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Improving the Properties of Ni-ZrO_2 Composite Coatings by Sol-Enhanced Electroplating

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ZrO_2 powder has been used as a second phase in metal coatings which can significantly improve the wear resistance of composite coatings. By using newly developed sol-enhanced electroplating method, Ni-ZrO_2 composite coating has been deposited on mild steel samples. The microstructure, hardness and wear property of sol-enhanced electroplated a Ni-ZrO_2 composite coatings with different ZrO_2 sol concentration were analyzed using SEM, XRD, micro-hardness and wear tests. The effect of ZrO_2 sol concentration on the surface morphology, microstructure and mechanical property of electroplated coatings was discussed and compared with Ni-ZrO_2 composite coatings prepared by adding ZrO_2 powder. It was found that incorporation of ZrO_2 sol improves the mechanical property of Ni coatings in composite coatings. Compared with the traditional ZrO_2 powder method, Sol-enhanced method has better enhancement effect. The mechanical properties of Ni-ZrO_2 coatings reach the optimum value when the ZrO_2 sol concentration is 15 ml/L.

Keywords: mechanical property, Ni-ZrO_2 composite coatings, sol-enhanced electroplating

1. INTRODUCTION

Co-depositing second-phase ceramic nanoparticles to form Ni or alloy based nanocomposite coatings has widely been used on the surfaces of metal substrates to improve the material’s surface mechanical properties [1-4]. For Ni or alloys based composite coatings, it is well-known that closely dispersed second phase ceramic particles can provide strong dispersion strengthening effect [5-8]. A wide range of hard second-phase ceramic nanoparticle is studied to obtain better properties of Ni based nanocomposite coatings, such as SiC, CeO_2, Al_2O_3, ZrO_2, WC, CNTs, etc. [9-11]. ZrO_2 powder has been used as a second phase in Ni coatings and can significantly improve the mechanical properties of the composite coatings [12–14].

However, in the process of adding ZrO_2 powder to electroplating solution to produce a Ni-ZrO_2 composite coating, fine particles agglomeration cannot be completely avoided due to the large surface energy of nanometer ZrO_2 particles [15-17]. One effective to further improve composite coating properties is to avoid nanoparticle agglomeration in the plating solution which can affect the coating properties [18]. A novel technique-the sol-enhanced coating method was developed by our team [18]. It can effectively reduce nanoparticle aggregation in the plating solution and form highly dispersed nanoparticles in the coating matrix, resulting in significantly improved mechanical properties [18]. Several Ni or alloy based composite coatings (such as Ni-TiO_2, Ni-Co-TiO_2, Ni-B-TiO_2, Ni-P-TiO_2 and Ni-P-ZrO_2) have been prepared and studied using this method, [18-22].

In this work, sol enhanced Ni- ZrO_2 nanocomposite coatings are prepared onto mild steel by electroplating. The microstructure, micro-hardness and wear property of Ni-ZrO_2 composite coatings with different ZrO_2 sol concentration are discussed and compared with Ni-ZrO_2 composite coatings prepared by adding ZrO_2 powder.

2. EXPERIMENTAL

In the preparation of ZrO_2 sol and Ni- ZrO_2 nanocomposite coatings, all commercial AR purity chemicals are directly used without additional purification.

2.1 Preparation of ZrO_2 sol

Transparent ZrO_2 sol is prepared in three steps, the details of which are shown in Table 1. In the first step, 61.8 ml anhydrous ethanol and 5.6 ml diethanolamine (DEA) are constantly stirred and mixed in a 250 ml beaker. In the second step, 22.6 ml zirconium(IV) n-propanol(70 wt. % solution in 1-propanol) is added to the mixed solution in the beaker and is constantly stirred until the solution is completely mixed.

Table 1. Process for Preparation of ZrO_2 sol

Symbol	Chemical substances	Quantity(mL)	First step	Second step	Third Step
A	zirconium(IV) n-propanol	22.6		Mixing A with F, and kept stirring, to generate H	H and G Mixed, and vigorous stirring to form a fresh sol
B	anhydrous ethanol	61.8	B and C mixed to generate F		
C	diethanolamine (DEA)	5.6			
D	deionized water	0.92	D and E mixed to generate G		
E	anhydrous ethanol	9.0			

At the same time, 0.92 ml deionized water and 9 ml anhydrous ethanol are mixed in another beaker. In the third step, mix the solution in the two beakers are mixed stirred until fully fused to form the ZrO_2 sol.

