納米級陶瓷粉體膠粒性質與形成鎳基複合電鍍材料之特性分析(2/2)

Analysis on Colloidal Properties of Nano-Sized Ceramic Powder and Material Properties of Electro-Plated Ni-Based Composite Layer

中英文摘要

具有 30-50 奈米之碳化矽及氧化鋁之超微粉體在胺基磺酸鎳鍍液中以電鍍法形成複合鍍層，使用各型電子顯微鏡、微硬度儀及磨耗機予以分析。微結構顯示 7 vol%微粒均質分散於鎳基底中，使鎳晶粒增加成核數，並大幅減小基底粒徑，尤其在 400°C 24 小時熱處理之樣品，添加超微顆粒之複合鍍層具有極佳之耐磨性，硬化及耐磨之機制在文內有詳細之討論。

Ultra-fine SiC and Al_2O_3 particles with 30 to 50 nm sizes were used to co-deposit with Ni in a sulfamate bath to form composite coatings. The microstructure and mechanical properties of the layers were investigated by scanning and transmission electron microscopies (SEM and TEM), high resolution TEM, micro-indentation, and wear testing. The microstructural results revealed that 7 vol% of SiC or Al_2O_3 particles dispersed randomly in the Ni matrix. The addition of the ultra-fine SiC or Al_2O_3 powder into the Ni matrix increases the nucleation density and inhibits the grain growth of the Ni. The micro-hardness and wear resistance were improved by the addition of SiC and Al_2O_3 particles, especially for SiC/Ni samples after the heat treatment at 400°C for 24 h. The mechanism of hardening of Ni-based electroplating layers are discussed.

關鍵字：複合電鍍，鎳，碳化矽，界面，硬度，磨耗

Keywords: composite plating, Ni, SiC, interface, hardness, wear.

1、 Introduction

For a nanocomposite contained nickel matrix and abrasive ceramic phases, the electrochemistry route is one convenient and economic way to reach full density without high temperature treatment. [1] By controlling the electroplating parameters, it is possible to synthesize nanostructured materials in pore-free state at ambient temperature. The simultaneous deposition of hard particles and metal phases to form composite coating results in an improvement of physical and mechanical properties of the metal layer. The composite plating included hard particles is potentially for nowadays industrial applications of precision molds (DVD or CD), electroforming coating in the LIGA process, and the electrical contacts and electronic parts.[2]

It is well known that second-phase inclusion retards the grain growth and hardens the matrix. As the inclusion size decreases, the Zener criteria[3] predicts a critical grain size (D_{crit}) at which grain growth stops because of a homogeneous distribution of spherical particles of radius, (r), in a volume fraction (V_f). The relationship is:

$$D_{crit} = \frac{4r}{3V_f} \qquad (1)$$

Equation (1) shows that, if the volume percentage of second phase keeps constant, the finer the second phase, the more particles available in the matrix, and the finer the grain size of matrix. According to Hall-Petch relationship, the strength (σ) or hardness (H) of material increases by the decrease of grain size (D)[4]

$$\sigma = \sigma_0 + kD^{-1/2}$$

$$H = H_0 + kD^{-1/2} \qquad (2)$$

The use of ultra-fine ceramic powder to improve the tribological properties of metallic materials is important in several engineering applications, e.g., a hard coatings on the cylinder surface of hot engine, ceramic reinforced Al composites used in areo-space aircraft, etc. Therefore, the electroplating process, as one of mature fabrication methods, was planned to prepare nanosized ceramic particle reinforced Ni-based composite layers.

2、 Experimental

Two kinds of ultra-fine ceramic powders were used in this study, one is a plasma-synthesized ultra-fine SiC (PJ-PL-SiC, PlasmaChem, GmbH, Germany) and the other is a nano-sized δ-phase Al_2O_3 powder (PJ-PL-ALO, Wah Lee, Taiwan). The ultra-fine SiC shows a major phase 3C and the average particle size in 62 nm. The Al_2O_3 powder has an average particle size of 30 nm with δ phase.

