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The microstructure and wear resistance characteristics of electroformed nickel and partially stabilized zirconia composite coatings

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Ni-PSZ composite coatings with various PSZ particle content were prepared by the electroforming technique. The microstructure and surface components of the coatings have been examined by optical microscopy, electron microscopy and X-ray photoelectron spectroscopy analysis and the wear properties of the coatings tested on a reciprocating wear test machine. The results show that the PSZ particles are uniformly dispersed in the coatings and thus increase the wear resistance of the coatings by inhibiting plastic deformation of the nickel matrix. The co-deposition of the PSZ particles in the electrolyte is mainly in the form of agglomeration and is accompanied by the incorporation of $Ni(OH)_2$. When the PSZ content in a coating is higher than a critical value, the wear resistance of the coating could deteriorate because of the decrease in the integrity of the nickel matrix. After heat-treatment at high temperature, $Ni(OH)_2$ in the coating is turned into Ni_2O_3 and NiO which can wet the PSZ particles and increase the bonding strength between the PSZ and nickel. In addition, the agglomerated PSZ particles are sintered when heat-treated. These are all beneficial to increasing the wear resistance of the coating. *© 2000 Kluwer Academic Publishers*

1. Introduction

Metal matrix composite (MMC) materials containing a fine dispersion of particles are rapidly increasing in importance in modern engineering application due to their enhanced hardness, wear and corrosion resistance when compared to metal or alloy. The conventional processes for the production of MMC include powder metallurgy, hot pressing, co-spraying and metal infiltration. Elecroformed composite coatings are prepared by co-depositing inert particles suspended in an electrolyte with growing metal during electrodeposition [1, 2]. As one of the techniques for producing MMC, electroforming has obvious advantage over other fabrication methods in many respects. This technique does not require high temperature or pressure. Moreover, a variety of composite forms and shapes can be produced with little or no postmaching operations [3].

The electroforming co-deposition processes are often conducted at the temperature less than 90°C, at which neither inert particles dispersed in metal matrix can be sintered, nor chemical interactions can occur between the particle/metal matrix interfaces. The improved properties of electroformed composites heavily depend on the content and nature of particles in the coatings. Therefore, control of the content and nature of particles incorporated in the coatings is essential for the production of composites with expecting properties. In addition, the nature of the particle/metal matrix interfaces plays an important role in determining the stability and mechanical properties of the composite coating [4–6]. In this study, the microstructural characteristics of the electroforming nickel and partially stabilized zirconia (PSZ) composite coatings in the as-plated and vacuum-annealed conditions are investigated. Furthermore, the effects of the bonding state of PSZ/Ni interfaces and the content of PSZ particles in the composite coatings on the wear resistance of these coatings are discussed.

2. Experimental

2.1. Preparation of composite coatings

The electroforming of Ni-PSZ composite coatings was carried out employing sediment electrodeposition (SED) technique in a nickel sulfamate bath which has the following composition: 600 g/L nickel sulfamate, 10 g/L nickel chloride, 30 g/L boric acid. All chemicals are of analytical reagent grade. The plating bath temperature was held to 50 °C and the pH of the bath was maintained at 3.5 by sodium hydroxide or dilute

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sulfuric-acid. The cathode current density was controlled at 20 A/dm^2.

Three mol.% yttria PSZ powder with a specific gravity of 5.85 was chosen to co-deposit with nickel in this experiment; the average size of the particles is 0.3–0.5 μm. It is composed of t- and m-phases, and the relative amount of m-phase is about 42%. The concentration of PSZ particles in the bath varied from 0 to 90 g/L. The particles were kept suspended in the bath by magnetic stirring and allowed to settle, after the stirring period, on a horizontal cathode during the quiescent period. The stirring time was fixed on 30 sec and the quiescent period was kept at the range of 0–60 sec. Using this technique, composite coatings with a PSZ particle content from 0 to 37.5 vol% could easily be obtained (Table I). The particle content in the composite coatings was determined by chemical analysis.

2.2. Characterization of composite coatings

In the microstructure and components examination, carbon steels were used as the substrates (30 × 20 × 2 mm) for depositing the Ni-PSZ composite coatings. The vacuum-annealing of the composites was conducted at 250–1000 °C for 1 hr. The nature and distributions of PSZ particles in the composite coatings were studied using an optical microscope, a transmission electron microscopy (TEM, CM12/STEM) and a scanning tunneling microscopy (STM, TMX2000Discoverer). The hardness of the composite coatings was measured using a NANO INDENTER$^{\text{IM}}\prod$. In addition, a x-ray photoelectron spectroscopy (XPS, ESCA750) was employed to analyze the surface components of the composite coatings.

2.3. Wear tests

The wear properties of the composite coatings were tested on a reciprocating wear test machine, as shown in Fig. 1. A 12.7 mm-diameter steel ball, on which a composite coating about 400 μm thick was deposited, is coupled with a plate of GCr-15 steel with a hardness of HRC 60. The steel ball is fastened in a columnar jig. The plate is fixed, while the steel ball moved in reciprocating sliding over the plate. The experimental parameters were: applied load 70 N, frequency 5 Hz, stroke 50 mm. All experiments were run at room temperature and used chemical pure liquid paraffin as lubrication.

