

Nano-particles dispersion effect on Ni/Al₂O₃ composite coatings

Sheng-Lung Kuo^{a,*}, Yann-Cheng Chen^b, Ming-Der Ger^c, Wen-Hwa Hwu^c

^a Department of Chemical Engineering, National Chinyi Institute of Technology, No. 35, Ln. 215, Sec. 1, Chung-Sun Road, Taiping, Taichung, Taiwan, ROC

^b Graduate School of Defense Science, Chung Cheng Institute of Technology, National Defense University, Taipei, Taiwan, ROC

^c Department of Applied Chemistry, Chung Cheng Institute of Technology, National Defense University, Taipei, Taiwan, ROC

Received 7 May 2003; received in revised form 5 November 2003; accepted 5 November 2003

Abstract

Nano-alumina particles (80 nm) are easily agglomerated into larger particles in a nickel sulfamate bath with an average diameter of about 1109 nm. This leads to low alumina content in the composite coating. In this study, the diameter of alumina agglomerates was reduced with the decrease in electrolyte concentration. Alumina agglomeration was reduced to 178 nm at a bath concentration of 0.20 M nickel ions under 5 W l⁻¹, with 40 min ultrasonic energy treatment. Effective alumina particle dispersion in the electrolyte solution creates more opportunities for loose and strong adsorption of alumina particles onto the electrode. The Ni/Al₂O₃ composite coating was prepared with electrolyte concentration variations under reasonable electrochemical conditions. The alumina particle volume content in this composite coating was increased from 8.37 vol.% to a maximum value of 26.78 vol.%. The homogeneity of the composite coating is promoted with effective dispersion.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Dilute Ni bath; Alumina; Composite coating; Dispersion

1. Introduction

Composite coatings are produced by co-deposition of fine inert particles into a metal matrix from an electrolytic or electroless bath. This technique is receiving increased interest because of its ability to produce films with excellent mechanical properties such as wear resistance, corrosion resistance and lubrication [1–7]. These properties depend on the morphology of the inert particles in the composite coating. Furthermore, metal matrix nano-composite coatings exhibit unique magnetic, mechanical and optical properties and are promising materials for micro-devices. Nano-composite deposition may be useful in fundamental studies of their nano-metric nature.

Nano-Ni/Al₂O₃ composite coating is used primarily to increase the wear resistance of metal surfaces in micro-devices. Although the micro-Ni/Al₂O₃ composite coating grades have progressed tremendously, certain problems persist in its preparation. The volume content of alumina particles in Ni/Al₂O₃ composite coating cannot be controlled quantitatively and the particles are frequently agglomerated together in the composite coating. Breaux and Podlaha [8]

reported that the alumina particles are very easily agglomerated in the electrochemical electrolyte. This makes poor mechanical properties in composite coating. Podlaha [9] tried to alleviate this problem. The alumina weight content in the composite coating can be promoted from 3.5 to 14.6% using pulse-reverse (PR) electrodeposition. The mechanical properties are also improved.

However, the fine alumina particle dispersion is still a dilemma in composite coating preparation. The smaller inert particles are more difficult to embed into the deposition layer because of the inert particle dispersion difficulties in the electrolyte [10–13]. The content volume of the nano-particles in the composite coating was very low in many researches under common operating conditions [6,14,15].

Particles dispersed in a continuous electrolyte solution are in constant Brownian motion. When two particles approach one another, energies exist between the particles that determine whether the particles will separate or agglomerate. Generally, particle agglomeration occurs as a result of larger attraction energy than repulsion energy between the particles. The magnitude of the net forces involved in producing an agglomerated structure clearly depends on the conditions and the nature of system. Knowledge of the interfacial region structure is an important factor in understanding the dispersion stability of solid particles with the electrolyte.

* Corresponding author. Tel.: +886-2-04-2392450 ext. 7510;

fax: +886-2-04-23926617.

E-mail address: kuosl@chinyi.ncit.edu.tw (S.-L. Kuo).

