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ARTICLE

Effect of Surfactant on the Ni/Nano-WC Composite Electrocoatings

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Abstract: Nickel matrix composite coatings reinforced by nano WC were prepared by pulse current (PC) electrodeposition. The effects of surfactant sodium dodecyl sulfate (SDS) concentration and wet-milling treatment of WC particles on surface morphologies, distribution of particles, microstructures and microhardness values of Ni/nano-WC composite coatings were all investigated and the results were discussed. The results reveal formation of compact coatings with high contents of embedded WC particles and uniform distribution in presence of SDS and under wet-milling treatment of WC particles. The microhardness of the composite coatings is also improved. The optimal coating is obtained by adding 0.15 g/L SDS under wet-milling for 10 h.

Key words: electrodeposition; microstructure; nano-composite tungsten carbide coatings; microhardness

Electroplating is an important method for preparing new composite materials due to its low requirement in equipment combined with simple process. Electrodeposition of hard particles on metal matrices is widely used in aerospace and automotive industry. The properties of metal matrix composites can be changed by incorporating second phase particles[1], which might be hard oxides like TiO_2[2], SiO_2[3], Al_2O_3[4], carbide particles like WC[5] and SiC[6, 7], diamond[8], and liquid containing microcapsules[9]. Electrodeposition can be employed to deposit composite materials on surface of substrates to improve their hardness, wear resistance, and corrosion properties.

Metallic carbides have attracted considerable attention due to their unparalleled chemical and physical properties, such as high melting point, elevated hardness, and excellent chemical and thermal stability[9,10]. Tungsten carbide is an important ceramic material that is widely used in cutting tools, rock drills, punches, and wear-resistant coating materials[11]. The performance of composite coatings heavily depends on sizes of embedded particles. Fine particles have negative effects on electrodeposition and reduce the content of particles embedded in the coating since they are more prone to agglomeration than coarse particles. However, the reduction in particle size could improve the performance of composite coatings[12,13]. Higher incorporated percentages and more uniform distribution of inert particles in metal matrices would have positive impact on wear-resistant, anti-corrosion, and mechanical properties of coatings. The incorporation of particles is affected by a number of interrelated process variables, such as current density, pH value, particle size and shape[14-16], and presence of organic surfactants[17].

Recent studies have extensively reported that addition of organic surfactant should enhance the particles contents in composite coatings[18]. The addition of cetyltrimethyl ammonium bromide (CTAB) may prevent agglomeration of SiC particles in the electroplating bath, yielding coatings with elevated concentrations of uniformly distributed SiC particles. The embedded particles depend on content of effective particles in the electroplating bath. To this end, surfactants are often used as dispersants to yield better suspension of particles and improve the effective content of particles in slurries[19]. In addition, continuous magnetic

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stirring for 24 h was used in experiments to ensure that the particles are fully wetted and suspended in the plating solution before performing electrodeposition[20]. However, the preparation of composite coatings embedded fine WC particles with good properties remains to be studied.

In this study, composite coatings with good properties containing certain amounts of tungsten carbide were prepared by mixing self-made WC particles (80 nm in diameter) with appropriate amounts of surfactant (SDS) followed by wet milling. The percentage and distribution of WC particles in the coatings, as well as the morphologies and microhardness values were investigated and the results were discussed. A possible formation mechanism of composite coatings was proposed and optimum parameters were identified.

1 Experiment

Ni/nano-WC composites were electrodeposited from an organic free Watt's nickel electrolyte containing suspended ultrafine WC particles. The electroplating process conditions are provided in Table 1. The average size of WC particles was around 80 nm (Fig.1). To prevent agglomeration of WC particles, they were diluted in deionized water and sodium dodecyl sulfate (SDS) was added followed by wet-milling for a certain time. The electrolyte containing WC particles and SDS was ultrasonically blended at 350 r/min for 30 min to uniformly suspend all WC particles in the electrolyte.

