

# Investigation on the Constitution and Mechanical Characteristic of Composite Containing Silicon-Carbide Produced by Electroless Co-deposition

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The constitution and mechanical characteristics of the composites containing silicon carbide and Ni-P alloy matrix produced by electroless co-deposition were investigated in this article. The experimental results indicate that SiC particles with high hardness obviously strengthen the Ni-P alloy matrix, leading to an increase in both the hardness and surface roughness of the composites in comparison with pure Ni-P alloy. The hardness of the composites reaches the maximum value when heat treated at 673 K for 1 h. During the friction and wear process, the wear resistance of SiC composites is higher than that of Ni-P alloy and hard chromium plating, although the friction coefficient of the composite is comparatively high, which is attributed to the worn-resistant hard phase.

**Keywords** composite, electroless co-deposition, mechanical, silicon carbide

## 1. Introduction

Electroless-deposited Ni-P alloys show a series of excellent physical, chemical, and mechanical properties, which can be used to prevent machine parts from corrosion and/or wear.<sup>[1,2]</sup> Via electroless co-deposition of many insoluble particles such as SiC, Al<sub>2</sub>O<sub>3</sub>, diamond, and PTFE, the metal matrix composites containing these particles are naturally produced, resulting in a broad range of applications of Ni-P alloys.<sup>[3,4]</sup>

The co-deposition process makes it possible to design the constitution and to control the properties of metal matrix composites. The Ni-P alloys acted well as composite matrix, and their composition and heat treatment to a certain extent<sup>[5,6]</sup> can tailor the properties. As a result, the process leads to a combination between a certain type of second-phase particles and Ni-P alloy matrix,<sup>[7]</sup> and the obtained composite is a new material produced with a variety of properties. According to the theory of alloy design, solute atoms dissolved in the alloy cause the lattice distortion of matrix phase, accompanying an increase in the hardness and strength of the alloy due to the occurrence of the solution strengthening effect. The strengthening effect is dependent on some factors such as the fraction, relative size, and valency electron number of the solute atom. When the solute atom fraction exceeds the solid solubility limit, a supersaturated solid solution becomes metastable to precipitate

fine and uniformly distributed second phase after aging treatment, the strengthening effect called "age strengthening" or "precipitation strengthening," usually occurs. However, the particles as second phase can be artificially entrapped in matrix materials to bring about the strengthening effect called "dispersion strengthening;" features such as the fraction and the size and distance between particles, naturally, all have influence on the strengthening effect.<sup>[8]</sup>

The strengthening processes of Ni-P alloy are correlated to the strengthening mechanism mentioned above. Nickel is a transition metal with face-centered cubic and phosphorus orthorhombic lattices. There exists 12% difference between the atom radii of nickel and phosphorus, and the solid solubility limit of phosphorus in nickel is only 0.17 wt.%. Our previous studies revealed<sup>[9,10]</sup> that Ni-P alloy with low phosphorus content (about < 7) is a supersaturated solid solution of nickel, causing the solution strengthening in as-plated state wt.% and precipitating the second-phase Ni<sub>3</sub>P with the precipitation strengthening effect as heat treated to a suitable temperature; while the high-P alloy with the content higher than 7 wt.% characterizes as an amorphous nickel alloy and crystallizes into Ni<sub>3</sub>P phases and nickel with the heat treatment temperature. Ni<sub>3</sub>P gradually becomes matrix over nickel, resulting in the dispersion strengthening effect in the alloy with the temperature. After comparatively higher temperature treatment, the high-P alloy resists the softening effect from the temperature with a higher wear resistance than the low-P alloy, which can be ascribed to the strengthening effect of Ni<sub>3</sub>P hard phase.

When hard phase SiC is co-deposited within the Ni-P alloy matrix, the composites with the Ni-P alloy matrix and SiC reinforced phase will be produced. To take advantage of the combined characteristics of the Ni-P alloy matrix and SiC particles, we prepared the composite containing silicon carbide in the Ni-P alloy matrix by electroless co-deposition. This paper presents the investigation on the constitution and mechanical properties of the composite, aiming at designing the composites with the comprehensive strengthening effect to gain a new set of properties.

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## 2. Experimental

The plain low carbon steel was used as the substrate in the deposition. The samples with the size of  $20 \times 20 \times 10 \text{ mm}^3$  were manufactured for the microhardness measurement and microstructure characterization and those of  $7 \times 7 \times 80 \text{ mm}^3$  for the wear test.

