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Effect of wear conditions on tribological properties of electrolessly-deposited Ni−P−Gr−SiC hybrid composite coating

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Abstract: The friction and wear properties of the electrolessly-deposited Ni−P−Gr−SiC composites were investigated. The effects of graphite content, load and rotation speed on the friction coefficient and wear resistance of the composite coatings were mainly investigated. The worn surface and cross section of the coatings were characterized by scanning electron microscopy and energy-dispersive X-ray analysis. The results show that the composite coatings reveal good antifriction and wear resistance due to the synergic effect of graphite and SiC particles. The formation of graphite-rich mechanically mixed layer (GRMML) on the surface of Ni−P−Gr−SiC coating contributes to the good tribological behavior of the wear counterparts and SiC particles play a load bearing role in protecting GRMML from shearing easily.

Key words: electroless composite coating; Ni−P coating; graphite; SiC; tribological property; self-lubrication; synergic effect

1 Introduction

Composite coatings have various properties, such as wear resistance, self-lubrication and oxidation resistance depending on the second phases. Self-lubricants are used for the production of bearing materials and generally considered for use where oil lubricants cannot be used [1,2]. Several kinds of these solid lubricating materials, such as graphite, polyfluorotetraethylene (PTFE), CaF_2, MoS_2, and mica are used as self-lubricants with a metal matrix, such as Ni or Cu and its alloys [3,4].

The Ni−P alloy coatings fabricated by electroless plating have been widely applied into chemical, mechanical and electronic industries because of their good corrosion resistance and anti-wear, weldability, etc. Based on the electroless nickel plating process, the electroless composite plating has been well developed in recent years by adding various particles, such as silicon carbide, aluminium oxide, graphite and PTFE, into electroless nickel plating bath according to demands [5−9].

Self-lubricant composite materials, especially Ni−P−PTFE and Ni−P−Graphite, are widely used because of their low friction coefficient. However, their strength and wear resistance are low due to the weakening effect of PTFE and graphite [10,11]. In theory, introducing hard particles can offset the mechanical and tribological properties loss of such materials. Therefore, the hybrid composite coatings containing both hard and lubricating particles are attracting many interests in recent years. HUANG et al [12] discussed the microstructure and properties of Ni−P−PTFE−SiC. CHI et al [13] and GAO et al [14] prepared the electroless Ni−P−PTFE−SiC composite coatings and evaluated its friction properties. Additionally, LOSIEWICZ et al [15] analysed the phase composition and surface morphology of electrolytic Ni−P−TiO_2−PTFE composites for an electrochemical reaction electrode [15]. GUO et al [16] prepared electrodeposited Re−Ni−W−SiC−PTFE composite and evaluated its properties. GUO and TSAO [17] studied the tribological behaviour of aluminium/SiC/nickel-coated graphite hybrid composite synthesized by the semi-solid powder densification method. It is well known that the graphite is one of the frequently used solid lubricant materials just like PTFE, and SiC used as one kind of hard particles. Therefore, metal reinforced with SiC and graphite particles, draws special attentions [18]. However, few reports involved in deep discussion about the effect of wear condition on tribological properties and mechanism.

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The investigations in preparation and mechanical properties of the electroless Ni−P−Gr−SiC coating have been conducted lately by the authors [19,20]. In this work, the tribological properties of the coatings with different graphite contents were evaluated at different loads and rotation speeds, respectively. The anti-friction and wear mechanism of the hybrid composites were discussed.

2 Experimental

Ni−P−Gr−SiC coatings, 40 μm in thickness, were deposited on mild carbon steel substrates by the electroless composite plating. The experimental details were described in other paper by the authors [19]. The dry sliding wear tests were performed using a ring-on-plate type wear machine at an air humidity of 48%±10% at room temperature. The materials of the ring and plate were GCr15 steel (a kind of chromium-bearing steel, AISI 52100) and 45# steel with the hardness of HRC(62±3) and HRC(42±3), respectively, the size of which is shown in Fig. 1. Prior to the wear test, all contact surfaces were polished, cleaned in acetone and dried. The sample surfaces prepared in this way had an average roughness R_a=1.2 μm and the surface of the ring was polished to a roughness of R_a=0.9 μm. The test time for each specimen was 20 min considering the thickness of coatings. The wear loss and normalized wear rate were evaluated by mass loss which was measured by a electric

