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Effects of addition of rare earth on properties and structures of Ni-W-B-SiC composite coatings^①

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[Abstract] The effects of rare earth (RE) on the composition, phase structures, surface morphologies and hardness of electrodeposited RE-Ni-W-B-SiC composite coatings were discussed. The results show that W and SiC contents in the coatings increase with the increase of RE in the bath. When RE is added in the coatings, the grains are refined and the trend of formation of amorphous coatings is increased. Moreover, the thermal stability of the RE-Ni-W-B-SiC composite coatings is enhanced. The hardness of the coatings is increased with the increase of heat treatment temperature, and it reaches the peak value when heated at 400 °C. Besides, the hardness of the RE-Ni-W-B-SiC coatings is higher than that of the Ni-W-B-SiC coatings.

[Key words] RE-Ni-W-B-SiC composite coating; properties; electrodeposition

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1 INTRODUCTION

Electroless Ni-B-SiC composite coatings have been studied at home and abroad because of their better cohesion, wear resistance and higher hardness in recent years^[1~4]. Rare earth (RE) plays an important role in electroless Ni-B alloys and Ni-B-SiC composite coatings, and it enables solid particles such as SiC, Al₂O₃ and so on to co-deposit effectively with alloys such as Ni-P and Ni-B alloys, increasing solid particles contents in the composite coatings, raising hardness and wear resistance of the coatings and intensifying oxidation resistance at high temperature^[5~7]. Application of RE in the electrodeposition of Ni-W-B-SiC composite coatings has been hardly studied recently^[8]. So the effects of CeO₂ on the structure and properties of Ni-W-B-SiC composite coatings have been approached in this paper.

2 EXPERIMENTAL

Bath composition and plating conditions are as follows:

NiCl₂·6H₂O, 30 g/L; complex agent (GZ-1), 40 ~ 80 g/L; complex agent (GZ-2), 0 ~ 15 g/L; KBH₄, 2.0 ~ 3.0 g/L; Na₂WO₄·2H₂O, 50 ~ 70 g/L; SiC(3.0 ~ 3.5 μm), 60 g/L; CeO₂(0.5 ~ 1.0 μm), 5 ~ 14 g/L; pH, 13.5; current density, 6 ~ 9 A/dm²; temperature, 40 °C; agitation style, air agitation.

The matrix materials is A₃ carbon steels, the matrix size is 40 mm × 40 mm × 3 mm.

The composition of the Ni-W-B-SiC composite coatings was measured by EDAX 9100 multiple functional electronic spectrum, and five points average was needed. The surface morphologies of the coatings were observed by ASM-SX electron scanning microscopy. The structures of the coatings were analyzed by Japanese 3015 X-ray diffraction. The hardness of the coatings was measured by means of HX-1 microhardness meter, and load was 100 g.

3 RESULTS AND DISCUSSION

3.1 Effects of CeO₂ on composition of Ni-W-B-SiC composite coatings

Effects of the amount of CeO₂ in the bath on the composition of the composite coatings are shown in Table 1. It is known that the contents of SiC particle, tungsten and CeO₂ in the deposits increase with increasing the amount of CeO₂ in the bath. And they reach peak values when the concentration of CeO₂ in the bath is up to 8 g/L. The contents of CeO₂, SiC and W in the coatings, however, decrease with the continuous rise of the concentration of CeO₂ in the bath. It is clear that the appropriate amount of CeO₂ in the bath can improve the co-deposition of SiC particles with Ni-W-B alloy. Because the addition of rare earth in the bath enables SiC particles to absorb more positive charges, and a lot of SiC particles to co-deposit with Ni-W-B alloy under the effect of electrical field force. But the surfaces of SiC particles in the bath are saturated when the concentration of CeO₂ in the bath is raised continuously, i.e. the positive charges are not increased. So the content of SiC parti-

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cles in the deposits decreases^[8].

