# Structure and characteristics of electrodeposited RE- Ni- W- P- B₄C- PTFE composite coatings[①]

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[Abstract] Hardness, friction and wear characteristics of electrodeposited RE- Ni- W- P- B₄C- PTFE composite coatings were studied, and the reason for these fine characteristics was explained in respect of structure. The results show that 1) the structure of RE- Ni- W- P- B₄C- PTFE composite coatings experiences a transformation process from amorphous to mixture then to crystal as the heat- treatment temperature rises; 2) incorporating of B₄C greatly increases the hardness of the coating; 3) the wear resistance of the coating is best with heat- treatment for 1 h at 300 ℃, which is greatly superior to that of the other traditional coatings.

[Key words] electrodeposited; RE- Ni- W- P- B₄C- PTFE composite coatings; structure; hardness; wear- resistance

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## 1 INTRODUCTION

Ni-W-P alloy possesses excellent magnetism, strength, good heat-resistance and ideal wear and corrosion resistance, which has attracted the surface finishing and engineering communities for many years[1, 2]. B₄C is a kind of ceramic power with high hardness and fine wear-resistance, and PTFE is self-lubricating high polymer[3, 4]. Rare earth can increase the solid particle content in composite coatings[5~7]. In order to increase further wear resistance of Ni-W-P alloy and decrease its microcrack, B₄C and PTFE are added into the bath.

There are many studies on basic composite coatings such as Ni-P, Ni-W, Au, and Ag etc[8], and more and more attention is paid to the Ni-W-P-based composite coatings. But the research for more complex coatings with more components is very rare, not to say the study of their structure.

This paper mainly describes friction and wear characteristics of the electrodeposited RE-Ni-W-P-B₄C-PTFE composite coatings. It also explains the fine characteristics in view of structure.

## 2 EXPERIMENTAL

### 2. 1 Basic bath composition and plating condition

| | |
|---|---|
| NiSO₄•H₂O | 20~ 40 g/ L |
| NaWO₄•2H₂O | 80~ 100 g/ L |
| NaH₂PO₄•H₂O | 10~ 14 g/ L |
| Complex | 80~ 100 g/ L |
| Rare earth ( CeO₂) | 6~ 10 g/ L |
| B₄C | 30~ 60 g/ L |
| PTFE | 10~ 20 ml/ L |
| Current density | 0. 10~ 0. 16 A/ m² |
| Temperature | 40~ 70 ℃ |
| pH | 4. 5~ 7. 5 |
| Time | 2 h |

When PTFE particles were added into bath, they were not wetted completely. It is necessary to add a certain surfactant into the bath. Also, all particles could be uniformly suspended in the plating solution by circulating them, using a tubing pump. The deposition rate was 45 μm/ h, and the RE- Ni- W- P- B₄C- PTFE composite coating of 90 μm thick was deposited on the matrix.

### 2. 2 Matrix material

15 mm × 20 mm × 1. 5 mm A3 steel, $d$ 16/ 40 mm × 10 mm 45[#] steel, $d$ 16/ 40 mm × 10 mm GCr₁₅ steel( quenching state).

### 2. 3 Test Method

HX- 1 microhardness tester was used to measure the hardness of the coating under a load of 0. 1 kg throughout.

Chemical composition of the coating was determined by EDAX9100 type electron probe X- ray analyzer.

Wear- resistance of the coating was examined by M 2000 abrasion tester. The mass difference of an unit area of standard wear samples before and after abrasion was examined.

Phase structure of the coating was determined by 3015 diffractometer.

Heat- treatment was carried out in CHOY type

resistance furnace.

# 3　RESULTS AND DISCUSSION

## 3. 1　Chemical compositions of RE-Ni-W-P-B$_4$C-PTFE composite coatings

The chemical compositions of the coating deposited under the above-mentioned condition is given in Table 1.

