A Study on the Composite Electrodeposition of Nickel With α-Al2O3 nanoparticles

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A highly concentrated and stable suspension of a-Al2O3 nanoparticles was prepared and added to Watts nickel electrolyte to deposit Ni/a-Al2O3 nanocomposite. EPMA analysis found that the nano-a-Al2O3 particles were incorporated into the nickel deposit uniformly with a ratio between 1~3Wt%. FESEM analysis observed that the nickel grain size became refined with the a-Al2O3 incorporation. And with XRD spectrum it was found that the composite coatings showed a preferred Ni(111) orientation compared with Watts nickel coatings which showed a preferred Ni(200) orientation. The obtained nanocomposite has high hardness (Hv 479) and improved resistance to wear and corrosion, which makes it a potential material for functional coatings.

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Introduction

Composite plating is a very mature process for depositing metal matrix composite(MMC) materials[1]. Usually, Ni or Cu is the selected metal matrix and SiC or Al_2O_3 is the common used particle. A lot of work[2-4] has been investigated in the electrodeposition of Ni/SiC or Ni/ Al_2O_3 MMC. However, the SiC or Al_2O_3 existed as micron or submicron particles in these researches.

Recently, with the development of nanotechnology, nanometer particles have been widely used to manufacture MMC. Lee et al [5] investigated the direct and pulse plating of Ni and nanometer diamond and found that the microhardness of the composite was greatly increased, especially under pulse plating. Wang et al[6] found that the nano- particles were more difficult to co-deposit than the micron ones, but with the addition of ultrafine powders into the Ni matrix, the size of Ni grains were reduced and the microhardness and wear resistance were improved, which was also proved by Jakob et al[7]. Benea et al[8] discovered that the nickel reduction curve shifted to more positive potentials in the electrodeposition of Ni and nano-SiC MMC.

In this work, a nano-a-Al_2O_3 suspension was first prepared and then added to a Watts based Ni plating bath to deposit Ni/a-Al_2O_3 MMC. The heat resistance and corrosion resistance of the obtained electrodeposit have been examined.

Experimental

Nanosuspension Preparation: The a-Al_2O_3 nano-particles (Degussa, average size: 13nm) were prepared into nano-suspensions (10Wt%) using FA25 (Fluko) high shear dispersing and emulsifying equipment according to the following procedures:

1. Add some dispersing agents to deionized water;
2. Mix the nanoparticles to a paste;
3. Emulsify the paste at a low rotation speed;
4. Disperse the suspension at a high rotation speed till a stable nanodispersion was formed.

Temperature was controlled below 35 °C with cooling tap water.

Sample preparation and deposition: Figure1 shows the schematic illustration of the plating system. Brass or low carbon steel with a dimension of 50mm×30mm×1mm was placed as the cathode after alkaline cleaning and dilute acid etching. The anode was a nickel plate. A Watts based bath containing 280 g/L $NiSO_4 \cdot 6H_2O$, 50 g/L $NiCl_2 \cdot 6H_2O$ and 45 g/L H_3BO_3 was used for nickel plating. 50 mL/L a-Al_2O_3 nano-suspension containing 5 g/L a-Al_2O_3 was prepared and added to the bath. Gentle air agitation kept the particles well dispersed. The bath temperature was controlled at 50±2°C, and the pH ranged from 4.0 to 4.8. Current density ranging from 1 to 6 A/dm^2 was applied to deposit the composite coatings.

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Material Characterization: The deposited composite was analyzed by Field Ejection Scanning Electron Microscope (FESEM, JSM-6330F, JEOL) to observe the surface morphology and by Electron Probe Microarea Analysis (EPMA, JXA-8800R, JEOL) to determine the quantity of the incorporated nano-a-Al2O3. To further insure that the incorporated particles were uniformly distributed, Al element mapping of the surface and the cross-section was analyzed by EPMA. X-ray Diffraction (XRD, DMAX-1200, Rigaku) was used to analyze the microstructure of the Watts nickel deposits and the composite nickel deposits before and after heat treatment.

