

# Wear mechanism of electrodeposited amorphous Ni-Fe-P alloys<sup>①</sup>

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**Abstract:** The wear mechanism of amorphous Ni-Fe-P coating was discussed. The wear resistance of the amorphous Ni-Fe-P coatings was tested on a Timken wear apparatus, and the wear track of the amorphous Ni-Fe-P coatings as deposited and heated at various temperatures was observed by SEM. The results show that the wear resistance reaches a maximum value at NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O concentration of 5 g/L, and heating at 400 °C. The wear mode of the coating will change with the heating temperature increasing from pitting+ plowing at 200 °C to pitting at 400 °C, and to plowing at 600 °C. The pits on the worn surface of the amorphous Ni-Fe-P coating result from the tribofatigue fracture. The cracks of spalling initiate at pits and propagate at certain angle with the sliding direction on surface, and then extend into sub-surface along the poor P layers or the interface between layers. Finally under repeated action of the stress in the rubbing process the cracks meet and the debris forms. The generation of the pits and spalling is related with the internal stress, brittleness and layer structure of the amorphous Ni-Fe-P coating.

**Key words:** Ni-Fe-P coating; amorphous alloy; wear mechanism

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## 1 INTRODUCTION

Amorphous alloys are characterized by high wear and corrosion resistance, together with many specific physical properties<sup>[1,2]</sup>. They have been used as functional materials in many fields extensively. The amorphous Ni-P alloy has been applied to automobile<sup>[3]</sup>, aircraft, computer, electronics, food processing, petroleum, and so on<sup>[4]</sup>.

Electrodeposition or electroless plating is one of the most simple, convenient and economic methods to obtain various amorphous alloys. The most attractive amorphous alloys consist of the elements of iron family (Fe, Ni, Co) and metalloid (P, B, S, C). The Ni-Fe-P alloys have soft magnetic properties<sup>[5]</sup> and wear resistance<sup>[6]</sup>. It can be used as a magnetic recording material. The metastable Ni-Fe-P amorphous alloy will crystallize and transform from metastable to stable state when it is affected by temperature<sup>[7]</sup> or pressure<sup>[8]</sup>. The inherent property of the amorphous alloy will disappear. However, fine, dispersed, intermetallic compound in the Ni-Fe-P amorphous alloy will be precipitated when being heated properly, and high hardness and wear resistance due to the dispersion strengthening will be obtained<sup>[9]</sup>.

The understanding of the structure of the amorphous alloy is clear, but the study on the wear mecha-

nism of the amorphous coating is few. In this paper, the wear mechanism of the amorphous Ni-Fe-P coating will be discussed and an effective method to improve its wear resistance will be proposed.

## 2 EXPERIMENTAL

The amorphous Ni-Fe-P coatings were deposited on a hardened and tempered steel 45<sup>#</sup> by electrodeposition process. The electrolyte compositions were: NiSO<sub>4</sub>·6H<sub>2</sub>O 100 - 200 g/L, FeSO<sub>4</sub>·7H<sub>2</sub>O 50 - 150 g/L, NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O 0.5 - 15 g/L, H<sub>3</sub>PO<sub>4</sub> 10 - 50 g/L, some buffering agents and complexants. The operating conditions were: pH= 0.5 - 2.0, temperature 60 - 80 °C, current density 3 - 20 A/dm<sup>2</sup>. The bath temperature was controlled by electro-contact thermometer, infrared ray lamp and transistor relay.

The wear tests were performed on a Timken wear apparatus (ring/block type) at a sliding speed of 1 m/s under 270 N load for 1 h while No. 20 machine oil was dripped onto the wear ring at 4 drops/min. The ring, made of quench hardened steel 45<sup>#</sup>, has the hardness of HRC 57 and the surface roughness of 0.51 - 0.76 μm. The Ni-Fe-P alloy was deposited on the block with the coating thickness of 50 - 100 μm. The friction coefficient was measured continuously by a dynamic strain gauge attached to the Timken wear apparatus. The worn surface morphology was observed on a Hitachi X-650 scanning electron micro-

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scope. The structure of the coating was examined on a Rigaku D/Max-RB automatic X-ray diffractometer under 50 kV, 150 mA,  $DS = 1^\circ$ ,  $SS = 1^\circ$ ,  $RS = 0.3$  mm, scanning speed of  $2^\circ/\text{min}$ , sampling step of  $0.02^\circ$ , using copper target and graphite monochromatic filter. The microhardness was determined on a 71-type microhardness tester under test load of 0.5 N and loading time of 15 s.

