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Composite Ni/UHMWPE coatings and their tribological performances

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ABSTRACT

Attempts have been made to develop Ni/UHMWPE composite coating by an electrophoretic deposition of UHMWPE particles in combination with an electroplating of nickel (two-step method). For comparison, Ni/UHMWPE coatings were also fabricated by traditional composite electroplating. The surface morphology, composition, roughness, residual stress, hardness, adhesive strength, and the tribological behaviors of the coatings fabricated by the two methods were compared and investigated. Results manifest that the two-step method is effective to enhance UHMWPE particle content in Ni/UHMWPE coatings and the performances of the coating are greatly affected by UHMWPE content. High particle contents increase the roughness and residual stress, but decrease the hardness and adhesive strength. However, with the increased ratio of UHMWPE particle, the tribological performances of the composite coatings are improved.

1. Introduction

Surface coating is a key technology for the industrial products. The purpose of applying the coating may be decorative, functional, or both. Recent coating technical advances allow the deposition of layers with properties that are not available even a decade ago.

Composite electro-deposition is one of the typical coating techniques, by which the powders as second phase are embedded in a metal or alloy matrix [1]. In the course of depositing, the implant particles are dispersed in a Watts-type bath and positioned into the matrix layer to form composite coatings. By selecting the type of particle material, desirable properties, such as high hardness [2], resistance of corrosion [3] and wear [1,2] can be achieved. However, these characters are mainly relied on the distribution and content of the co-deposited particles in coatings. Although some attempts have been made, such as adding different surfactants in the planting bath [2], the ultrasound agitation [4] and changing the current types [5], but the percent of particle in the composite coatings fabricated by traditional composite electro-deposition method is still very low.

Electrophoretic deposition is an electrochemical behavior wherein fine powders are shaped directly from a stable colloid by a DC electric field [6]. In 2001, the Tetsuo Saji group introduced an effective way to achieve Ni/Al_2O_3 composite coatings containing up to 60 vol% Al_2O_3 [7]. This method involves an electrophoretic deposition of Al_2O_3 particles film on substrate in combination with an electroless deposition of nickel (two-step method). A question then arises: is this two-step method applicable to any kinds of particle, especially for polymeric particles? Furthermore, what are the performance differences between the coatings produced by the traditional composite electroplating and the two-step technique? To date, there is still no available knowledge about this.

Herein, typical non-conductive ultra-high molecular weight polyethylene (UHMWPE) was chosen as the composite particles due to its superior friction and wear resistance. Attempts have been made to produce Ni/UHMWPE composite coatings via two-step and traditional composite electroplating techniques. The surface appearance and composition of the coating samples prepared by the two processes were compared and evaluated. The surface roughness, residual stress, microhardness and adhesive strength were investigated. The effect of UHMWPE content in the coatings on the tribological performances was analyzed.

2. Experimental details

2.1. Preparation of the coatings

In this paper, the Ni/UHMWPE composite coating was prepared using the electrophoretic deposition followed by electro deposition (two-step method). Copper substrates with the size of $\Phi 30 \times 3$ mm were mechanically grinded to a roughness value of Ra 0.08–0.10 μm. Then the substrate was put in an acidic bath to degrease and activate for 30 s followed by ultrasonic cleaning in distilled water. After that, the copper surface was deposited electrophoretically with a layer of the UHMWPE particles. In the second step, the UHMWPE electrophoresis

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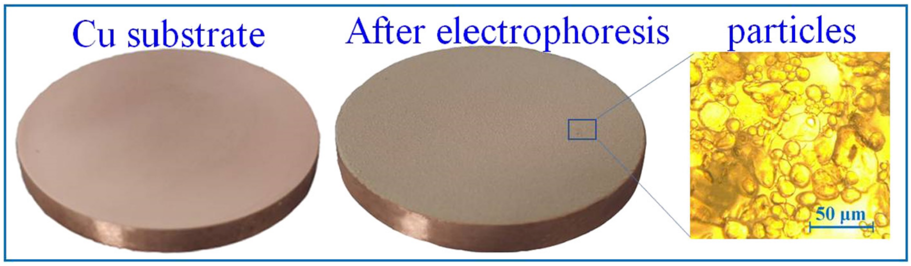

Fig. 1. Cu substrate before and after electrophoresis of UHMWPE particles.

film was covered by nickel coating through electroplating.