TABLE I PSZ content in composite coatings at various plating conditions

No.	Concentration of PSZ (g/L)	Quiescent time (sec)	PSZ content (vol%)
1	0	0	0
2	10	0	8.8
3	30	15	17.3
4	50	30	25.6
5	90	60	37.5

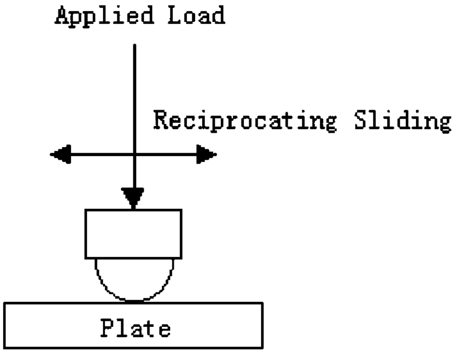


Figure 1 Schematic of reciprocating wear test machine.

During the wear experiment, a round scar was formed on the composite coating surface and progressively increased in diameter. The diameter of the worn surface was measured using a reading microscope. Thus the wear volume of the composite coating is calculated by

$$V = \frac{\pi}{3}\left(r - \sqrt{r^2 - \frac{d^2}{4}}\right)^2 \cdot \left[3r - \left(r - \sqrt{r^2 - \frac{d^2}{4}}\right)\right] \tag{1}$$

where V is the wear volume, r is the radius of the steel ball and d is the diameter of the worn composite coating surface.

With the increase in diameter of the worn surface, the load on per wearing area decreases. Therefore, the wear volume of the composite coating will tend to reach a constant and no longer increase with the increasing wear cycles, that is to say wear process will reach a steady state. The load on per wearing area in the steady state is defined as the wear limiting pressure

$$P = \frac{4N}{\pi \cdot d_{\max}^2} \tag{2}$$

where N is applied load, $d_{\max}$ is the maximum diameter of the worn surface after wear process reaching the steady state. The wear resistance of the composite coatings can be characterized by the value of its wear limiting pressures, the greater the wear limiting pressure, the greater the wear resistance.

In order to judge the wear mechanism of the composite coatings a scanning electron microscope (SEM) was used to observe the morphologies of the worn surfaces.

3. Experimental results and discussions

3.1. Microstructure

The Ni-PSZ composite coatings with the increasing PSZ particle content were polished and then observed using the optical microscopy to examine the distribution of the PSZ particles in the nickel matrix. The optical micrographs are shown in Fig. 2. It can be seen that the PSZ particles are uniformly distributed in the nickel matrix. Under the co-deposition conditions, the nickel matrix is a continuous phase in the composite coatings and no chemical interactions occur between the Ni/PSZ interfaces. Therefore, it is easily concluded that with the increasing PSZ particle content in the composite coatings, the integrity of the nickel matrix is gradually weakened.

Fig. 3 presents the TEM images of the PSZ particles in the as-plated composite coating. It is apparent that the PSZ particles co-deposited with the nickel in two ways: one is the occluding of a single particle in nickel crystal grain or crystal boundary (A point in Fig. 3a and c); another is the incorporating of the agglomerated