2.2 Sol-enhanced plating processes

We used the electroplating process for appiling coatings according to our previous report [23]. Ni-ZrO_2 composite coatings are electroplated onto a mild steel substrate (20×30×3 mm^3). Before electroplating, the stainless steel substrate underwent several processes such as mechanical polishing using SiC paper, ultrasonic cleaning in ethanol and immersing in HCl solution for 2 min at room temperature.

The plating system consists of a Ni plate as the anode and a mild steel sample as the cathode. Detailed bath composition and electroplating plating parameters as shown in Table 2. ZrO_2 sol is used to produce a composite coating. Six different concentrations of ZrO_2 (0 ml, 5 ml, 10 ml, 15ml, 20 ml, 30 ml) sol were added to the bath.

In order to study the comparative effects, a Ni composite coating was prepared by adding ZrO_2 powder. The preparation method was the same as the sol-enhancement process, with ZrO_2 sol replaced by ZrO_2 powder. The added amount of ZrO_2 powder with a mean diameter of 50 nm is 5 g/L, 10 g/L, 15 g/L, and 20 g/L respectively.

Table 2. Bath composition and electroplating parameters for Ni-ZrO_2 composite coatings

Bath composition and plating parameters	Quantity	Bath composition and plating parameters	Quantity(mL)
$NiSO_4$-$6H_2O$	250 g/L	Current density	20 mA cm^{-2}
$NiCl_2$-$6H_2O$	40 g/L	Stirring rate	500 rpm
H_3BO_3	35 g/L	Bath temperature	55 ^oC
Brightener additives	Certain amount	Time	30 min
PH	3.5	ZrO_2 sol	0~40 ml/L

2.3 Coating performance measurement

The surface morphologies and wear track images of coatings were characterized by high-resolution optical microscopy. The phase structure of coatings was characterized by X-ray diffraction (XRD). Vickers microhardness of coating surface was measured using a load of 100 g with a holding time of 15 s. The average of 5 measurements was used as the hardness. The wear property of coatings was tested using a micro-tribometer (Nanovea, USA) in air at room temperature. All wear tests were performed under a load of 3 N, a sliding speed of 2 m/min and a contact radius of 6 mm for a total sliding distance of 20 m.

3. RESULTS AND DISCUSSION

3.1 Surface of Ni-ZrO$_2$ composite coatings

The surface morphologies of Ni-ZrO$_2$ composite coatings are shown in Fig.1. The surface morphologies of Ni-ZrO$_2$ composite coatings prepared with ZrO$_2$ powder content of 5 g/L, 10 g/L, 20 g/L are shown in Fig.1 (a), Fig.1 (b), and Fig.1 (c), respectively. The surface morphologies of sol enhanced Ni-ZrO$_2$ composite coatings prepared with ZrO$_2$ sol content of 5 ml/L, 15 ml/L, 30 ml/L are shown in Fig.1 (d), Fig.1 (e), and Fig.1 (f), respectively. As the concentration of ZrO$_2$ powder or gel in the bath increases, the quantity and size of black points on the surface of the Ni-ZrO$_2$ composite coatings increases, especially when ZrO$_2$ powder is added. These large black particle clouds could be due to the agglomeration of ZrO$_2$ nanoparticles [23]. Compared with a Ni-ZrO$_2$ composite coating prepared by adding ZrO$_2$ powder, the Ni-ZrO$_2$ composite coating prepared by adding ZrO$_2$ sol has a smoother surface and a more uniform distribution of nanoparticles, which can effectively reduce the agglomeration of nanoparticles during electroplating.