### 3 RESULTS AND ANALYSIS

#### 3.1 Structure of amorphous Ni-Fe-P coating

The surface of the amorphous Ni-Fe-P coating as-deposited displays a lot of granular convexities, as shown in Fig. 1. The sizes of the granular convexities reduce with increasing phosphorus content<sup>[10]</sup>. The interfaces between these grains where the cracks are easy to nucleate make the continuity of the material destroyed, and result in stress concentration. The research results<sup>[11]</sup> by positron annihilation showed that in the amorphous alloy there are many structure defects which are characterized by the free volume and contain a few larger holes which have a size of 3–4 atomic vacancies referring to the crystalline state. These defects will play an important part in the plastic deformation.

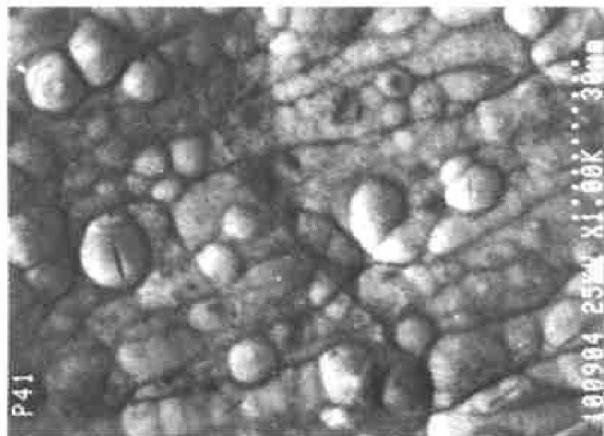


Fig. 1 Morphology of Ni-Fe-P coating surface

The microstructure of the electrodeposited Ni-Fe-P coating is shown in Fig. 2. The cross section of the coating by electrolytic etching exhibits a structure of alternate light and dark bands parallel to the surface. The light bands are generally wider than the dark ones. Some dark bands are clear while others are faint. The distance between successive dark bands varies from a fraction to several micrometers. The light bands contain more phosphorus than the dark bands<sup>[12]</sup> as Ni-P coating<sup>[13]</sup>. So the disorder degree of the light bands is greater than that of dark bands. The banded structure results from the variation of the phosphorus content. The dark bands containing less P, where the order degree is less destroyed during electrodeposition, may be at a mixed state of amor-

phous and crystal. The amorphous Ni-Fe-P coating has a layer structure in three dimensions. The interfaces of the layers are weak for the structure. The layer structure will play an important role in the wear behavior.