Copper plate with dimension 50 mm× 18 mm× 1 mm was used as working electrode. Before experiments, emery papers of different grades (600~1500) were used to polish the copper sheet, and surface oxide film was removed by degreasing with ethanol and acetone for 3 min. The copper sheet was then washed with deionized water and dried in air. A nickel plate (~ 99.99 % purity, dimension 50 mm× 36 mm×3 mm) was used as counter electrode. The pH of the solution was fixed to 4.2 and current density was set to 15 A/dm^2. The WC powders were added to the electroplating bath at concentration of 7 g/L, and different SDS loads of 0.05, 0.1, 0.15, and 0.2 g/L were added (Table 2) and the effects were studied. A thermostat water bath was used to stabilize the electrolyte temperature at 50 ℃. Magnetic stirring at 350 r/min was employed to maintain uniform dispersion of particles in bulk solution. The distance between the anode and cathode was fixed at 5 cm. Electrodeposition of Ni/nano-WC composites was carried out using PC deposition in Watt's bath according to the formula: $\text{d.c.}=t_{\text{on}}/(t_{\text{on}}+t_{\text{off}})$, where t_{on} is the time period under applied pulses and t_{off} is relaxation time. The total volume of the electroplating bath was fixed to 300 mL.

Table 1 Experimental conditions used for preparation of Ni/nano-WC composite deposits

Solution composition electrolyte (Watts)	Value
$NiSO_4\cdot 6H_2O$/g·L^{-1}	250
$NiCl_2\cdot 6H_2O$/g·L^{-1}	40
H_3BO_3/g·L^{-1}	35
SDS/g·L^{-1}	0.05, 0.1, 0.15, 0.2
WC powder/g·L^{-1}	7
Electrodeposition conditions	Value
pH	4.2
Temperature/℃	50
Duty cycle /d.c. %	50
Current density/A·dm^{-2}	15
Pulse frequency/kHz	1
Plating time/h	1

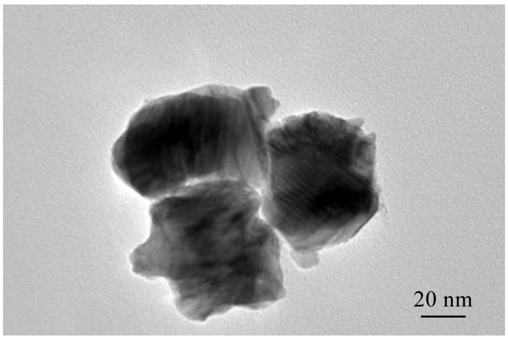

Fig.1 TEM image of the as-prepared nano-WC powders

Scanning electron microscopy (SEM, Nova Nano SEM450) was used to observe the structure, morphology and composition of both surface and cross-sectional profile of Ni/WC composites. The concentration of WC particles on the surface was evaluated by energy-dispersive X-ray spectroscopy (EDS). The phase structure of each composite coating was analyzed by X-ray diffractometry (XRD, Bruker D8 X-ray diffractometer Focus) using Cu Kα radiation. The microhardness of each material was assessed by Microhardness tester (HXS-1000A) at load of 200 g for 15 s.

Table 2 Composition of solution used for electrodeposition

Wet-milling time/h	SDS concentration/g·L^{-1}	WC concentration /g·L^{-1}	Solution No.
0	0	0	1
0	0	7	2
0	0.15	7	3
10	0.05	7	4
10	0.1	7	5
10	0.15	7	6
10	0.2	7	7
2	0.15	7	8
5	0.15	7	9
15	0.15	7	10

2 Results and Discussion

2.1 Structure and morphology

The surface morphology of each coating was studied by SEM. In Fig.2a, the surface of pure nickel coating showed bimodal grain structure with "truncated pyramidal type" [21]. The addition of WC nanoparticles to the plating solution led to their precipitations at grain interfaces, affecting the grain growth direction. This transformed the structure from pyramidal to global (Fig.2b). As a result, fairly rough surface morphology was observed due to agglomerated particles during electrodeposition. Upon addition of SDS, the surface of the coating became relatively more compact (Fig.2c), with obvious case depicted in Fig.2d.