**Table 1**　Chemical compositions of coating deposited under above-mentioned condition (%)

| Ni | W | P | B$_4$C | PTFE | RE |
|---|---|---|---|---|---|
| 68. 8 | 5. 8 | 9. 7 | 8. 2 | 1. 6 | 5. 9 |

## 3. 2　Hardness of RE-Ni-W-P-B$_4$C-PTFE composite coatings

3. 2. 1　Influence of heat treatment temperature on hardness of RE-Ni-W-P-B$_4$C-PTFE composite coatings

The influence of heat treatment temperature on the hardness of the RE-Ni-W-P-B$_4$C-PTFE composite coatings is shown in Fig. 1.

It can be seen that with increasing temperature, the hardness increases accordingly, and at 400 ℃, it reaches peak value. But as the temperature rises furthermore, it then decreases.

Fig. 2 shows the XRD patterns of the RE-Ni-W-P-B$_4$C-PTFE composite coatings at various heat temperatures, which helps to explain the above-mentioned phenomenon.

In Fig. 2(a), there is a bread-shaped peak (where $2\theta = 45°$), and the area of amorphous is very wide. It can't be determined that as-deposited coating is absolutely amorphous, because there is a char-
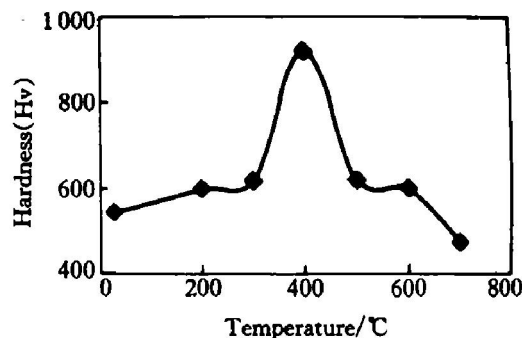


**Fig. 1**　Effect of heat treatment temperature on hardness of Ni-W-P-B$_4$C-PTEF composite coating (heat treated for 1 h)

acteristic peak of not only B$_4$C and CeO$_2$(RE), but also Ni and W at the same position. Although the peak is very weak, it is the typical characteristic of crystalline state. So it can be stated that in low temperature, the coating is mainly amorphous and partly crystallized.

After heat treated at 400 ℃, the diffraction peak becomes more narrow (Fig. 2(b)), and the area of amorphous contracts greatly, i. e. it is easy for atom to migrate and diffuse. A great amount of Ni, W phase appears in crystal area with strong characteristic peak. There also appears strong Ni$_3$P phase, which is the typical characteristic of crystalline state. All results show that as a result of heat treatment, coating's tendency of crystal rises and the coating is in the stage of transformation from amorphous to crystal, which is called "the mixture". The occurrence of FeNi phase is the result of Ni in coating permeating to the Fe-base. In this way, the adhesive force between the composite coatings and matrix is raised greatly.
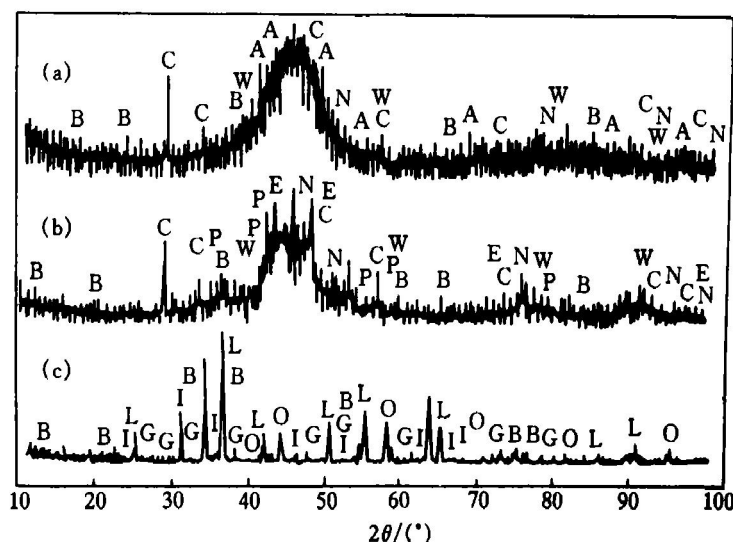


