Formation of Compositionally Graded Ni-P Deposits Containing SiC Particles by Jet Electroplating

Hiromitsu Takeuchi[†], Yoshiki Tsunekawa and Masahiro Okumiya

Toyota Technological Institute, Hisakata, Tempaku, Nagoya 468, Japan

This paper presents a new electroplating process that uses an electrolyte jet containing SiC particles for the formation of electrodeposited Ni-P matrix composite coatings. The electrolyte jet remarkably increases the limiting current density in electroplating, so that the deposition rate will be approximately 10 times faster than that of conventional electroplating without an electrolyte jet. The fast deposition rate is caused by the thin diffusion layer adjacent to the cathode surface due to the electrolyte jet. The jet velocity determines the volume fraction of SiC particles in the range of 0–30 vol% without changing the particle concentration in electrolytes. The phosphorus content in deposits is also controlled by the jet velocity without changing the phosphinic acid concentration in electrolytes. Hence, the jet electroplating realizes SiC particle/Ni-P deposits with a compositional gradient regarding the phosphorus content and the particle volume fraction with an extremely fast deposition rate.

(Received July 17, 1996)

Keywords: electroplating, electrolyte jet, composite coating, deposition rate, limiting current density, compositional gradient, SiC particle, nickel-phosphorus matrix

I. Introduction

In automotive industries, material substitutions from ferrous components to aluminum alloys or other low-density materials have been promoted from weight-lightening and fuel economy viewpoints. Since aluminum alloys are not hard enough to use in wear resistant applications with high load bearing, surface modification, such as surface alloying or coating, must be carried out. Composite electroplating containing ceramic reinforcements or self-lubricant particles is a typical surface coating process. For example, composite electroplating of a SiC particle/Ni-P system has been applied to the bores of cylinder blocks⁽¹⁾. However, the composite electroplating process even now has serious problems, such as a slow deposition rate and difficulty in controlling particle volume fraction.

The authors⁽²⁾ applied an electrolyte jet to the composite electroplating of an Al₂O₃ particle/nickel system, since jet electroplating has been known as a fast deposition process in copper electroplatings without any ceramic reinforcements⁽³⁾⁽⁴⁾. The electrolyte jet enables not only a fast deposition rate because of a rise in the limiting current density, but also makes possible volume fraction control of the particles by changing the jet velocity⁽²⁾.

In the present research, an electrolyte jet containing SiC particles is applied to the composite electroplating of a SiC particle/Ni-P system. In this particular composite system^{(1)(5)–(8)}, it is known that the deposit characteristics are influenced by the phosphorus content as well as the volume fraction of SiC particles⁽⁵⁾. In addition to an improvement in deposition rate and control of the particle volume fraction, this research is aimed at making control

of the phosphorus content possible by the use of the electrolyte jet. As a typical application of the volume fraction of SiC particles and the phosphorus content control, we discuss the compositional gradient Ni-P deposits in relation to the particle volume fraction and the phosphorus content, which increase in the thickness direction.

II. Experimental Procedures

A piece of extruded aluminum alloy (Al-10.2 mass% Si-7.68 mass% Cu) was employed as a substrate. The circular plating area was 6 mm in diameter and the rest of the area was insulated by an epoxy resin coating. Prior to electroplating, the substrates were polished by buffing with fine Al₂O₃ powder and water, and then pretreated through a conventional galvanizing process to suppress poor adhesion of deposits due to oxide films on the substrate. A nickel sulfamate bath was used as the fundamental electrolyte, to which phosphinic acid was added as a phosphorus source alloyed with nickel matrix. The chemical composition of the electrolyte and the electroplating conditions are listed in Table 1. As an incorporated ceramic reinforcement, α -SiC particles with an average diameter of 0.7 μ m were supplied. The particles were a massive type shown in the scanning electron micrograph of Fig. 1.