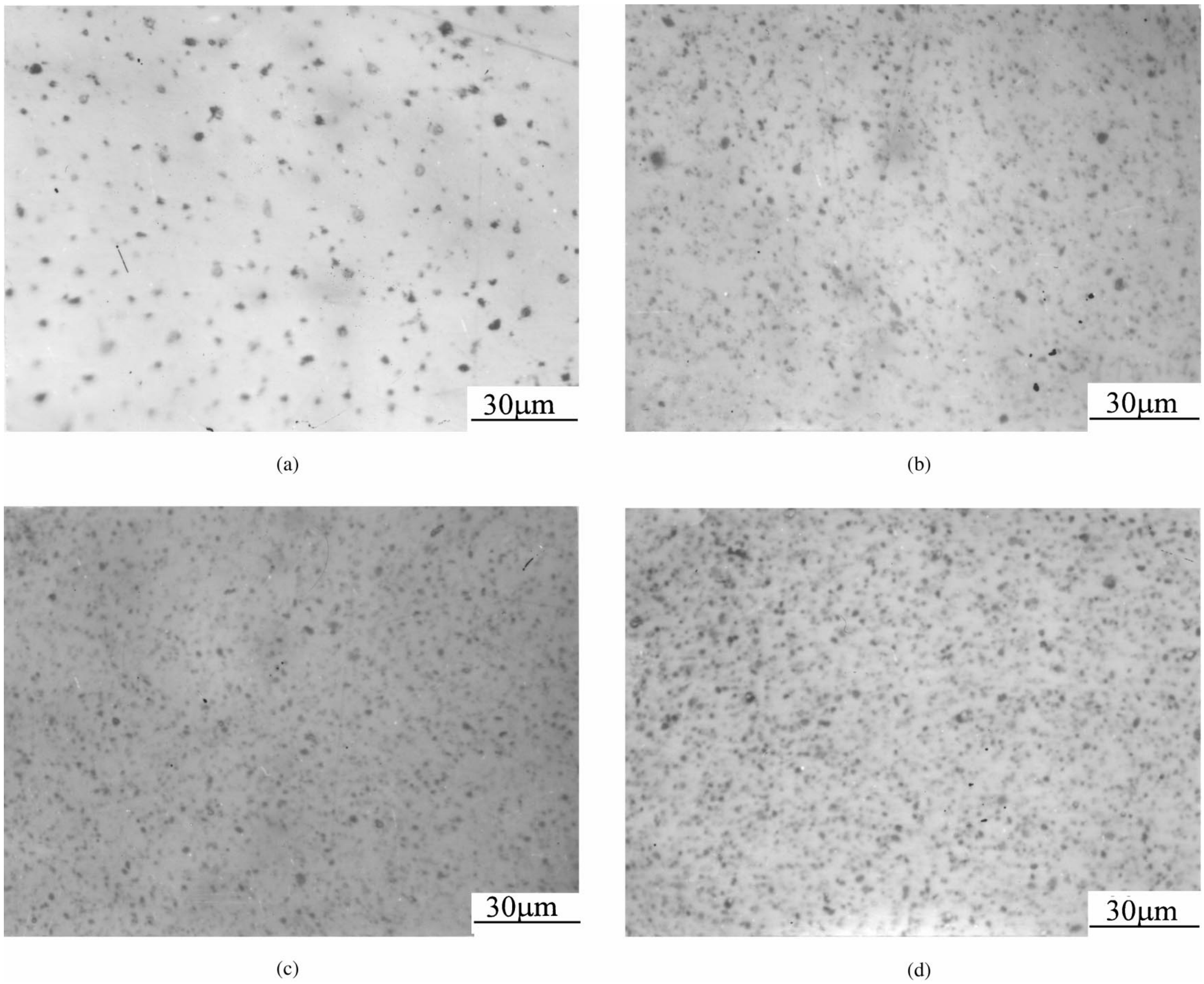


Figure 2 Optical micrographs of Ni-PSZ composite coatings with various PSZ content: (a). Ni-8·8PSZ; (b). Ni-17·3PSZ; (c). Ni-25·6PSZ; (d). Ni-37·5PSZ.

particles merely in nickel crystal boundary (B point in Fig. 3a,b and c), indicating that the agglomerated PSZ particles incorporated can inhibit nickel crystal growth. Because the PSZ particles are too small to disperse completely in the nickel sulfamate electrolyte, the co-deposition of the PSZ particles in the nickel matrix is mainly in the form of agglomeration. Fig. 3d shows the selected-area diffraction pattern corresponding to the agglomeration area of the PSZ particles in Fig. 3c. It indicates that the agglomeration area is actually a mixture consisting of the PSZ particles and the metal nickel with infinitely small grain.

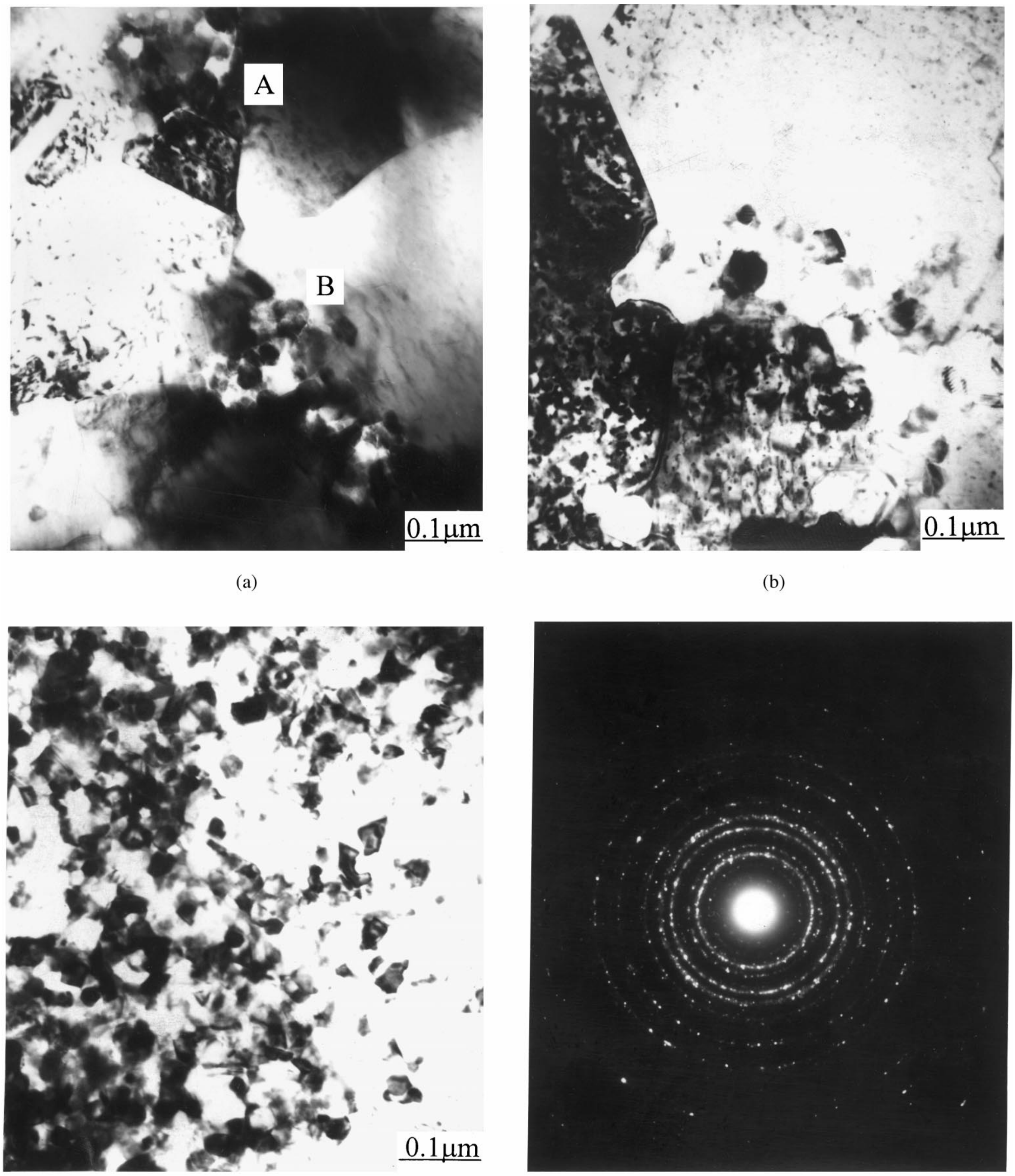
Fig. 4 shows the STM image of a PSZ particle occluded in the nickel matrix. No cavity or crack is observed between the PSZ particle and nickel interface. This proves that the interfaces between the PSZ particles and nickel matrix are close.