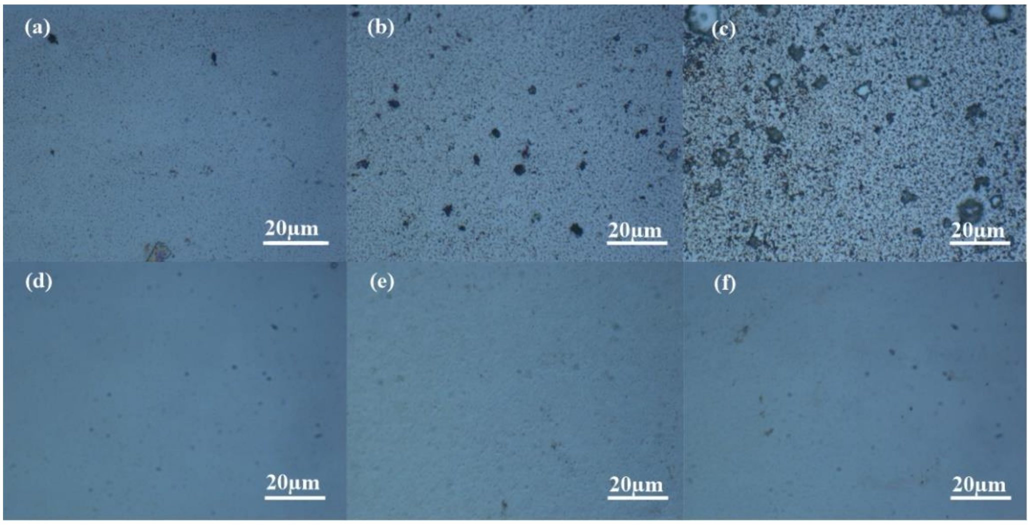

Figure 1. Surface morphologies of Ni–ZrO$_2$ composite coatings: (1) ZrO$_2$ powder:(a) Ni–ZrO$_2$ (2.5 g/L), (b) Ni–ZrO$_2$ (10 g/L), (c) Ni–ZrO$_2$ (20 g/L); (2) ZrO$_2$ sol-enhanced:(d) Ni–ZrO$_2$ (5 ml/L), (e) Ni–ZrO$_2$ (15 ml/L), and (f) Ni–ZrO$_2$ (30 ml/L) .

3.2 Microstructure of Ni-ZrO$_2$ composite coatings

The XRD patterns of sol enhanced Ni-ZrO$_2$ composite coatings with different concentration of ZrO$_2$ sol addition are shown in Fig.2. From Fig.2, the Ni-ZrO$_2$ composite coating is a polycrystalline structure of face-centered cubic (*fcc*) lattice structure, and the characteristic peaks of Ni coatings are Ni (111), Ni (200) and Ni (220), respectively. The peaks at 65.0^{o} can be assigned to Fe from the mild steel substrate. No ZrO$_2$ peaks can be detected from the Ni–ZrO$_2$ composite coatings, probably due to the low quantity of ZrO$_2$ and high intensity of Ni diffraction peaks.

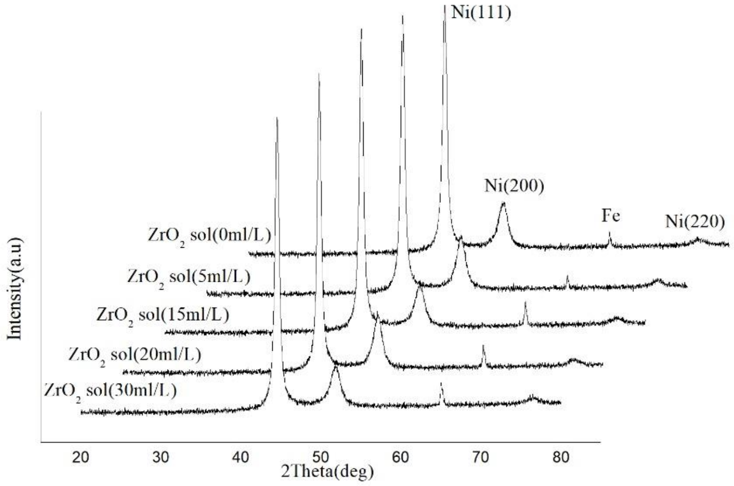

Figure 2. XRD patterns of sol enhanced Ni-ZrO_2 composite coatings with different concentration of ZrO_2 sol addition.