More specifically, before the particle electrophoretic deposition process, 7.5 g/L UHMWPE particle was dispersed in an ethanol bath with $MgCl_2 \cdot 6H_2O$ (1.0 g/L) to improve conductivity. The ethanol solution was agitated by ultrasonic dispersion for 30 min to form stable suspension. Then, the copper substrate as cathode was put vertically with a space of 1 cm paralleling to a 304 stainless steel plate. The electric field strength of 45 V/cm was applied for 2 min. For this process, the charged UHMWPE particles in ethanol solution move directionally to the copper surface (electrophoresis) and a UHMWPE film forms due to the particle accumulation (deposition). Fig. 1 gives the macro and micro morphologies of the electrophoretic deposition layer of UHMWPE particles on Cu substrate.

The substrate covered with the UHMWPE particles film was dried in air and then put in the plating solution (see Table 1) without any particles. The copper covered with the UHMWPE was used as cathode and a pure nickel plate was fixed as anode in the circuit. After 1.5 h of depositing, the coating sample was rinsed with distilled water.

For comparison, pure nickel and Ni/UHMWPE coatings were also prepared by traditional composite electroplating technique with different concentrations of UHMWPE particle. The mixture was agitated with a magnetic stirrer for 30 min. Detailed experimental conditions for the traditional co-deposition were presented in Table 1. The plating time is 1.5 h for each sample.

After preparing, the thickness of the coatings was measured by cutting the samples across the diameter. The value of each sample was averaged from five points. The pure nickel coating presents the largest average thickness of 11 ± 1 μm, the co-deposited samples of Ni/UHMWPE are in the range of 9 ± 1 μm and the thickness of coating prepared by two-step method is about 8 ± 1 μm.

2.2. Characterization of the coatings

The microstructures of the coating surfaces were investigated by scanning electron microscope (SEM, JSM-6480LV). The EDS and elementally X-ray map analyses were executed to obtain the element content and distribution. Surface roughness of the coatings was determined by an optical 3D profiling system. The macro-residual stress of the samples was tested using an X-ray diffractometer with Ni Kα radiation. Micro-hardness was measured by a Vickers hardness instrument with a load of 300 g for 10 s. The adhesive force between the coating and the copper substrate was estimated using scratch test with the loading speed of 20 N/mm. The tribological behaviors of the coatings were evaluated using a ball-on-disc tester under dry sliding condition. A standard 304 stainless steel ball (diameter 4.0 mm) was used as the counterpart. Each test was performed at a sliding speed of 0.1 m/s with a normal load of 2 N. The worn surfaces of the tribo-pairs were analyzed by SEM and 3D profiler.

Table 1
Bath compositions and electroplating condition.

Compositions and conditions	
Nickel sulfate, $NiSO_4 \cdot 6H_2O$ (g/L)	200.0
Nickel chloride, $NiCl_2 \cdot 6H_2O$ (g/L)	45.0
Particle content (g/L)	0, 7.5, 10, 12.5
Saccharin sodium (g/L)	1.0
Sodium dodecyl sulfate (g/L)	2.0
Boric acid, H_3BO_3 (g/L)	40.0
pH	4 ± 0.5
Current density (A/dm^2)	1.0
Temperature (°C)	20
Magnetic stirring (rpm)	150

3. Results and discussion

3.1. Surface morphology of the coatings

The SEM images of pure Ni and Ni/UHMWPE composite coatings fabricated by electroplating and two-step techniques are given in Fig. 2, respectively. The surface of pure Ni coating is relatively smooth (see in Fig. 2a), while the micro-bulge structures are observed for the composite coatings (Fig. 2b–e). However, for samples produced by co-deposition technique, with the increased concentration of UHMWPE in the plating solution, the growth of the particle incorporated in the matrix is unremarkable according to the analysis of EDS and the elementally X-ray map of carbon. Even the concentration of particle reaches to 12.5 g/L, only 9.99 wt% mass fraction of UHMWPE incorporates in the coating. One possible reason could be due to the surface hydrophobicity of UHMWPE particles. Although the surfactant of sodium dodecyl sulfate was used, UHMWPE particles in the plating solution cannot be dispersed uniformly.