High temperature heat-treatment on the composite coatings at the vacuum condition does not affect the distribution of the PSZ particles in the nickel matrix, but can sinter the agglomerated PSZ particles. Fig. 5 shows the TEM images of the PSZ agglomeration area vacuum-annealed at 500°C and 1000°C, respectively, for an hour and corresponding diffraction patterns. The PSZ particles in agglomeration area are gradually burn together with the increase in heat-treatment temperature. After annealing at 1000°C, the agglomerated PSZ particles have become a cross-linked network structure, in which contains some tiny nickel crystal grains.

3.2. XPS analysis

Fig. 6 represents XPS spectra of the nickel matrix in the composite coatings with the increasing PSZ content, in which the two peaks are identified as Ni and $Ni(OH)_2$, respectively. According to the reaction mechanism during nickel electrodeposition, hydrogen reduction reaction occurs in the sulfamate bath. The hydrogen evolution happens on the surface of the cathode and increases the local pH. Because the concentration of nickel ion in the electrolyte is high, $Ni(OH)_2$ is formed and incorporated in the coating. The co-deposition of the PSZ particles has a significant effect on hydrogen evolution. On the other hand, the PSZ particles adsorb on the cathode and prevent OH^- from being released into the solution, which also results in more $Ni(OH)_2$ in the coating [7, 8]. Therefore, the amount of $Ni(OH)_2$ in the coatings increases with the increase in the PSZ content.

As shown in Fig. 7, $Ni(OH)_2$ in the composite coating turns into Ni_2O_3 and NiO after vacuum-annealing at 1000°C for an hour due to losing water.



(a) (b) (c) (d)

Figure 3 TEM images of the PSZ particles in as-plated composite coating: (a), (b) and (c). Images of the PSZ particles in coating; (d). Diffraction pattern of (c).

3.3. Wear tests

Fig. 8 shows the wear curves of the as-plated composite coatings with various PSZ content. Initially, the wear volume of the composite coating rapidly increases with the increasing wear cycles. Then, the wear process reaches progressively the steady state until the end of the test due to the decrease in the load on per wearing area. The values of the wear limiting pressures (P) of these composite coatings are tabulated in Table II. One can see that the values of P increase with the increase in the PSZ content in the coatings. Consequently, the incorporation of the PSZ particles improves the wear resistance of the coatings. However, when the PSZ content is up to 37.5%, the composite coating appears to be even poorer wear behavior than the pure nickel coating.

The wear curves of the composite coatings containing 37.5% PSZ vacuum-annealed at various temperature are shown in Fig. 9, and the corresponding wear limiting pressures are listed in Table III. It can be seen that the heat-treatment can pronouncedly increase the wear resistance of the composite coating. The composite coating which wear limiting pressure is larger than that of the as-plated Ni-25·6PSZ coating has the best wear resistance after vacuum-annealing at 1000°C for an hour.