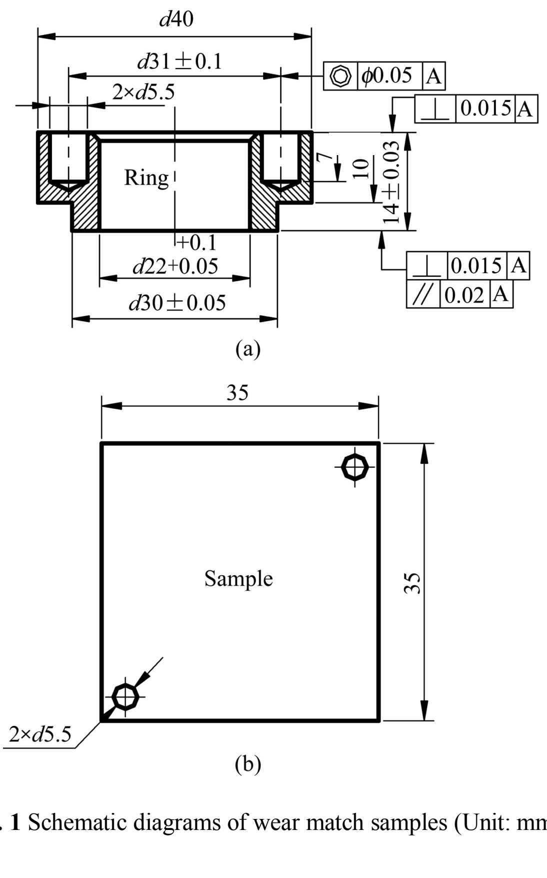

Fig. 1 Schematic diagrams of wear match samples (Unit: mm)

balance with 0.1 mg accuracy. The worn surfaces and subsurface stratum were analysed by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDAX).

3 Results and discussion

3.1 Tribological behavior of coatings with different graphite concentrations

Figure 2 shows the friction coefficient curves of the composite coatings deposited in the electroless plating bath containing the constant 8 g/L SiC and 0, 6, 9, 12 g/L graphite, respectively, at 70 N and rotation speed of 50 r/min. It is demonstrated that the friction coefficient of the composite coatings sharply decreases with the increase of graphite content, especially from 6 g/L to 9 g/L in the electroless plating bath, correspondingly increasing of the graphite content in the coating. Also, the vibration of the friction coefficient goes slightly and the wear system becomes more stable with high graphite content. When the graphite content rises up to 12 g/L, the friction coefficient also falls to 0.46 in the average value, but not a slash compared to the difference from 6 to 9 g/L graphite content.

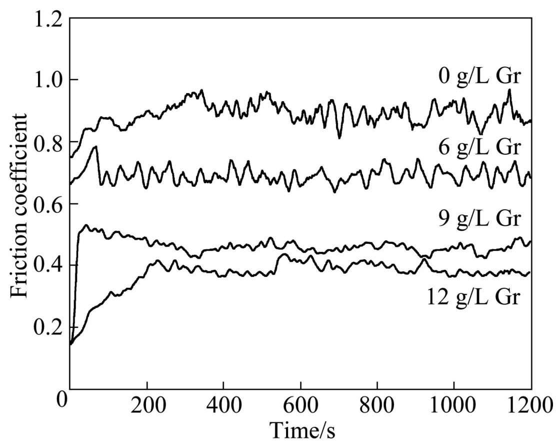

Fig. 2 Friction coefficient of composite coating with different graphite contents in electroless bath at 70 N load with rotation peed of 50 r/min

The wear tracks at different graphite contents are characterized in Fig. 3. For the Ni−P−SiC coating without the graphite, the worn surface has the wide grooves and irregular craterlets which results from grinding abrasion during sliding with the hard GCr15 counterpart. The discontinuous dark parts on the worn surface are produced when introducing 6 g/L graphite to the electroless bath. The whole worn surface becomes uniform and contact, and corresponding friction coefficient obviously decreases for 9 g/L graphite introduction. It can be concluded that the mixed parts play an important role in the antifriction properties of