While for the coating prepared by the two-step technique, as well as 7.5 g/L UHMWPE particle concentration is used during the electrophoretic process, the amount of particle inset increases obviously. And the C content in the coating approaches 17.54 wt%, which has doubled compared with electroplating process (see in Fig. 2d and e). The result confirms two important facts: 1) the Ni/UHMWPE composite coating can be produced by means of electrophoretic and electroplating depositions; 2) compared with the co-deposition, the two-step technique can effectively enhance the amount of UHMWPE in the coating while using low concentration of particles in ethanol solution. However, the side effect is that the agglomeration of particles in coating increases according to the elementally X-ray map (see Fig. 1e). Besides, with the increasing percent of the particles, pinholes appear on the coating surfaces (see Fig. 2d and e), which may originate from the passive effect of hydrogen evolution during the electroplating process.

3.2. Surface roughness of the coatings

Fig. 3 shows the surface roughness of the coatings fabricated by the two kinds of method. Analyzing the obtained profiles, one may remark that the particles entrapped in a coating strongly influence the surface quality. The average roughness Ra changes from 0.05 μm for the pure Ni deposition to 0.84 μm for the composite coating prepared using two-step method. And the roughness of the composite coatings fabricated by co-electroplating falls somewhere in the middle. Such results are in

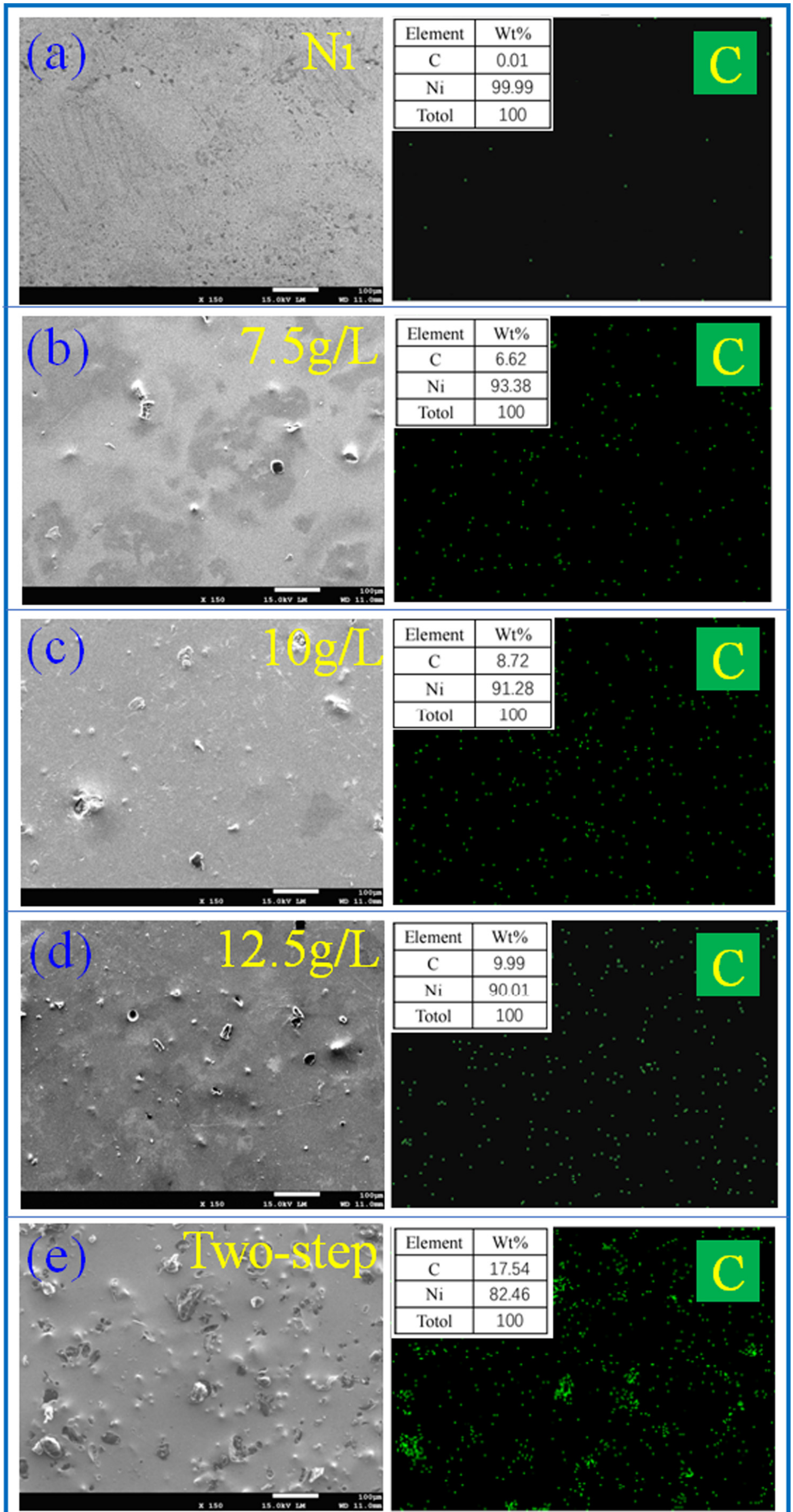

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Fig. 2. SEM images of pure Ni and Ni/UHMWPE coatings, and corresponding elementally X-ray maps for C.