**Fig. 2**　XRD patterns of RE-Ni-W-P-B$_4$C-PTFE composite coatings heat treated at various temperatures
X —Amorphous; A —Ni$_2$P; B —B$_4$C; C —CeO$_2$; E —FeNi; G —WO$_3$; I —Ni$_2$P$_2$O$_7$; L —Fe$_2$O$_3$; N —Ni; O —NiO; P —Ni$_3$P; W —W
(a) —As-deposited; (b) —400 ℃, 1 h; (c) —800 ℃, 1 h

Compared with Fig. 2(a) and Fig. 2(b), crystal characteristics in Fig. 2(c) are more distinct. The diffraction peak becomes sharp, at the same time, the number of peak increases and big area of amorphous can not be seen. At 800 ℃, Fe-base, Ni and W are oxidized into $Fe_2O_3$, NiO and $WO_3$ respectively. $Ni_3P$ is oxidized into $Ni_2P_2O_7$ furthermore. After heat treated at 800 ℃ for 1h, the coating is entirely crystallized. $B_4C$ is very stable at high temperature since there still is its characteristic peak in Fig. 2(c).

In conclusion, at low temperature, the coatings are mainly amorphous, with a lower hardness correspondingly. When the temperature increases to 300~400 ℃, the distortion of crystal lattice is very severe, and the intermediate phase $Ni_3P$ appears, which is an intermetallic compound possessing very high hardness. At the same time supersaturated Ni solid solution forms, which has the function of precipitation and hardening. All of these continue to increase the hardness of the coating. Then at 400 ℃, hardness reaches maximum value and the coating is the mixture of amorphous and crystal. With increasing temperature, the coating crystallized. Although the quantity of $Ni_3P$ increases, the growth of crystal and the reverse effect prevail. As a result, crystalline grain coarsens; the internal stress decreases, and then gathers together. By contrast, contribution of the increase of $Ni_3P$ amount to the hardness is less, and can not resist lowing of the tendency of hardness. So the coating softens and the hardness decreases. The maximum hardness can reach to as high as 920Hv. Compared with the other coatings (Table 2), it can be stated that incorporating of $B_4C$ greatly increases the hardness of the coatings.

**Table 2**   Comparison of harness and wear resistance between RE-Ni-W-P-B₄C-PTFE composite coating and other coatings

| Material | Hardness (Hv) | Wear amount / ($mg \cdot cm^{-2} \cdot h^{-1}$) |
|---|---|---|
| RE-Ni-W-P-B₄C-PTFE [*] [△] | 920 | 0.65 |
| Ni-W-P [*] [△] | 500~600 | 1.85 |
| Ni-W-P [△] | 200~350 | 2.55 |
| Ni-W-P-SiC [△] | 550~700 | 2.93 |
| Ni-P-SiC [*] [△] | 700~800 | 3.43 |
| Ni-SiC [△] | 450~550 | 22.5 |
| Hard chromium [△] | 800~900 | 23.8 |

[*]  Heat treated at 400 ℃ for 1h
[△]  Determined by M2000 abrasion tester.
     Load 490N, number of circulating 6×10⁴

3.2.2 Influence of heat treatment time on hardness of RE-Ni-W-P-B₄C-PTFE composite coatings

Fig. 3 shows the influence of heat treatment time on the hardness of the RE-Ni-W-P-B₄C-PTFE com-
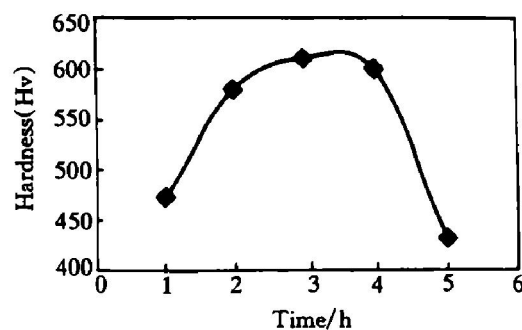


**Fig. 3**   Effect of heat treatment time on hardness of RE-Ni-W-P-B₄C-PTFE composite coatings ( heat treated at 700 ℃)

posite coatings at 700 ℃.

It can be seen that the curve ascends first, then descends, and reaches peak value 3h. While heat treated, precipitating and hardening of $Ni_3P$ phase leads to hardness increasing of the coating. After treated for 3h, the growing of crystal and the reverse effect prevail, so crystalline grain coarsens, the internal stress decreases, and gathers together resulting in hardness lowering.