To produce good alumina particle dispersion in a nickel sulfamate bath, a change in the inter-particle interfacial region by either chemical or physical methods is necessary. The chemical effect occurs when the particles contain adsorbed surfactants or macro-molecules to form electrostatic or steric interference within the inter-particles. Under certain conditions, this interference leads to repulsion arising from adsorbed layer mixing and loosing the configuration entropy in the inter-particles [16]. Conversely, the physical effect occurs when the particles absorb destructive energy such as ultrasonic energy. The propagation of ultrasonic waves in the liquid medium generates giant pressure (reaching thousands of pressure atmospheres), causing a mammoth stress that destroys the binding energy of the inter-particles. Gas bubbles from the cavity then intrude into the new inter-particle crevices to decrease the alumina particle agglomerated diameter. In our previous work [17], the average alumina agglomerate diameters in de-ionic water and nickel sulfamate baths, without applying ultrasonic energy, were 183 and 1109 nm, respectively. It seems that the ionic strength effect of the solution on the particle agglomeration cannot be ignored in the Ni bath. The average alumina agglomerated particle diameter can be reduced to 280 and 448 nm, respectively, using physical dispersion with applied ultrasonic energy and chemical dispersion from adding surfactants into the Ni bath.

Although the physical and chemical dispersion are considered in nano-composite coating electrochemical preparation, these methods limitedly dispersed the fine inert alumina particles in the nickel sulfamate bath. Because the ionic concentration of the electrolyte is considered an important factor in alumina particle effective dispersion, alumina particle dispersion is investigated in a diluted nickel sulfamate bath in this study. The corresponding effect on the composite coating is also discussed.

Table 1

Electro-co-deposition parameters of preparing Ni/Al₂O₃ composite coating

Component	Bath compositions (g l ⁻¹)	Parameter	Conditions
Ni(NH ₂ SO ₃) ₂	38–308	Temperature	50 °C
NiCl ₂ ·6H ₂ O	10	pH	4
H ₃ BO ₃	40	Current density	3 A dm ⁻²
Al ₂ O ₃ particle (80 nm)	5	Magnetic stirrer	5 cm
		Stirring rate	200 rpm

Every experiment runs under 5 W l⁻¹, 40 min ultrasonic energy treatment.

Table 2

Ni baths and their corresponding Ni²⁺ concentrations used in this research

Ni bath	Ni(NH ₂ SO ₃) ₂ (g l ⁻¹)	NiCl ₂ ·6H ₂ O (g l ⁻¹)	[Ni ²⁺] _{total} (M)
Ni-1	308.0	10	1.27
Ni-2	154.0	10	0.65
Ni-3	77.0	10	0.35
Ni-4	38.5	10	0.20

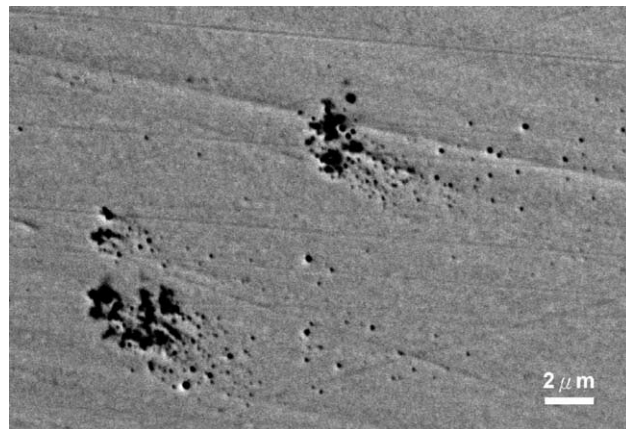
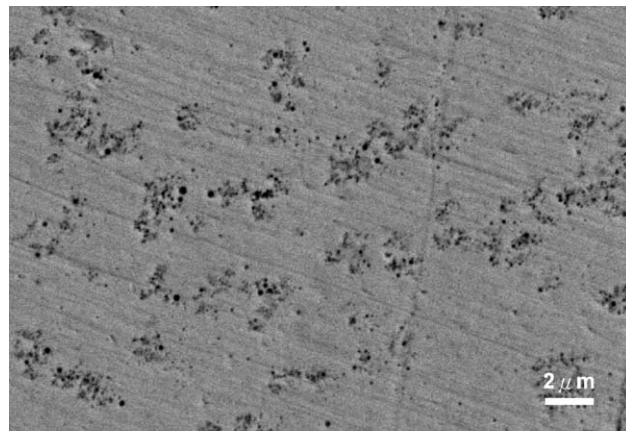
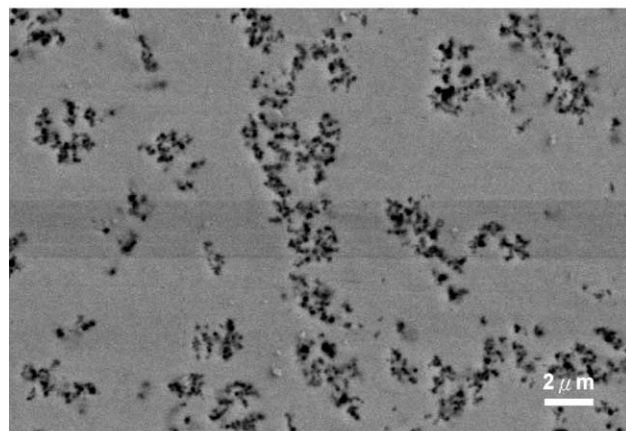


