

## Influence of SiO<sub>2</sub> nano-particles on microstructures and properties of Ni-W-P/CeO<sub>2</sub>-SiO<sub>2</sub> composites prepared by pulse electrodeposition

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**Abstract:** Ni-W-P base composites containing CeO<sub>2</sub> and SiO<sub>2</sub> nano-particles were prepared on common carbon steel surface by pulse co-deposition of Ni, W, P, CeO<sub>2</sub> and SiO<sub>2</sub> nano-particles. The influence of SiO<sub>2</sub> concentrations in bath on microstructures and properties of Ni-W-P/CeO<sub>2</sub>-SiO<sub>2</sub> composites was studied, and the characteristics were assessed by chemical compositions, element distribution, surface morphologies, deposition rate and microhardness. The results indicate that when SiO<sub>2</sub> concentration in bath is controlled at 20 g/L, the composites possess the fastest deposition rate, the highest microhardness, compact microstructures, smaller crystallite sizes and uniform distribution of W, P, Ce and Si within Ni-W-P matrix metal. Increasing SiO<sub>2</sub> concentration in bath from 10 to 20 g/L leads to the refinement in grain size and the inhomogeneity of microstructures. While when SiO<sub>2</sub> concentration is increased to 30 g/L, the crystallite sizes increase again and some bosses with nodulation shape appear on the surface of composites.

**Key words:** pulse electrodeposition; nano-particle; composite; microstructure and property

### 1 Introduction

The need for composites with improved resistance to highly aggressive environments is high as a result of a growing demand for extended safe service life of industrial objects. Composite electrodeposition is a valuable new surface intensification technology to obtain particle-reinforced metal matrix composites allowing to co-deposit inorganic and organic solid particles with matrix metal[1–4]. The composites possess comprehensive performance of matrix metal and second phase particle. At present, there are some reports about Ni-W-P base multi-element composites prepared by direct current electrodeposition[5–9], while studies on components design, preparation technology, microstructures and properties of the multi-element composites prepared by pulse electrodeposition are not sufficient

owing to the existing problems of complexity of the bath system and plating device.

The grain sizes, chemical compositions, microstructures and properties of the composites not only depend on bath compositions, but also process conditions [10–14]. W is a hard element and high mass fraction in the composites is helpful for improving microhardness [15]. CeO<sub>2</sub> and SiO<sub>2</sub> nano-particles deposited into Ni, Ni-P or Ni-W-P can lead to refinement in grain size and increase microhardness, wear and oxidation resistance [16–19]. Compared with the direct current electrodeposition, pulse electrodeposition can improve cathode activation polarization and decrease concentration polarization, avoiding the shortages of single direction and persistence of direct current by means of utilizing the relaxation of pulse current. Therefore, it is more favorable for preparing the composites and has already attracted much attention. In this work, Ni-W-P base

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composites containing  $\text{CeO}_2$  and  $\text{SiO}_2$  nano-particles were prepared under different  $\text{SiO}_2$  concentrations in bath.

## 2 Experimental

The basic compositions of electroplating bath used for electrodeposition Ni-W-P/ $\text{CeO}_2$ - $\text{SiO}_2$  composites were as follows: 75 g/L  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , 120 g/L  $\text{H}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$ , 100 g/L  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , 6 g/L  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , 20 g/L  $\text{SiO}_2$  (average size: 30 nm) 10 g/L  $\text{CeO}_2$ , (average size: 30 nm), and 6 mg/L cationic surfactant. Bath temperature was maintained at 60 °C, pH value was about 5.5 and plating time was 2 h. Double-pulse parameters were as follows. Forward and reverse pulse duty cycles were controlled at 10%, forward and reverse pulse average current densities were controlled at 6 A/dm<sup>2</sup> and 0.6 A/dm<sup>2</sup>, and forward and reverse pulse working times were controlled at 100 ms and 10 ms, respectively.