The deposition device is made up of two cylindrical troughs. The outer trough is heated directly by electroheater, and the temperature of the inner trough (solution container) is supplied by water bath. In the co-deposited process, the samples were vertically positioned in the solution, and the solution was magnetically stirred for maintaining SiC particles in suspension, so that the particles in movement could be prevented from falling and grouping. The particles were transferred forcibly to the sample surface in succession and covered gradually by deposited nickel. The co-deposition of the particles was proceeded with the deposition of the Ni-P alloy. The composition of the co-depositing solution and operating condition are listed below:  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  20 to 30 g/L,  $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$  15 to 25 g/L,  $\text{Na}_3\text{-Cit}$  25 to 30 g/L, SiC (3 to 5  $\mu\text{m}$ ) 1 to 10 g/L. All the samples were co-deposited at temperatures ranging 80 to 90 °C and pH 5.0 to 5.6 to obtain the composites. During co-deposition, the pH value was adjusted continuously to and the principal to components were replenished in time due to the evaporation and reaction. When the deposition was completed, SiC particles were filtered out of the solution and dried for reuse.

As the composite was produced, the appearances of the samples were evaluated. The samples were normal if the surface showed a thin white color and abnormal if the surface was dim black and had burrs or other defects. After rinsing in boiled water, the samples were treated in common case and salt-bath furnaces (used at temperatures higher than 673 K) to protect the surface from oxidation at temperatures ranging from 373 to 873 K for 1 h.

The composite microhardness measurement was carried out on the surface using a 71-type microhardness tester (made in Yixian Tester Co. Ltd., Yixian, China) under a 1 N load for 30 s. Three readings were taken on each sample and the values were then averaged. Sliding wear testing with boundary lubrication was performed employing a Amsler-135 wear tester (made in Switzerland Instrument Co. Ltd., Berne, Switzerland) under a load of 49 N; the counterpart sample was made of the steel-bonded hard alloy (HRC63) with the revolving speed of 400 r/min. The width of the worn trace was read using a DM-5 digital microscope; several readings were taken and then converted into the wear volume according to the formula wear volume  $V = Bb^3/12r$  (where  $B$  is the worn length, mm;  $b$  the worn width, mm; and  $r$  is the counterpart radius, mm), so the relation curve of the wear loss vs the rubbing time can be drawn out. The worn scraps were collected to prepare the specimen in the oil diluted into 10:1, 100:1, and 1000:1, respectively, to carry out the ferrographic spectrum analysis on a TRF-1 ferrographic meter (made in Beijing Scientific Instruments Co. Ltd., Beijing, China). The surface worn morphology and microstructure of the composite were characterized using a S-570 scanning electron microscope and H-800 transmission electron microscope (both made in Hitachi Co. Ltd., Tokyo, Japan).

## 3. Results and Discussions

### 3.1 Influential Factors on Co-Deposition of SiC with Ni-P Alloy and the Constitution

When SiC particles were added into the electroless deposited Ni-P alloy solution, the bath became unstable in thermodynamic state and inclined to decompose naturally. The stabilizer with the right amount must add to the bath to prevent the solution from decomposition and failure. With the electroless deposition of Ni-P alloy based on a redox reaction, SiC particles were physically incorporated into the Ni-P alloy matrix in the co-deposition process.

In fact, the co-deposited amount of SiC particles is related to the particle size, added amount, operating conditions, and other factors. (1) When the added amount of SiC is lower, the co-deposited fraction in the Ni-P alloy increases with SiC particles; when the amount reaches 40 to 50 g/L, the fraction attains the maximum value and does not increase with further addition (as shown in Fig. 1). (2) SiC particles are adhered onto the sample surface owing to the electrostatic and mechanical force effect. It was found that the stirring intensity has a great influence on the co-deposited fraction of the particles. If the solution is stirred slightly, SiC particles will sink into the bottom of the solution owing to the high gravity and cannot disperse throughout, resulting in less co-deposition. Stirring the solution violently, though the co-deposited temperature is well distributed and SiC particles dispersed uniformly in the solution, the particles and the solution revolve so fast that the selective absorption of the particles on the sample surface is destroyed, leading to a great decrease of co-deposition. Thus, suitable stirring must be provided to ensure SiC floating and co-deposition. (3) The deposited rate and phosphorus content of Ni-P alloy also depends essentially upon the pH-value of the solution.<sup>[11]</sup> When the pH value is less than 3, the solution hardly reacts; the lower the pH value, the higher the phosphorus content in the alloy. But it also can be found from Fig. 1 that the pH value has little influence on the co-deposited amount of the SiC particles.