The grain size of the composite coatings is calculated from the measured XRD spectra. (111) peak broadening of *fcc* nickel is used to determine the average crystallite size of the nickel matrix. Equation (1) (Scherrer equation) is used to calculate the crystallite sizes.

$$L = \frac{\lambda}{\beta \times \cos\theta} \qquad (1)$$

Where, L is the crystallite size, λ is the X-ray wavelength, β is the effective line broadening and θ is the Bragg angle. Grain size of sol enhanced Ni-ZrO_2 composite coatings with different ZrO_2 sol addition concentration is shown in Table 3. The grain size first decreases and then increases with the increase of ZrO_2 sol concentration. When ZrO_2 sol is not added to the plating solution, the pure nickel coating has a grain size of 11.5 nm. As the ZrO_2 sol concentration increases, the grain size of the coating gradually decreases from ~11.5 nm to ~9.8 nm. When the addition of ZrO_2 sol concentration is 15 ml/L, the grain reaches a minimum value of 9.8 nm.

Table 3. Grain size of sol enhanced Ni-ZrO_2 composite coatings with different ZrO_2 sol addition concentrations

Composition and conditions	Grain size(nm)
Ni coating	11.5±0.1
Ni- ZrO_2 (5ml/L) composite coating	11.1±0.1
Ni- ZrO_2 (10ml/L)composite coating	10.7±0.1
Ni- ZrO_2 (15ml/L)composite coating	9.8±0.1
Ni- ZrO_2 (20ml/L)composite coating	10.3±0.1
Ni- ZrO_2 (30ml/L)composite coating	10.4±0.1

During electrodeposition of composite coating particles suspended in plating solution get adsorbed on the growing metal matrix and inhibit further growth of the crystals while enhancing the crystals nucleation [5, 23-25]. Small ZrO_2 nanoparticles could provide a large number of nucleation centers and accelerate the deposition rate. The addition of ZrO_2 would increase deposition overpotential [26] and the large number of nucleation sites with ZrO_2 nanoparticles perturbs the growth of the nickel matrix, this leads to the formation of finer grains [27, 28]. Hence the grain sizes were decreased. When the ZrO_2 sol concentration is more than 15ml/L, the agglomeration effect of nanoparticles is enhanced, the nucleation center is reduced, the effect of inhibiting grain reduction is weakened, and the grain size is enlarged. The grain size increases to ~10.4 nm when the ZrO_2 concentration reaches 30 ml/L. It can be seen that adding an appropriate concentration of ZrO_2 sol can effectively decrease the grain size of Ni-ZrO_2 composite coatings.

Compared with the sol enhancement method, the grain size of the Ni-ZrO_2 composite coating prepared by adding ZrO_2 powder is the same as that of the sol enhancement method, and the grain size decreases first with the increase of ZrO_2 powder, and then increases, but the decrease is much smaller. This may be because ZrO_2 powder nanoparticles are easily reunited, and the nucleation center formed to promote the growth of grains is not as good as the sol competition method. The grain size of Ni-ZrO_2 composite coating prepared by adding ZrO2 powder is shown in Table 4.

Table 4. Grain size of Ni-ZrO_2 composite coatings with different ZrO_2 powder addition concentration

Composition and conditions	Grain size(nm)
Ni coating	11.5±0.1
Ni- ZrO_2 (5g/L) composite coating	11.2±0.1
Ni- ZrO_2 (10g/L)composite coating	11.0±0.1
Ni- ZrO_2 (15g/L)composite coating	10.6±0.1
Ni- ZrO_2 (20g/L)composite coating	11.1±0.1