The wear properties of the Ni-PSZ composite coatings strongly depend on their constitution and microstructure. The PSZ particles dispersed in the nickel matrix block, or at least delay, the movement of dislocations in the metal nickel and thus inhibit plastic deformation [9], which result in an increasing hardness

(Fig. 10) and improve the wear behaviors of the coatings. Furthermore, the co-deposition of the PSZ particles can generate a lot of dislocations in the nickel matrix and strengthen the nickel matrix. SEM observations of the worn surfaces of the coatings are shown in Fig. 11. From Fig. 11a and b, wide and deep grooves, spalling pits and plastic deformation are observed on the worn surface of the pure nickel coating, indicating severe adhesive wear occurred [10]. The worn surface of the Ni-25·6PSZ coating shows a completely different appearance when compared with the pure nickel coating. As Fig. 11c shows, some small bulges are found and the abrasion grooves are uncontinuous and disordered. This confirms that the incorporation of the PSZ particles suppresses the plastic deformation and enhances the mechanical properties of the metal nickel. However, the toughness of the composite coatings will gradually be reduced with the increasing PSZ particle content in the coatings because the PSZ is a discrete

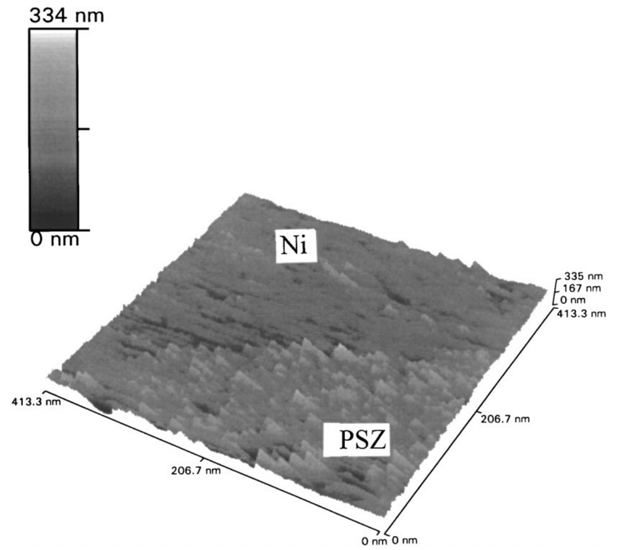
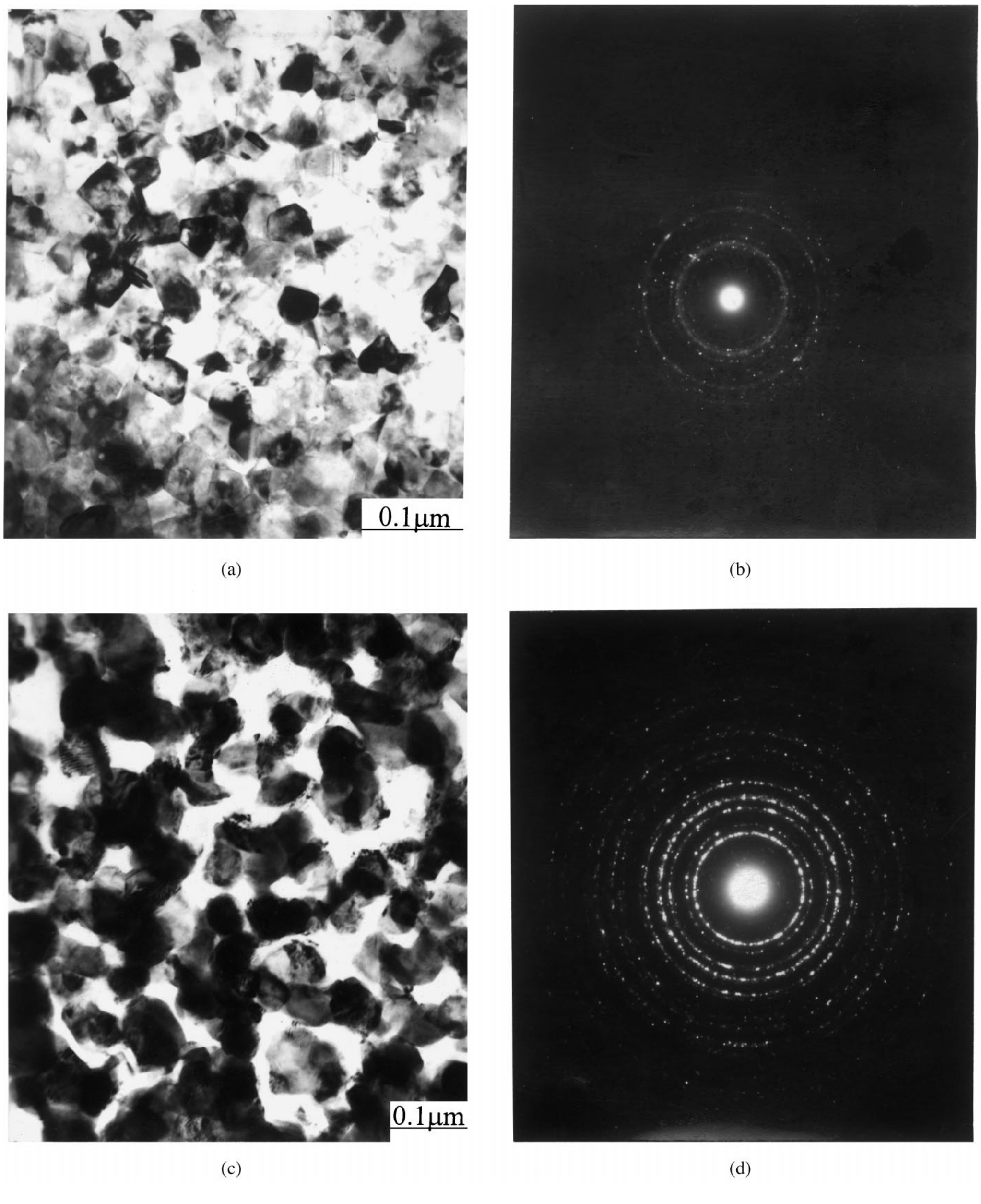


Figure 4 STM micrograph showing bonding state between a PSZ particle and the nickel matrix.