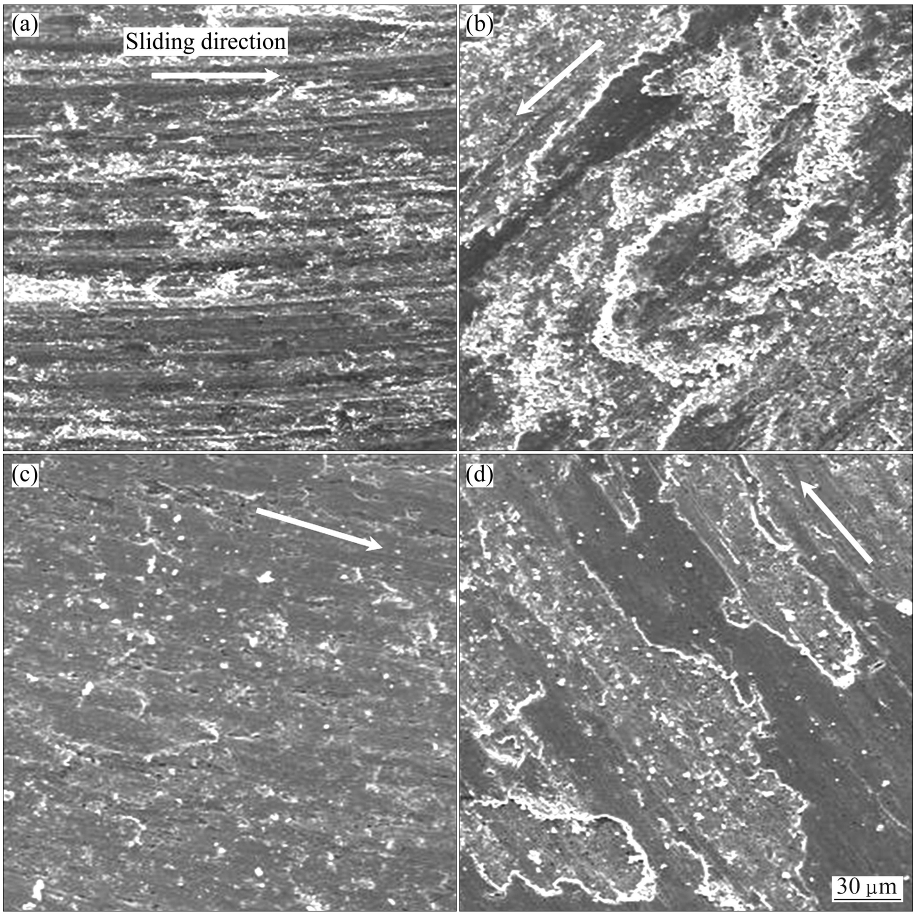

Fig. 3 Worn surface morphologies of composite coating with different graphite contents in electroless bath under 70 N load and 50 r/min: (a) 0 g/L Gr; (b) 6 g/L Gr; (c) 9 g/L Gr; (d) 12 g/L Gr

the hybrid composite coatings. This would be explained in details lately. For 12 g/L graphite content, the worn surface still keeps smooth, but is partly detached and the fresh mixed layers are being formed.

The average friction coefficient, wear loss of the composite coatings and counterparts at 70 N load with rotation speed of 50 r/min are listed in Table 1. The results reveal that the wear loss of the hybrid composite coatings increases with the increase of graphite content, especially for 12 g/L graphite content. The tendency is converse for the counterpart, namely the wear loss keeps decreasing with the increase of the graphite content, even becomes minus value, which means getting mass for 12 g/L graphite content. This mainly attributes to the descending mechanical properties because of the increasing content of graphite in the composite coating, which causes the severe wear of test samples, whereas can protect GCr15 counterpart from wear loss, even get mass by transferred wear debris from samples. By comparing the friction coefficient and wear loss, the hybrid composite coatings with 9 g/L graphite content (HCC98) in the electroless bath has the best friction properties, which is therefore selected for further study.