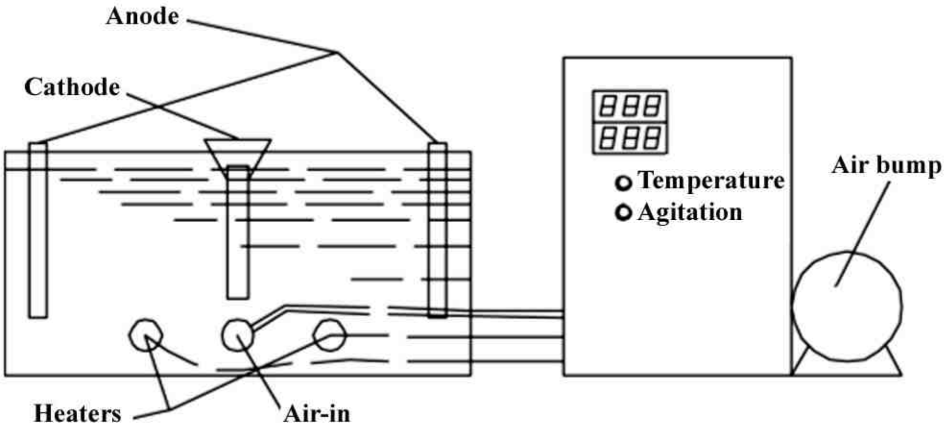

Fig. 1. Schematic Illustration of Plating System

Performance Characterization: The heat resistance of the composite coatings was analyzed with Differential Scanning Calorimeter (DSC 204, NETZSCH) and Thermal Gravimeter (TG 209, NETZSCH). Corrosion resistance was indicated by the time lasted in 1:1(v) HNO3 at 40 °C until the first bubble emerged from the brass substrate. Microhardness was tested with HXD-1000 microhardness tester and wear resistance was measured with LKY-Contour and Friction Coefficient In-situ Synchrometer.

Results and Discussion

Figure 2 shows the surface FESEM micrographs of Watts Ni deposit and Ni/a-Al2O3 composite. EPMA analysis probed that the weight percentage of nanoparticles in the composite layer was 1.5%. The nickel grains became refined with the inclusion of the particles and the surface morphology changed. Further investigation found that the particles incorporated into the nickel matrix uniformly, which can be illustrated by the Al element mapping graphs (Fig. 3). Fig. 3(b) of the cross-sectional Al mapping analysis confirmed the well dispersion of the included a-Al2O3 particles.

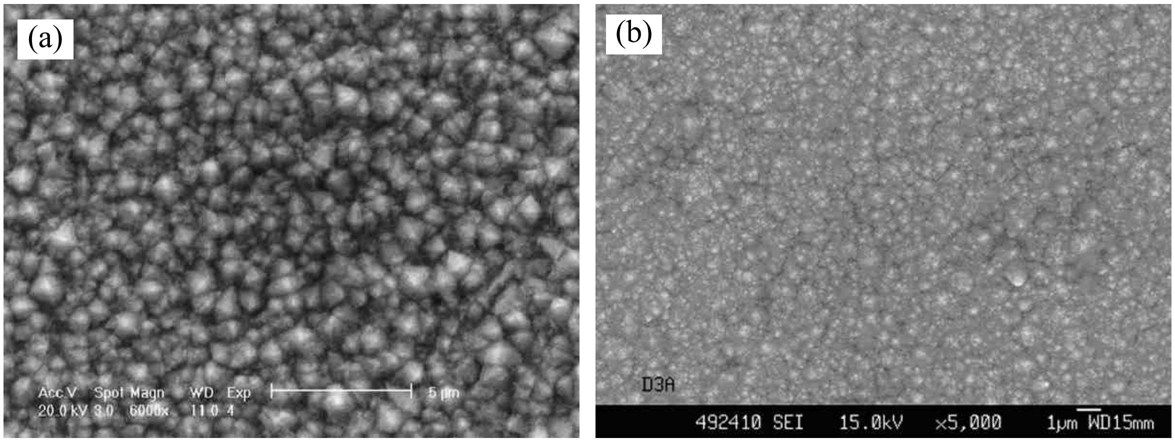

Fig. 2 FESEM Micrographs of (a) Watts Ni deposits and (b) Ni/a-Al2O3 Deposits

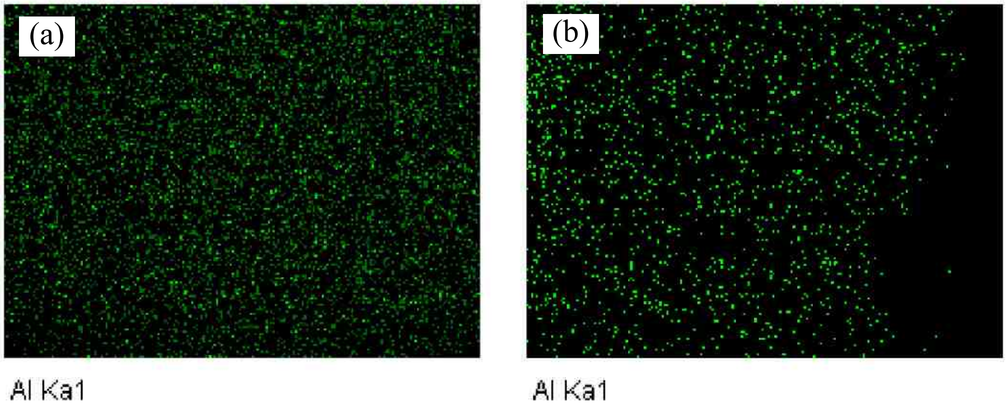

Fig. 3 Al Mapping Graphs of (a) Surface and (b) Cross-section of Ni/a-Al2O3 Deposits

XRD results of pure Ni and Ni/a-Al2O3 composite deposits are shown in Figure 4. From the comparison of Fig. 4(a) and 4(b) we can know that the preferred plane of the Watts Ni prepared by our electrodeposition is (200) plane, which differs from that prepared by Wang et al [9]. Obviously, with the incorporation of nano-a-Al2O3, the Ni matrix changes its orientation from preferred (200) plane to preferred (111) plane.