Figure 2 shows a schematic diagram of the jet electroplating system used in the present study. It consists of a jet electroplating cell to form SiC particle/Ni-P composite coatings and a stirring bath to disperse the particles uniformly into the electrolyte. The electrolyte containing a given amount of particles was impinged on the substrate through a nozzle with a diameter of 9 mm. Then the electrolyte was constantly recirculated back in the stirring bath. The electrolyte jet velocity was controlled by

[†] Graduate Student, Toyota Technological Institute.

Table 1 Bath composition and electroplating conditions.

Chemicals	Concentration (kg/m ³)
Ni(NH ₂ SO ₄)·4H ₂ O	430
NiCl ₂ ·6H ₂ O	15
H ₃ BO ₃	45
H ₃ PO ₂	0.5, 5.0
C ₇ H ₅ NO ₃ S	5
Bath temperature (K)	328
pH	2.0
Electricity (C)	55

Fig. 1 Scanning electron micrograph of α -SiC particles with an average diameter of 0.7 μm .

Fig. 2 Schematic diagram of the jet electroplating system.

an inverter and a valve. The nozzle was made of pure nickel which was used as an anode. The nozzle tip was made of an acrylic resin pipe so as to prevent a change in diameter during electroplating.

The particle volume fraction in deposits was calculated using stereology⁽⁹⁾. The fields of vision were firstly selected at a given position of cross-sectional deposits, in which all the cross-points (N_a) were arranged equidistantly. Then, the number of cross-points (N_p) inside the cross-sectional particle peripheries was counted. The ratio of N_p to N_a in the field of vision is the area fraction

of particles, which is approximately equal to the particle volume fraction in deposits. In the present research, we took optical micrographs with a magnification of 1000 showing the cross-sectional deposits. Then, we placed 400 cross-points in an equidistant arrangement within every field of vision. The volume fraction was an average value obtained from 10 fields of vision.

Optical microscopy observations and electron probe microanalysis (EPMA) were performed to characterize the electrodeposited nickel alloy matrix composites. Hardness profiles were also determined on the cross-sectional deposits with a Knoop hardness tester. The phosphorus contents in deposits were measured with a photoelectric spectrometer.

III. Results and Discussion

1. Improvement of deposition rate by electrolyte jet

According to Faraday's law, deposition rate depends on cathode current density (i) if current efficiency is constant. It is necessary that electroplating is carried out at high i to obtain a fast deposition rate. At first, the relationship between jet velocity (v_j) and limiting current density (i_L) was clarified in jet electroplating, as shown in Fig. 3, as a function of v_j , where the SiC particle concentration (C_{SiC}) in electrolyte was 100 kg/m³. The relation obtained in the electrolyte without any particles was also described in Fig. 3 for comparison with that in the electrolyte mixed with particles. The electroplating at $v_j = 0$ m/s was conventional one in which only aeration and no jet was employed. The i_L obtained with particles is consistent at any v_j with those without particles, regardless of the amount of particles in electrolytes. Therefore, i_L does not depend on C_{SiC} in the electrolyte, but rather on v_j . A rate of increase in i_L gradually decreases as v_j increases, although an increase of 4.0 m/s in v_j causes an increase of 120×10^2 A/m² in i_L , which is 15 times larger than in conventional electroplating without a jet. Hence, the application of an electrolyte jet to composite electroplating remarkably improves the deposition rate.

Fig. 3 Effect of jet velocity on limiting current density in SiC particle/Ni-P jet electroplating.

Fig. 4 Optical micrographs of cross-sections of SiC particle/Ni-P deposits electroplated for 240 s ($C_{\text{SiC}}=50 \text{ kg/m}^3$), (a) jet plating ($v_j=1.2 \text{ m/s}$, $i=80 \times 10^2 \text{ A/m}^2$), (b) conventional plating ($i=8 \times 10^2 \text{ A/m}^2$).

