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Microstructure and Debris Fracture for Crystalline Ni-P-Cnts Composite Coatings After Wear

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Abstract:
The purposes of this study are to determine the effects of CNTs on Microstructure and wear Fracture for Crystalline Ni-P-CNTs Composite Coatings after Wear. Crystalline Ni-P-CNTs composite coatings were prepared via brush electroplating technology. Then wear tests for the coatings were carried out. The deformation of the microstructures in the coatings after wear was analyzed by TEM. The results showed that loads make mainly a dislocation movement and proliferation that causes dislocation configuration changes in crystalline Ni-P/CNTs composite coating. As the applied load increases, the dislocation configuration changes from dislocation tangles to the formation of cell, again to cell deformation. Abrasive debris was collected for SEM observation which is helpful to understand the microscopic mechanism of wear crack nucleation and propagation. Fracture modes for the debris in crystalline Ni-P/CNTs composite coating are micro-plastic deformation intergranular, cleavage and quasi-cleavage. Fracture characteristics on the abrasive debris are cleavage steps, micro-cutting stripes, grain groups and torn edges. Crack nucleation sites for the debris generally are inter-granular defects, such as dislocation piles and cell walls, and grain boundaries. The crack propagation paths are cleavage planes and grain boundaries.

Keywords:
CNTs, Coating, Wear, Microstructure, Fracture

1. Introduction

Composite coatings applied by electroplating provide hardness and Corrosion resistance characteristics to the surface of a material. Carbon nanotubes (CNTs) that exhibit extremely strong mechanical characteristics and unique hollow structures are ideal reinforcement for fabricating high-quality composites. So the composite coatings are expected to perform good friction and wear properties under high friction condition.

The complex nature of wear has delayed its investigations and resulted in isolated studies towards specific wear mechanisms or processes. Some commonly referred to wear processes include: Adhesive wear, Abrasive wear, Surface fatigue, Fretting wear, Erosive wear and so on. But we studied wear mechanisms in a new view of fracture. A dust was looked as the result of a fracture from the material. So the wear can be regarded as a series of debris fracture.

Although composite coatings added to CNTs have been studied extensively [1–5] in labs, but the role of CNTs in improving friction and wear properties remains unknown. Previous studies have reported that CNTs as reinforcement in coatings affect the micromechanism of the wear deformation and fracture. Complex stress and plastic deformation are observed on a worn surface and its layer during the friction and wear process [6–10].

In the process of sliding wear, no loss of material would occur when the interaction between the contact points is a completely reversible elastic deformation process. Wear is the process of plastic deformation and fracture of the surface and subsurface of materials, including the localized accumulation of plastic deformation; formation, expansion, and merger of wear and tear crack; and material separation. Abrasive debris is the product of wear fracture. Similar to a fracture, the surface of abrasive debris records large amounts of information of the wear fracture process. Thus, a study on abrasive debris helps understand the microscopic mechanism of wear.

2. Experiments

2.1. Compositions of Brush Electroplating Bath

The components of the brush electroplating solution are as follows: nickel sulfate ($NiSO_4 \cdot 7H_2O$), 200 g/L to 250 g/L; nickel chloride (NiCl), 40 g/L to 60 g/L; sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), 20 g/L to 30 g/L; additives, 60 g/L to 100 g/L; and suitable amounts of surfactants. The acidity–alkalinity (pH) of the solution was 1.5 to 2.5.

Table 1. *Compositions of the composite coatings.*

Coating	Nickel–phosphorus (Ni–P) plating solution	Added CNT (g/L)
Ni–P		/
Ni–P/0.5 g CNTs		0.5
Ni–P/1 g CNTs		1.0
Ni–P/2 g CNTs		2.0

Four groups of coating samples with different amounts of CNTs added in the plating solution were obtained, as shown in Table 1.

2.2. CNTs

The CNTs were prepared by catalytic chemical vapor deposition (CCVD)[11]. The CNT wall was clear, with few defects and impurities. Only a few amorphous carbons and graphite sheets were attached on the CNTs. The CNTs were long and slightly curved(as shown in Fig. 1), with a measured length longer than 700 nm. The inner diameter of the CNT was approximately 5 nm to 20 nm, and the outer diameter was approximately 20 nm to 40 nm.

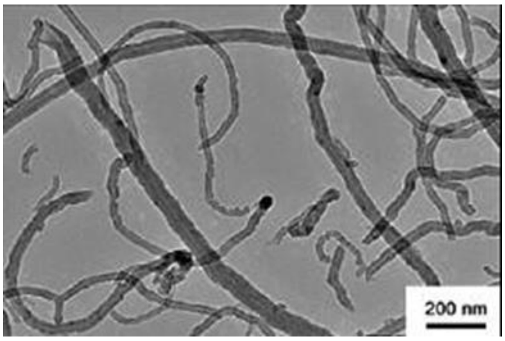

Figure 1. *TEM image of CNTs prepared by CCVD.*

2.3. Brush Electroplating Process

After the CNTs with different weights were added into the plating solution using a 10,000 r/min electric mixer to agitate the solution for 5 min, a uniformly dispersed and suspended compound bath was obtained.

