

Effect of Addition of Polytetrafluoroethylene (PTFE) and Silicon Carbide (SiC) on Properties of Electroless Nickel Alloy Coatings

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Abstract: Electroless nickel (copper)-phosphorus-silicon carbide (SiC)-polytetrafluoroethylene (PTFE) composite coatings were prepared by adding SiC and PTFE into electroless nickel (copper)-phosphorus alloy baths. The effects of addition of SiC and PTFE on depositing rate, microhardness, wear resistance and anti-friction of the resulted composite coatings were studied. The results indicated that electroless nickel (copper)-phosphorus alloy coatings were greatly improved in depositing rate, microhardness, wear resistance and antifriction by co-deposited proper amount of SiC and PTFE.

Keywords: Electroless deposition; Silicon carbide; Polytetrafluoroethylene; Composite coatings

IN RECENT YEARS, electroless deposition has become an important technology to prepare composite materials^{[1][2]}, especially the metallic matrix composite materials with characteristics of Ni-P alloy and composite phases, and the prepared process which can be used to design the functional materials^{[3][4]}. Both the electrolytic and electroless codeposited composites display the flexibility and potential advantages^{[5][6]}.

The ternary and even the polyalloys (such as Ni-Co-P, Ni-Mo-P, Ni-Cu-P, Ni-W-P-B) have much more advantaged properties than the binary alloy Ni-P (or Ni-B)^{[7][8]}. In high technology fields (electronic, space, communication field etc.), the demands for advanced materials are more and more strong. While the electroless polycomponent depositions have provided effective methods to the material fabrication processing. Using electroless deposited polycomponent alloy as the matrix, many new functional materials with properties can be designed. In this study, the PTFE and SiC were codeposited into composite coatings as to improve the wear properties of the pure alloy coating during the process of the electroless Ni(Cu)-P alloy deposition. What's more, the better wear resistant materials can be obtained.

1. Experimental

Specimens as deposited substrate were made by aluminum and mild steel. Before electroless deposition, the specimens were degreased, descaled, activated in acid, and zinc impregnated. Then the treated SiC and PTFE were added to the electroless nickel(copper)-phosphorus alloy deposition solution (SiC and PTFE decentralized by surfactant and

ultrasonic treatment). The deposition lasted for 2 ~3 hours, and the deposits' thickness was about 30 ~40 μm . The compositions of the solution and the operational conditions are shown of follow : For Ni(Cu)-P deposition , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (18-24g) , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (10-15g) , $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (20-25g) , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ (40-50g) , Pb^{2+} (0.001g) , T ($^{\circ}\text{C}$) (75-85 $^{\circ}\text{C}$) , PH (5.0-5.6) . For Ni

(Cu)-P-SiC-PTFE deposition , $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (20-25g) , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (10-18g) , $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (20-25g) , $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ (20-40g) , Pb^{2+} (0.001) , SiC (3-5 μm) (15-40g) , PTFE (10-30) , T ($^{\circ}\text{C}$) (80-85 $^{\circ}\text{C}$) , PH(5.0-5.6) .After preparation of the composite coatings, heat treatment in vacuum was performed at temperature of 200~300 $^{\circ}\text{C}$ for 1 hour.

The morphology and microstructure of composite coating were characterized using Olympus optical microscope, HITACHI S-570 scanning electron microscope (SEM), H-800 TEM, Regaku D-max/rB XRD (Cu target, 40kV, 100mA). The microhardness measurements were taken on the microhardness instrument (model 71), kept with a load of 1N for 30s.