(a) (b)

(c) (d)

Figure 5 TEM images of the PSZ particles in Ni-37·5PSZ coating after heat-tement: (a). Image of the PSZ particles in coating heat-treated at 500°C; (b). Diffraction pattern of (a); (c). Image of the PSZ particles in coating heat-treated at 1000°C; (d). Diffraction pattern of (c).

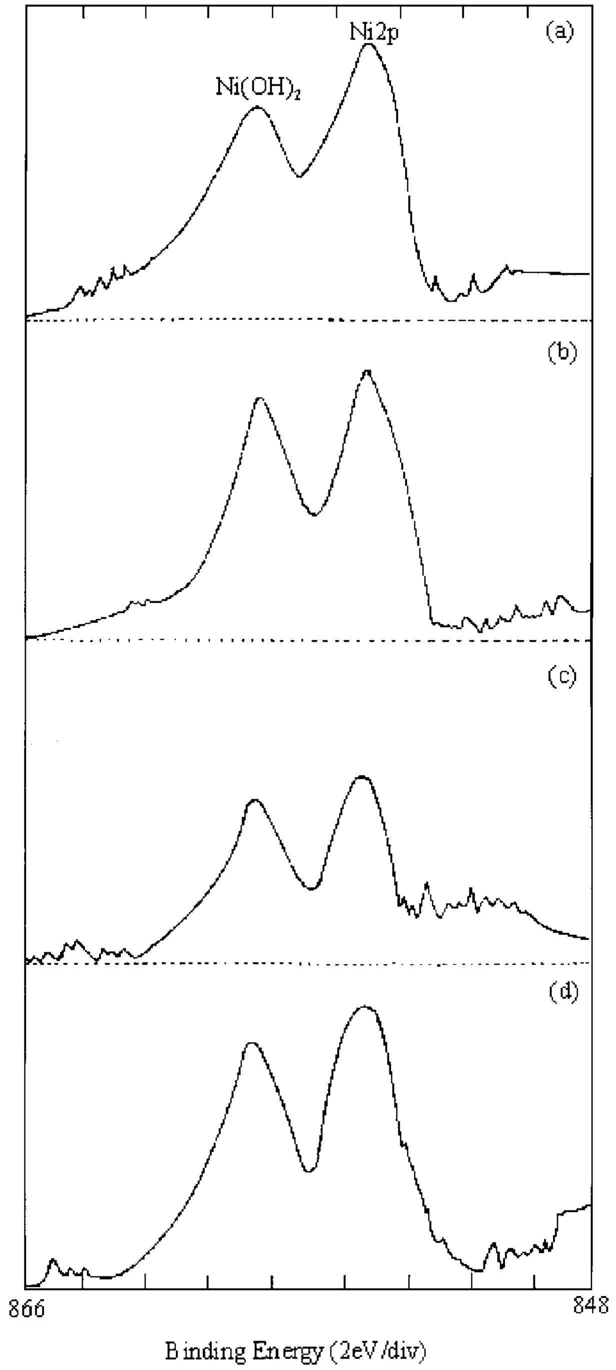


Figure 6 XPS analysis of the nickel in composite coatings: (a). Ni; (b). Ni-8·8PSZ; (c). Ni-25·6PSZ; (d). Ni-37·5PSZ.

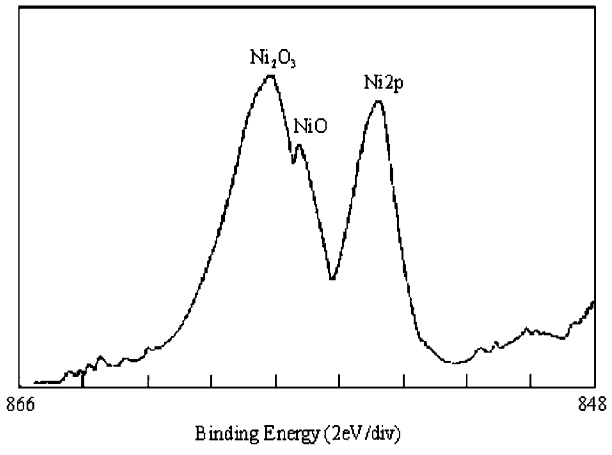


Figure 7 XPS analysis of the nickel in Ni-37·5PSZ coating heat-treated for 1 h at 1000°C.