To guarantee better dispersion of  $\text{CeO}_2$  and  $\text{SiO}_2$  nano-particles within Ni-W-P matrix metal, before pulse electrodeposition, the electroplating bath was dispersed by ultrasonic for 30 min. Then, mechanical stirring was used during the experiments and the stirring speed was controlled at 750 r/min. 316L stainless steel was used as anode material, common carbon steel with dimensions of 30 mm×60 mm×2 mm was used as substrate materials. Each experiment was carried out with a fresh solution.

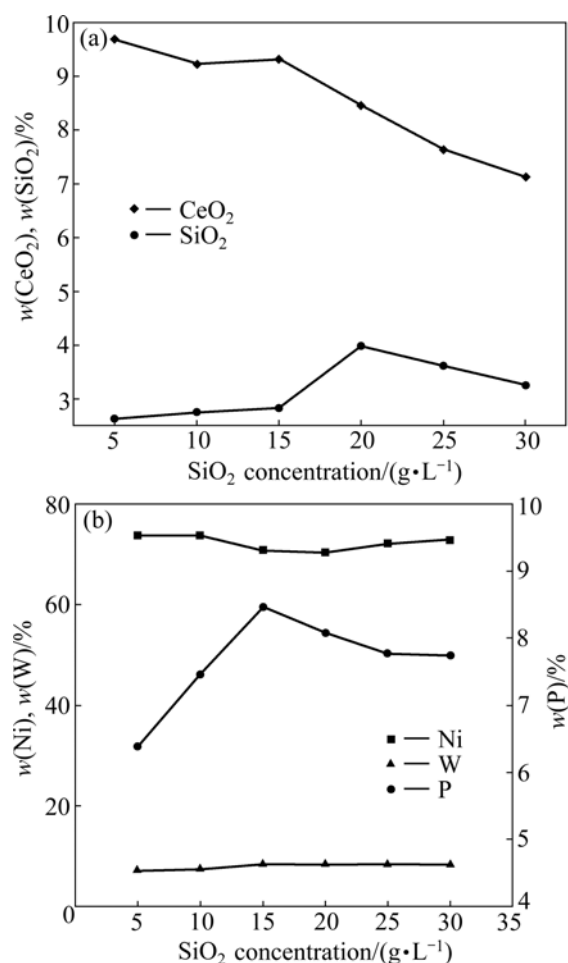
The chemical compositions, element distribution, deposition rate, microhardness and microstructures were evaluated as the characteristics of the composites. The microhardness was tested by 401MVA microhardness tester. The thickness was measured by metallurgical microscope and deposition rate was expressed by the thickness deposited in unit time. The microstructures, element distribution and chemical compositions were examined by scanning electron microscope (XL30 ESEM) and energy disperse spectroscopy (PHOENIX type).

## 3 Results and discussion

### 3.1 Influence of $\text{SiO}_2$ concentrations in bath on chemical compositions of composites

Fig.1 shows the influence of  $\text{SiO}_2$  concentrations in bath on chemical compositions of Ni-W-P/ $\text{CeO}_2$ - $\text{SiO}_2$  composites. As shown in Fig.1, mass fraction of  $\text{SiO}_2$  in the composites increases with increasing  $\text{SiO}_2$  concentrations in bath. When the concentration is controlled at 20 g/L,  $\text{SiO}_2$  mass fraction reaches the highest value of 3.98%; but over 20 g/L, it begins to decrease again. While mass fraction of  $\text{CeO}_2$  decreases