Fig. 1. SEM diagram of electrochemical composite coating comes from traditional Ni bath ([Ni²⁺] = 1.27 M), no ultrasonic energy treatment (Al₂O₃ = 1.42 vol.%); (temperature = 50 °C; pH = 4; current density = 3 A dm⁻²; Al₂O₃ = 5 g l⁻¹).



(a) physical dispersion (Al₂O₃: 4.16 vol.%)



(b) chemical dispersion (Al₂O₃: 6.78 vol.%)

Fig. 2. Ni/Al₂O₃ composite coating SEM diagram of electrochemical composite coating comes from (a) after 5 W l⁻¹, 40 min ultrasonic treatment and (b) the added surfactant (cetyltrimethyl ammonium bromide, CTAB) (temperature = 50 °C; pH = 4; current density = 6 A dm⁻²; Al₂O₃ = 5 g l⁻¹).

2. Experimental

The plating electrolyte is a nickel sulfamate bath. The bath composition and experimental process parameter ranges are shown in Table 1. Low carbon steel ($2.5\text{ cm} \times 4\text{ cm}$) was used as the electrode. Initially, the weighted (5 g l^{-1}) nano-alumina powder (80 nm, purity 98.0%, PL-PJ-ALO, Wah Lee Industrial Co., Taiwan) was placed into different concentrations of the original or diluted nickel sulfamate bath. The nickel ion concentration in different nickel sulfamate bath concentrations is shown in Table 2. After proper ultrasonic energy treatment, the particle size distribution was measured using the Zeta Plus (Brookhaven Instruments Co., New York, USA) instrument. The particle size analysis discusses the effect of Al_2O_3 particles dispersion in the electrolyte. The ultrasonic energy used in these experiments (Microson XL-2000 Ultrasonic Cell Disruptor, Misonix, USA) was 5 W in 1 l of Ni bath (W l^{-1}) at 40 min.

The electrochemical preparation of $\text{Ni}/\text{Al}_2\text{O}_3$ composite coating was performed at designated conditions in a well-stirred bath for 8 h. The composite coating morphology was observed using a SEM (S-3000, Hitachi) instrument in BSE (Back Scattered Electron) mode. The volume content, particle distribution and alumina particle weight content in the $\text{Ni}/\text{Al}_2\text{O}_3$ composite coating were analyzed using the

image analysis (Matrox Inspector 2.2) and EDX test methods, respectively.

3. Results and discussion

The nano-alumina particle agglomerate diameter (80 nm) in the Ni-1 bath without surfactant and ultrasonic energy treatment was 1109 nm. This leads to an ultra-low alumina content within the composite coating, as shown in Fig. 1. The alumina particle volume content in this composite coating was about 1.42 vol.% with an agglomerated structure. The average diameter of the alumina agglomerated particles could be reduced to 280 and 448 nm, respectively, using physical dispersion with applied ultrasonic energy and chemical dispersion with surfactants added into the Ni bath. The alumina particle volume contents in the electrochemical composite coating were 4.2 and 6.8 vol.% for the physical and chemical dispersions, respectively. These results are shown in Fig. 2. The fine inert alumina particles were limitedly dispersed in the Ni bath using these two methods because of the high electrolyte concentration and ionic valence of the bath. The bath concentration effect on the alumina particle dispersion was therefore investigated using a diluted nickel sulfamate bath.