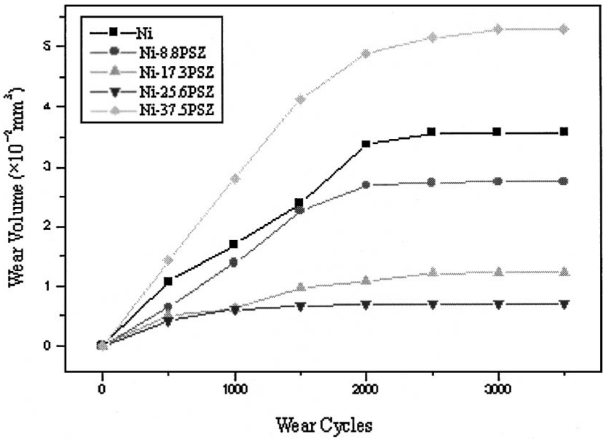


Figure 8 The effects of the PSZ particle content on the wear properties of as-plated composite coatings.

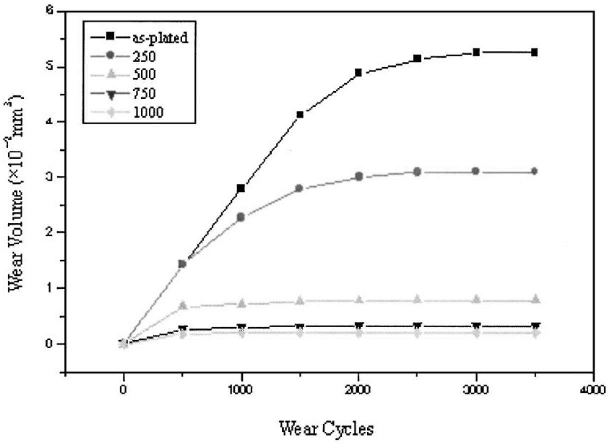


Figure 9 The effects of heat-treatment temperature on the wear properties of Ni-37·5PSZ coating.

phase and no interactions occur between the PSZ particles and nickel matrix interfaces. When the PSZ particle content reaches a critical value, the mechanical properties of the composite coatings will be abruptly deteriorated. As shown in Fig. 11d, more cracks and spalling pits are found on the worn surface of the as-plated Ni-37·5PSZ coating. The grooves on the worn surface are shallow. It suggests that the as-plated Ni-37·5PSZ coating is weaker in fatigue resistance than the pure nickel and Ni-25·6PSZ coating [11]. The PSZ particles are easily pulled out from the worn surface and lead to the largest volume loss and appearance of cracks and pits. Fig. 11e and f demonstrate that the wear resistance of the Ni-37·5PSZ coating is obviously improved after vacuum-annealing at high temperature.

TABLE II The effects of PSZ content on the wear limiting pressure *P* of composite coatings

Coatings	Ni	Ni-8·8PSZ	Ni-17·3PSZ	Ni-25·6PSZ	Ni-37·5PSZ
P (N/mm^2)	41.8	47.7	72.0	96.8	34.4

TABLE III The effects of heat-treatment temperature on the wear limiting pressure *P* of Ni-37·5PSZ composite coating