For the composite plating, a nickel sulfamate bath containing 90 g/L nickel sulfamate (EP grade, Phibrochem Inc., USA), 3 g/L nickel chloride (EP grade, SHOWA, Japan), and 40 g/L boric acid (EP grade, SHOWA, Japan) were used. A copper plate with dimensions of $10 \times 6.5 \times 0.25$ mm^3 was used as cathode and the anode was a Ti basket containing small nickel ingots. Before plating, a sequence of cleaning and acidic etching of the Cu plate by diluted sulfuric acid was carried out to remove the contamination and greasiness on the surface.

The solid loading of the added powder in the plating solution was of 1 vol% based on the bath volume. Gentle stirring of the suspension by air bubbles kept the solution well dispersed. The current density was 4 A/dm^2 (ASD). The bath temperature was controlled at 50±2°C and the pH ranged from 4.0 to 5.0, which was adjusted by H_3BO_3 or $NiCO_3$.

Crystalline phases of the composite layers were

identified by X-ray diffractometry (PW1792, Philips Instrument, Netherlands). The codeposition layer was cut and polished, then the cross section was examined with scanning electron microscopy (SEM, XL30 Philips, Netherlands) equipped with EDS (EDS DX4, EDAX Corp., USA). Thin foil sample of 3 mm diameter prepared from the coating layer was prepared and characterized by transmission electron microscopy (TEM, 100CXII, or HRTEM, FX-400E, JEOL, Japan or HRAEM, Hitachi HF-2000 Equipped with EDX: Noran, Voyager1000)

The coating samples were heat-treated in an atmosphere controlled furnace vented with N_2 and operated at 400°C for 24 hr, or kept at constant temperatures either at 100°C, 200°C, ... or 600°C for 1 hr. The hardness of the cross section of the layer was measured by a Vicker's indentor (AKASHI, MVK-EII, Japan) with a load of 50 gf and lasted for 15 s. The tribological properties of the composite layer, including wear resistance and friction coefficient, were measured by a block-on-wheel method (TE53, Plint & Partiners Ltd., England). The wearing wheel was made by a heat-treated steel (NSOH/B01) with a hardness 65HRc (830 Hv). The block specimens in a cross section of 5×13 mm^2 were tested by a load of 67 N in air at room temperature. The rotational speed of the wheel was 200 rpm and the number of cycles were between 3000 and 8000.

3 · Results and Discussion

3.1 Microstructure

The cross sections of the SEM micrographs, as shown in Fig. 1, display the distribution of ultra-fine SiC, and ultra-fine Al_2O_3 in the Ni matrix. The ceramic particle contents for both the composite layers are 7 vol%. The SiC particle shows a random distribution in the Ni matrix, and individual round feature in size of 0.1 μm can be found in the highly magnified images. It is close to the mean particle size of SiC. It indicates that the agglomeration of SiC in the electroplating solution is hardly occurred.

Fig. 2 shows the TEM micrographs of cross-section of pure Ni, ultra-fine SiC/Ni, and ultra-fine Al_2O_3/Ni composite layers. The Ni matrix in the blank specimen shows columnar grains with the longitudinal axis or growth direction perpendicular to the Cu substrate. The average grain dimensions are 0.23 μm in diameter and 2 to 3 μm in length. However, for an as-plated composite specimen with ultra-fine SiC or Al_2O_3 particles, the grain size of the Ni is very small and the shape becomes equiaxial due to the presence of the second phases. The mean grain size of the Ni reduces to 78 nm and 89 nm, respectively, by the addition of the ultra-fine SiC and Al_2O_3 particles.