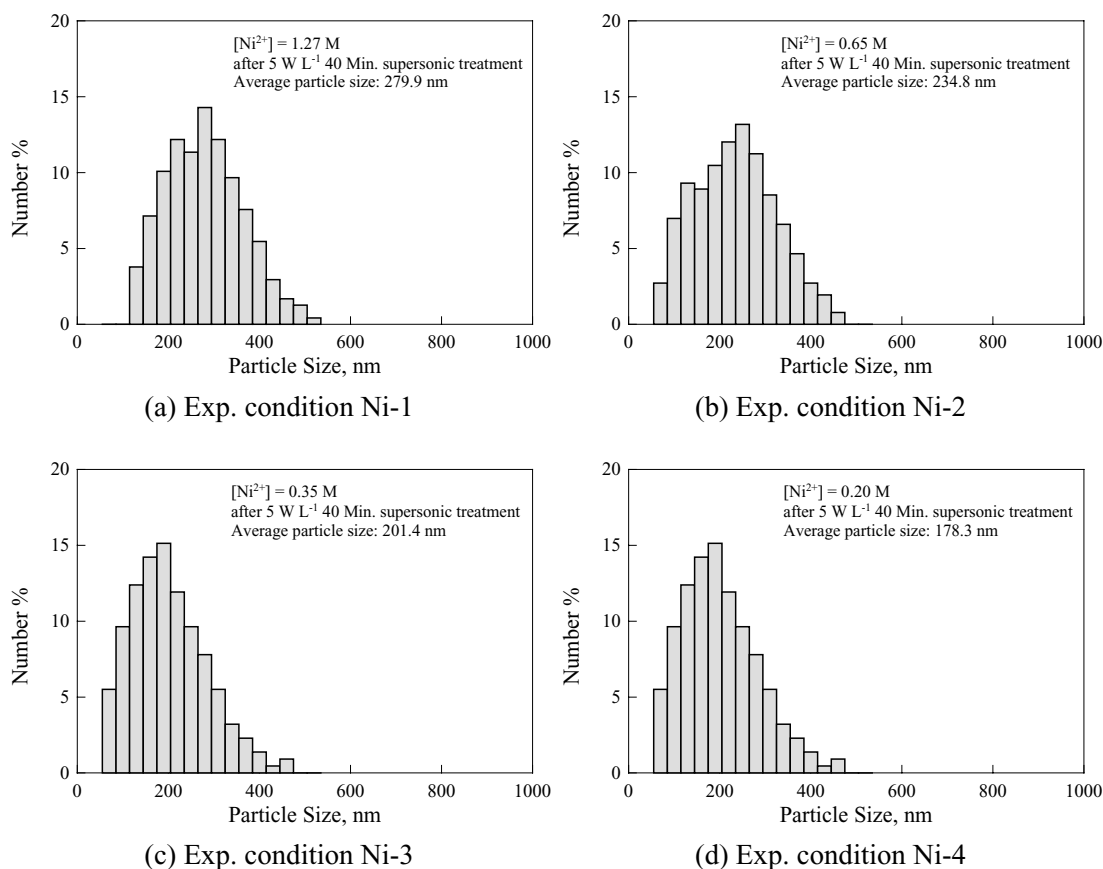


Fig. 3. Shows the average diameter of alumina agglomerates in different nickel baths: (a) Ni-1; (b) Ni-2; (c) Ni-3; (d) Ni-4.

Although the nano-alumina particles are easily agglomerated in the electrochemical electrolyte, the average agglomerate diameter can be reduced using decreased electrolyte concentrations. Fig. 3(a) shows the average diameter of the alumina agglomerates in the Ni bath under 5 W l^{-1} and 40 min ultrasonic energy treatments. To promote nano-alumina particles dispersion, the nickel ion concentration in the electrolyte was decreased. Fig. 3(b)–(d) shows the nickel ion concentration effects on the average alumina agglomerate diameter under 5 W l^{-1} and 40 min ultrasonic energy treatment. The average alumina particle agglomerated diameter was lowered to 178 nm at a bath concentration of 0.20 M nickel ions. The average alumina agglomerate diameter was influenced by the nickel ion concentration in the electrolyte.

