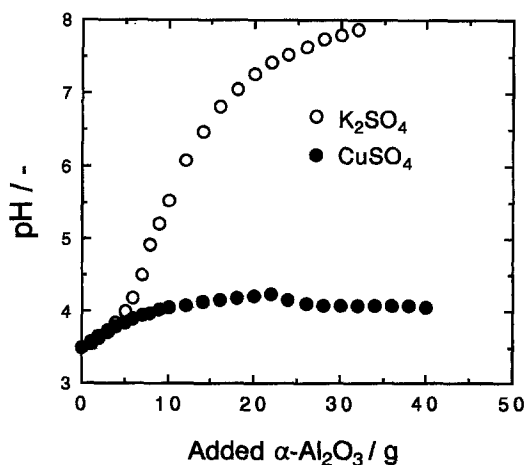


Fig. 6. pH shift for successive particle addition: 0.5M CuSO₄, 0.5M K₂SO₄ initial pH = 3.5.

Although the mechanism described above can interpret the codeposition behavior when the zeta potential of particles shows positive sign, it never accounts for the codeposition behavior of negatively charged particles whose zeta potential is negative.

Results of this study clearly indicated that the amounts of incorporated α -alumina particle from an acid copper sulfate bath can reach more than 5 w/o, in spite of their negatively charged state. Considering various conflicting reports on the codeposition behavior, the interaction at the interface between the particles and the solution should be examined more profoundly.

When the α -alumina particle is in contact with an acid copper sulfate bath, the following three reactions can take place: Reaction between H^+ in the bath and the surface of the oxide, Reaction between Cu^{2+} in the bath and the surface OH groups, and Adsorption of SO_4^{2-} on the surface of the oxide.

Reaction between H^+ in the bath and the surface of the oxide.—The surface of the sparingly soluble oxides is generally covered with OH groups.¹⁵ When the oxides are placed in a solution, adsorption of H^+ or dissociation of the surface OH groups begins. Consequently, the surface of the oxides becomes charged. Such acid-base reactions depend not only on the nature of the solid oxide but also the solution pH.

When the amount of surface excess H^+ is equal to that of OH^- , the observed solution pH value should correspond to the pzc (point of zero charge) of this system. In the pH ranges below the pzc, the excess H^+ will be adsorbed on the oxide surface, while in the pH ranges above the pzc, the oxide surface will adsorb excess OH^- or release H^+ .

The surface-chemical characteristic values of the oxides such as IEPS or pzc that have been compiled from a number of sources are based on the measurements in the presence of 1:1 type supporting electrolyte. The adsorbed species on the oxide particle and their quantity can be estimated from the pzc of the oxide, surface area of the oxide, and the solution pH, under the condition that only H^+ and OH^- interact with the oxide surface.

Reaction between Cu^{2+} in the bath and the surface OH groups.—The amount of adsorbed Cu^{2+} was determined to be $(2.2 \pm 0.1) \times 10^{-6}$ mol/g-alumina. As shown in Fig. 6, the EABP of the α -alumina particle in acid copper sulfate bath was lower than the pzc. The same tendency was also observed for a copper nitrate bath. As a result of acid-base reaction of α -alumina and the bath, pH value at the oxide surface may increase with the formation of copper hydroxide as a result. In such a case, the pH value should approach 4.1, the value at which the copper hydroxide starts to precipitate. The observed pH value for α -alumina particle addition converged to 4.1. These results indicate that Cu^{2+} interacts with the oxide surface as a consequence of Brønsted basic behavior of the oxide in the bath.

Adsorption of SO_4^{2-} on the surface of the oxide.—The zeta potential of α -alumina particles in acid copper sulfate bath was found to be negative. According to the Stern model, the electrical double layer is divided into two parts, compact layer and the diffuse layer. The zeta potential is equal to the potential at the slipping plane which is located in the diffuse double layer. From adsorption analysis, it was found that excess amounts of SO_4^{2-} are adsorbed on the

α -alumina surface. The adsorbed SO_4^{2-} compensates the excess positive charge resulting from adsorbed H^+ and Cu^{2+} , and gives excess negative charge to the surface and develops a net negative zeta potential. There is a possibility that SO_4^{2-} adsorption on the oxide surface enhances the interaction between Cu^{2+} and surface OH group.

In order to incorporate the particle into the metal matrix, the particle must attach to the cathode during the codeposition process. Codeposition of the α -alumina particle is possible both from an acid copper sulfate bath and a copper nitrate bath. As shown above, Cu^{2+} ions interact with the surface of the oxide regardless of the anion in the bath and shift the EABP to values smaller than the pzc. The α -alumina particle can be incorporated into the metal matrix when Cu^{2+} ions are adsorbed on the surface of the particle.

Conclusion

In a concentrated solution such as a plating bath, zeta potential of suspended particles can be measured using streaming potential method as well as in dilute solution. The zeta potential obtained gives important information concerning the charged state of the particles and the chemical species adsorbed on the surface of particles in the plating bath.

α -alumina particles of 0.5 μm (AKP-20) can be codeposited from a copper sulfate bath and, amounts of codeposited particles were found to be greater than those reported for 0.3 μm α -alumina in the literature, in spite of the negative sign of zeta potential. This indicates that the electrostatic interaction between the particles and the cathode is not the essential factor in the codeposition process.

The EABP value of α -alumina particles in the acid copper sulfate bath was much lower than the pzc of the particles. This indicates that the surface of the oxide interacts not only with the protons and hydroxide ions but also with Cu^{2+} ions in the plating bath.

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