In the presence of SDS under wet-milling treatment of WC particles, both nickel and WC particles were deposited on the surface and nickel gradually grew on WC particles to cover the gaps between grains (Fig.2c and 2d). SDS molecules interacted with WC particles to form macroscopic monolayers or micelles[18]. The WC particles should completely be wet in the plating solution to achieve dispersed and uniform suspension, conductive to deposition of improved quality of composite coatings. The wetting of the coating surface was improved by micelle structure, and tension at the solid-liquid interface reduced. Thus, compactness of the coating surface significantly improved (Fig.2d). In Fig.2, deposits with more dispersed and homogenous structures were obtained by addition of SDS under wet-milling treatment.

The SEM-backscattered electron micrographs of cross-sectional profile of Ni/nano-WC deposits under various SDS contents are shown in Fig.3. The embedded WC particles in the nickel matrix were well distributed to form compact coatings. EDS spot analysis showed that the gray-colored areas of the coatings presented Ni crystallites and white areas were WC. Higher participation of WC particles in the coatings occurred as surfactant concentration increased to the optimal level of 0.15 g/L. The distributions of WC particles in the coatings were identified by dispersion of the particles in the electroplating bath. The composite coating fabricated from solution 4 presented obvious WC particles agglomeration with many voids (Fig.3a). SDS could be absorbed on the surface of WC particles, leading to particles with the same charge and mutual repulsion between particles. In other words, the addition of surfactant promoted the co-deposition and uniform distribution of insoluble particles in the coating [20]. This gradually reduced the number of micropores in co-deposition layer, leading to formation of more uniform and compact coatings as SDS content increased (Fig.3b, 3c). However, exceeding the optimal value of added SDS led to declined contents of WC particles in the coatings (Fig.3d). In other words, when SDS concentration exceeded the optimum value, larger repulsion forces were induced between the surfactant layer near the cathode and approaching particles[4].

Representative SEM micrographs of the cross-sectional profile of Ni/WC composite coatings under different wet-milling time are illustrated in Fig. 4. The distribution of WC particles and porous structure in the coating were clearly visible. At wet-milling time of 10 h and compared to Fig.4a, 4b, the coating showed relatively more uniform distribution of particles with almost no pores (Fig.4c). As wet-milling time was prolonged, the quality of the coatings improved for the same added SDS concentration since WC powders were fully wetted to form uniform and dispersed suspension. However, the quality of the coating had no significant improvement by extending the wet-milling time (Fig.4d). The coating prepared from solution 6 looked fully compact, which might improve its mechanical properties.

To investigate the effects of surfactant concentration on content of WC particles in composite coating, the SDS concentration was varied from 0.05 to 0.2 g/L. The content of WC particles on each surface was determined by EDS analysis and the results are depicted in Fig.5. The maximum amount of WC content reached 4.19 wt% for the surface prepared from solution 6. Proper amount of SDS would raise the concentration of WC particles in coatings. SDS is an anionic surfactant with one end containing hydrophobic hydro carbonic chain and the other end is hydrophilic. The

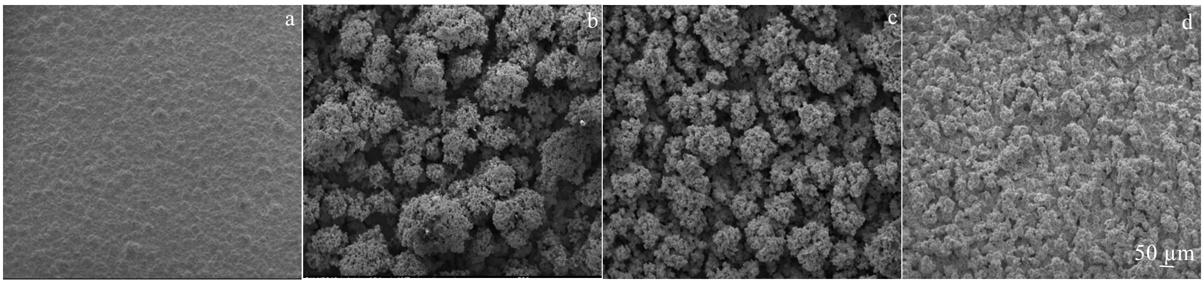

Fig.2 SEM images of pure nickel coating deposited from solution 1 (a), Ni/nano-WC coatings deposited from solution 2 (b), Ni/nano-WC coatings deposited from solution 3 (c), and Ni/nano-WC coatings deposited from solution 6 (d)