Table 1 Effects of addition of CeO₂ on contents of W, SiC and CeO₂ in composite coatings

| Concentration of CeO ₂ in bath/(g·L ⁻¹) | Contents of W, SiC and CeO ₂ | | |
|---|---|----------|------------------------|
| | w(W)/% | w(SiC)/% | w(CeO ₂)/% |
| 0 | 0.38 | 4.28 | 0 |
| 5 | 0.42 | 5.67 | 0.58 |
| 8 | 0.66 | 10.74 | 1.12 |
| 11 | 0.47 | 7.85 | 0.97 |
| 14 | 0.60 | 7.60 | 0.21 |

3.2 Effects of CeO₂ amount on surface morphology of composite coatings

Fig.1 shows that the surfaces of the Ni-W-B-SiC composite coatings tend to level, cracks become small and grains get fine with increasing the concentration of CeO₂ in the bath. Because much more amount of rare earth is absorbed on the surface of electrode with the rise of concentration of rare earth in the bath, and the structure of electric double layer between electrode and solutions is changed, and the polarization of cathode is enhanced and grains of the composite coatings are fined^[9]. But the cracks of the coatings get wide when the concentration of rare earth in the bath

is raised greatly. So the concentration of rare earth in the bath must be controlled within 8 ~ 11 g/L.

3.3 Effects of addition of CeO₂ on structure of composite coatings

X-ray diffraction patterns of Ni-W-B-SiC and RE-Ni-W-B-SiC composite coatings are shown in Fig. 2. It is clear that the width of diffraction peak of RE-Ni-W-B-SiC composite coating is much wider than that of Ni-W-B-SiC composite coating, furthermore, there is no peak of Ni₄B₃ in the diffraction pattern of RE-Ni-W-B-SiC composite coating. It is displayed that the addition of CeO₂ enables Ni-W-B-SiC coating to change from crystal to amorphous status. In addition, there are some new phases such as Ni₂B, NiB and WB appearing in the patterns of the coatings after heat treated at 500 °C for 1 h. It is known from Ni-B binary phase diagram that the solubility of boron in nickel is only 0.03%, and atom radius of boron is $r_B = 0.97 \text{ \AA}$ and that of nickel is $r_{Ni} = 1.246 \text{ \AA}$, ($r_{Ni} - r_B$)/ $r_{Ni} = 22.2\%$. Therefore, boron and nickel will form solid solution, moreover, the structure of solid solution is the same as that of metal solution^[10]. Ni and B will form supersaturated gap solid solution with increasing contents of boron in the coatings, and supersaturated solid solution of nickel will change into