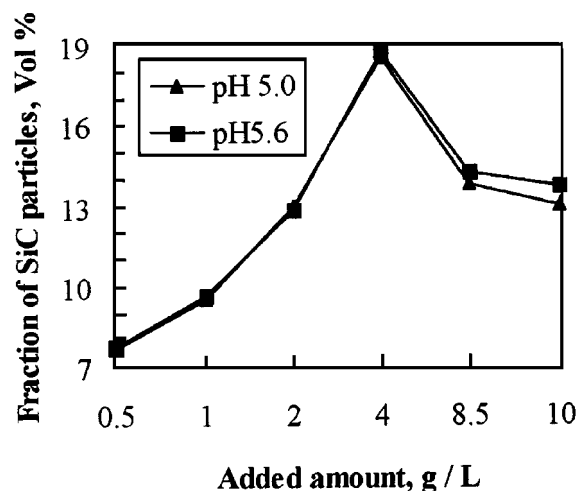
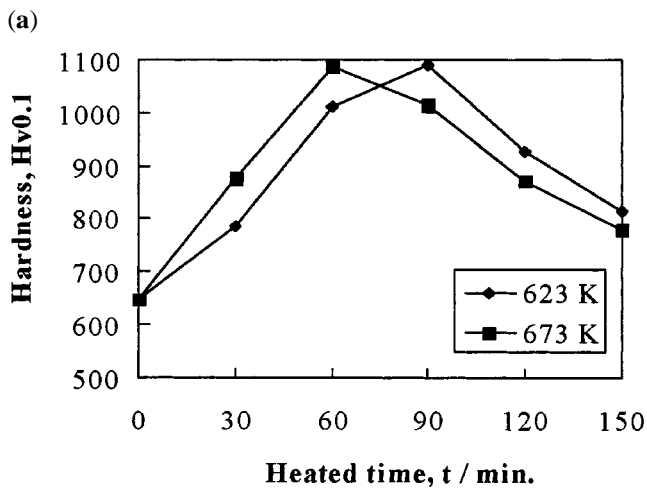
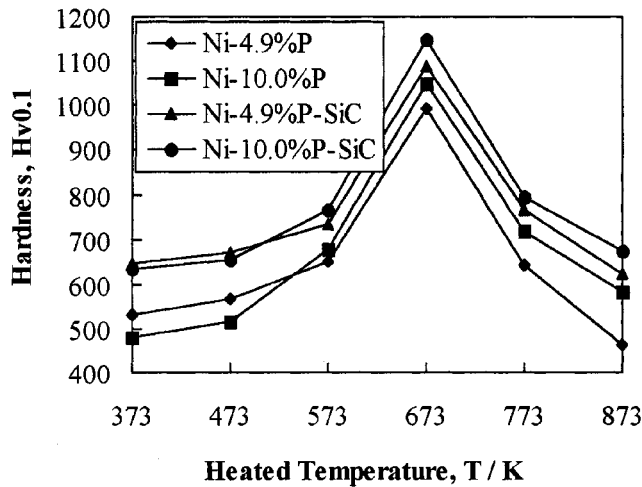


Fig. 1 Effect of SiC added amount on the fraction in the composite

### 3.2 Strengthening Effect of SiC Particles on the Composite

The SiC particles of co-deposition obviously increase the hardness of the composites in the as-deposited and heat-treated state compared to the Ni-P alloy, as shown in Fig. 2(a). The 4.9% P alloy underwent the strengthening process in accordance with the precipitation strengthening mechanism.<sup>[10]</sup> The precipitated second-phase Ni<sub>3</sub>P enhances the plastic deformation resistance of the alloy with the hardness reaching the highest value at 673 K. With a further increase in temperature, the second-phase Ni<sub>3</sub>P gathers and coarsens, leading to the softening of the alloy and a decrease in the hardness. Although the phase transformation of the amorphous 10% P alloy is different from that of the 4.9% P alloy, the change tendency in the hardness is similar, and the value also goes to the maximum as it is heated at 673 K. Especially when heated at relatively higher temperature, the higher the phosphorus content, the higher the hardness, because the Ni<sub>3</sub>P fraction increases with the temperature and phosphorus content.<sup>[10]</sup> The Ni-P alloys with the strengthening effects meet the requirements as the matrix for the composite.