Table 1 Wear results of composite coating with different graphite contents in electroless bath at 70 N load with rotation speed of 50 r/min

Index	Graphite content in electroless bath			
	0 g/L	6 g/L	9 g/L	12 g/L
Average friction coefficient	0.892	0.690	0.464	0.373
Wear rate of coating(10^{-6} g·m^{-1})	1.84	4.36	8.14	25.69
Wear loss of counterpart (10^{-3}mg)	34	26	0.8	−0.12 (mass gain)

3.2 Effect of load and rotation speed on friction properties

The effect of load and rotation speed on the wear rate of HCC98 is displayed in Fig. 4. The wear rate of HCC98 obviously increases with increasing load from 50 N to 90 N, whereas has a low rise with the load increasing from 90 N to 120 N, and then sharply increases when the load exceeds 120 N, which means the severe wear of the coatings. By contrast, the wear rate of the counterparts keeps irregular with the load from 50 N to 150 N, however, totally presents increasing tendency, as shown in Fig. 5. Comparatively, the wear rate with rotation speed of 50 r/min is larger than that with 100 r/min below the load of 90 N, then it changes a little with the load increasing and is much less than that with the speed of 100 r/min above load 90 N. The analysis means that the load and rotation speed in heavy load range have great influence on the wear rate of the counterpart. In addition, the wear rate of the counterpart is much lower than that of the composite coating, which means that the wear matching system avoids the severe wear of the counterpart.

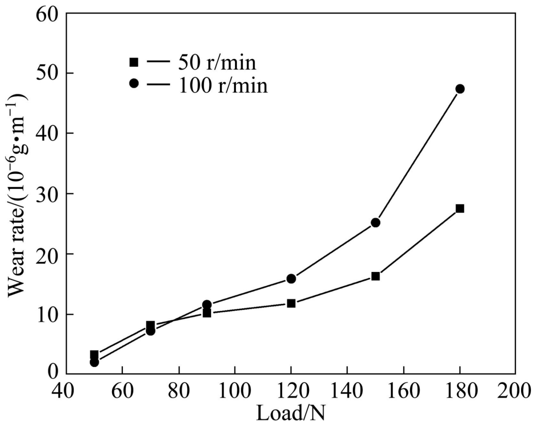

Fig. 4 Variation of wear rate of composite coating at different loads and rotation speeds

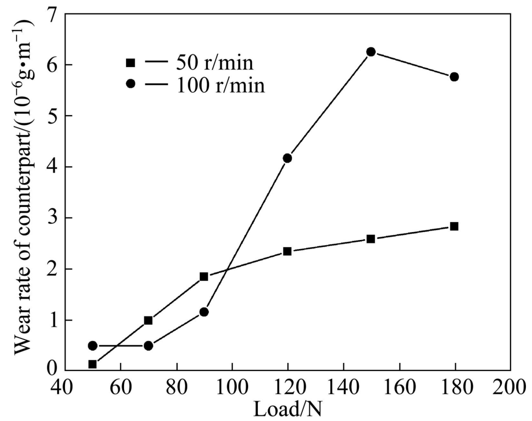

Fig. 5 Variation of wear rate of counterpart at different loads and rotation speeds

The friction coefficient can also be affected by the load and rotation speed. As listed in Table 2, the average friction coefficient has a little decrease with the load increasing from 50 N to 150 N and the rotation speed from 50 r/min to 100 r/min, however, it goes up sharply to high value at load of 180 N with speed of 100 r/min. The large change of the friction coefficient possibly results from the hard flaky detachments clipped between the matching samples, even worn out of the composite coating under heavy load.