2. Results and Discussion

2.1 Deposited Rate of Ni-P-SiC- PTFE Composite Coatings

Ni (Cu)-P alloy was used as the matrix of the Ni-P-SiC-PTFE composite coatings. Generally, in order to get the pure Ni (Cu)-P alloy, the concentrations of the Ni^{2+} and Cu^{2+} in the solution must be adjusted. If so, codeposition of Ni and Cu could occur, otherwise there was no Cu or pre-Cu deposition in the resultant coating. When adding SiC and PTFE into the plating solution, the components changed and should be set in a suitable range. Not only the Ni (Cu, P) codeposited, but also the PTFE and SiC codeposited together in the composite plating solution. For these, the $\text{Ni}^{2+}/\text{Cu}^{2+}$ ratio was determined among 5.2 to 6.3 after a series test and optimization.

Figure 1 shows the changes of Ni (Cu)-P-SiC-PTFE composite coatings in the deposited rate. At the beginning of codeposition, as the addition of PTFE and SiC increased, the codeposited rate also increased. When the addition reached the critical value (PTFE 15g/L, SiC 25g/L), the deposited rate did not increase any more. If the added quantity was large enough, the rate oppositely decreased. When the PTFE and SiC were added properly, there were more active centers

formed on the surface of specimens^[9], which could increase the nucleation probability and accelerate the co-deposition, leading to a higher deposited rate.

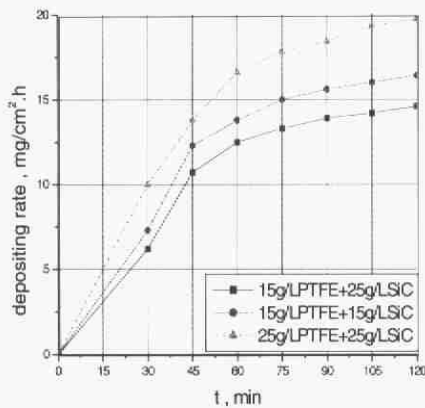


Fig.1 Deposited rate of Ni(Cu)-P-SiC-PTFE composite coatings

2.2 Microstructure of Ni (Cu)-P-SiC-PTFE Composite Coatings

During the process of the codeposition, the quantity of the surface-active agent and the stirring must be controlled to keep the PTFE and SiC uniform distribution in the solution. Under the action of stirring force and electrostatic force, the PTFE and SiC moved to the specimen surface and adsorbed on the surface, co-deposited with the Ni (Cu)-P alloy. When the stirring was strong enough, the particles could not stay firmly at the surface, and always being washed away, that was harmful to the codeposition during coatings' formation. If the temperature was maintained around 80°C, raising temperature could increase the deposited rate, but on the other hand it would make PTFE easily form the white floccule in the solution which prevented PTFE from codeposition. The surface appearances of the Ni (Cu)-P-SiC-PTFE composite coatings are shown in Fig.2, SiC and PTFE co-deposition changed the surface appearances compared with the Ni(Cu)-P alloy matrix.

Through changing the Ni (Cu)-P matrix alloy solution and the addition of PTFE and SiC, we could obtain the Ni (Cu)-P-SiC-PTFE composite coatings with different composition and microstructure. Fig.3 shows the X-ray diffraction patterns of the Ni (Cu)-P alloy and its composite coatings. Fig.3 shows that the Ni (Cu)-P alloy has two states (crystalline state and amorphous state). Adding PTFE and SiC, the crystallization with the diffraction maximum Ni (111) or the amorphous structure could both be obtained, but as the addition of PTFE and SiC increased, the amorphous structure exposed the Ni (111) and Ni (200) diffraction, which showed that the amorphous state had changed into the crystalline state. For there was no echo among the PTFE, SiC and the matrix, the particles distribution changed the solution composition, as a result, the Ni(Cu)-P matrix alloy and depositing