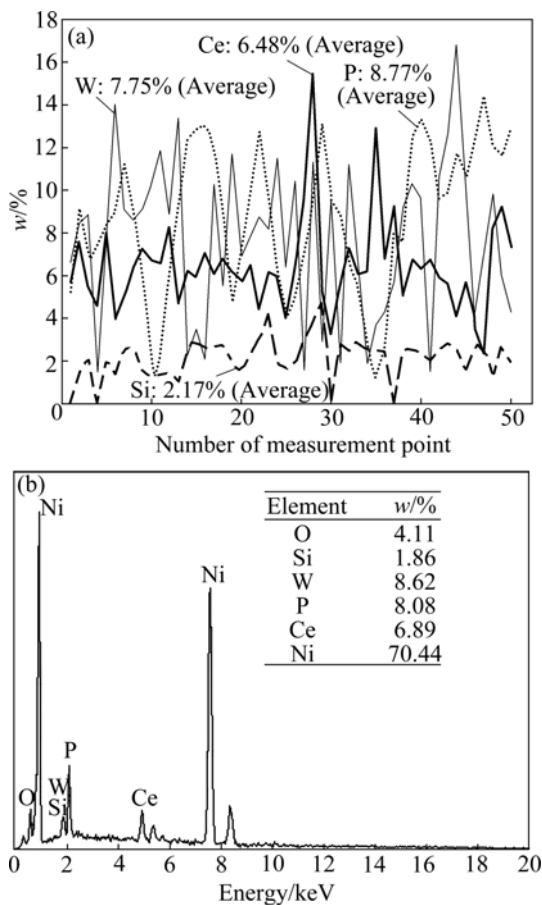
with the increase of  $\text{SiO}_2$  concentrations in bath. The mass fraction of P is the highest when  $\text{SiO}_2$  concentration is controlled at 15 g/L and the change of W mass fraction is little. The main reason may be that when  $\text{SiO}_2$  concentration is lower than 20 g/L, with increasing its concentration, the amounts of  $\text{SiO}_2$  nano-particles in bath increase and the probability imbedded into Ni-W-P matrix metal increases on the cathodic surface, leading to the increase of  $\text{SiO}_2$  deposition amounts and mass fraction in the composites. When  $\text{SiO}_2$  concentration is over 20 g/L, too high particle concentrations in bath result in the increase of electrolyte viscosity and serious coagulation of nano-particles absorbed on the cathodic surface. Therefore, the area offered electric chemical reaction is deduced and true density current is improved, leading to hydrogen evolution increasing on the cathodic surface and the decrease of deposition amounts. In addition, increasing  $\text{SiO}_2$  concentration in bath leads to the increase of  $\text{SiO}_2$  particle deposition amounts on the cathodic surface, making the probability of  $\text{CeO}_2$  nano-particles imbedded in the composites decrease, so the deposition amounts in the composites are also reduced.



**Fig.1** Influence of  $\text{SiO}_2$  concentrations in bath on chemical compositions of composites: (a)  $\text{SiO}_2$  and  $\text{CeO}_2$ ; (b) Ni, W and P

### 3.2 Influence of SiO<sub>2</sub> concentrations in bath on element distribution of composites

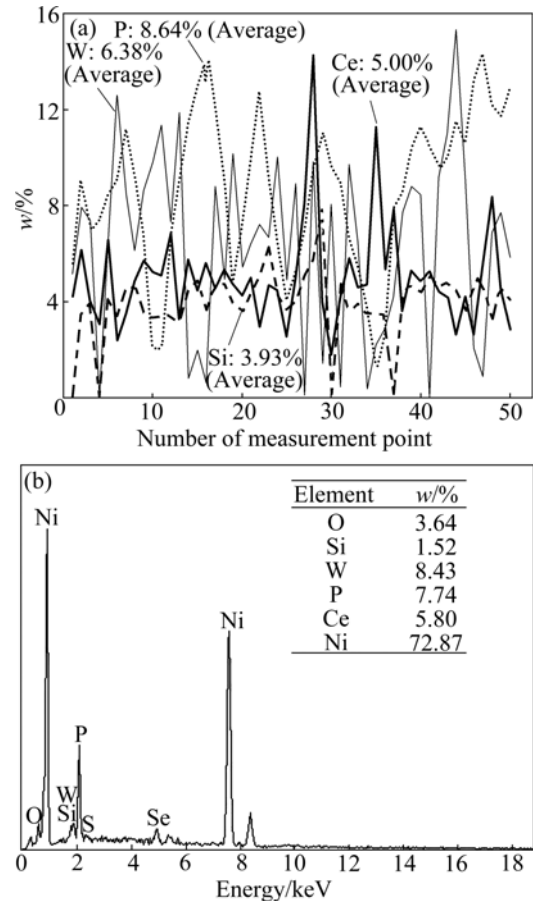
When SiO<sub>2</sub> concentration in bath is controlled at 20 g/L, the energy spectrogram analysis results of line scanning and area scanning are shown in Fig.2. As shown in Fig.2(a), on the level measurement points of line scanning, the mass fraction of W is 1.53%–16.85% (Average 7.75%), that of P is 1.23%–14.46% (Average 8.77%), that of Ce is 3.24%–15.74% (Average 6.48%) and that of Si is 0–4.84% (Average 2.17%). It can be seen from Fig.2(b) that the result of area scanning is close with that of line scanning, displaying that the distribution of every element in the composites is very uniform.