3.3 Characterization of worn surface

From above analyses, the friction properties of the composite coatings are greatly affected by the load and rotation speed. By characterizing the worn surface achieved at different loads, the wear mechanism under different wear conditions can be clarified. As displayed in Fig. 6, the worn surface presents obvious differences. Particularly, the worn surface at load of 50 N is not smooth and distributes many flaky “knots”, marked as ‘K’ in Fig. 6(a), which are proved as graphite-rich mechanically mixed layer (GRMML) in our previous work [20]. Owing to the low load, the wear debris produced by ploughing function is not enough to form continuous GRMML. Conversely, these knots are hardened, but are not further plastically deformed and not fully spread out on the surface due to the low load. The convexes cause the vibration of the wear system and unstable running. The plastic deformation of GRMML is strengthened and produces large continuous layers with the load increasing, which are detailed in Figs. 6(b) and (c), where the friction coefficient keeps low and the wear system is stable. However, the GRMML is partially destroyed when the load goes up to 150 N and badly deformed and detached at 180 N because the transverse shearing stress increases and finally exceeds the deformation strength of GRMML according to the adhesion theory [21]. Obviously, undetached GRMML is smoother than that at low load since full deformation happens and there are few knots. The changes in friction coefficient at different loads are shown in Fig. 7. The results reveal that the friction coefficient becomes lower with the load increasing and the vibration of the wear system is indirectly reflected from the change of the friction coefficient. Generally, the vibration is relatively violent at the low load and stable at high load.

Table 2 Average friction coefficient of composite coating at different loads and rotation speeds

Rotation speed/(r·min^{-1})	Load					
	50 N	70 N	90 N	120 N	150 N	180 N
50	0.553	0.48	0.467	0.424	0.403	0.417
100	0.549	0.493	0.438	0.415	0.380	0.504

3.4 Wear mechanism of hybrid composite coatings

According to the discussion in Section 3.3, the worn surfaces of the Ni−P matrix with the graphite and SiC are covered by GRMML. To further clarify the wear mechanism of the hybrid composite coatings at different loads, the cross-sectional micrographs of subsurface stratum at the loads of 50 and 100 N are shown in Fig. 8. It is obviously seen that the GRMML at load of 50 N is discontinuous and very thin (Fig. 8(a)). Also, it seems that the GRMML has no strong adhesion to the substrate and can be easily detached from it. At a low load, the subsurface stratum is lightly deformed and micro-