**Fig. 2** (a) SiC volume fraction as 18.5%, same as below (b) Ni-4.9% P-SiC. Dependence of hardness of the composites upon (a) heat-treating temperature and (b) time

The hard phase SiC is as high as 2483 K in melting point and 32,000 MPa in hardness, which greatly increases the plastic deformation resistance and thermal stability of the composite. Like Ni-P alloy matrixes, the composites reach their maximum hardness value at 673 K. When the heat-treated temperature rises to higher than 673 K, the hardness begins to reduce but is still higher than that of the Ni-P alloy. At higher temperature, the attribution from the Ni<sub>3</sub>P strengthening effect gradually degenerates. However, the dispersion strengthening from the hard phase SiC makes the hardness drop slowly with further increasing heat-treating temperature. The similar changing trend in hardness appears under the isothermal condition at 623 and 673 K (Fig. 2b).

It can be explained that the hard phase particles of co-deposition obstruct the movement of dislocation, resulting in an increase in both the energy of the dislocation motion and deformation resistance of the composite. As a result, the strength and hardness both rise. According to the reference,<sup>[12]</sup> the influence of the particle size and intervals between particles on the composite strength can be inferred from the following formula:

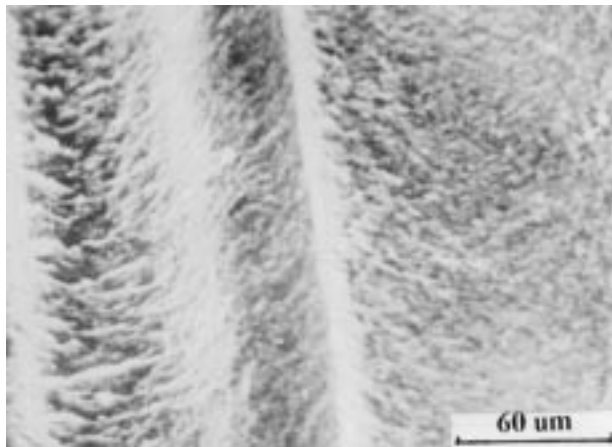
$$\sigma_f = f(d)/(D - d) + \sigma_0$$

where  $\sigma_f$  represents the strength of the composite,  $\sigma_0$  the yield strength of the matrix alloy,  $D$  the distance between the particle centers,  $d$  the diameter, and  $f$  the volume fraction of the particles. When the matrix is given,  $f(d)$  is related to  $d$ :  $f(d) = (4/3)\pi(d/2)^3/D^3$ .

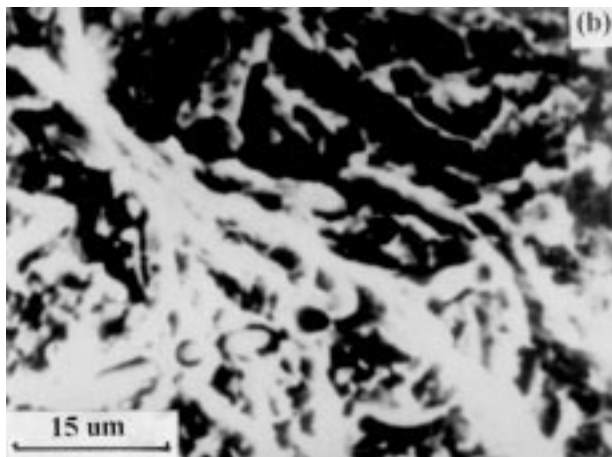
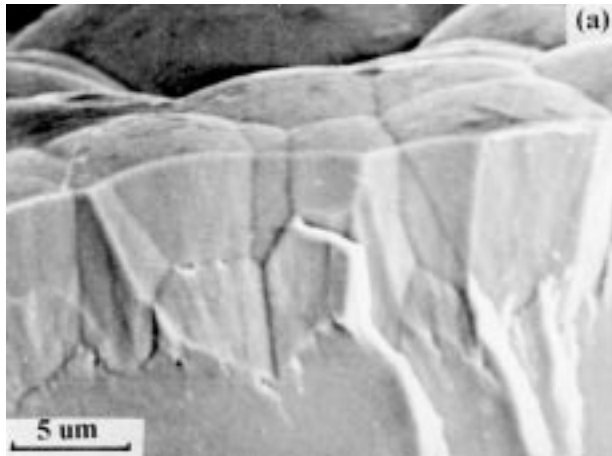
From the formula above, it can be found that the hardness will increase with an increase in both the SiC fraction in the composite and  $\sigma_0$  and with a reduction  $D$ . In fact, SiC particles cannot be co-deposited in the composite in limitless amount. As the SiC fraction rises, the  $(D - d)$  value tends to be zero, it seems that  $\sigma_f$  should be great. However,  $\sigma_f$  decreases apparently due to increasing brittleness in the composite. The volume fraction percent of the particles increases and the distance between them decreases in the composite after heat treatment. Though there existed a possibility that SiC particles react with the Ni-P matrix into the free Ni<sub>3</sub>Si phase<sup>[13]</sup> at temperatures higher than 873 K, the recrystallization and grain growth of the composites can be inhibited to some extent, and thus, the composites maintain a high strength and hardness.