Electrodeposition is generally composed of three elemental steps: a transfer of metal hydration ions, a transfer of electrical charges and crystallization. The deposition rate is governed by the transfer of metal hydration ions, which is the slowest of the three steps. The application of an electrolyte jet to electroplating improves the transfer of metal hydration ions due to the forced supply of nickel hydration ions. In electrodeposition, there exists a diffusion layer with a concentration gradient of nickel hydration ions formed adjacent to the cathode surface. If i exceeds the i_L , the concentration of nickel ions becomes nearly zero on the cathode surface because of the excess consumption of nickel ions due to fast crystallization and the lack of supplied nickel ions. The electrochemical reaction will be thereby stopped. However, the electrolyte jet forcibly supplies a great quantity of nickel hydration ions and makes the diffusion layer extremely thin. Consequently, the i_L becomes very high due to the electrolyte jet. The electrolyte jet, however, improves only the transfer rate of metal hydration ions, so that the i_L is saturated in a range governed by the transfer of electrical charges and crystallization.

It is known that composite coatings with the dispersed particle volume fraction of 5–15 vol% show good wear resistance⁽¹⁰⁾. By using an electrolyte containing SiC particles of 50 kg/m^3 , we formed Ni-P matrix composite coatings with SiC particle volume fraction (V_{SiC}) of 15 vol% as a typical example. Figure 4 presents optical micrographs showing a particle distribution of cross-sectional coatings formed by (a) jet electroplating and (b) conventional where both plating times were 240 s, and i was

$80 \times 10^2 \text{ A/m}^2$ and $8 \times 10^2 \text{ A/m}^2$, respectively, which corresponded to each i_L . The thickness ratio of deposit (a) to (b) is approximately 10, which is the same as the i ratio in both electroplatings. Hence, the deposition rate of jet electroplating increases 10 times faster than in conventional one at $V_{\text{SiC}}=15 \text{ vol\%}$, although the rate depends on the required V_{SiC} .

2. Control of particle volume fraction by jet velocity

In order to clarify the effect of jet velocity (v_j) on the volume fraction of SiC particles (V_{SiC}) in deposits, we performed jet electroplating at various v_j with a particle concentration (C_{SiC}) of 50 kg/m^3 in the electrolyte. Typical optical micrographs are shown in Fig. 5. Measured V_{SiC} values are approximately (a) 15 vol%, (b) 5 vol% and (c) 0 vol%, respectively. The results concerning the amount of incorporated SiC particles show a tendency for V_{SiC} to decrease with increasing v_j . Although all deposits should have the nearly same volume of Ni-P matrix because of the same electricity in electroplating, the deposit (a) containing 15 vol% of SiC particles is the thickest of them. The difference in thickness arises from the V_{SiC} , the change in which is summarized in Fig. 6 as a function of v_j . While the current density (i) was selected to be the limiting current density (i_L) at each v_j , V_{SiC} is changed from 30 vol% to approximately 0 vol%, corresponding to $v_j=0.5 \text{ m/s}$ to 16.0 m/s . Herein, V_{SiC} is controlled by changing v_j at constant C_{SiC} in the electrolyte. Since v_j also affects the i_L , as mentioned previously, the application of an electrolyte jet to electroplating realizes composite coatings containing the required V_{SiC} with an extremely fast deposition rate.

The codeposition mechanism of jet electroplating seems to be as follows. Nickel hydration ions exist as anion clusters on the surfaces of SiC particles in the electrolyte. SiC particles enveloped by nickel hydration ions are forcibly transferred to the cathode surface by an electrolyte jet. Then, nickel hydration ions adsorbed on the SiC particles become nickel atoms after dehydration and reduction immediately adjacent to the cathode surface. In contrast, the particles directly contact the cathode surface and are simultaneously covered with crystallized nickel. In the previous research on the jet electroplating of an Al_2O_3 particle/nickel system⁽²⁾, we also confirmed that the volume fraction of Al_2O_3 particles decreases with increasing v_j . However, compared with the jet velocity of the present SiC particle/Ni-P system, the volume fraction of Al_2O_3 particles obtained in the jet electroplating is smaller than the V_{SiC} incorporated at the same v_j . This difference presumably arises from the amount of nickel hydration ions adsorbed on each particle surface, which have different specific areas and dielectric constants.