Fig. 3 shows the lattice image of two partially adhered Al_2O_3 particles embedded in Ni matrix. An amorphous layer was found on the surface of the Al_2O_3 particle. The interface between Al_2O_3 and Ni is integrated. As marked in Fig. 4, the concave region of the adhesive Al_2O_3 particles has several Moiré fringes, which correspond to the interference between two Ni grains having similar orientation which rotate each other in a

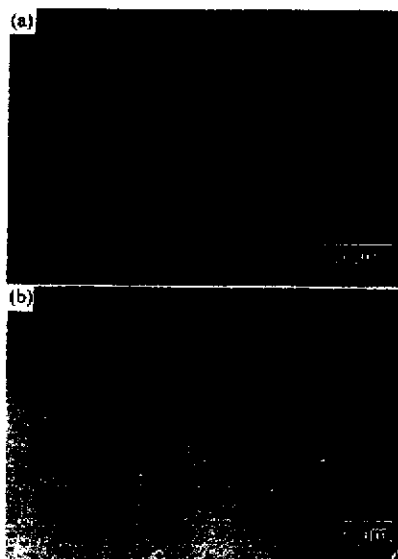small angle. It implies that the ceramic phases can

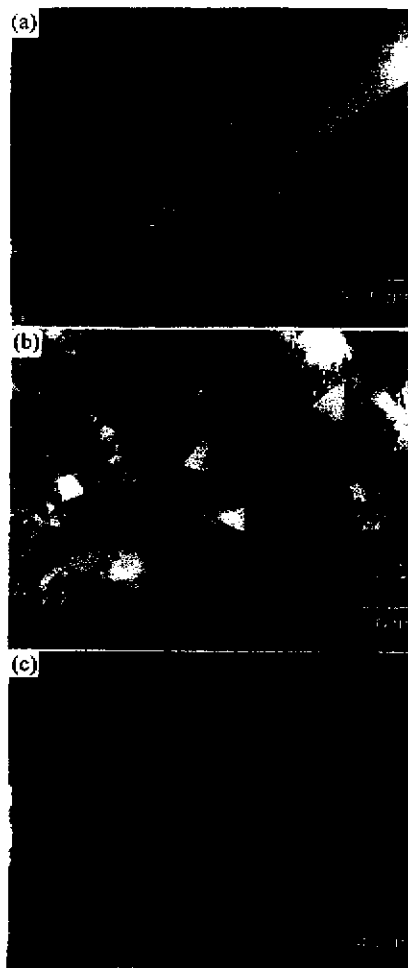Fig. 1 SEM micrographs of (a) ultra-fine SiC/Ni, and (b) ultra-fine Al_2O_3/Ni composites.

Fig. 2 TEM micrographs of the cross section of (a) pure Ni, (b) ultra-fine SiC/Ni, and (c) Al_2O_3/Ni composite layers.

Fig. 3 HRTEM micrograph of the lattice image of the interface of Al₂O₃ and Ni.

become heterogeneous nucleation sites of Ni grain during electro-plating. The tiny Ni grains grow and fill the concave space, then the grain size of Ni increases as the distance from the ceramic particle increases. This heterogeneous nucleation and growth of Ni grains also appear in the SiC/Ni composite. The addition of the ultra-fine SiC and Al₂O₃ powder into the Ni matrix can not only increase the nucleation density of the Ni but also inhibit the grain growth. Both the effects can significantly refine the Ni grain and change the grain shape from columnar to equiaxial.

3.2 Mechanical Properties

Fig. 4 shows the evolution of the friction coefficient (μ) of the SiC/Ni and Al₂O₃/Ni composites compared to that of a pure Ni coating. The friction coefficient is independent of the wear time and seems to remain in the same level after heat treating at 400°C. Although the value of the friction coefficient is very close between these three kinds of deposited layers, the pure Ni seems to have a minimal value. It may be partially due to the fact that the existence of ultra-fine SiC and Al₂O₃ particle increases the surface roughness of the deposit layers.