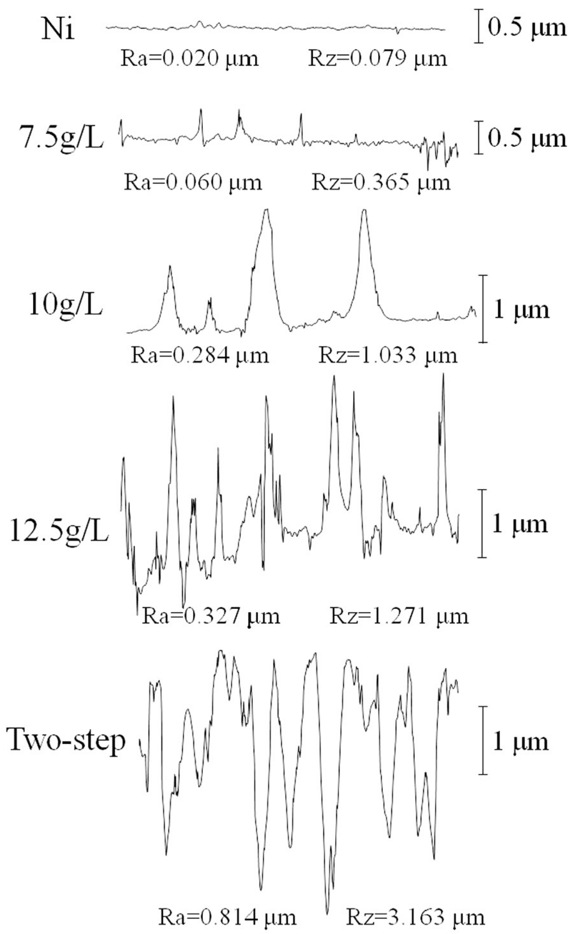

Fig. 3. Surface profile of pure Ni and Ni/UHMWPE coatings.

agreement with the data of SEM images presented in Fig. 2. The other measured characteristics of the surface, ten-points Rz height of irregularities also support the results. The higher percent of the UHMWPE particles the coating is, the larger roughness it presents. Such phenomenon may arise from the increment of the local current density on the matrix surface owing to the particle blocking effect [8].

3.3. Macro-residual stress of the coatings

Fig. 4 illustrates the macro-residual stress of the coatings. For each sample, four positions in the radial and circumference directions were tested. It can be found that all the specimens present tensile stress. For pure Ni coating, the residual stress is about 84 MPa, which is roughly equivalent to the value reported in ref. [9]. Residual stress of the co-deposited coatings enhances with the increment of the particle concentration in electrolyte. Obviously, the Ni/UHMWPE coating fabricated by two-step method expresses the highest value of residual stress.

In general, the existence of particles in the coatings will disturb the growth of nickel crystals and lattice distortions in Ni matrix are inevitable, which generate residual stress during the process of deposition [10]. Besides, the hydrogen theory could also be proposed to explain the stress raising [11]. As mentioned above, the introduction of particle increases the local current density as well as the hydrogen evolution, which will also result in the non-uniform distribution of the grains. Thus, the residual stress enhances with the increasing UHMWPE particle content.