The Ni/ Al_2O_3 composite coating was prepared using electrolyte concentration variations under the conditions shown in Table 1. Fig. 4 shows the alumina particle volume content in the Ni/ Al_2O_3 composite coating with decreased electrolyte concentrations. The alumina particle volume content in this composite coating was increased from 8.37 vol.% to

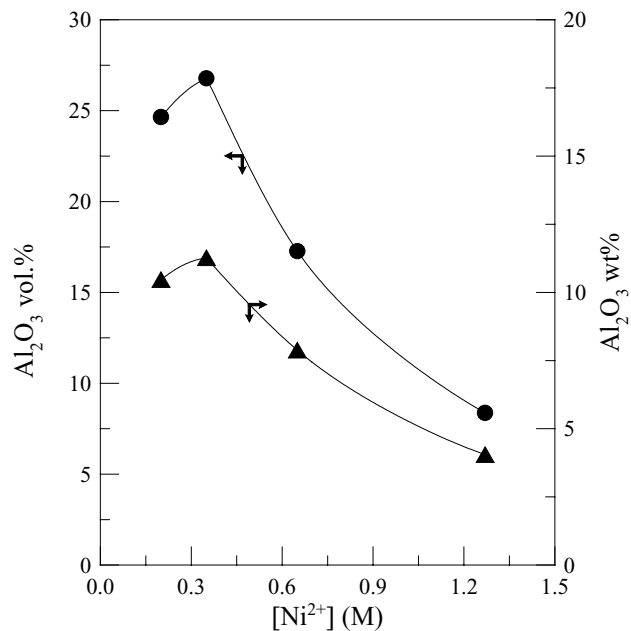
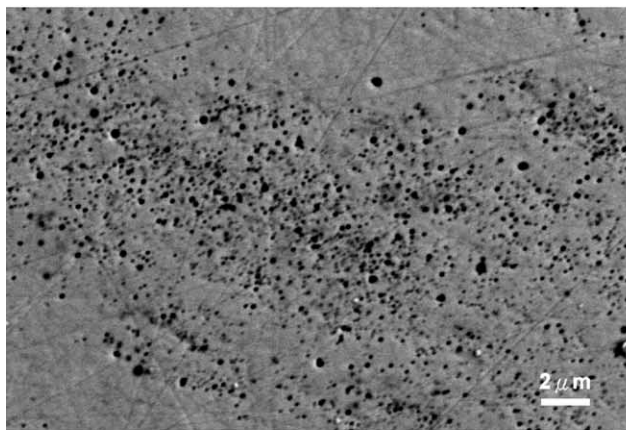
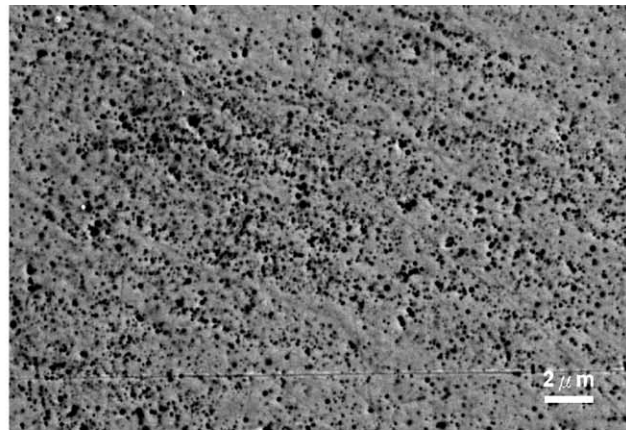


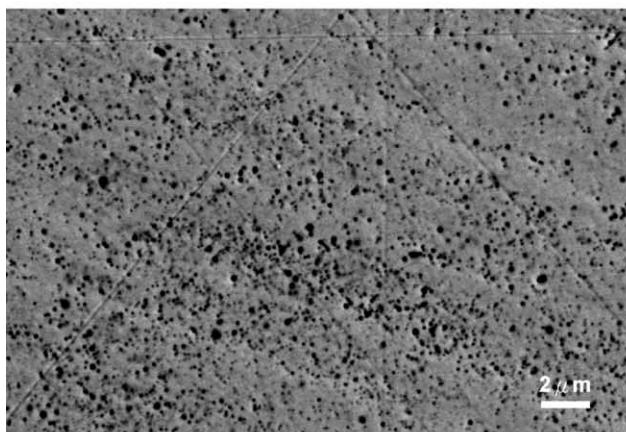
Fig. 4. Al_2O_3 (vol.%) by image analysis and wt.% by EDX test in Ni/ Al_2O_3 composite coating.