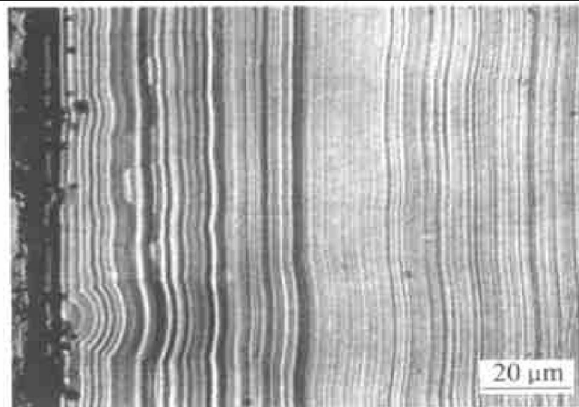


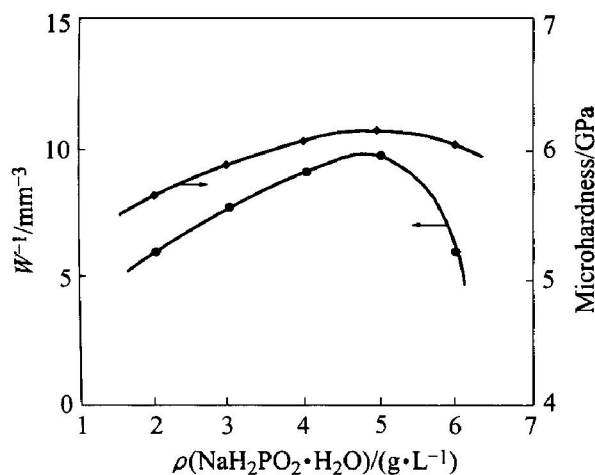
Fig. 2 Metallograph of amorphous Ni-Fe-P alloy electrolytically etched (SEM)

There is no long-range order in the amorphous alloy that is different from crystal. Sadoc et al<sup>[14]</sup> considered that two P atoms are never first neighbours according to the results of partial interference and radial distribution function, that is, there are no adjacent double P-P atoms in the amorphous Ni-P type alloy. It has a tetrahedral close packing (TCP) structure with P atoms spreading out in this matrix without long-range order and surrounded by 9 metallic atoms. So it is considered that during electrodeposition of amorphous Ni-Fe-P alloy, because P atoms have larger chemical affinity with Ni and Fe atoms and produce chemical action with them, the atom colonies are formed with central P atoms enveloped in Ni and Fe atoms. These atom colonies destroy the long-range order degree in the structure of Ni and Fe. The higher the P content, the greater the disorder degree of the coating.

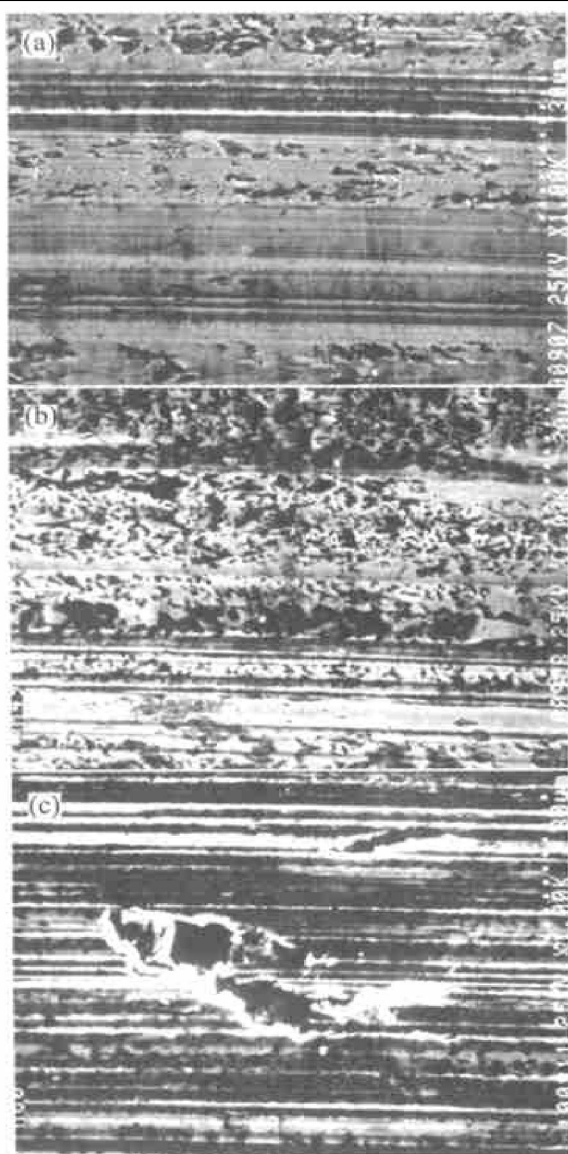
#### 3.2 Influence of P content on wear resistance

The effects of the  $\text{NaHPO}_2 \cdot \text{H}_2\text{O}$  concentration on the microhardness and the wear resistance of the Ni-Fe-P coating are shown in Fig. 3. The microhardness and wear resistance reach their maximum values when  $\text{NaHPO}_2 \cdot \text{H}_2\text{O}$  concentration is increased to 5 g/L. The wear resistance decreases remarkably when the  $\text{NaHPO}_2 \cdot \text{H}_2\text{O}$  concentration is higher than 5 g/L.