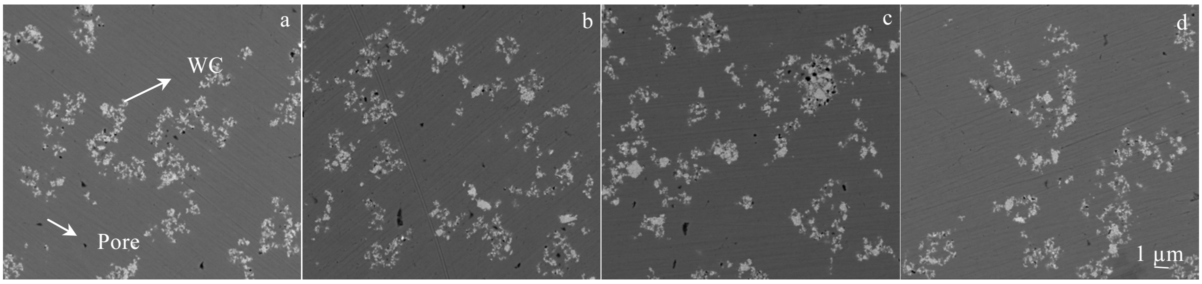

Fig.3 SEM backscattered electron micrographs of cross-profile of Ni/nano-WC deposits prepared from SDS of different concentrations: (a) 0.05 g/L, (b) 0.1 g/L, (c) 0.15 g/L, and (d) 0.2 g/L

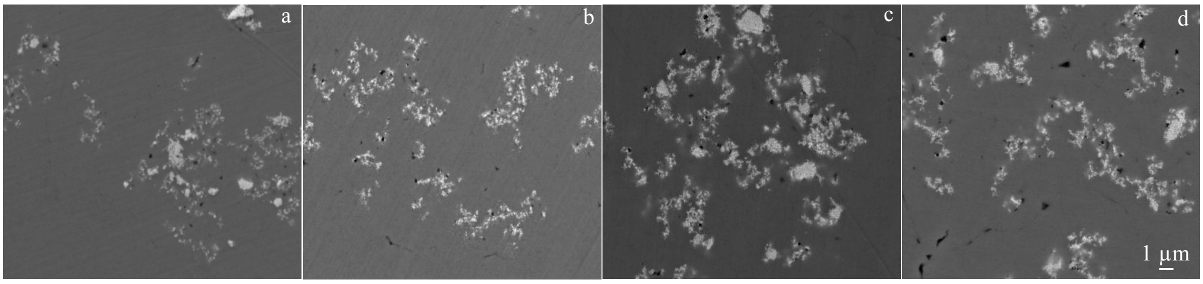

Fig.4 SEM backscattered electron micrographs of cross-profile of Ni/nano-WC deposits prepared at different wet-milling time: (a) 2 h, (b) 5 h, (c) 10 h, and (d) 15 h

increase of WC particles in the coating was linked to formation of micelles through reaction of SDS molecules with the suspended particles in solution. The adsorption of negatively charged SDS molecules to WC particles raised the absolute zeta potential of particles, leading to enhanced repulsive electrostatic forces between the particles in the plating solution. This, in turn, should be conducive for improving the dispersion of particles in the bath[7]. In addition, the particles might be surrounded by nickel cations and strengthen the second stage of the Guglielmi model, thereby promoting Ni/nano-WC co-deposition and increasing the number of particles in the coating. However, when SDS concentration exceeded the ideal value, the extra molecules acted as electrolyte and increased the ionic strength of the bath[20]. Meanwhile, the electrostatic forces were disturbed among particles, reducing the electrostatic repulsions and raising the number of agglomerated particles [22].