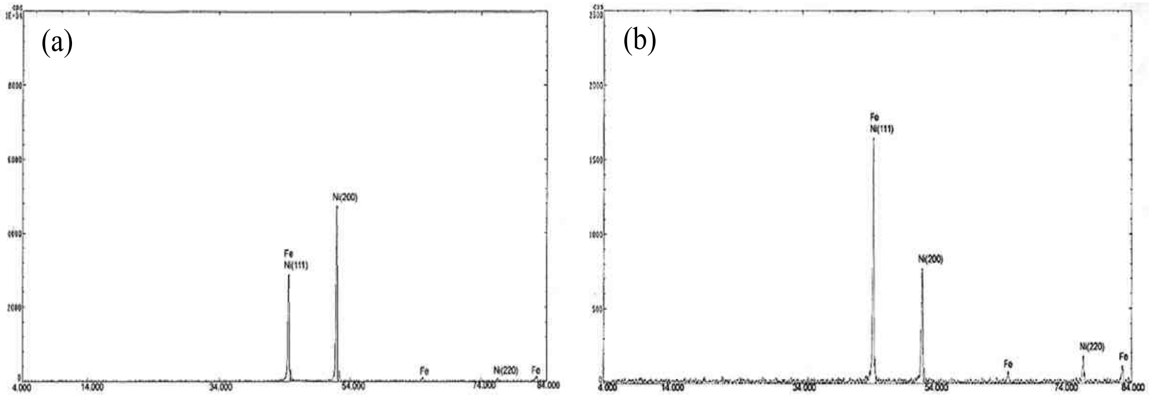

Fig. 4 XRD patterns of (a) Watts Ni and (b) Ni/a-Al2O3 composite deposits

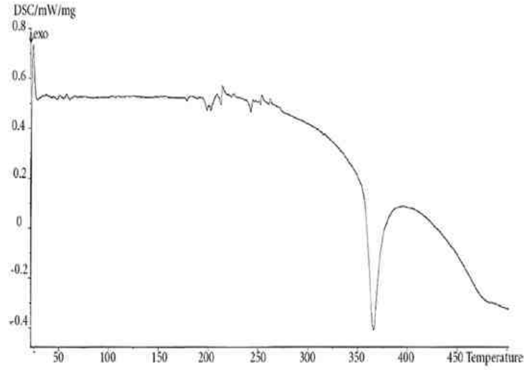

Fig. 5 DSC analysis of Ni/a-Al2O3 composite deposits

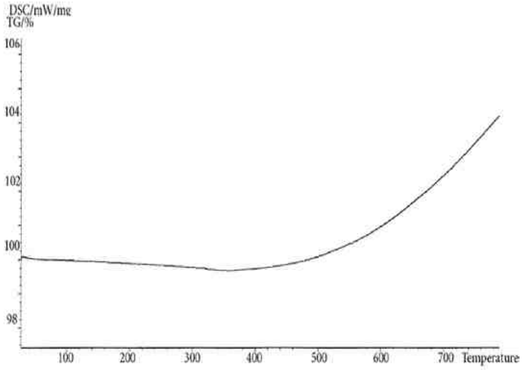

Fig. 6 TG analysis of Ni/a-Al2O3 composite deposits

The test results of heat oxidation resistance of Ni/a-Al2O3 composite deposits are displayed in Figure 5 and 6. DSC analysis found that the composite coatings started to absorb heat at 250 °C and a sharp dive was observed at 362 °C, which implies there may be some structure adjustment during heat treatment. TG analysis showed that the composite began its oxidation above 500 °C, that is to say, Ni/a-Al2O3 composite coatings was heat oxidation resistant under 500 °C.
Figure 7 displays the XRD results of Ni/a-Al2O3 composite after heat treatment at 400 °C and 800 °C. From Fig.7(a) and Fig.4(b), we can see that after heat treatment at 400 °C, the composite Ni matrix orientation changed from preferred (111) plane to preferred (200) plane. This structure change resulted in the corresponding dive in the DSC curve of Fig.5. Composite coatings after heat treatment at 800 v were partially oxidized into NiO and Fe3O4 (Fig.7(b)). From Fig.7(a) and (b) we can also draw a conclusion that Ni(200) plane is more stable than Ni(111) plane under high temperature.