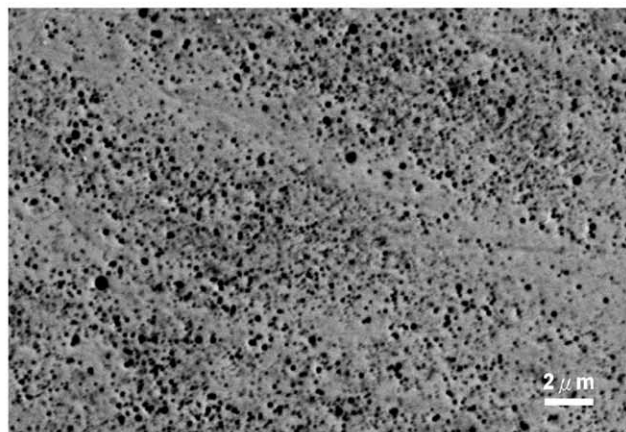
(a) Experiment condition Ni-1 (Al_2O_3 8.37 vol.%)



(c) Experiment condition Ni-3 (Al_2O_3 26.78 vol.%)



(b) Experiment condition Ni-2 (Al_2O_3 17.27 vol.%)



(d) Experiment condition Ni-4 (Al_2O_3 24.65 vol.%)

Fig. 5. The corresponding SEM diagram with the variation in nickel bath: (a) Ni-1; (b) Ni-2; (c) Ni-3; (d) Ni-4 (temperature = 50°C ; pH = 4; current density = 3 A dm^{-2} ; $\text{Al}_2\text{O}_3 = 5 \text{ g l}^{-1}$).

a maximum value of 26.78 vol.% initially, then slowly decreased to 24.65 vol.%.

According to Guglielmi's proposal [18] for the composite coating mechanism, this electrochemical reaction has two steps. The first step is called loose adsorption in that there is a layer of adsorbed ions and solvent molecules screening the interaction between the electrode and the particles. The second step is a strong adsorption that is thought assisted by the electric field, whereby a substantial electrochemical reaction produces strong particle adsorption onto the electrode. Effective alumina particle dispersion in the electrolyte solution creates higher particle density (particles per liter), and produces more opportunities for loose alumina particle adsorption onto the electrode. The smaller the agglomerated alumina particle groups, the higher the opportunity for attraction by the electric field, making effective strong adsorption.

Because the alumina particle dispersion within a nickel sulfamate bath is more effective when the electrolyte concentration is lower, it is not surprising that the alumina content volume of the Ni/Al₂O₃ composite coating is promoted with a lower nickel ion concentration in this electrochem-

Table 3

Current efficiency and alumina volume content in Ni/Al₂O₃ composite coating at different Ni bath (operation conditions as shown in Table 1)

Ni bath	Current efficiency (%)	Al ₂ O ₃ in composite coating (vol.%)
Ni-1	96.3	8.37
Ni-2	94.7	17.27
Ni-3	93.4	26.78
Ni-4	88.2	24.65

ical reaction. However, when the nickel ion concentration is too low, hydrogen ion reduction results in a lower current efficiency, as shown in Table 3. Therefore, the alumina particle volume content in the Ni/Al₂O₃ composite coating has a maximum value at about 26.78 vol.%.

The corresponding SEM diagram with the various electrolyte concentrations is displayed in Fig. 5. From this figure, the particle distribution in the composite coating is more uniform with a lower nickel ion concentration than with a concentrated electrolyte. Effective alumina particle dispersion in the electrolyte substantially benefits composite coating preparation in this electrochemical process. A