3. Control of phosphorus content by current density and jet velocity

In order to understand the relationship between the phosphorus content (C_P) and current density (i), we used two types of electrolytes, in which the phosphinic acid concentrations were 5.0 kg/m^3 and 0.5 kg/m^3 , respec-

Fig. 5 Optical micrographs of cross-sections of SiC particle/Ni-P deposits with jet velocity of (a) 1.2 m/s, (b) 6.0 m/s and (c) 16.0 m/s, $C_{\text{SiC}} = 50 \text{ kg/m}^3$, current density=limiting current density, electricity=55°C.

tively. As shown in Fig. 7, C_P decreases as i increases in both electrolytes. Brenner⁽¹¹⁾ and Ross⁽¹²⁾ also earlier reported that C_P decreases as i increases in conventional electroplating, which is consistent with the present result. It is known that metalloid atoms such as phosphorus and boron are not directly electrodeposited from electrolytes⁽¹³⁾⁽¹⁴⁾. Phosphorus atoms seem to be incorporated by nickel deposit in such a way that phosphorus atoms are adsorbed on the nickel on the cathode, and then nickel atoms successively deposit around the adsorbed phospho-

Fig. 6 Effect of jet velocity on volume fraction of SiC particles in deposits.

Fig. 7 Effect of current density on phosphorus content in deposits.

Fig. 8 Effect of jet velocity on phosphorus content in deposits.

rus atoms. At lower i , that is, a slower deposition rate, there is enough time for the phosphorus adsorption on nickel atoms electrodeposited on the cathode. As a result, C_P increases as i decreases at constant v_j , although the deposition rate is remarkably fast in jet electroplating.

Using the same electrolytes as above, the effect of v_j on C_P is determined, as shown in Fig. 8. Herein, C_P increases with v_j which is a second variable at constant i . A diffusion layer with a concentration gradient of phospho-

rus is also formed on the cathode surface. The fast v_j makes for a thin diffusion layer, because it supplies phosphorus atoms forcibly on the cathode surface. Since C_P increases with v_j at constant i , C_P is controlled by changing i and v_j without having to prepare the electrolytes with different phosphinic acid concentrations.

4. Formation of SiC particle/Ni-P deposits with a compositional gradient

(1) Deposits with a compositional gradient of phosphorus

We attempted to form the composite coatings with a phosphorus content (C_P) gradient by jet electroplating,

Fig. 9 Characteristic X-ray intensity and microhardness profiles in a deposit with a compositional gradient of phosphorus. Electroplating conditions: jet velocity = 1.2 m/s, current density = (a) 80, (b) 60, (c) 50, (d) 35 and (e) 30×10^2 A/m².

Fig. 10 Characteristic X-ray intensity and microhardness profiles in a deposit with a compositional gradient of SiC particles. Electroplating conditions: jet velocity = (a) 16, (b) 9.0, (c) 4.0, (d) 2.0 and (e) 1.2 m/s, current density = (a) 135, (b) 90, (c) 55, (d) 40 and (e) 20×10^2 A/m².

so the volume fraction of SiC particles (V_{SiC}) was kept constant. The codepositions were performed with changing current density (i) at a constant jet velocity (v_j) of 1.2 m/s. With the electrolyte containing 50 kg/m³ of the SiC particles and 0.5 kg/m³ of phosphinic acid, we selected the intermittently decreasing i according to the results in Fig. 7. The change in i gives C_P values of 0.3, 0.4, 0.5, 0.6 and 0.7 mass% in the layers in the thickness direction.

An optical micrograph showing a particle distribution of the cross-sectional deposit obtained is presented in Fig. 9, which also includes the characteristic X-ray intensity profiles of EPMA, and the microhardness measured after the heat-treatment at 573 K for 3.6 ks. The phosphorus characteristic X-ray (P-K α) intensity profile clearly shows that the objective gradient of C_P is obtained by this technique. In the layer, V_{SiC} is constant in the thickness direction, and the microhardness increases with C_P .