Fig. 4 shows the worn surface of the Ni-Fe-P coating with various P content. There are a lot of pits and plowings on the worn surface of the coating with 7.8% P content, as shown in Fig. 4(a). The size of the pits increases with the increase of P content. When the P content is beyond certain limit, the peeling in large block (Fig. 4(c)) appears. The marked increase of the wear loss can result from the increased brittleness of the coating due to excess P, even



**Fig. 3** Effect of  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  content on wear resistance and microhardness of coating



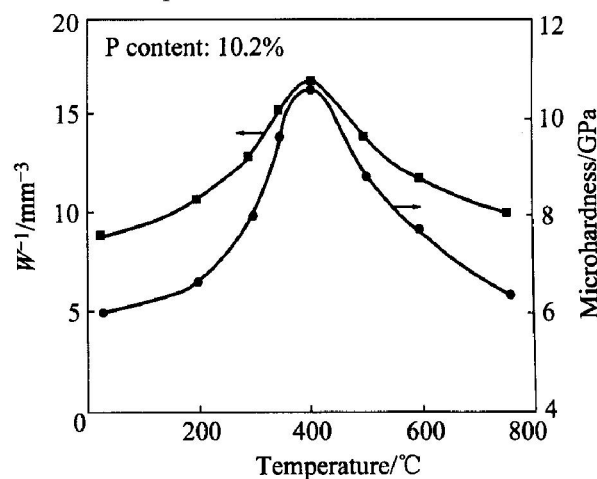
**Fig. 4** Worn surfaces of NiFeP alloys with various P contents (SEM)  
(a) -7.8% P; (b) -10.2% P; (c) -15.0% P

though the microhardness of the coating electroplated at 4 g/L  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  is nearly the same as that at 6

g/L. The wear debris cut the coating surface repeatedly and the plowings are formed. When the  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  concentration is less than 5 g/L, the increase of the wear resistance with the concentration results mainly from the increase of the microhardness.

### 3.3 Effect of heating temperature on wear resistance

The variation of the microhardness and wear resistance of NiFeP alloy with heating temperature is shown in Fig. 5. The microhardness of the alloy as-deposited is 5 880 MPa. The microhardness increases rapidly when heating temperature is between 300 °C and 400 °C, and then decreases markedly when the temperature is over 400 °C. The highest microhardness of the coating heated at 400 °C is 10 760 MPa. The wear resistance of the coating goes through a maximum value with increasing temperature, and reaches the peak at 400 °C. However the wear resistance of the coating heated at 750 °C is still higher than that as-deposited.



**Fig. 5** Effect of heating temperature on wear resistance and microhardness of NiFeP coating

When the coating is heated below 300 °C, there might be some hydrogen released, atom regrouping or structural relaxation, which make the hardness increase and internal stress decrease. As a result, the wear resistance is increased. When being heated between 300 °C and 400 °C, the coating is crystallized. New metastable phases are first formed and then transformed into stable phases of Ni(Fe) and  $(\text{Fe}, \text{Ni})_3\text{P}$  [7]. In this temperature range the wear resistance is increased because the grains of these crystalline phases just formed are very fine, and the fine  $(\text{Fe}, \text{Ni})_3\text{P}$  grains with very high hardness are distributed in the matrix of Ni(Fe). For this kind of structure the load is mainly carried by the hard second phase particles in wear process. The wear resistance depends mainly on the properties, number and distribution of the second phase particles. In general, the

harder and the more the particles, the better the wear resistance of the material. Above 400 °C the wear resistance decreases because the hardness of the coating decreases markedly. The wear resistance of the coating heated at 750 °C, however, is still higher than that of the amorphous alloy as-deposited. This demonstrates that the crystallized structure forms in the fine and dispersed Ni(Fe) and (Fe, Ni)<sub>3</sub>P phases and its wear resistance is higher than that in amorphous state.