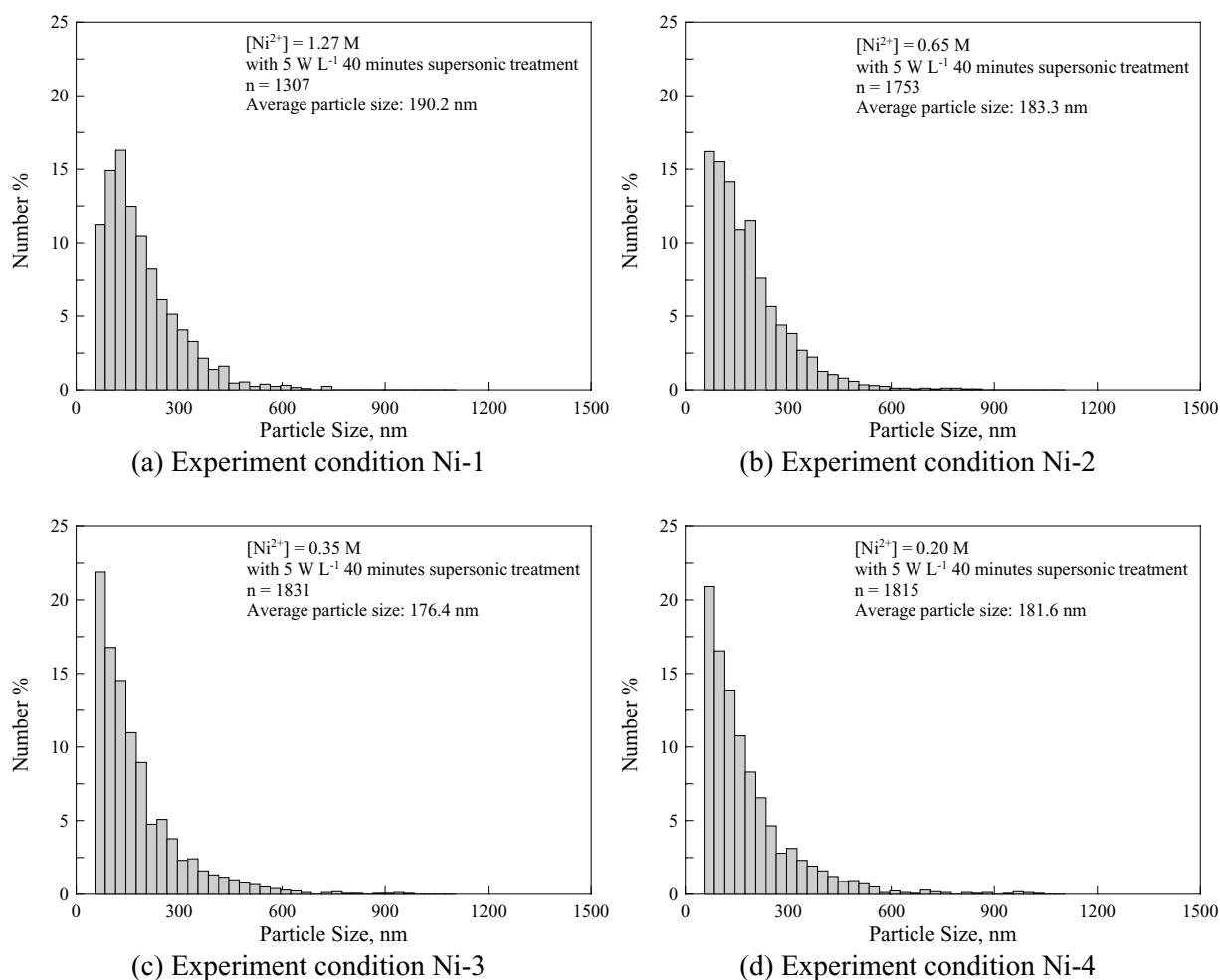


Fig. 6. The composite coating particle distribution corresponding to Fig. 5.

particle group will be engulfed by the growing metal when brought in contact with an electrode with enough foothold to remain on the electrode [19]. That is, a particles group could be embedded into the metal matrix when the attraction force between the particle group and electrode is stronger than the removing force on the electrode. Because it has a larger reactive area, the adsorption ability of a smaller particle group on the electrode from the applied potential in electrochemical process is stronger than that for larger particle groups. Therefore, the relative removing force of smaller particles is smaller than that for larger particles. It is also reasonable that the effective alumina particle dispersion in the electrolyte drastically benefits the increase in alumina particle content in Ni/Al₂O₃ composite coating preparation.

Fig. 6 exhibits the particle distribution of a composite coating corresponding to Fig. 5. The amount of alumina particles in the composite coating increased with the decrease in nickel ion concentration. The average diameter of the alumina agglomerates in the composite coating decreased slightly with the decrease in nickel ion concentration. The ratio of smaller particles in the coating was drastically increased with a dilute electrolyte concentration. However, the amount of alumina particles in the coating from the Ni-4 bath with an eight-fold dilute nickel ion concentration was not high as expected owing to the lower current efficiency. The hydrogen evolution on the cathode hinders alumina particle adsorption and leads to a lower particle content volume in the Ni/Al₂O₃ composite coating.