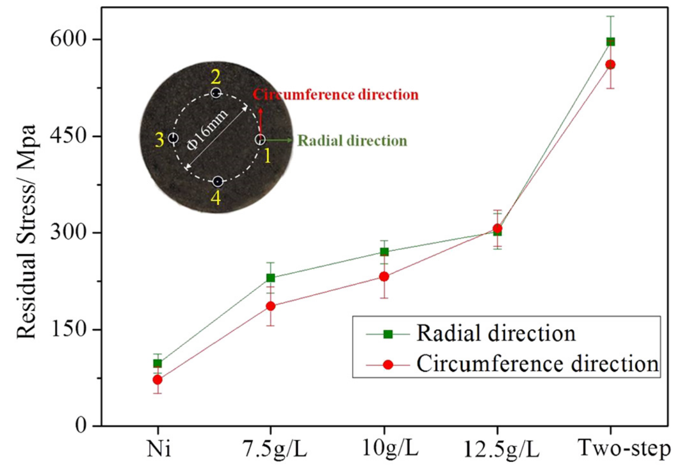

Fig. 4. Residual stress of Ni and Ni/UHMWPE coatings.

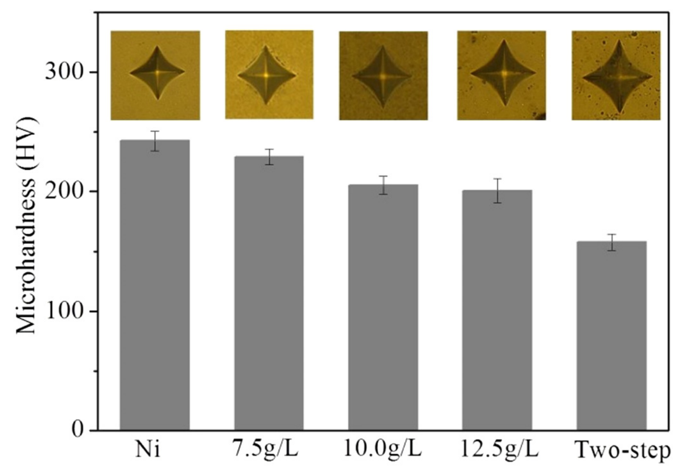

Fig. 5. Micro-hardness of Ni and Ni/UHMWPE coatings.

3.4. Micro-hardness and adhesive strength of the coatings

Micro-hardness measurements quantify the resistance of a material to plastic deformation. Fig. 5 presents the micro-hardness of the five coating samples generated by the two methods. The final data was the average of 10 measurements for each sample. The typical value for nickel coating is about 250 HV. And the values decrease as UHMWPE particles incorporated in nickel matrix. As shown in Fig. 5, the coating fabricated by two-step method expresses the lowest hardness. Different from hard particles, such as SiC [12] and Al_2O_3 [2], the hardness of UHMWPE is usually below 10 HV [13], which is much lower than that of Ni matrix. This could be the main reason of the hardness decline. Similar result was also observed for Cu/PTFE composite coatings and the reduced hardness was ascribed to the soft nature of PTFE powder [8].

Fig. 6 presents the results of adhesive strength of the coatings by using a scratch test. A vertical load applied to an indenter is increased continuously, and the load, at which the first crack emerging in the coating is defined as the critical load. Usually, this load can be used to describe the adhesive strength between the coating and substrate. Similar to the micro-hardness, the pure Ni coating shows the highest adhesive strength and the critical load of the coating fabricated by two-step method is the lowest. As mentioned in ref. [14], the internal stress may markedly affect the interface bonding performance. Taken account