The XRD patterns of Ni/nano-WC composite coatings prepared under different conditions are displayed in Fig. 6. Both coatings presented face-centered cubic (fcc) crystal structure but with different preferred orientation. Typical peaks corresponding to pure nickel coating with crystal face of (111), (200) and (220) were recorded. In addition, peaks of (001), (100), (101) crystalline face of tungsten carbide were also observed. The composite coating prepared from solution 8 obviously depicted preferred orientation of (111) crystalline face, which was higher than those of (200) and (220) faces. The height of the diffraction peak of (111) crystalline face was about three-fold that of (200) crystalline face. Moreover, the height of each peak for coatings prepared in the presence of SDS under wet-milling treatment was superior to that of coating prepared from solution 2. On the other hand, the half-height width of diffraction peaks of the coating prepared from solution 2 was smaller than that of the coating obtained in solution 8. Hence, WC particles in the presence of SDS coupled with wet-milling treatment can refine the grain of coatings.

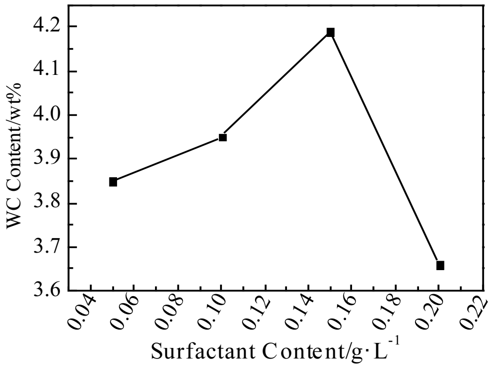

Fig.5 Content of WC in composite coatings under various SDS contents

The grain size of each coating can be estimated by the Scherrer's formula[23]:

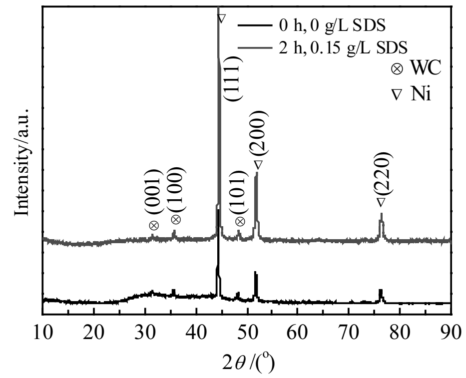

Fig.6 XRD patterns of Ni/nano-WC composite coatings produced under different conditions

$$D = K\lambda/\beta\cos\theta \tag{1}$$

where D is the main grain size of the produced film, K is the Scherrer constant (K=0.89), β represents width at the half-height width of the diffraction peak, λ is X-ray wavelength (λ=0.154 056 nm), and θ denotes the Bragg angle.

Grain refinement mainly depends on continuous nucleation of new crystals, which can be realized by adding convenient grain refining agents, reinforcing the second phase to the plating bath or applying deposition current pulses[24]. The grain size of the composite coating obtained in solution 2 was estimated to be 71.78 nm, while that of Ni/nano-WC composite coating prepared from solution 8 was 46.13 nm. Therefore, the electrodeposited layer resulted from competition between nucleation and grain growth. In sum, the presence of SDS in the plating bath combined with wet-milling treatment of WC particles contributed to grain refinement of the nickel matrix.

2.2 Mechanical properties

The mechanical properties of composite coatings would be improved by adding WC particles as hard ceramic powder. The microhardness values of Ni/WC composite coatings prepared under different process conditions were measured and the results are compiled in Fig.7 and 8. The microhardness of nickel coating significantly enhanced in the presence of WC powders. Also, the microhardness of the coatings distinctly varied in the presence of different SDS concentrations and under different wet-milling time. At SDS concentration of 0.15 g/L and wet-milling time of 10 h, the maximum Vickers microhardness value reached 3134 MPa. As SDS doping content further rose, the microhardness of the coating decreased slightly. The higher microhardness of nickel matrix composite coatings when compared to pure nickel coating might be due to grain refinement strengthening that can be explained by the Hall-Petch law (HPL):

$$H = H_0 + Kd^{-1/2} \tag{2}$$

where H is macro yield stress, H_0 represents the lattice friction resistance generated when moving a single dislocation, K is a constant, and d is the average grain diameter.