4. Conclusion

Nano-alumina particles are easily agglomerated in traditional electrochemical electrolyte that makes Ni/Al₂O₃ composite coating preparation difficult. The mean agglomerated diameter for alumina agglomerates was 1109 nm in a nickel sulfamate bath. The diameter of the agglomerated alumina particles could be reduced by applying ultrasonic energy or adding surfactants to the Ni bath. However, the resulting dispersion is limited using these two methods. Our results show that the alumina agglomerate diameter was further reduced with the decrease in electrolyte concentration. The alumina particle agglomeration diameter was reduced to 178 nm at a bath concentration of 0.20 M nickel ions under 5 W l⁻¹ and 40 min ultrasonic energy treatment.

Effective alumina particle dispersion in the electrolyte solution creates more opportunities for loose alumina particle adsorption onto the electrode. Smaller agglomerated alumina particle groups have a higher attraction force from the electric field that produced effective adsorption. The alumina particle volume content in the Ni/Al₂O₃ composite coating was increased from 8.37 vol.% to a maximum value of 26.78 vol.%. The homogeneity of the composite coating was better under effective dispersion.

Acknowledgements

The financial support from The National Science Council under Contract No. NSC-91-2214-E167-001 is gratefully acknowledged.

References

- [1] M. Ghouse, M. Viswanathan, E.G. Ramachandran, *Met. Finish.* 78 (3) (1980) 31.
- [2] C. Buelens, J.P. Celis, J.R. Roos, *J. Appl. Electrochem.* 13 (1983) 541.
- [3] J. Zahavi, J. Hazan, *Plat. Surf. Finish.* 70 (2) (1983) 57.
- [4] A. Hovestad, L.J.J. Janssen, *J. Appl. Electrochem.* 25 (6) (1995) 519.
- [5] H. Ferkel, B. Müller, W. Riehemann, *Mater. Sci. Eng. A234–A236* (1997) 474.
- [6] L. Benea, P.L. Bonora, A. Borello, S. Martelli, F. Wenger, P. Ponthiaux, J. Galland, *J. Electrochem. Soc.* 148 (2001) C461.
- [7] A.B. Viderine, E.J. Podlaha, *J. Appl. Electrochem.* 31 (2001) 461.
- [8] A.E. Breaux, E.J. Podlaha, in: *Proceedings of the 195th Society Meeting of the Electrochemical Society*, vol. 99-1, 1999 (abstract 2.13).
- [9] E.J. Podlaha, *Nano Lett.* 1 (8) (2001) 413.
- [10] G. Maurin, A. Lavanant, *J. Appl. Electrochem.* 25 (1995) 1113.
- [11] I. Garcia, J. Fransaer, J.P. Celis, *Surf. Coat. Technol.* 148 (2001) 171.
- [12] S.Y. Park, R.H. Kim, J.S. Kim, C.K. Kim, *J. Korean Surf. Eng.* 25 (2) (1992) 73.
- [13] K.H. Hou, M.D. Ger, L.M. Wang, S.T. Ke, *Wear* 253 (2002) 994.
- [14] I. Shao, P.M. Vereecken, R.R. Cammarata, P.C. Searson, *J. Electrochem. Soc.* 149 (11) (2002) C610.
- [15] S.C. Wang, W.C.-J. Wei, *Mater. Chem. Phys.* 78 (2003) 574.
- [16] Th.F. Tadros, *Solid/Liquid Dispersions*, Academic Press/Harcourt, Brace and Jovanovich, New York, 1987 (Chapter 1).
- [17] S.L. Kuo, Y.C. Chen, W.H. Hwu, M.D. Ger, X.L. Chen, *Physical and chemical dispersion effects on the preparation of Ni–Al₂O₃ composite coating*, *J. Chin. Inst. Chem. Eng.*, in press.
- [18] N. Guglielmi, *J. Electrochem. Soc.* 119 (1972) 1009.
- [19] J. Fransaer, J.P. Celis, J.R. Ross, *J. Electrochem. Soc.* 139 (1992) 413.