Fig. 2 Surface morphology of the Ni (Cu)-P-SiC-PTFE composite coatings

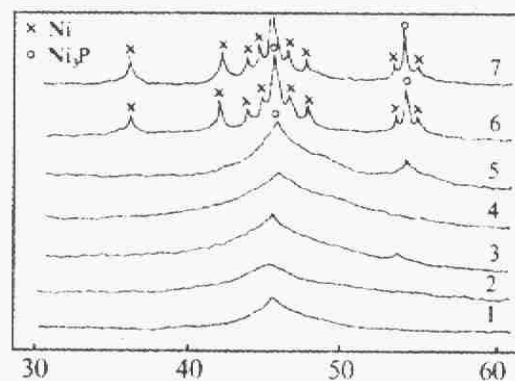


Fig.3 X-ray diffraction patterns of the Ni (Cu)-P-SiC- PTFE composite coatings

- 1.Ni (Cu)-P I ; 2. Ni (Cu)-P II ; 3. Ni (Cu)-P-SiC-PTFE I ;
- 4. Ni(Cu)-P-SiC-PTFE (SiC+15g/L PTFE) II ; 5. Ni (Cu)-P-SiC-PTFE (SiC+25g/L PTFE) II ; 6. Ni (Cu)-P-SiC-PTFE I ,600 °C ; 7. Ni (Cu)-P-SiC-PTFE (SiC+15g/L PTFE) II 600°C

performance changed. After heat treatment, amorphous (Cu)-P alloy and its composite coatings both turned to crystalline state. When $2\theta = 45^\circ$, the broaden diffraction lines changed to the diffraction with (111) peak. If the heat treated temperature increased gradually, the Ni₃P phase would precipitate from the Ni(Cu)-P alloy. The microscopic structure is shown in Fig.4.

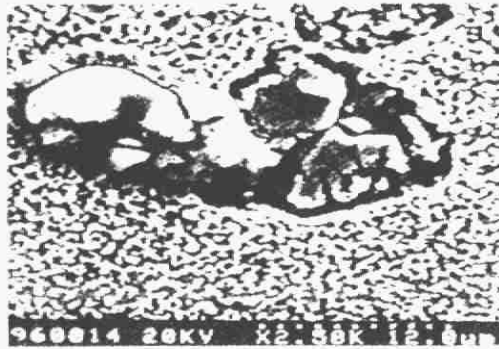


Fig. 4 Microstructure of Ni(Cu)-P-SiC-PTFE coating heat treated at 500°C

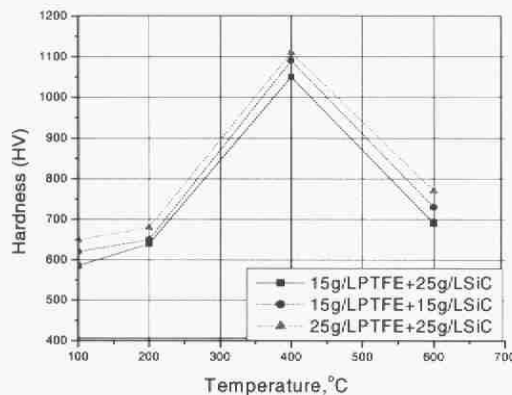
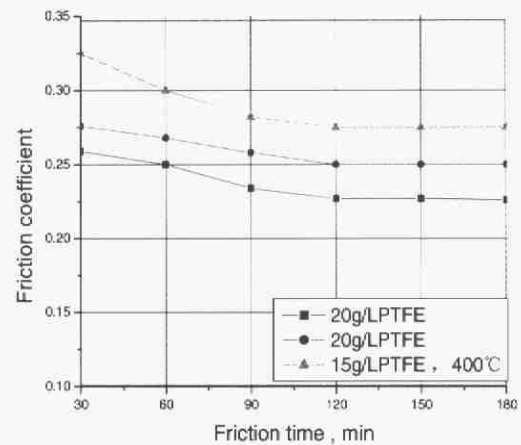