(2) Deposits with a compositional gradient of SiC particles

A smaller volume fraction of particles is desired immediately adjacent to the substrate from an adhesion viewpoint. The particle volume fraction at the deposit surface, however, should be a required value predicted through the wear conditions and the counterbody. In order to realize this situation on deposits, we formed deposits with a compositional gradient of particles in the thickness direction by changing v_j during the jet electroplating process.

With the electrolyte containing SiC particles of 50 kg/m³ and phosphinic acid of 0.5 kg/m³, we selected intermittently decreasing v_j according to the results in Fig. 6 and also decreasing i to maintain constant C_P according to the results in Figs. 7 and 8. The change in v_j and i gives V_{SiC} values of 0, 4, 8, 12 and 15 vol% in respective layers, in the thickness direction. The electroplating time was decided so that the amount of nickel reduction was the same in each layer.

An optical micrograph showing the cross-sectional deposit formed is presented in Fig. 10, which also includes characteristic X-ray intensity profiles of EPMA, and a microhardness profile measured after the same heat-treatment as previously mentioned. The characteristic X-ray (Si-K α) intensity profile clearly shows that the objective gradient of V_{SiC} is obtained by this technique. In the layer, C_P is constant in the thickness direction, and the microhardness increases from $H_K 770$ to $H_K 940$ with V_{SiC} . Hence, composite coatings with a compositional gradient of SiC particles are realized by jet electroplating. In addition to the successful formation of codeposits with a compositional gradient, the deposition rate in the jet electroplating is remarkably high compared with that in conventional electroplating.

IV. Conclusions

An electrolyte jet containing SiC particles was used in the formation of Ni-P matrix composite coatings with a

compositional gradient of the phosphorus content and the particle volume fraction. The following results were obtained:

(1) The electrolyte jet remarkably increases the limiting current density, so that the deposition rate in jet electroplating is 10 times faster than that in conventional electroplating without a jet.

(2) The particle volume fraction decreases with increased jet velocity, so the particle volume fraction is controlled by jet velocity without changing the particle concentration in electrolytes.

(3) The phosphorus content is controlled not only by current density, but also by jet velocity without changing the concentration of phosphinic acid in electrolytes.

(4) Jet electroplating realizes SiC particle/Ni-P deposits with a compositional gradient of the phosphorus content and the particle volume fraction in the thickness direction with an extremely fast deposition rate.

Acknowledgment

Financial support from the Tatematsu Foundation is gratefully acknowledged.

REFERENCES

- (1) K. Funatani, K. Kurosawa, P. A. Fabiyi and M. F. Puz: SAE Tech. Paper Series, 940852, (1994).
- (2) M. Okumiya, H. Takeuchi and Y. Tsunekawa: J. Japan Inst. Metals, **59** (1995), 640.
- (3) R. C. Alkire and T. J. Chen: J. Electrochem. Soc., **129** (1982), 2424.
- (4) R. C. Alkire and J-B. Ju: J. Electrochem. Soc., **134** (1987), 294.
- (5) K. Masui: J. Surf. Finish. Soc. Japan, **40** (1989), 440.
- (6) X. Huang and Z. Deng: Plat. and Surf. Finishing, **80** (1993), 62.
- (7) O. Berkh, A. Bodnevas and J. Zahavi: Plat. and Surf. Finishing, **82** (1995), 62.
- (8) X. C. Zonggang and Z. Lijun: Plat. and Surf. Finishing, **75** (1988), 54.
- (9) E. E. Underwood: *Quantitative Stereology*, Addison-Wesley Pub. Co. MA, (1970), p. 37.
- (10) M. Onoda and T. Tsuchiya: J. Surf. Finish. Soc. Japan, **40** (1989), 1121.
- (11) A. Brenner, D. E. Couch and E. K. Williams: J. Res. Natl. Bur. Stand, **44** (1963), 109.
- (12) C. A. Ross, L. M. Goldman, and F. Spaepen: J. Electrochem. Soc., **140** (1993), 91.
- (13) R. L. Zeller and U. Landau: J. Electrochem. Soc., **139** (1992), 3464.
- (14) T. Watanabe, T. Kanayama: J. Surf. Finish. Soc. Japan, **40** (1989), 425.