3.3 Micro-hardness of coatings

The Vickers hardness values of the sol enhanced Ni-ZrO_2 composite coatings are shown in Fig.3. The hardness increases first and then decreases with the increase of ZrO_2 sol concentration in the plating bath. The hardness of pure Ni coating is ~410 HV. When the ZrO_2 sol concentration reaches 15 ml/L, the hardness value of Ni-ZrO_2 composite coating reaches a maximum of 588 HV. The increase in hardness may be due to the effect of ZrO_2 nanoparticles dispersion strengthening. The decrease in hardness with further increasing the amount of ZrO_2 concentration can be due to more serious particle agglomeration which tends to cause a porous structure [23]. Compared with the sol enhanced method, the hardness of the Ni-ZrO_2 coating prepared by adding ZrO_2 powder is not better than the Sol method. When the ZrO_2 powder concentration reaches 10g/L, the hardness value of Ni-

ZrO_2 composite coating reaches a maximum of 498 HV, which was 90 HV less than the maximum of the Sol method.

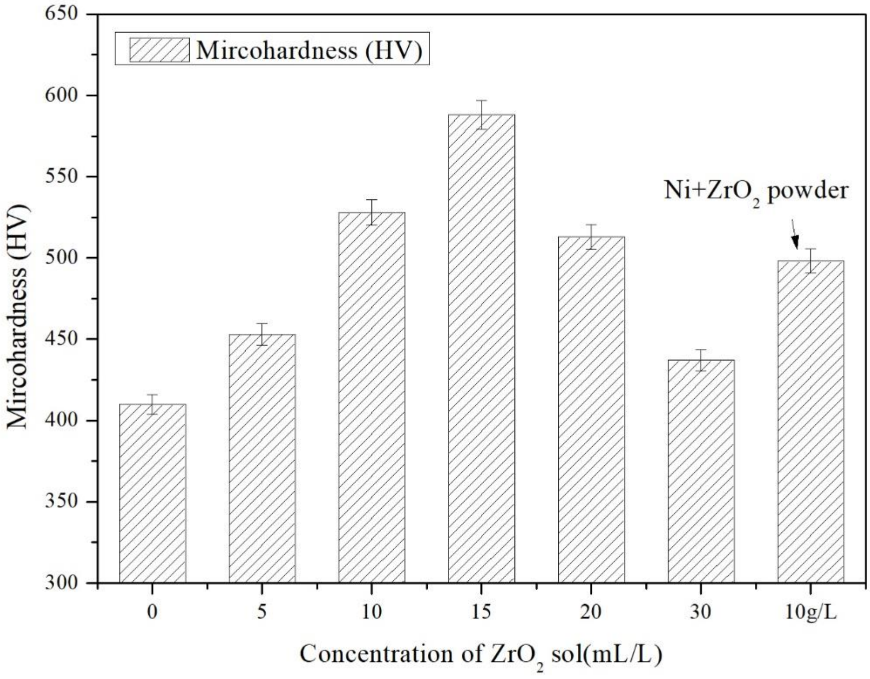

Figure 3. Microhardness of sol enhanced Ni- ZrO_2 composite coatings with different concentration of ZrO_2 sol addition concentration.

3.4 Wear property of coatings

The wear track images of sol enhanced Ni-ZrO_2 composite coatings are shown in Fig.4. The wear track width of (a) Ni coating, (b) Ni-ZrO_2 (5 ml/L) coating, (c) Ni-ZrO_2 (10 ml/L) coating, (d) Ni-ZrO_2 (15 ml/L) coating, and (e) Ni-ZrO_2 (20 ml/L) coating are ~185 μm, ~170 μm, ~145 μm, ~130 μm, and ~160 μm, respectively. These widths first decrease and then increase with increasing ZrO_2 sol concentration in the plating bath, and follow the same trend as the ZrO_2 powder concentration in the plating bath results. In all the Ni-ZrO_2 composite coatings prepared by adding ZrO_2 powder, when the ZrO_2 powder concentration reaches 10g/L, the wear track width of Ni-ZrO_2 composite coating reaches a minimum of 135 μm as shown in Fig.4 (f), which is 10 μm more than the minimum of the sol enhanced Ni-ZrO_2 composite coating. The main reason for this phenomenon is that the wear track width is mainly determined by the hardness of the coating. When the ZrO_2 sol concentration reaches 15 ml/L, the hardness value of Ni-ZrO_2 composite coating reaches a maximum, so his wear track width was also minimal.