The pretreatment process of the samples was as follows: Electrocleaning (voltage: +12 V) → activation (voltage: ±12 V) → second activation (voltage: ±18 V) → nickel plating (voltage: ±12 V). Plating was carried out at temperature at room temperature, the current was 3 A to 6 A, the relative moving speed was 8 m/min (0.13 m/s) to 12 m/min (0.2 m/s), and the voltage was 12 V.

The Ni-P CNT coatings with different CNT content were made on a pin by the technique. The initial thickness of the Ni-P CNT composite coatings were about 0.6-08mm.

2.4. Friction and Wear Tests

The dry sliding friction coefficient and wear loss of the coating were measured in the atmosphere with an M-200-type abrasion tester. The mount ring was quenched 45 steel (0.45% C) with 53 HRC hardness and 38.2 mm diameter. The test block was normalized 45 steel with surface coating. The sample was immobile and the mount ring rotated at a rotation speed of 0.4 m/s for 3 min. A 1 load of 100, 200, or 300 N was applied to the sample block through weights and leverage.

2.5. TEM and SEM Analysis

A 0.5 mm-thick sheet was cut from the coating parallel to the worn surface. The sheet was placed on a metal plate and ground into 50 μm or less. Finally, a thin film was prepared as observation sample. The Hitachi 8100 Transmission Electron Microscope with 200 kV, fourth beam spot, and 0.144 nm line resolution was used. The electron microscope was equipped with a Philips DK-4 energy-dispersive spectroscope, which can be used for chemical composition analysis.

The abrasive debris of coating was collected for surface morphology analysis. The Hitachi S-450-type scanning electron microscope (SEM) was used for this observation.

3. Experimental Results and Analysis

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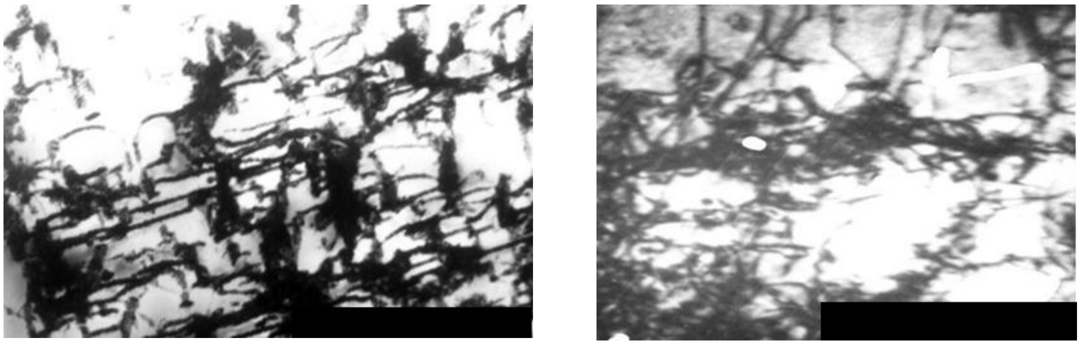
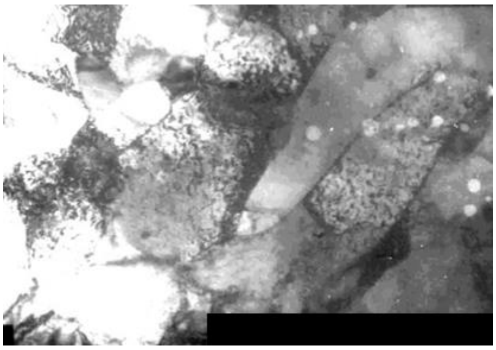
Stacking faults and twins were not found in the surface layer of crystalline nickel-phosphorus base composite coating. And the main deformation mechanisms are dislocation movement and proliferation. Figure 2 showed the effect of the friction loads on the dislocation movement and proliferation. As the load increases, the dislocation configuration changes from pile-up and tangles to cell formation then to cell deformation.

(a) 100N, 0.4m/s (b) 100N, 0.4m/s



(c) 200N, 0.4m/s (d) 200N, 0.4m/s



(e) 300N, 0.4m/s

Figure 2. *Changes of dislocation configuration with loads (crystalline Ni-P/1g CNT).*

Under the condition of a smaller load, certain amount of dislocations glide in the intragranular and tangle, as showed in Figure 2(a). Part of dislocations glide to the vicinity of the carbon nanotubes and pile up, causing microstress concentration and CNTs deformation (Figure 2(b)). As the load increases, the deformation of the surface layer increases, followed by the proliferation of dislocations and corresponding densities. The increment of yield strength caused by the increase of dislocation density can be expressed as [12]：

$$\Delta\sigma_s \approx G_m b \rho^{1/2} \quad (1)$$

Where G_m is the elastic modulus of the matrix metal, b is the Burgers vector, is a dislocation density. As showed in Figure 1 (c), it is estimated that the dislocation density is $10^{12}/cm^2$ magnitude. However, this refers to the average value.

In fact, the dislocation distribution is uneven in a severe deformation region.