### 3.3   Influence of heat treatment temperature on wear-resistance of RE-Ni-W-P-B₄C-PTFE composite coatings

The influence of heat treatment temperature on the wear-resistance of the RE-Ni-W-P-B₄C-PTFE composite coatings is shown in Fig. 4.
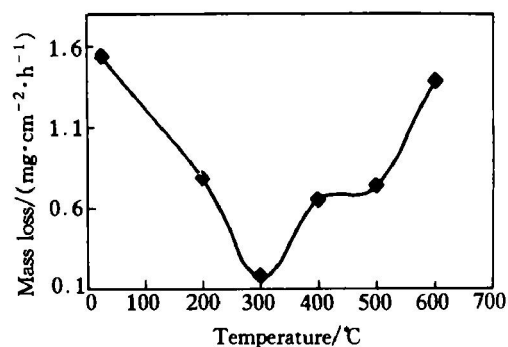


**Fig. 4**   Effect of heat treatment temperature on wear-resistance of RE-Ni-W-P-B₄C-PTFE composite coatings ( heat treated for 1h)

When temperature is below 300 ℃, as the temperature increases, the abrasion degree of the coating decreases accordingly. When temperature is over 300 ℃, the abrasion degree increases. In view of the above-mentioned phenomena, it is just because of the excellent self-lubricating characteristic of PTFE. What takes the main effect of anti-friction on the coating is PTFE, instead of the oxide layer of the coating. Below 300 ℃, the reason for wear-resistance of the coating tending to be better with the increase of temperature lies in the migrating and diffusing of P

atoms, which causes crystal lattice distortion. This distortion arouses the interaction between the elastic energy resilience and dislocation, then increases the resistance of dislocation movement. As a result, wear amount decreases. In addition, it can be seen in Fig. 1, the hardness of the coating increases during this period of temperature, which is also beneficial to increasing the wear resistance of the coating. When heat treatment temperature increases to 300~ 400 ℃, wear-resistance decreases with increasing temperature. Because PTFE is a high polymer with a relatively low melting point and it will decompose in high temperature. Generally speaking, the higher a coating's hardness, the more excellent its wear resistance. But at 400 ℃, the coating has the highest value of hardness, wear resistance of the coating is not so good as that at 300 ℃. According to Fig. 2(b), which has no PTFE characteristic peak, it can be known that PTFE, as self-lubricant, decomposes more at 400 ℃ than at 300 ℃. Above 400 ℃, the intermediate phase $Ni_3P$ gathers together, coarsens, and distortion of lattice disappears, resulting in not only the hardness decreasing but also the coating's wear-resistance lowering. Furthermore, at the moment, PTFE has decomposed completely. It can be concluded that in the process of increasing temperature from as-deposit to 400 ℃, the wear resistance of RE-Ni-W-P-$B_4$C-PTFE composite coatings is best at 300 ℃, as a result of the competing of the PTFE decomposition in high temperature and the coating's crystallization. Moreover, according the abrasion degree shown in Table 2, the wear resistant characteristics of the coating is greatly superior to that of other coatings.

## 4　CONCLUSIONS

1) According to XRD patterns, the structure of RE-Ni-W-P-$B_4$C-PTFE composite coatings experiences a transformation process from amorphous to mixture then to crystal with increasing heat treatment temperature.

2) Under the condition of heat treatment, there emerge the particles of $Ni_3P$ in the coating, which bring about dispersion hardening. As a result, the hardness of the RE-Ni-W-P-$B_4$C-PTFE composite coatings increases, and at 400 ℃, it reaches its peak value. Compared to convention Ni-W-P alloy coatings, the hardness of RE-Ni-W-P-$B_4$C-PTFE composite coatings is greatly increased.

3) Under the condition of heat treatment, the wear resistance of RE-Ni-W-P-$B_4$C-PTFE composite coatings is best at 300 ℃, as a result the competing of the PTFE decomposition in high temperature and the increase of the hardness of the coating are greatly superior to that of other conventional Ni-W-P alloy coatings.

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