The low-P alloy, a supersaturated solid solution with phosphorus atoms dissolved in the nickel, has a large lattice distortion, resulting in the formation of very fine grains, as demonstrated in the fractal morphology of the alloy shown in Fig. 3. The broadening of the x-ray diffraction of the alloy in high angle position further proved the result.<sup>[10]</sup> The high-P alloy in an amorphous state has the same strengthening tendency as the low-P alloy.<sup>[10]</sup> The brittleness of the alloy in deposited state is relatively high because of the remaining hydrogen; the fracture exhibits a morphology with a small smooth plane of brittle fracture, as shown in Fig. 4(a). The ductility of the alloy will be improved to some extent after heat treatment. The same fracture feature of the high-P alloy as the low-P alloy has also been observed.

The Ni-P alloy, as the matrix of the composites, is cut apart by SiC particles, as shown in Fig. 4(b). The dispersed hard phase obviously changes the path of the crack propagation in the composite, causing an increase in the energy for the crack to propagate. The strengthening effect of the composites becomes

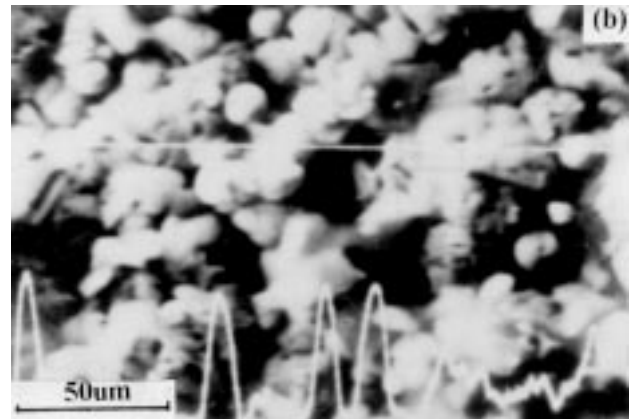
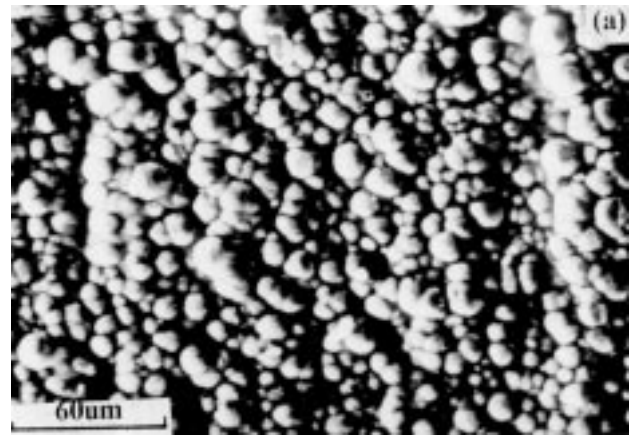


**Fig. 3** Fracture microstructure of Ni-4.9% P alloy in as-deposited state



**Fig. 4** Fractorgraphics of (a) Ni-4.9% P alloy and (b) its composite in as-deposited state

more evident with the increase of the fraction of particles and the Ni-P matrix after the heat treatment.