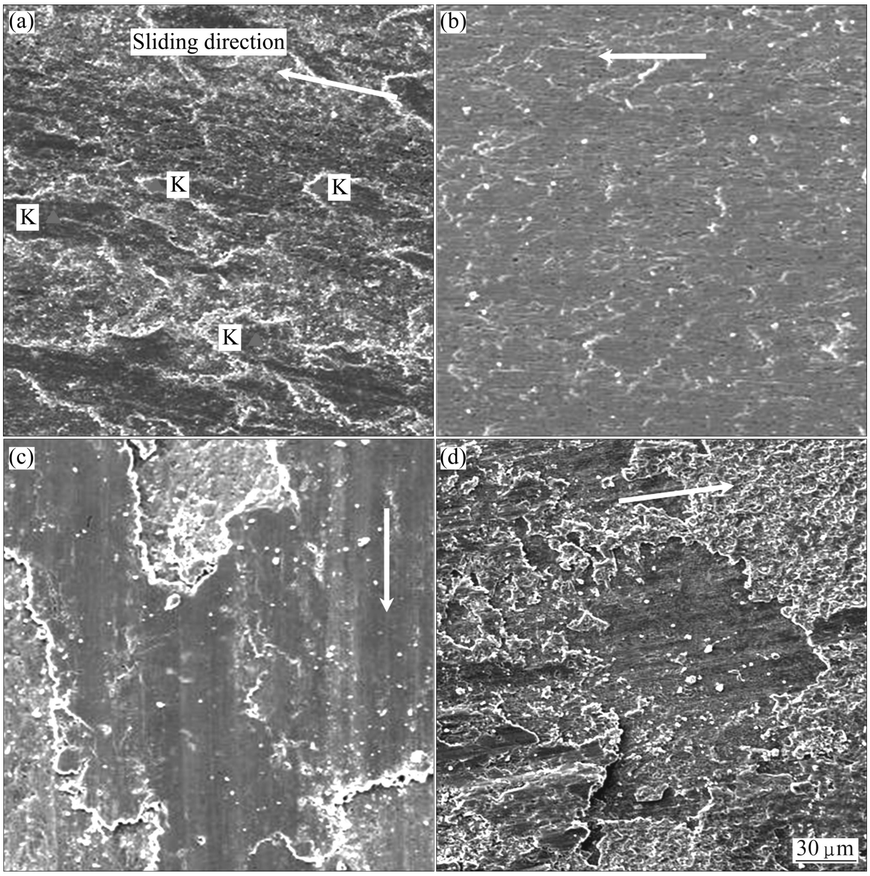

Fig. 6 Worn surfaces of Ni−P−Gr−SiC composite coatings at different loads: (a) 50 N, 50 r/min; (b) 90 N, 50 r/min; (c) 150 N, 50 r/min; (d) 180 N, 100 r/min

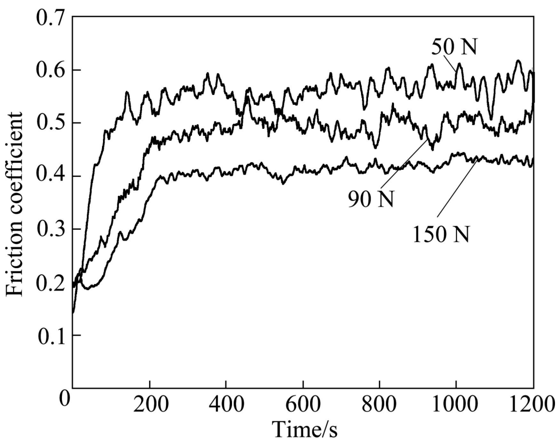

Fig. 7 Friction coefficient of HCC98 at different loads with rotation speed of 50 r/min

prominences on the surface of the counterparts are difficult to press into the test samples, then no much wear debris is produced under weak shearing action and full GRMML is difficult to form. However, the discontinuous GRMML at low load has no great influence on the tribological behavior of the hybrid composite coatings. With the increasing of load, the subsurface stratum of composite coatings is greatly deformed and the thickness of GRMML is apparently enhanced, as seen in Fig. 8(b). At high load, large plastic deformation of micro-prominences and full spreading of GRMML happen on the surface and more GRMML can also be transferred into the surface of the counterparts. Resultantly, the wear system becomes more stable and the friction coefficient is less than that at the low load. Additionally, more or less GRMML can be transferred into the surface of the counterparts during the wear, depending on the wear conditions. As seen from Fig. 9(a), the worn surface of the counterpart reveals similar features and contains all elements, such as Ni, C, Si and P from the composite coatings besides Fe and Cr from the counterpart by the EDAX analysis in Fig. 9(b). Clearly, the more transferred GRMML can avoid the direct action between the hard GCr15 and the sample. Finally, the wear interface shifts to the wear between GRMMLs. The GRMML is yet easily fractured and detached from the surface at heavy load because of the low shearing strength itself. When the detached rate of GRMML is higher than its generating rate, the severe wear happens and the composite coating is quickly worn out at heavy load. This can be proved from Fig. 8(b) that the interface between the subsurface stratum and GRMML is indiscernible, where many micro-fractures are produced.

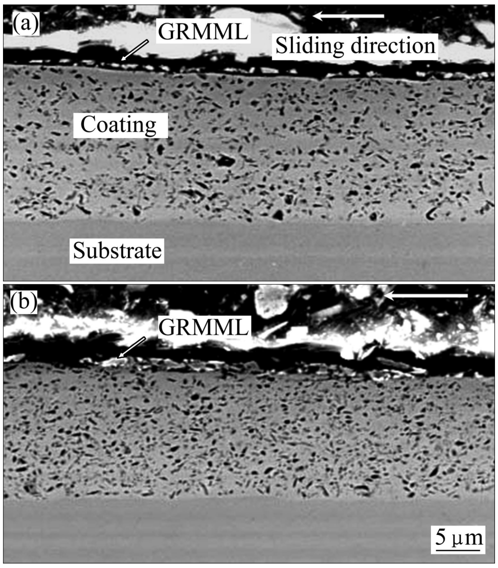

Fig. 8 SEM images of subsurface region at load of 50 N (a) and 150 N (b)