The wear results for the composite layers and pure Ni are plotted in Fig. 5. The wear rate of the SiC/Ni or
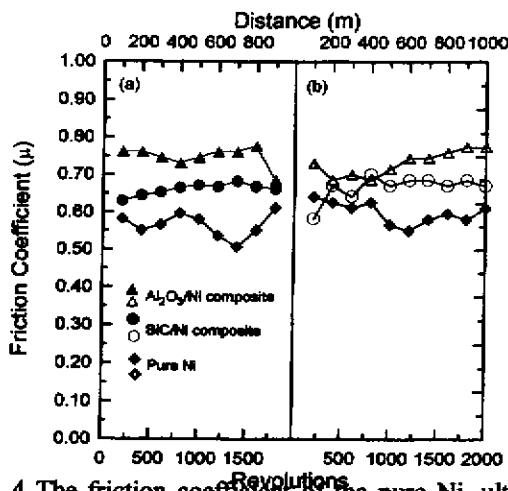

Fig. 4 The friction coefficient of the pure Ni, ultra-fine SiC/Ni, and Al₂O₃/Ni composite layers worn against tempered steel. (a) as-plated and (b) heat treated at 400°C for 24 h.

Al₂O₃/Ni composite layer without heat-treatment is in an average of 6×10^{-9} or 8×10^{-9} cm³/N·m, respectively. It is apparently better than that of pure Ni. Moreover, after 400°C heat treatment for 24 hr, the wear rate of a treated composite layer remains at a similar level, while the wear rate of the treated pure Ni increases about 50 times.

Fig. 6 shows that the hardness of the pure Ni, ultra-fine SiC/Ni and Al₂O₃/Ni composite layers changed upon varying the temperatures for 1 h. At room temperature, the hardness increases as the ceramic particles are added into the Ni matrix. When the specimens were treated at
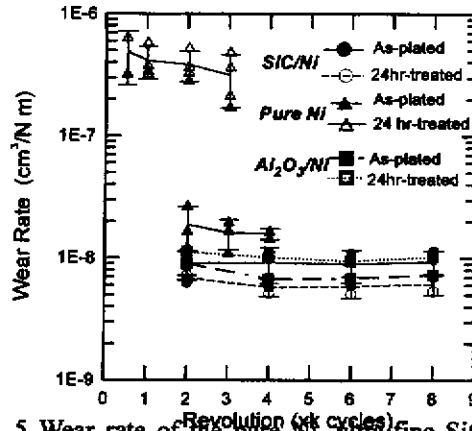

Fig. 5 Wear rate of the pure Ni, ultra-fine SiC/Ni, and Al₂O₃/Ni composite layers of as-plated or after heat treated at 400 °C for 24 h in N₂ atmosphere.
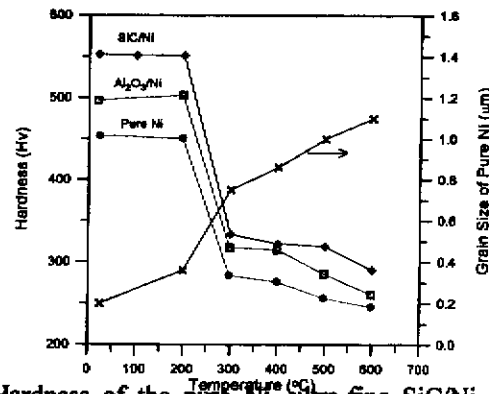

Fig. 6 Hardness of the pure Ni, ultra-fine SiC/Ni and Al₂O₃/Ni composite layers and grain size of pure Ni changed with various heat-treated temperatures for 1 h.

specified temperatures for 1 hr, the hardness decayed. The SiC/Ni composite layer has the highest hardness at all testing temperatures among these Ni coated layers. When the heat-treated temperature is higher than 300°C, the hardness of the composite layers decreases and remains constant at 300~500°C. But as the temperature is higher than 600°C, the hardness reduces further. The average grain size of pure Ni variation with different heat treating temperature for 1 h that also shown Fig. 6 with solid circle. It shows that the grain size of Ni starts to grow at 300°C, then reduces significantly at temperatures higher than 400°C.