The addition of appropriate amount of SDS combined with proper wet-milling of WC particles before plating led to full wetting and even dispersion of WC particles in the plating solution, helpful for improving the content of WC in the coating (Fig.5). WC particles acted as new nucleation sites on the nickel matrix surface, leading to refinement of the grains. Moreover, reinforced adsorption of anions from the catholyte to the metallic surface under pulse plating regime was achieved during relaxation time, facilitating the re-nucleation process during subsequent on-pulses and refining the grains[24,25]. According to HPL measurements, the microhardness increased with grain diameter. Meanwhile, the higher hardness of Ni/ nano WC composite coatings when compared to pure Ni coating might be explained by dispersion strengthening through the Orowan mechanism. The addition of WC particles for refining the grains led to enlargement in grain boundaries to prevent motion of dislocations. This, in turn, increased microhardness[22]. However, the microhardness of the coating decreased beyond the optimal concentration of SDS (0.15 g/L) since excess molecules served as electrolyte. This reduced the electrostatic repulsions among particles and increased the number of agglomerates. In addition, the high amount of surfactant enhanced the surface energy between the substrate and particles, resulting in declined amounts of WC particles adhered on the cathode surface[20, 22].

In Fig.8, the hardness of coating increased with wet-milling time since wet-milling promoted the wetting of WC particles, conductive to the increase in deposited WC particles. However, hardness of the coating did not significantly change when wet-milling time exceeded 10 h, which may be due to complete wetting of WC powder after 10 h that rendered the effect of continued wet-milling unimportant.

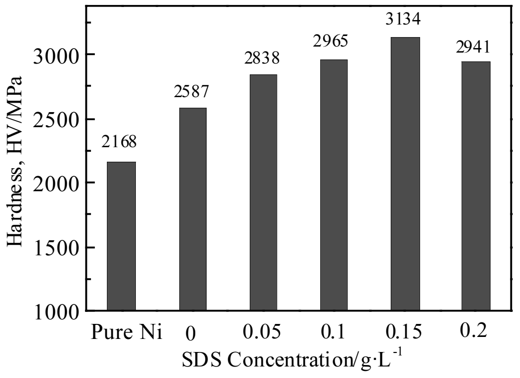

Fig.7 Microhardness with different SDS concentration

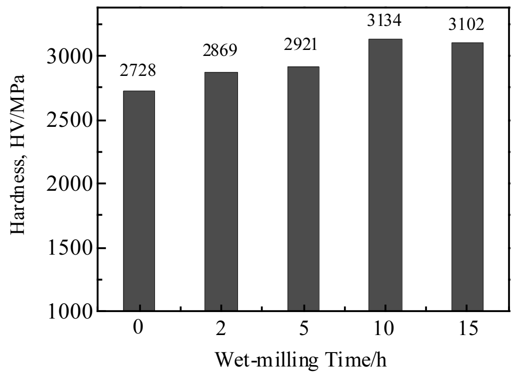

Fig.8 Microhardness under different wet-milling time

2.3 Electrodeposition mechanism

WC is thermodynamically unstable and can be oxidized in the presence of water or oxygen at room temperature. The WC powders were received in the oxidized form, with oxidized surface mainly consisting of WO_3[26]. The WO_3 might be hydrated and -OH groups dominated the surface, resulting in negative surface charge according to Eq. (3).