**Fig. 5** Surface morphology of (a) Ni-4.9% P alloy and (b) its composite in as-deposited state

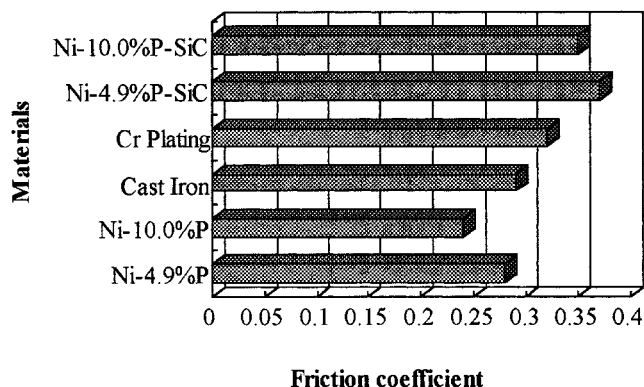
### 3.3 Mechanical Characteristics and Wear Behavior of SiC Composite

Compared to electrodeposition, electroless can be applied on different substrates, and the obtained Ni-P alloy has a very homogeneous distribution regardless of the substrate geometry. Consequently, the outline of the deposited substrate is well reserved. However, the surface morphology of the composites is varied by the co-deposited SiC particles in comparison with pure Ni-P alloy, as shown in Fig. 5. The surface roughness value of the composite increases remarkably because of the incorporation and the projection of SiC particles, as indicated in Table 1, where the value of hard chromium plating and the Ni-P alloy is comparatively lower. Surface roughness, as an important parameter to the tribological system, has a great influence on the friction feature originated between the counterparts. The counterparts with low surface roughness get into the normal and stable wear stage easily, resulting in a reduction in friction resistance with lower friction coefficient.

The low friction coefficient can improve antiseizing and antiadhering capacity for the wear resistant materials. The Ni-P alloy with lower friction coefficient is due primarily to the fact that the surface roughness is relatively lower. Although the nickel of face-centered-cubic lattice usually tends to adhere to steel, the low-burning point element phosphorus, inducing the

**Table 1 Surface roughness (Ra  $\mu\text{m}$ ) of several materials**

Materials	Ni-4.9% P	Ni-10% P	Ni-4.9% P-SiC	Ni-10% P-SiC	Cast iron	Cr plating
Ra	0.48	0.46	0.58	0.59	0.63	0.44

**Fig. 6** Illustration of the friction coefficient of several materials

formation of nickel phosphide, brings about the solid-lubricating effect and a decrease in the friction coefficient. In contrast, the co-deposition of SiC particles will alter the surface features, leading to the composite with comparatively high surface roughness and higher friction coefficient, though the composite is composed of the particles and Ni-P with nonmetallic feature surface (Fig. 6).

It can be found from the worn feature curve of Fig. 7(a) that the wear volume of the composite increases beyond Ni-P alloy at the beginning, implying that a longer time will be taken to reach the stable wear stage for the composite. Evidently, the worn loss of the composite at the first stage is larger than that of the Ni-P alloy. After the SiC composite rubbed against the counterpart for a while, the surface roughness and the friction resistance decreased gradually, and as a result, the wear process was inclined to be stable and the worn loss fixed at a level lower than that of hard Cr plating and Ni-P alloys.

Figure 7(b) shows the influence of heat treatment on wear resistance of the Ni-P alloy and the composite. After the resultant materials with low phosphorus content are heat treated at 673 K for 1 h, the hardness and wear resistance reach their optimum values. Also, the wear loss heat treated at higher temperature is lower than that at lower temperature; the compared temperature ranges are around 673 K. It can be discerned that the decrease of the hardness does not mean the reduction of the wear resistance, and the microstructure also affects the properties of heat treatments at temperatures higher than 673 K. For high phosphorus materials, although the hardness decreases gradually with the temperature when exceeding 673 K, the wear resistance continuously rises. The result indicates that the microstructure with a two-phase mixed compound of Ni + Ni<sub>3</sub>P together with SiC particles plays a key role in the raising of the wear resistance, and the hardness is not the only dominant influencing factor on the wear resistance of Ni-P alloys and the composites. The high hardness of Cr plating is due to the

severe lattice distortion caused by the absorbed hydrogen. The hardness of the plating drops with heat treatment.<sup>[13]</sup> On the contrary, SiC composites with comprehensive strengthening effect bring about higher hardness, even though heated at higher temperature, leading to a better wear resistance than Cr plating.