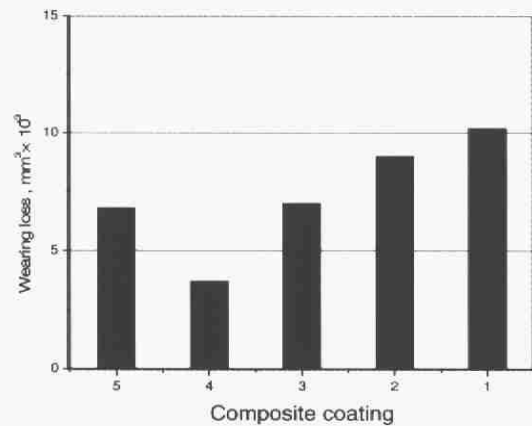
Fig. 5 Dependence of microhardness on heat treatment temperature for Ni(Cu)-P-SiC-PTFE composite coatings

2.3 Hardness and Wear Performances of Ni (Cu)-P-SiC-PTFE Composite Coatings

The hardness changes of Ni (Cu)-P-SiC-PTFE composite coatings are shown in Fig.5. It was found that as the addition of the PTFE increased, the hardness decreased; but the content of SiC increased, the hardness increased too. The effect of the SiC reinforcement could retain the PTFE degeneration in the composite coatings. The heat treatment can increase the hardness for the composite coatings. The heat treatment effect on the hardness was similar to that of Ni (Cu)-P alloy^[10], after 400°C treatment, the hardness of the composite coatings ascended due to Ni₃P dispersion strengthening effect from the Ni (Cu)-P alloy matrix. Thus, it can be also concluded that the hardness changes of the composite coatings related to the microstructure characteristics of the alloy matrix.



(a) Friction coefficient changes of the composite coatings



b) 2h worn loss of the composite coatings

Fig.6 Friction coefficient and worn loss of the Ni (Cu)-P-SiC-PTFE composite coatings

1.Ni (Cu)-P; 2: Ni (Cu)-P-SiC-PTFE; 3: Ni (Cu)-P-SiC-PTFE, 200°C heat treatment; 4: Ni (Cu)-P-SiC-PTFE, 400°C heat treatment; 5: Ni (Cu)-P-SiC-PTFE, 600°C heat treatment.

Though the PTFE could decrease the hardness of the coatings, on the other hand, it could also obviously decrease the friction coefficient, the more the PTFE added, the greater the effect. Even if the hard phase SiC existed in the coatings, the friction coefficient was still lower. It was ascribed to that the solid lubrication characteristic of PTFE could result in good anti-friction performance, as shown in Fig 6(a). While the codeposition of the SiC could strengthen the composite coatings, the anti-friction characteristic still existed during the friction and wear. Fig.6(b) shows that the wear loss in the Ni (Cu)-P-SiC-PTFE composite coatings is much less than that of Ni (Cu)-P alloy matrix, which proved that composite coatings had better wear performance. The friction coefficient of Ni (Cu)-P-SiC-PTFE composite coatings via heat treatment decreased a little. When treated at 400°C,

Ni₃P precipitated from the alloy matrix that also had antifriction property, resulting in decrease of the wear loss greatly. After heat treatment at 400°C, the hardness of the coatings reached to the maximum value, so the wear resistance got to the optimum. Heat treatment at 600°C, though the hardness decreased a little, the wear loss was less than both the as-deposited state and the 200°C treated state. It was obvious that the heat treatment could be used to improve the wear performance. So the Ni (Cu)-P-SiC-PTFE composite coatings not only possessed the strength effect, but also performed with good antifriction properties.

3. Conclusion

Adding PTFE to the Ni (Cu)-P-SiC composite solution, the Ni (Cu)-P-SiC-PTFE composite coatings can be successfully obtained by co-deposition. The deposited rate can be adjusted by changing the components and the contents of the solution. When the addition was maintained at 25g/L SiC+15g/L PTFE, the deposited rate is the fastest and the most stabilized. Compared with the Ni (Cu)-P alloy, the Ni (Cu)-P-SiC-PTFE composite coatings have better reinforcement and wear properties. Heat treatment can improve the wear performance further.

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