**Fig.2** Energy spectrogram analysis results of line scanning and area scanning (SiO<sub>2</sub> concentration: 20 g/L): (a) Line scanning; (b) Area scanning

When SiO<sub>2</sub> concentration in bath is increased to 30 g/L, the energy spectrogram analysis results of line scanning and area scanning are shown in Fig.3. As shown in Fig.3(a), on the level measurement points of line scanning, the mass fraction of W is 0.03%–15.35% (Average 6.38%), that of P is 1.14%–14.58% (Average 8.64%), that of Ce is 1.74%–14.24% (Average 5.00%) and that of Si is 0–7.85% (Average 3.93%). It can be seen from Fig.3(b) that there is the large deviation from

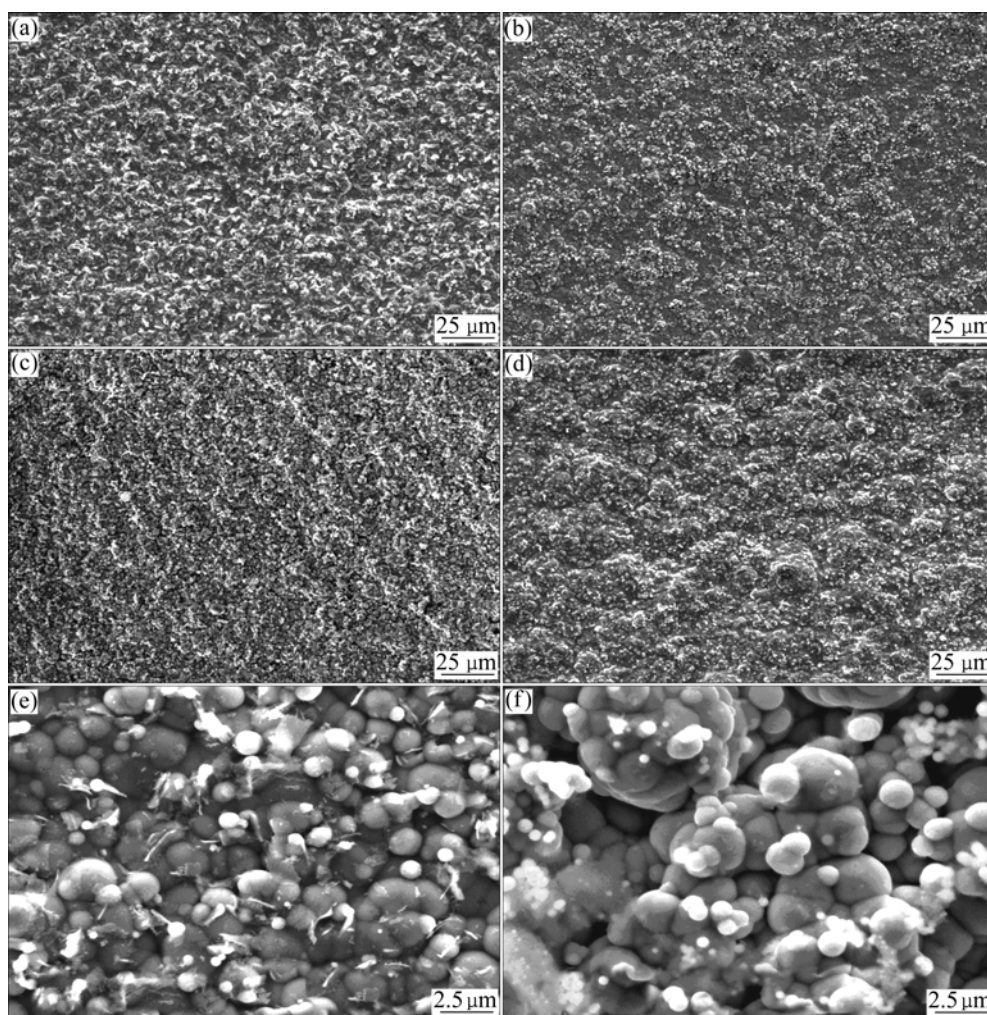
the results of line scanning. In particular, the average content of Si obtained by area scanning is obvious lower than that by line scanning. It can be concluded that the distribution of SiO<sub>2</sub> in the composites is very uneven and may have a serious coacervation under too high SiO<sub>2</sub> concentration in bath.