3.3. Hardening Effects by Ultrafine Particles

There are two possible hardening mechanisms for the Ni composite layers incorporated with nano-

particulates. One is the refinement of the grain size, which can be defined simply as the Hall-Petch (H-P) effect.[5] The other is from the contribution of volume fraction of hard particles. SEM micrographs of the acid-etched surfaces of the pure Ni and two ceramic added composites are shown in Fig. 7. All three specimens have been heat-treated at 400°C for 24 h. The Ni grains have grown from ca. 80 nm (Fig. 2) to micrometric sizes. The average Ni grain size of the treated pure Ni, SiC/Ni and Al$_2$O$_3$/Ni are 14, 1.0, and 1.4 μm, respectively. The data depict that the growth of Ni is significantly retarded by the SiC or Al$_2$O$_3$ particles.

The average Ni grain size of the composite layers strongly affects micro-hardness. If the hardness and the grain size (d) of the pure Ni layers are formularized by an H-P relationship, the data can be plotted as Fig. 8, and shown the relationship is shown below.

$$H_1 = 155\ d^{-0.5} + 101 \qquad (3)$$

The hardness changes linearly with the square root of the gain size of Ni in the region larger than 0.2 μm. For SiC/Ni and Al$_2$O$_3$/Ni composites, the average Ni grain sizes are 78 and 89 nm, respectively. The hardness of these two composite layers predicted by eq. (2) is 656 or 621 Hv, as the solid line shown in Fig. 8. The experimental hardness of the SiC/Ni and Al$_2$O$_3$/Ni layers is softer than the predicted value. If a dash line is plotted in Fig. 8 connecting the data given by El-Sherik et al.[6] to the point of 0.2 μm, the second H-P relation is obtained.
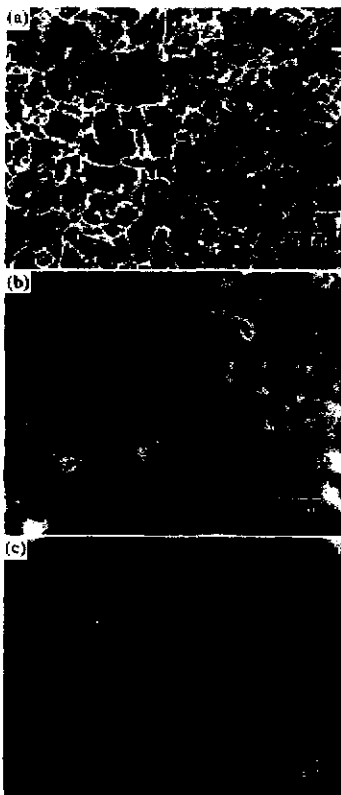

Fig. 7 SEM micrographs of acid-etched surfaces of the cross-sections of (a) pure Ni, (b) ultra-fine SiC/Ni, and (c) Al$_2$O$_3$/Ni composite layers. These specimens were heat-treated at 400°C for 24 h.
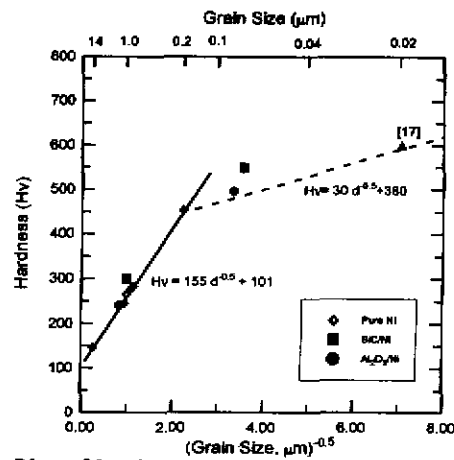

Fig. 8 Plot of hardness versus square root of the grain size of pure Ni, also included the hardness of the composite layers with either ultrafine SiC or Al$_2$O$_3$.