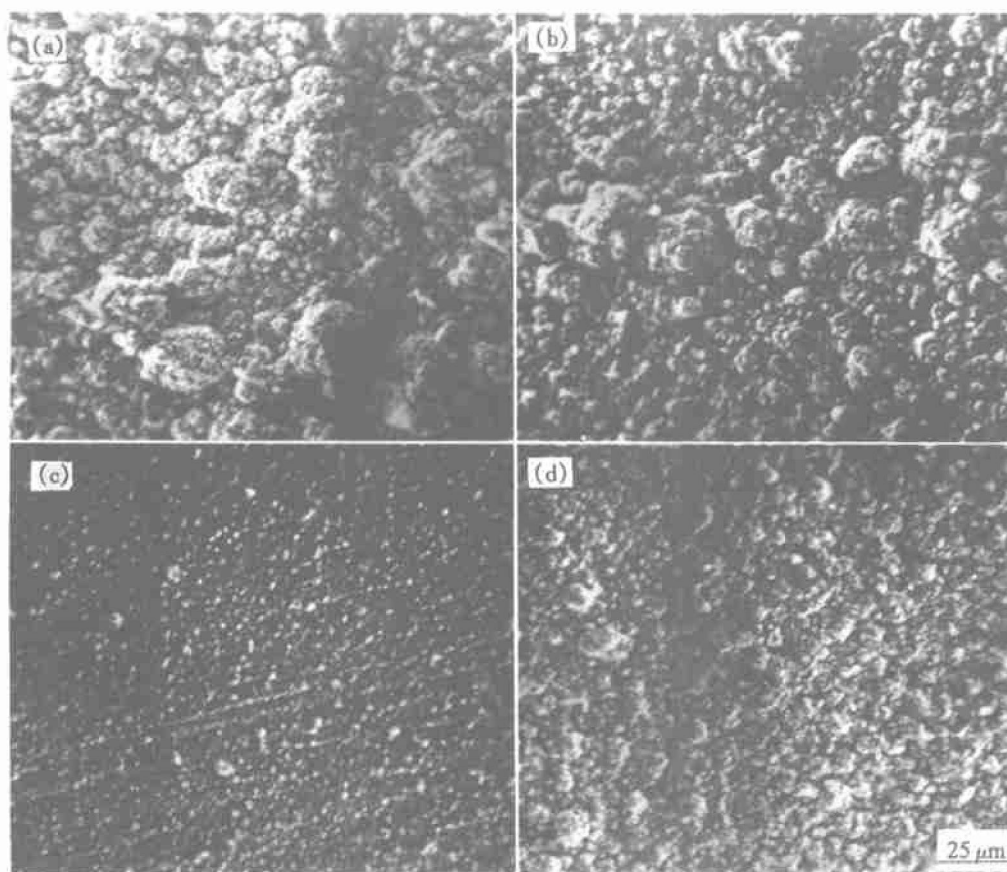


Fig.1 Effects of addition of CeO₂ on surface morphologies of composite coatings

(a) —5 g/L CeO₂; (b) —8 g/L CeO₂; (c) —11 g/L CeO₂; (d) —14 g/L CeO₂

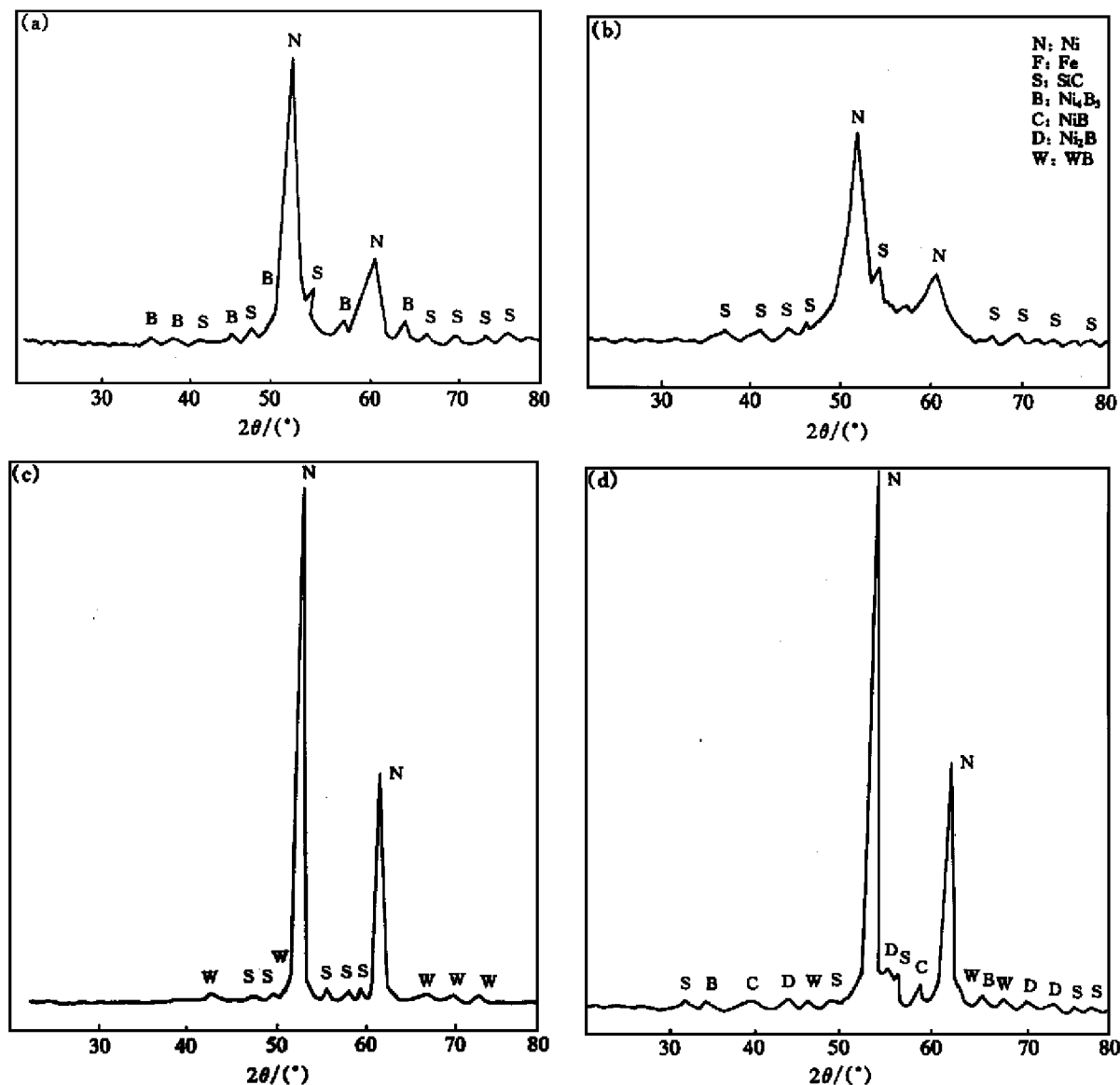


Fig.2 X-ray diffraction patterns of composite coatings

- (a) — Ni-1.52%W-2.15%B-4.55%SiC composite coating as deposited;
 (b) — Ni-1.64%W-2.35%B-4.48%SiC-1.24%CeO₂ as deposited;
 (c) — Ni-1.52%W-2.15%B-4.55%SiC composite coating after heat treated at 500 °C;
 (d) — Ni-1.64%W-2.35%B-4.48%SiC-1.24%CeO₂ after heat treated at 500 °C

boride and equilibrium phase of nickel when the composite coatings are heat treated. So a lot of new phases show up in the diffraction patterns.

3.4 Effects of addition of CeO₂ and heat treatment temperature on hardness of composite coatings

Effects of addition of CeO₂ and heat treatment temperature on hardness of Ni-W-B-SiC and RE-Ni-W-B-SiC composite coatings are shown in Fig.3. It is known that the hardness of the composite coatings changes greatly with increasing temperature of heat treatment. The hardness of the two kinds of composite coatings reaches peak values at 400 °C, but they decrease linearly with continuously raising heat treatment temperature. This is because that when the heat

treatment temperature is very low, the structures of the composite coatings hardly change and the hardness increases a little; when the temperature increases, the structures turn into crystal from mixture, the supersaturated solid solution of nickel forms, the crystal lattice distorts greatly and the hardness rises obviously.