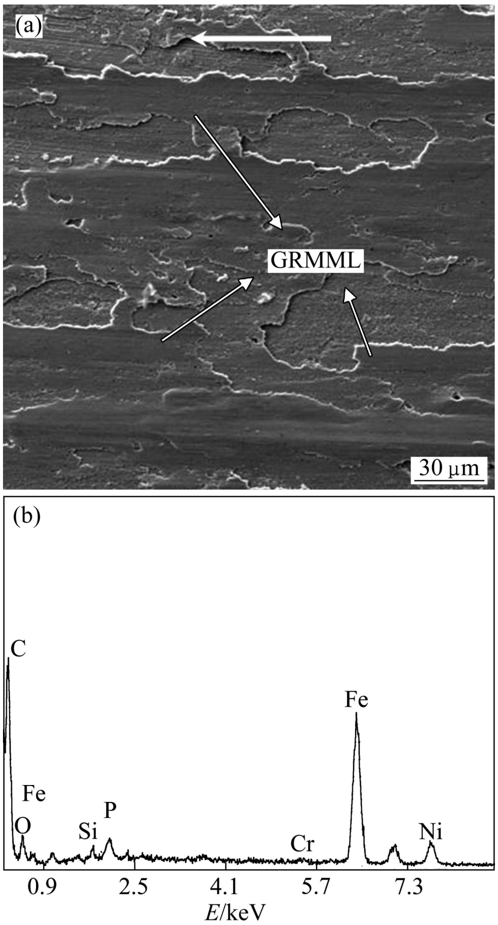

Fig. 9 SEM images (a) and EDAX spectrum (b) of worn surface of counterparts at load of 150 N

In the case of hybrid composite coating containing both self-lubricating graphite and hard SiC particles, it presents good antifriction and wear resistance, especially at high load. On one hand, the graphite has small shearing stress and easily slips between lamellar structures which play an important role in the decreasing of the friction coefficient. On the other hand, SiC particles on the worn surface are ground and mixed into the GRMML during the wear. Under the bearing of hard SiC, the GRMML is not easily deformed so that there is enough time to form new fresh GRMML. In a word, the Ni−P−Gr−SiC coating demonstrates a combination of the advantages of the Ni−P−SiC coating with higher load-bearing and the Ni−P−Gr coating with a low friction coefficient.

4 Conclusions

1) The hybrid composite coating has good antifriction and wear resistance because of the synergic effect of the graphite and SiC, compared to the composite coating with unitary particle.

2) The friction properties can be improved by the introduction of graphite at any content, and the wear resistance has different performance, depending on the content of both graphite and SiC. When the content of graphite and SiC are 9 g/L and 8 g/L in the electroless plating bath, respectively, the hybrid composite coatings present the best tribological properties.

3) It is found that the test conditions have a large influence on the tribological properties of the hybrid composite coatings. Particularly, the abrasive wear dominates at low load of 50−90 N and the delamination wear does at high load over 150 N. In general, the composite coating has well integrated antifriction and wear resistance at load of about 100 N.

4) The GRMML formed on the worn surface is responsible for the good antifriction properties and SiC particles mixed with GRMML play a load bearing role in protecting the GRMML from shearing easily.

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摩擦条件对化学混杂复合镀层 Ni−P−Gr−SiC 摩擦性能的影响

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摘 要：研究化学复合镀层 Ni−P−Gr−SiC 的摩擦磨损性能，主要研究石墨复合量、载荷及转速对复合镀层摩擦性能的影响。采用 SEM 和 EDAX 对磨损表面和截面进行磨痕形貌和成分分析。结果表明，由于石墨和碳化硅两相颗粒的协同作用，复合镀层显示出良好的减摩性能和耐磨性。分析表明，摩擦试样的亚表层形成的富石墨机械混合层对摩擦体系保持良好的摩擦性能起到重要作用，同时碳化硅颗粒的承载作用有效避免富石墨机械混合层在摩擦剪切力作用下的断裂。

关键词：化学复合镀层；Ni−P 镀层；石墨；SiC；摩擦性能；自润滑；协同作用

(Edited by YUAN Sai-qian)