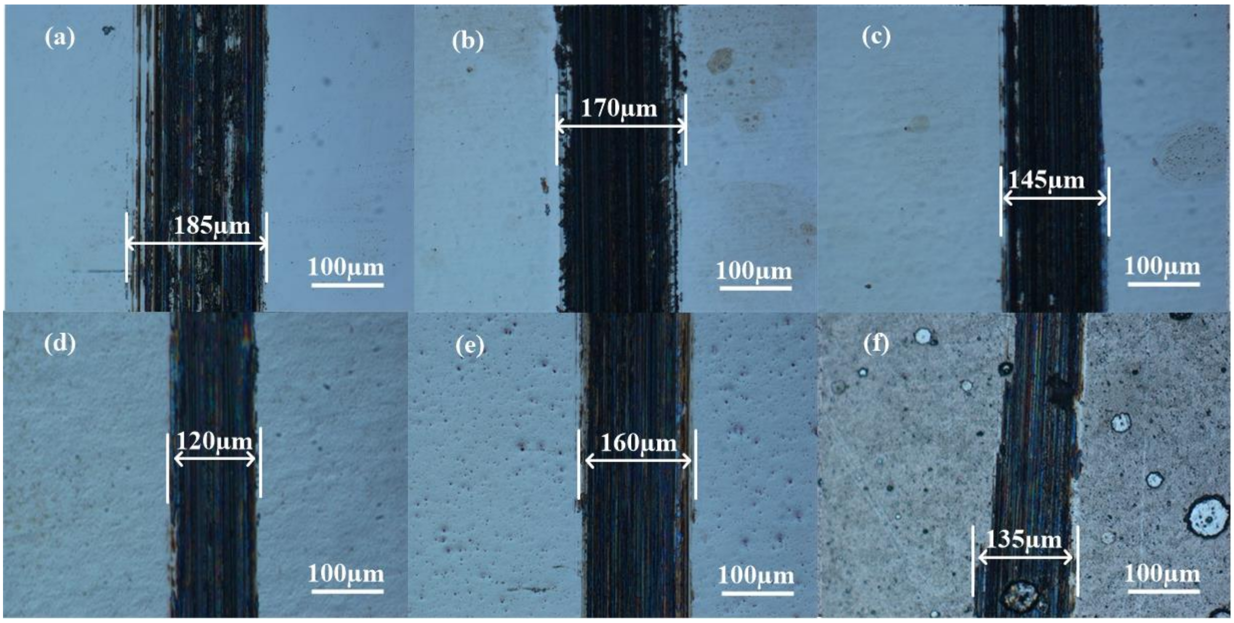

Figure 4. Wear track image of Ni composite coatings, prepared by adding ZrO_2 sol: (a) Ni coating, (b) Ni–ZrO_2 (5ml/L) coating, (c) Ni–ZrO_2 (10ml/L) coating, (d) Ni–ZrO_2 (15ml/L) coating, (e) Ni–ZrO_2 (20 ml/L) coating, and prepared by adding ZrO_2 powder: (f) Ni–ZrO_2 (10 g/L) coatings.

4. CONCLUSIONS

Sol enhanced Ni-ZrO_2 nanocomposite coatings are prepared on mild steel by an electroplating method. The microstructure, micro-hardness and wear property of sol enhanced Ni-ZrO_2 composite coatings with different ZrO_2 sol concentration are studied and compared with the Ni-ZrO2 composite coatings prepared by adding ZrO_2 powder. With increasing ZrO_2 sol concentration in the electroplating solution, the hardness value first increases and then decrease, the grain size and the wear track width first decrease and then increase. The mechanical properties of the sol enhanced Ni-ZrO_2 composite coatings are better than those of the Ni-ZrO_2 composite coatings prepared by the addition of ZrO_2 powder. The mechanical properties of sol enhanced Ni-ZrO_2 coatings reach the optimum value when the ZrO_2 sol concentration is 15 ml/L. A suitable ZrO_2 sol concentration could effectively improve the mechanical characteristics of Ni-ZrO_2 nanocomposite coating and broaden the application field of Ni-ZrO_2 nanocomposite coating.

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