Figure 7(c) shows the effect of the alternation of the counterpart material on the wear resistance of SiC composite. When rubbed against the Ni-P alloy, the SiC composite compatibly forms a suitable worn couple because of the suitable difference in both hardness and surface feature between them. The wear loss is naturally lower. Rubbed against low alloy cast iron with higher surface roughness and lower hardness (Hv 110), the wear volume is considerably high. The adhesive and abrasive wear easily occur as a result of the composite contacting with the relatively soft and rough material, leading to the transfer of the worn chips between the couples and an increase in the wear loss.

The properties of the composites can be supplemented by the co-deposition of SiC particles and Ni-P alloy. The SiC particles are supported by the Ni-P alloy matrix of relatively high strengthening; the composites thereby can be strengthened and obtain a high effective hardness. The dispersed particles serve as the first sliding plane and the Ni-P alloy matrix as the second in the friction and wear process. The participation of the matrix and SiC particles creates the resistance to wear, which corresponds to the surface worn morphology, as shown in Fig. 8(a) for the composite. The SiC particles may strip from the matrix and drop with the rubbing time (Fig. 8b); the Ni-P alloy matrix then participates the wear.

Generally, the abrasive wear rate can be indicated as the formula  $W = K^*L/H$ , where  $K^*$  is the proportion constant,  $H$  the hardness of the materials, and  $L$  the load of the wear. It is well known that the wear rate of the materials can be inferred from the effective surface hardness, so the high hardness of the composites is one of the requirements to improve the wear resistance.

The SiC particles are well combined with the matrix, which ensures the composites without deformation under a general load density. The composites also can keep certain mechanical and thermal coherence with the substrate, resulting in the high adhesion strength from mechanical lock force and van der Waals force, preventing the interface failure. Therefore, the composites with SiC particles and the Ni-P alloy matrix meet the requirements of the constitution and mechanical characteristics, which really can serve as a wear resistant material.

## 4. Conclusions

The added amount of SiC particles in the solution and operating parameters have a key influence on SiC co-deposited

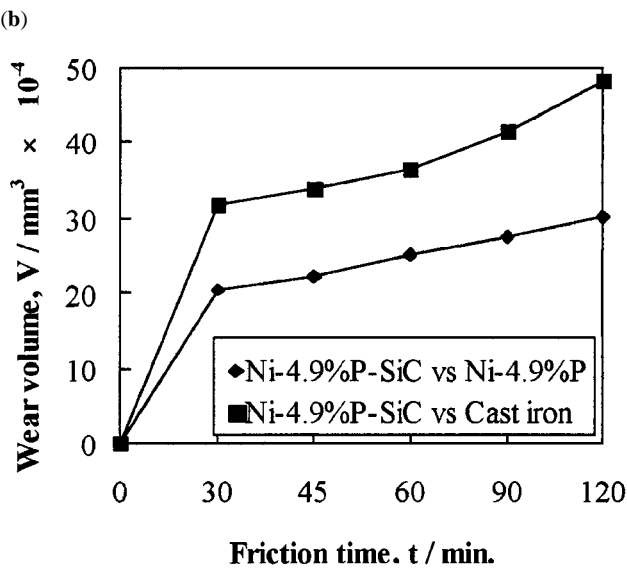
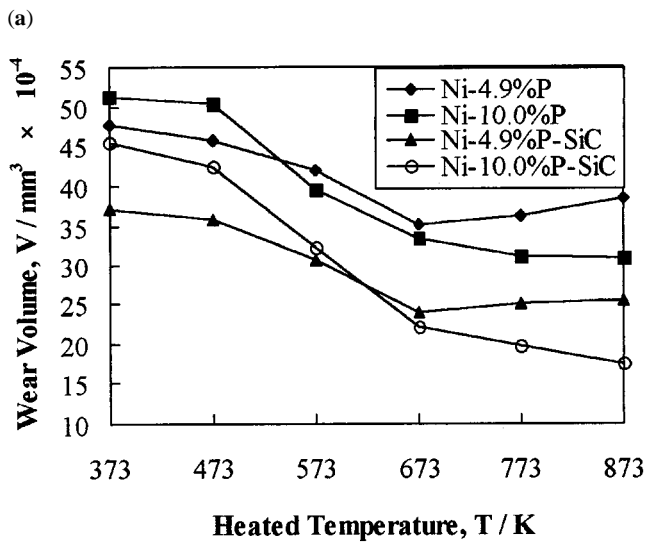
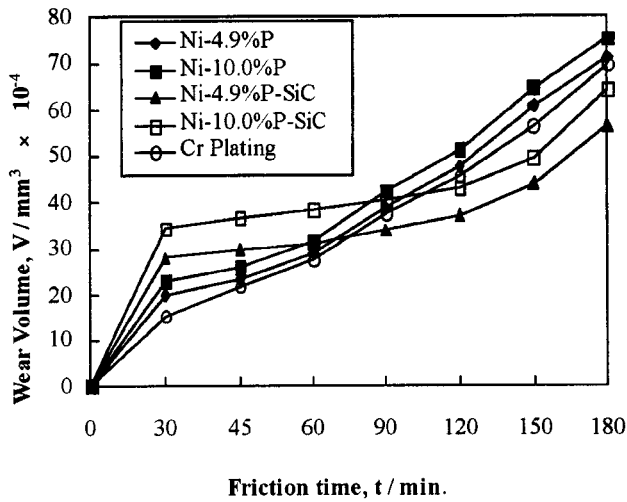