$$H_2 = 83\ d^{-0.5} + 235 \qquad (4)$$

Obviously, the slope of the eq. (4) is much smaller than eq. (3). In the other words, the constant k in the equation (2) decreases as the grain size of Ni smaller than 0.2 μm. According to the dislocation model for a Hall-Petch equation, the grain boundaries act as a barrier to dislocation motion. The physical meaning of k is "locking parameter" which represents the ability of dislocation pile-up, or the relative hardening contribution of the grain boundaries. It is function of the critical shear stress, τ_c, for dislocation to continue slip past the grain-boundaries barriers, shear modulus, G and Burger's vector of the pile-up dislocation, b.[7] The hardness of SiC/Ni composite is about 50 Hv larger than that predicted by the dash line in Fig. 9. It implies that, beside the grain size refinement, the dispersive harden mechanism shows a visible effect in the composite system. Based on the Orowan's equation, the distance between two particles, λ, reduces when the number of hard inclusion increases. Thus, the critical stress τ_c increases, and the constant k in the Hall-Petch relationship increases. The results can be verified in the Fig. 9 that all the data points of SiC/Ni or Al$_2$O$_3$/Ni composite are above the H-P relation line.

4. Conclusion

In this study, 7 vol% of ultra-fine SiC or Al$_2$O$_3$ particles were codeposited with Ni and formed random distribution in Ni matrix. The columnar Ni grains in pure Ni layer with the dimensions of 0.2×2 μm change to equiaxial shape of 78 nm and 89 nm for SiC/Ni and Al$_2$O$_3$/Ni composites, respectively. The concave regions of the ceramic particles become heterogeneous nucleation sites during the electro-plating. Tiny Ni grains are found in the regions, which show the dimensions much smaller than the mean grain size.

The micro-hardness of the composite Ni layer increases as the ultra-fine ceramics in Ni matrix increases. The increment of the hardness is higher than the composite with coarse SiC or estimated by the rule of mixture. The effect can be described by two Hall-Petch equations, and is contributed by the matrix grain

refinement,

The friction coefficient of ultra-fine SiC/Ni and Al_2O_3/Ni composite layers is higher than of the pure Ni. But the wear resistance of SiC/Ni and Al_2O_3/Ni composite coatings are significantly better than that of pure Ni coating after 400°C heat treatment for 24 h. The ultra-fine ceramic particles significantly inhibit the grain growth of Ni grains above 300°C, and improve the wear resistance of the Ni matrix.

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Reference

[1]. U. Erb, G. Palumbo, B. Szpunar and K. T. Aust, "Electrodeposited vs. Consolidated Nanocrystals: Differences and Similarities," *NanoStructured Materials*, 9, 261-270 (1997)

[2]. M. Hepel, Ch. Mahoney, T. Tannahill, The 1997 Joint International Meeting, 31 August-5 September, Meeting Abstracts, Paris, p.641, 1997

[3]. C. Zener, as communicated by C. S. Smith, "Grains, Phases, and Interfaces: An Interpretation of Microstructure," *Trans. Am. Inst. Min. Metall. Eng.*, 175,15-51 (1948)

[4]. N. J. Petch, "Cleavage Strength of Polycrystal," *J. Iron Steel Inst. London*, 174 [1], 25-28, (1953)

[5] M. Furukawa, Z. Horita, M. Nemoto, R. Z. Valiev, and T. G. Langdon, "Microhardness Measurements and The Hall-Petch Relationship in An Al-Mg Alloy with Submicrometer Grain Size," *Acta Mater.*, 44 [11], 4619-4626 (1996)

[6] A. M. El-Sherik, U. Erb, G. Palumboand K. T. Aust, " Deviation From Hall-Petch Behavior in As-perpared Nanocrystalline Nickel," Scr. Metall. Mater., 27 [9], 1185-1188, (1992)

[7] G. E. Dieter, Mechanical Metallurgy, SI Metric Edition, Chap.6, 184-240, McGraw-Hill Book Co., London, 1988.