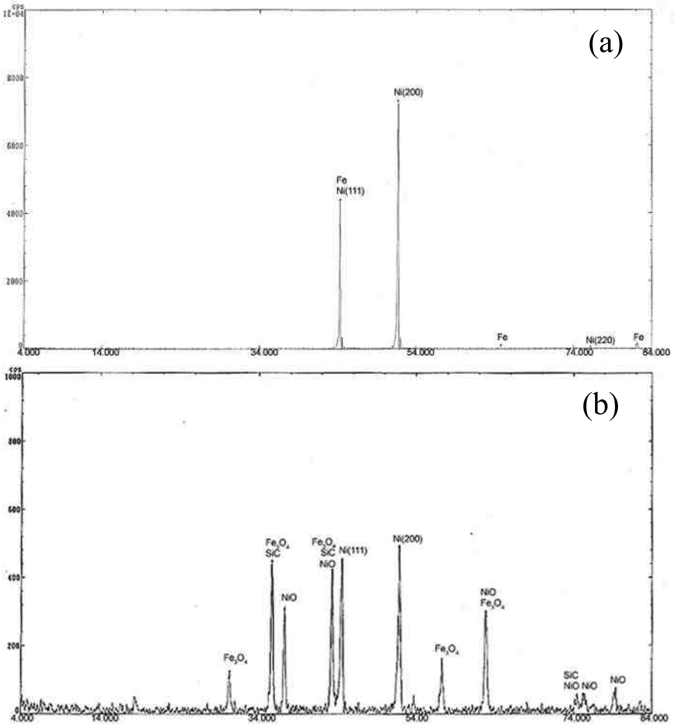

Fig. 7 XRD Patterns of Ni/a-Al2O3 after Heat Oxidation at (a) 400 °C and (b) 800 °C

The test results of the corrosion resistance, wear resistance and microhardness of Ni/a-Al2O3 and Watts Ni deposits are listed in Table 1. All these properties were greatly improved except the friction coefficient. The microhardness doubled and the wearing depth decreased by 80%. These improvements may be explained by the dispersion hardening effect of nanoparticles in the Ni matrix. The friction coefficient remained almost the same because the incorporated small particles were well dispersed in the Ni matrix, and the surface roughness was weakened. Although the surface roughness didn't increase, the porosity was greatly reduced by the nanoparticles inclusion. As a result, the corrosion resistance was improved remarkably.

Table 1 Properties of Ni/a-Al2O3 and Watts Ni Deposits

Items	Ni/α-Al_2O_3	Watts Ni
Friction coefficient	0.482	0.473
Wearing depth (μm)	1.25	5.94
Microhardness (Hv)	493	234
Corrosion resistance(min)	24.3	9.0

Conclusion

Ni/a-Al2O3 nanocomposite coatings with 1~3Wt% incorporation of nano-a-Al2O3 have been electrodeposited from a Watts based nickel plating bath. The included particles are well dispersed in the Ni matrix and thus leads to the Ni grain refinement and the change of Ni plain orientation from preferred (200) to (111). With heat treatment under 500 °C, the structure of the composite is modified from preferred (111) orientation to (200); with temperature above 500 °C, the composite is slowly oxidized into NiO and Fe3O4. The composite shows good hardness and resistance to corrosion and wear, which makes it a potential material for functional anti-corrosion or anti-wear coatings.

Acknowledgements

Financial support by Guangzhou Sci-tech Bureau (P.R. China), is gratefully acknowledged.

References

1. A. Hovestad and L.J.J. Janssen, J. Appl. Electrochem. 1995, 25:519-527
2. F.K. Sautter, J. Electrochem. Soc. 1963, 110(6):557-560
3. P. Nowak, R.P. Socha, M. Kaishev and et al, J. Appl. Electrochem. 2000, 30:429-437
4. N. K. Shrestha, I. Miwa and T. Saji, J. Electrochem. Soc. 2001, 148(2):C106-C109
5. W.H. Lee, S.Ch. Tang and K.Ch. Chung, Surf. Coat. Technol. 1999, 120-121:607-611
6. Sh. Ch. Wang and W.Ch. Wei, Mater. Chem. & Phys. 2003, 78:574-580
7. C. Jakob, F. Erler and R. Nutsch et al, Proc. 197th Meeting Electrochem. Soc. Toronto, 2000, 1:329
8. L. Benea, P.L. Bonora, A. Borello and et al, J. Electrochem. Soc. 2001, 148(7):C461-C465
9. Sh. Ch. Wang and W.Ch. Wei, J. Mater. Res. 2003,18(7):1566-1574