Fig. 7 Wear volume of Ni-P alloy and Ni-P-SiC composites: (a) wear volume vs friction time; (b) wear volume vs heated temperature; and (c) wear volume vs counterpart material

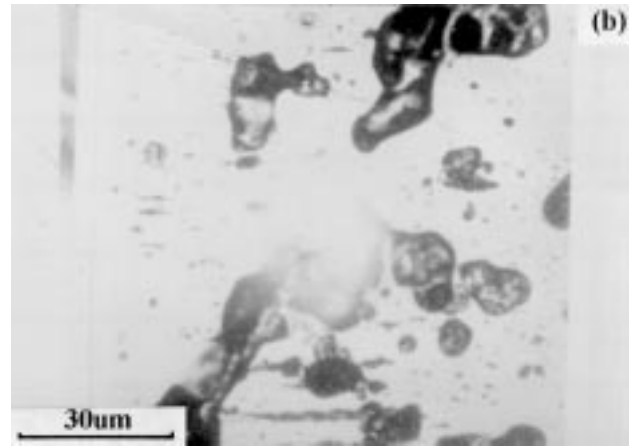
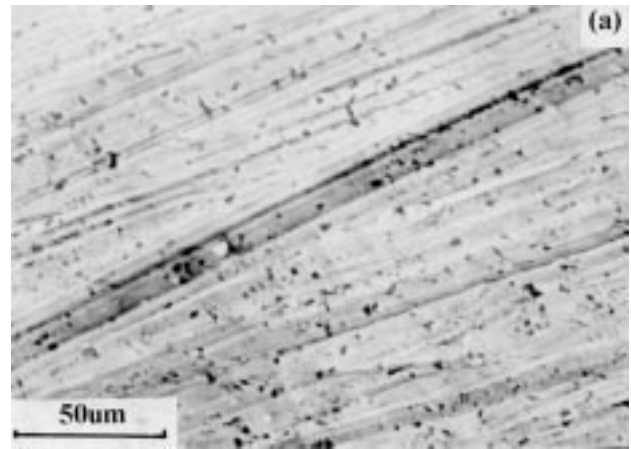


Fig. 8 Worn micrographs of Ni-4.9% P-SiC composite in as-deposited state: (a) surface morphology and (b) ferrographic morphology

fraction in the composite. The constitution of the composites dominates the microstructure and the properties. SiC particles with high hardness are well dispersed in the composite and bring about the dispersion strengthening effect. The hardness of SiC composites is higher than that of Ni-P alloys, which increases with heat treatment temperature, and reaches the maximum value at 673 K  $\times$  1 h such as the matrix. The SiC particles of co-deposition change the original surface features of the Ni-P alloy, leading to an increase in the surface roughness and the friction coefficient. The composites bring about a relatively high hardness and wear resistance beyond hard Cr plating and Ni-P alloys. In addition, the particles also can combine with the matrix, producing an excellent antiabrasive wear effect, so the SiC composites are satisfied as a kind of wear-resistant material with potential applications.

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