In Ni^{2+} acidic aqueous solution, surface complexes could be formed at the interface of WC particles following Eq. (4). This could subsequently increase the absorption of Ni-W and H cations on the particles, forming surface complexes[27]. In addition, the decrease in the number of H^+ would suggest that SDS wetting agent might promote the hydrogen evolution reaction, which can reduce the number of holes in the coating.

$$\text{W-OH} \leftrightarrow \text{W-O}^- + \text{H}^+ \tag{3}$$

$$\text{W-OH} + \text{Ni}^{2+} + \text{Cl}^- \leftrightarrow \text{W-O}\cdot\text{Ni}^{2+}\text{Cl}^- + \text{H}^+ \tag{4}$$

According to the Gugliemi's absorption model, the absorption force of particles on the electrode for Ni/nano-WC composite coating should overcome the repulsion forces[20]. The WC particles carried ions and solvent molecular films were adsorbed on the cathode surface through weak physical forces (step one). Subsequently, the WC particles under weak adsorption state excluded ions and solvation membranes for direct contact with the cathode surface to form irreversible electrochemical adsorption, which then transformed into strong adsorption (step two). During electrodeposition, strongly adsorbed particles were embedded within the coatings. The whole process is summarized in Fig. 9.

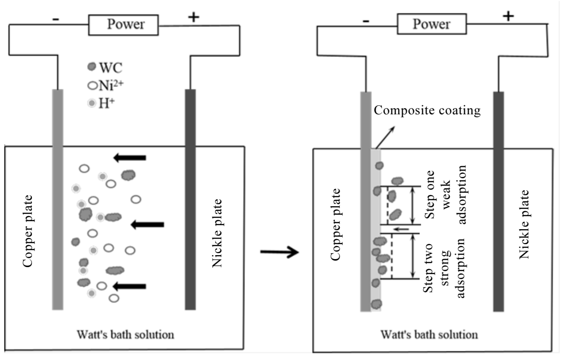

Fig.9 Schematic representation of the electrodeposition process mechanism of Ni with WC particles

3 Conclusions

1) Nickel matrix composite electrocoating with embedded nano-WC particles is electrodeposited from watts' bath.

2) The composite coatings prepared by adding surfactant SDS and under wet-milling process show better coating quality with more compact and fewer microvoids when compared to coatings prepared without the addition. The optimal conditions are determined as SDS concentration of 0.15 g/L and wet-milling time of 10 h. The addition of SDS promotes uniform distribution of WC particles in the coating and increases the embedded WC particles to 4.19 wt%. Moreover, the preferential growth orientation of crystal face (111) of the composite coatings prepared from the solution 8 is significantly enhanced. The addition of SDS combined with wet-milling treatment of WC particles contributes to refinement of the grains. The microhardness values of the composites reaches a maximum of 3134 MPa, which is higher than that of pure nickel coating. This is attributed to grain refinement mechanisms and dispersion strengthening.

3) The electrodeposition mechanism of Ni/nano-WC composite coatings is interpreted by the Guglielmi model. The coverage of WC particles by charged ions and solvents induces weak adsorptions (physical adsorption) as particles first moves outside the dense layer of the cathode. The adsorbed film on the particles is then eliminated under the action of electric field force at the interface. The charged particles become adsorbed on the cathode surface under the action of the electric field force to form strong adsorptions (chemical adsorption). The chemically adsorbed particles become buried by continuously deposited nickel to yield compact deposits.

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表面活性剂对 Ni/纳米 WC 复合电镀层的影响

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摘　要：采用脉冲电沉积法制备了纳米 WC 强化镍基复合镀层。探究了表面活性剂（十二烷基硫酸钠，SDS）添加量以及 WC 粉的湿磨预处理对 Ni/nano-WC 复合镀层表面形貌、颗粒分布、微观结构以及显微硬度的影响。表面活性剂的添加和对 WC 粉湿磨处理有助于细化镀层晶粒，得到 WC 颗粒分布均匀的致密镀层。镀层中 WC 含量以及镀层的显微硬度随着表面活性剂的添加量的增加而增加，但过量会使效果变差，理想的 SDS 添加量为 0.15 g/L，湿磨 10 h。

关键字：电沉积；微观结构；纳米 WC 复合镀层；显微硬度

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