Temperature (°C)	0	250	500	750	1000
P (N/mm^2)	34.4	44.7	89.2	141.1	176.4

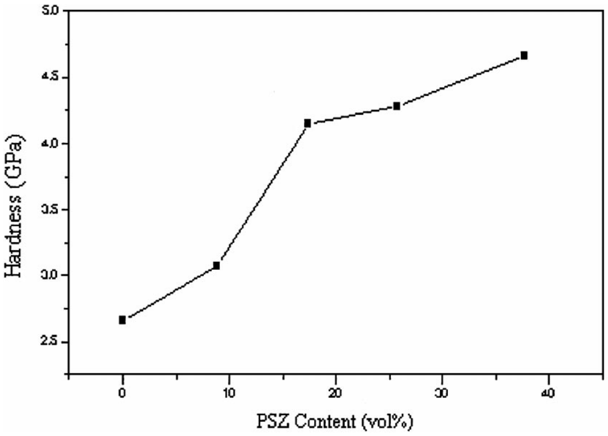
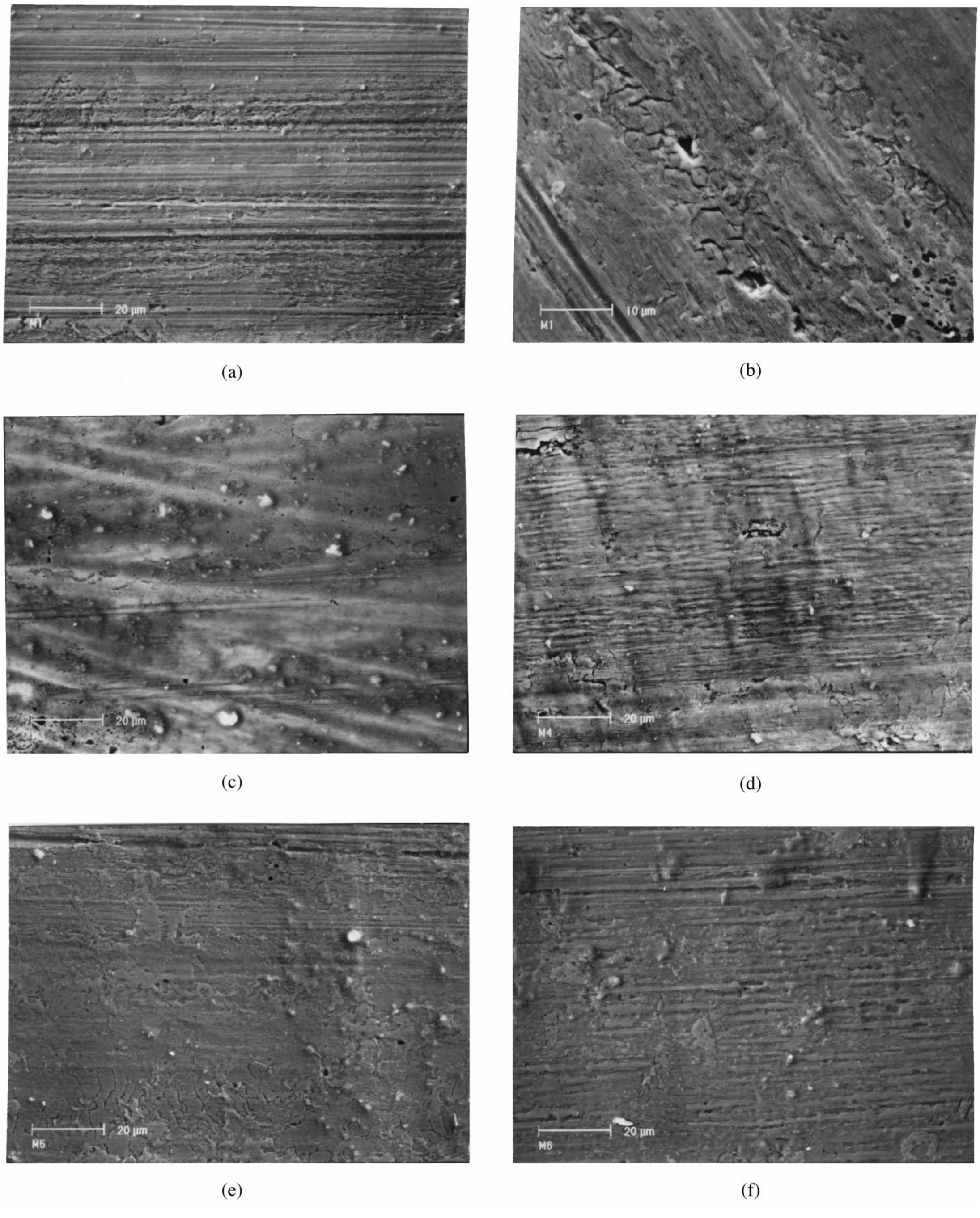


Figure 10 The effects of the PSZ particle content on the hardness of composite coatings.

The worn surface is very smooth and the cracks and pits are greatly reduced. Apparently, the one reason for the effects of heat-treatment on the wear resistance of the composite coating is that sintering of the agglomerated PSZ particles and the decrease in internal stress of the composite coating. The other reason is that the formation of NiO from $Ni(OH)_2$ in the coating. NiO can wet the PSZ particles and thus increase the bonding strengths between the PSZ and metal nickel [12]. Previous researches indicate that the coating wear life is controlled by crack initiation [11]. Crack initiation sites are at the interface between the particle and metal; cracks propagate rapidly along the particle and metal interface and link up leading to final failure. It may be deduced that the increase in bonding strength between



(a) (b) (c) (d) (e) (f)

Figure 11 The morphologies of the worn surfaces of composite coatings: (a). pure Ni (×500); (b). pure Ni (×1000); (c). Ni-25·6PSZ; (d). as-plated Ni-37·5PSZ; (e). Ni-37·5PSZ heat-treated at 500°C; (f). Ni-37·5PSZ heat-treated at 1000°C.

the PSZ and metal nickel play a more important role in the wear resistance of the composite coatings.

4. Conclusions

1. Ni-PSZ composite coatings with various PSZ content are obtained by changing the concentration of PSZ particles in the sulfamate electrolyte and the quiescent period in the sediment electroforming process.

2. The co-deposition of the PSZ particles with the nickel is mainly in the form of agglomeration. The PSZ particles uniformly disperse in the nickel matrix and improve the wear resistance because of inhibiting plastic deformation of the nickel.

3. The co-deposition of the PSZ particles with the nickel is accompanied by the evolution of hydrogen, which results in the increase in the value of the pH near the cathode. Thus, $Ni(OH)_2$ is formed and incorporated in the coating. $Ni(OH)_2$ is turned into Ni_2O_3 and NiO when the coating is vacuum-annealed at high temperature. NiO can wet the PSZ particles and increase the bonding strength between the PSZ and nickel.

4. The PSZ particles are a discrete phase in the coatings and no interactions occur between the PSZ particles and nickel matrix interfaces. Therefore, with the increasing PSZ particle content in the composite coatings, the integrity of the nickel matrix is gradually weakened. The Ni37·5PSZ coating has the poorest wear resistance. After heat-treatment at high temperature, the wear resistance of the Ni-37·5PSZ coating is obviously improved because of the sintering of the agglomerated PSZ particles and the wetting of NiO.

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