Moreover, a large number of fine Ni₂B particles precipitate and a hardening reaction appears at 400 °C for 1 h. So the hardness of the coatings reaches peak value. However, the grains of solid solution of nickel grow up and the Ni₂B particles coarsen and the coatings soften, resulting in the decrease of hardness with increasing temperature further^[10]. Besides, it is clear that the hardness of RE-Ni-W-B-SiC composite coar-

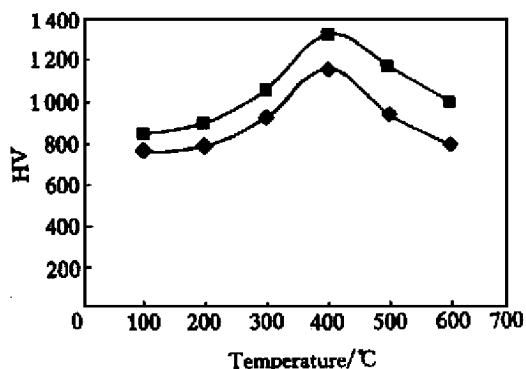


Fig.3 Effects of heat treatment temperature on microhardness of composite coatings

◆ — Ni-1.52%W-2.15%B-4.55%SiC;
 ■ — Ni-1.64%W-2.35%B-4.48%SiC-1.24%CeO₂

ting is higher than that of the Ni-W-B-SiC coating. This is because that the addition of rare earth in the bath can enable SiC particles in the bath to co-deposit with Ni-W-B alloy, and the content of SiC particles in the coating will be raised. At the same time, SiC particles in the coatings can obstruct the grains growing during the process of heat treatment.

4 CONCLUSIONS

1) Addition of rare earth has an important effect on the composition of Ni-W-B-SiC composite coatings, and the contents of W, SiC and CeO₂ in the deposits reach the peak values when the concentration of rare earth in the bath arrives at 8 g/L.

2) Addition of rare earth can enable SiC particles to co-deposit with Ni-W-B alloy, and refine the grains of the coatings.

3) Hardness of Ni-W-B-SiC and RE-Ni-W-B-SiC composite coatings increases with the increase of heat

treatment temperature, and it reaches the peak value at 400 °C. The hardness of RE-Ni-W-B-SiC composite coating is higher than that of the Ni-W-B-SiC composite coating.

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