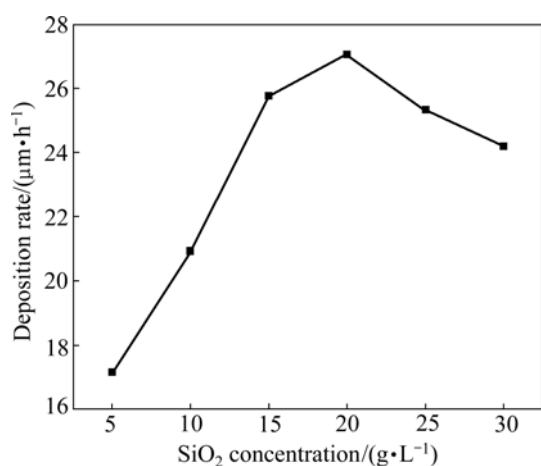
**Fig.3** Energy spectrogram analysis results of line scanning and area scanning (SiO<sub>2</sub> concentration: 30 g/L): (a) Line scanning; (b) Area scanning

### 3.3 Influence of SiO<sub>2</sub> concentrations in bath on microstructures of composites

Fig.4 shows the influence of SiO<sub>2</sub> concentrations in bath on surface morphologies of the composites. It can be seen from Fig.4 that increasing SiO<sub>2</sub> concentrations in bath from 10 g/L to 20 g/L leads to the refinement in grain size and the inhomogeneity of microstructures. While when SiO<sub>2</sub> concentration is improved to 30 g/L, the crystallite sizes begin to increase again and surface smooth decreases. The main reason may be that when SiO<sub>2</sub> concentration is lower than 20 g/L, increasing its concentration leads to the increase of deposition rate (as shown in Fig.5). So, the nucleation rate of crystallites is faster than the growing up rate. In the meantime, the increase of SiO<sub>2</sub> deposition amounts in the composites provides a large amount of nucleation points for matrix metal, hindering the continuous growth of Ni-W-P



**Fig.4** Influence of  $\text{SiO}_2$  concentrations in bath on surface morphologies of composites: (a) 10 g/L; (b) 15 g/L; (c) and (e) 20 g/L; (d) and (f) 30 g/L