The worn surface of the coating heated at different temperatures is shown in Fig. 6. There are a lot of plowings and pits on the surface of the coating heated below 400 °C. The pits of the coating heated at 200 °C appear as irregular, just as that of the coating as-deposited (Fig. 4(b)). The plowings on the worn surface of the coating heated at 400 °C are less and shallower because of its higher microhardness. With the phase transformation and the diffusion of atoms the band structure disap-

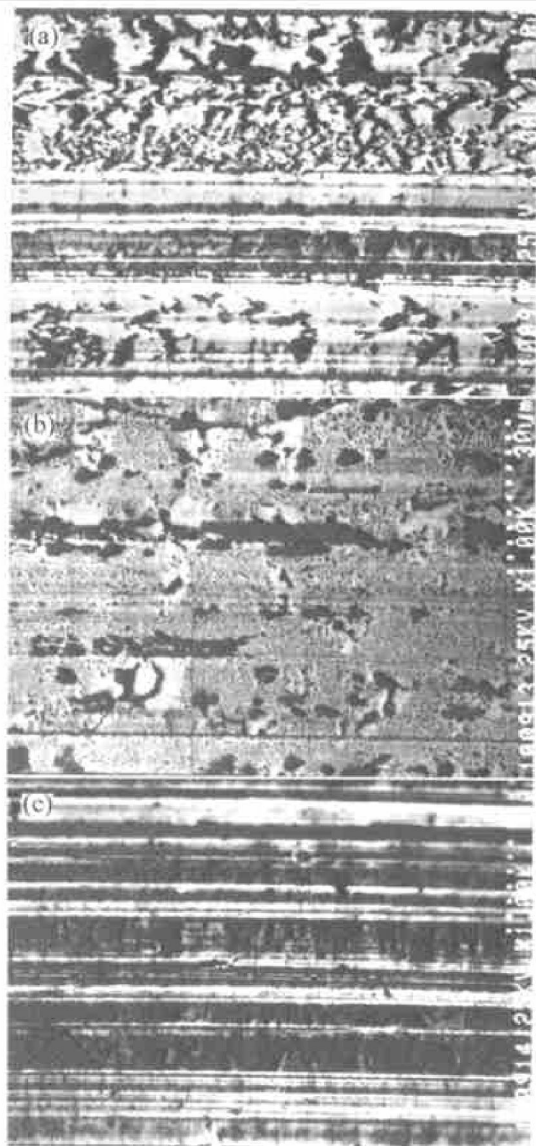
pear<sup>[6]</sup>. Internal stress relieves sufficiently at a higher temperature and toughness increases. Only plowings are observed on the worn surface of the coating heated at 600 °C. The plowings, however, are deeper since the microhardness decreases.

#### 4 WEAR MECHANISM OF AMORPHOUS Ni-Fe-P COATING

The wear track of the coating as-deposited appears as pits and grooves. The pits form for disengaging of the micro-particle from the surface. When the coating rubs against counterface, the asperities on the surface of the coating and the counterface will embed, impinge and extrude each other. Their roots bear large stress as a cantilever. The stress will relax partially by the plastic deformation of the root material. The stress concentration and damage accumulation of plastic deformation on the roots under repeated extrusion effect make the microcrack easy to form at the roots or the interface of the convexities on the coating surface. The brittleness and the tension stress on the coating surface will promote this process. The cracks nucleating at the roots are easy to propagate along the boundaries of the convexities and the weakness of the layer structure or through the defects of the amorphous coating, such as microhole. When the shearing stress on the friction surface is greater than the breaking strength of the remainder in the crack front, the asperities will fall off from the coating surface and then many pits are formed. The falling debris or the asperities will cut the deposit surface repeatedly and many grooves are formed on the worn surface. The wear mass loss of the amorphous coating by this mechanism is less relatively. Essentially, the formation of the pits is a tribo-fatigue process and is related to the brittleness and the stress condition of the coating.