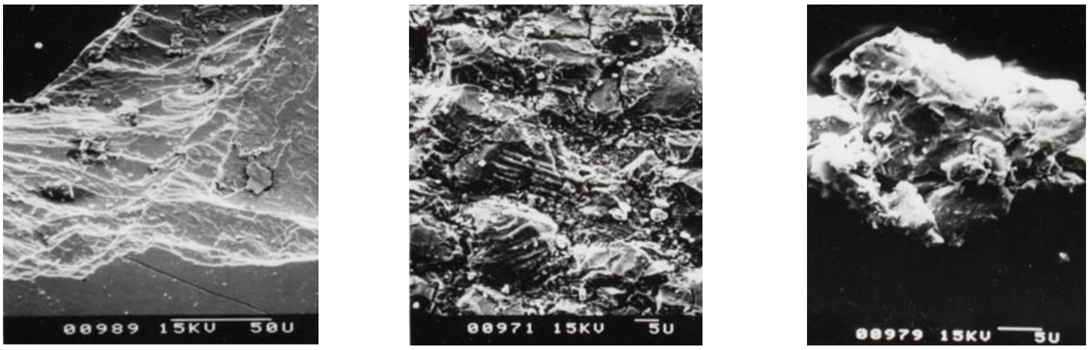
When there is little dislocation at some locations, usually a large amount of dislocations stack in the surrounding and form a cellular structure as indicated in Figure 1 (c) and d. In wear surface, the pile-up and tangle of dislocations in front of the carbon tube, together with the formation of sub-structure cell, hinder further dislocation movement, and result in microscopic strengthening effect, which can increase the micro-plastic deformation resistance of the crystalline nickel-phosphorus-based carbon nanotube composite coating. Consequently, anti-plowing adherent capability of the coating is improved. The friction coefficient and wear loss are significantly reduced [13].

The further increased loads lead to a large plastic flow in the surface layer. Some dislocation cells or sub-grains slip and rotate, resulting in elongated cells and thinner cell walls (Figure 1(e)). Cell wall thinning is actually attributed to the attraction and absorption of sliding dislocations to sub-grain boundaries, which means that the dislocations further aggregate in the sub-grain boundaries. After sub-grain boundaries attract and absorb sliding dislocations, the misorientations gradually increase to form small-angle grain boundaries, which eventually shift to large-angle grain boundaries. As a result, the interfacial bond strength is weakened and cracks nucleate. Thus, under the action of the further load, it is easy to form quasi-cleavage fracture pattern [14].

4. Main Microscopic Characteristics of Wear Fracture

The SEM morphologies of the abrasive debris from crystalline Ni-P base composite coatings are shown in Figure 3. Main fracture modes are cleavage and granular. The microscopic fracture characteristic and mechanism of the wear debriss are concluded in Table 2.

Hardness and inter stress of the coatings are not high [15-17]. In another word, the coating material does not constitute typical brittle materials. However, the fracture of abrasive debris is mainly characterized as a brittle fracture, which is a characteristic, as well as a disadvantage of wear fracture. The reason for this finding is related to the characteristics of friction and wear force, such as stress concentration and rapid dynamic, which cause severe plastic uneven damage and reduction of the response capacity of the material on load and embrittlement. From the energy point of view, crystalline Ni-P base composite coating has a small amount of ductile fracture characteristics, such as torn edges, which is benefit of absorb the works of the external forces. On the other hand, while the intensive cleavage steps change the direction of the main crack propagation, more energy can be consumed.



(a) quasi-cleavage (b) Granular mode with torn edges (c) Granular mode with torn edges

Figure 3. *The SEM images of the debris from crystalline Ni-P base composite coating (i-P/1g CNTs).*

Table 2. *Microscopic characteristics on the wear debris of the coatings.*

coating type	**microscopic characteristics**	**crack nucleation sites**	**crack propagation paths**	**Fracture natures**
crystalline nickel-phosphorus	cleavage edges	Intragranular defects	Cleavage planes, grain	Cleavage, quasi-leavage
base composite coating	micro-cutting stripes, grain groups and torn edges	dislocation piles and its cell walls, etc.,grain oundaries	boundaries	granular with micro-plastic deformation

5. Conclusions

In the process of friction and wear, severe plastic formation damages and structure changes occur at the worn surface. It mainly is the dislocation movement and proliferation that cause dislocation configuration changes in crystalline Ni-P based composite coating, and as the applied load increases, the dislocation configuration changes from dislocation tangles to the formation of cell and the cell deformation.

The surface of abrasive debris records a large amount of wear fracture information. Thus, the analysis of abrasive debris helps to understand the microscopic mechanism of wear crack nucleation and propagation. The wear fracture of crystalline nickel-phosphorus base composite coating is micro-plastic deformation inter-granular, cleavage and quasi-cleavage. The microscopic characteristics of abrasive dust are cleavage steps, micro-cutting stripes, grain groups and torn edges. Wear crack nucleation sites generally are intragranular defects such as dislocation piles and cell walls as well and at the grain boundaries. The crack propagation path is cleavage planes and grain boundaries.

Conflicts of Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “Microstructure and Debris Fracture for Crystalline Ni-P-CNTs Composite Coatings after Wear”.

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