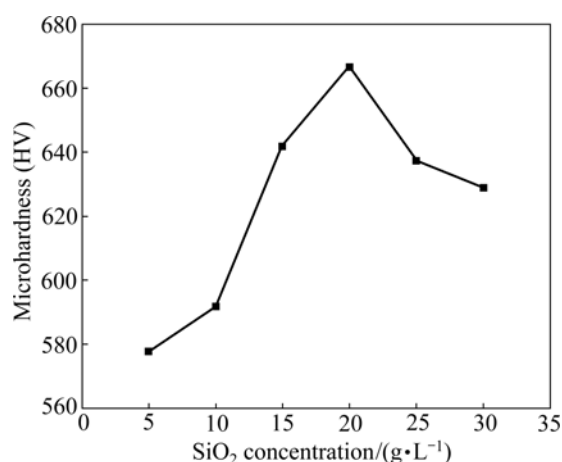
**Fig.5** Influence of  $\text{SiO}_2$  concentrations in bath on deposition rate of composites

matrix metal, and resulting in the refinement in grain size. When  $\text{SiO}_2$  concentration is improved to 30 g/L, too high particle concentrations in bath result in the serious coacervation of nano-particles, which is unfavorable to

refinement in grain size, so, the crystallite sizes increase again. As shown in Figs.4(e) and 4(f), it is obvious that when  $\text{SiO}_2$  concentration is controlled at 20 g/L, the outline of Ni-W-P matrix metal crystallites with spherical type is very clear, and the distribution of  $\text{CeO}_2$  and  $\text{SiO}_2$  nano-particles within matrix metal is uniform. When  $\text{SiO}_2$  concentration is improved to 30 g/L, the coacervation of nano-particles is serious and the distribution is very uneven. In the meantime, there appear a lot of small boss with nodulation shape on the composites surface.

### 3.4 Influence of $\text{SiO}_2$ concentrations in bath on microhardness of composites

Fig.6 shows the influence of  $\text{SiO}_2$  concentrations in bath on microhardness of the composites. Obviously, the microhardness increases with the increase of  $\text{SiO}_2$  concentrations in bath and reaches the highest value with HV666 at 20 g/L, but it will decrease gradually if  $\text{SiO}_2$  concentrations increase continuously.



**Fig.6** Influence of SiO<sub>2</sub> concentrations in bath on microhardness of composites

In general, the microhardness of the composites is relative not only with microstructures but with chemical compositions. CeO<sub>2</sub> particles can lead to refinement in grain size and increase the microhardness of the composites. Some mechanical properties such as microhardness and abrasion resistance can also be improved with increasing mass fraction of SiO<sub>2</sub> particle in the composites. In addition, the high W content in Ni, Ni-P or Ni-W-P base composites is also helpful for improving the microhardness. In this work, when SiO<sub>2</sub> concentration in bath is controlled at 20 g/L, mass fraction of SiO<sub>2</sub>, 3.98%, and mass fraction of W, 8.62%, are the highest, CeO<sub>2</sub> mass fraction of 8.46% is also higher. In the meantime, the grain size is small and the grain structure is compact (see Fig.4), so the microhardness is higher. When SiO<sub>2</sub> concentration in bath is improved to 30 g/L, the mass fractions of nano-particles decrease obviously, and their distribution in Ni-W-P matrix metal is also very uneven owing to the coacervation, leading to the decrease in the microhardness.

## 4 Conclusions

1) Ni-W-P-CeO<sub>2</sub>-SiO<sub>2</sub> composites were prepared on common carbon steel surface by pulse electrodeposition of Ni, W, P, CeO<sub>2</sub> and SiO<sub>2</sub> nano-particles in bath.

2) When SiO<sub>2</sub> concentration in bath is controlled at 20 g/L, the deposition rate is the fastest and microhardness is the highest. The average contents of W, P, Si and Ce are very close by means of line scanning and area scanning, displaying that the distribution of every element within the composites is very even.

3) Increasing SiO<sub>2</sub> concentration in bath from 10 g/L to 20 g/L leads to the refinement in grain size and the inhomogeneity of microstructures. The crystallite sizes increase again when the SiO<sub>2</sub> concentration is improved

to 30 g/L. In the meantime, there appear a lot of small boss with nodulation shape on the composite surface.

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