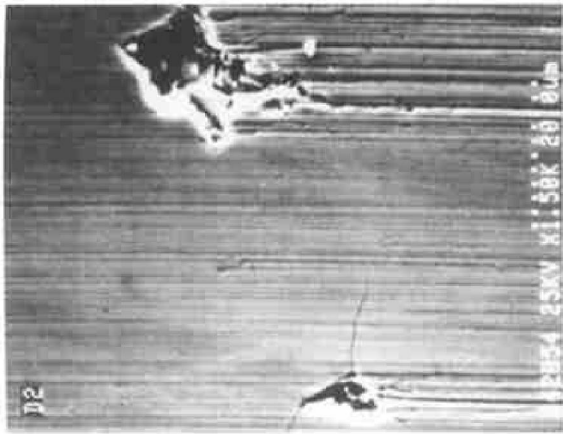
There appear a few pits as small cave by spalling on the worn surface of the coating with P content of 10.2% or as large cave on the worn surface of the coating with P content of 15.0%. The spalling takes its source at the pits. The cracks extend from pit to outside, as shown in Fig. 7. There is another larger pit in Fig. 7. The depth of the grooves on the two sides of the pit makes an obvious difference along the sliding direction.

According to the wear track the spalling starts from the pit. In frictional process by boundary lubrication the formed pits on the coating surface take effect in storing oil and lubricating. However, they lead to the discontinuity of the structure and stress concentration. The lubricating oil stored in the pits plays a role in transmitting force. Under combination of load and internal stress of the coating the cracks are easy to form at the pit rim and then propagate at an angle with sliding direction. In the subsurface the



**Fig. 6** Worn surfaces of Ni-Fe-P alloys heated at various temperatures

(a) —Heated at 200 °C; (b) —Heated at 400 °C;  
(c) —Heated at 600 °C



**Fig. 7** SEM photograph of worn surface of amorphous Ni-Fe-P alloy

structure of poor P layers (corresponding to the dark bands in the cross section) is approaching to the crystal. The plastic deformation, defect convergence and crack nucleation are all easy to perform at these layers. The crack will propagate along the poor P layers or the interface between layers. The pits extend gradually to a cave. The spalled debris will extrude and cut the coating, especially at back rim of the pit (shown in Fig. 7), which leads to the further spalling or plastic damage. It is an important reason why the pits are easy to connect into a cave along the sliding direction.

The spalling generally occurs when P content of the coating goes beyond certain limit or under heavier load. It is related to the brittleness, internal stress and layer structure of the coating. Consequently the amorphous coating is suitable to application under light-load and its P content cannot be too high. Reducing the internal stress and brittleness of the coating can be favorable for increasing the wear resistance of the coating. The layer spacing in the pulse-plated alloy is much thinner than that in the DC-plated alloy and appears more uniform<sup>[15]</sup>. So using pulse plating is expected to increase the wear resistance of the amorphous coating that has a layer structure.

## 5 CONCLUSIONS

1) The wear resistance gets a maximum value at  $\text{NaHPO}_2 \cdot \text{H}_2\text{O}$  concentration of 5 g/L, beyond which the spalling will appear on the worn surface of the amorphous Ni-Fe-P coating, hence the wear loss increases.

2) The pits on the worn surface of the amorphous Ni-Fe-P coating result from the tribo-fatigue fracture of the asperities. The cracks of spalling start at pit and propagate at certain angle to the sliding direction on surface, and then extend into sub-surface along the poor P layers or the interface between layers. The pitting and spalling are both related to the internal stress, brittleness and layer structure of the

amorphous Ni-Fe-P coating.

3) The wear mode of the coating will change from pitting + plowing at 200 °C to pitting at 400 °C, and to plowing at 600 °C, which is related to the phase transformation of the amorphous Ni-Fe-P coating during the heat treatment.

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