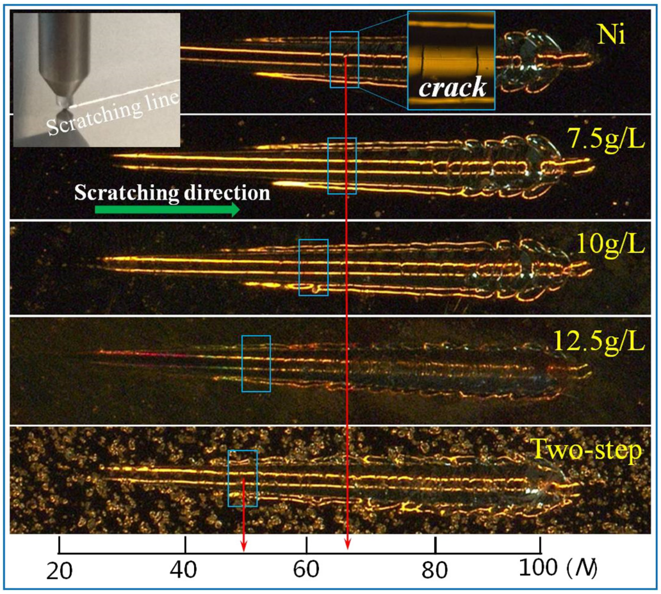

Fig. 6. Optical micrograph of a scratch created by an indenter with continuous loading.

of the different lattices between the matrix and particles materials, defects and/or lattice distortions are inevitable when introducing particles into Ni matrix. As confirmed in Section 3.3, significantly enhancement of the internal stress appears in the composite coatings, which should be responsible for the lowest adhesive strength of the coating fabricated by two-step technique.

3.5. *Tribological behaviors of the coatings*

Fig. 7 presents the friction curves of a 304 stainless steel ball sliding against the coatings. For pure Ni coating, the coefficient of friction increases at first and then achieves stability at approximately 0.7, which is the highest value among the five coating samples. Similar phenomena were found for the three Ni/UHMWPE coatings prepared by composite electroplating. And the friction coefficients decreased slightly, which could be due to the low content of the co-deposited UHMWPE particles (see in Fig. 2b–d).

It is interesting to find that the sample generated by two-step method, with the highest surface roughness (see in Fig. 3), presents the lowest and much more stable friction coefficient. Although the

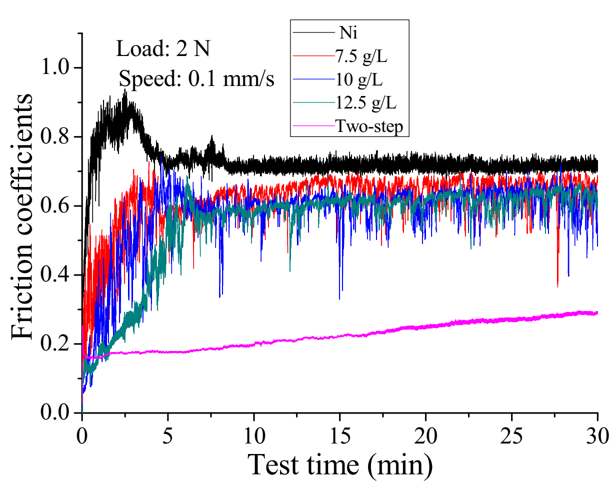

Fig. 7. The friction curves of Ni and Ni/UHMWPE coatings under dry sliding condition.

coefficient increased with the sliding time, it reached to about 0.3 at the end of the 30 min test and the value declined by 57% compared with pure Ni. Generally speaking, among the five samples, the friction coefficients decrease with an increased UHMWPE particles content in the coatings. Usually, the friction is dependent upon the shearing strength of the coatings. On the one hand, the import of UHMWPE decreases the coating hardness and causes an easy deformation during the shearing process; on the other hand, high amount of UHMWPE on the rubbing surface may present excellent self-lubricating and anti-sticking properties [15].

Fig. 8 shows the SEM, EDS and 3D images of the worn surfaces after 30 min friction test. Plastic deformation and delamination were observed for all the coating samples. For pure Ni coating, distinct scratches, adhesion and heavy peeling phenomena were found along the wear track (see Fig. 8, Ni), indicating adhesive wear mechanism mainly. Although element C was detected on the worn surface, similar phenomenon was observed for Ni/UHMWPE coating deposited using 7.5 g/L UHMWPE.

With the increased particle concentration in the plating solution, the degree of plastic deformation reduced and the worn surfaces revealed slight adhesion wear with narrow scratch lines paralleling to the sliding direction (see Fig. 8, 10 g/L and 12.5 g/L). The coating fabricated by two-step method presented the smallest width of the wear track among the five samples and the track was almost invisible from the 3D profile (see Fig. 8, two-step). It was also found in the SEM observation that the wear track is not continuous on the coating surface.

Fig. 9 shows the optical images of the worn surface on the counter balls. As can be seen, the wear scar is near to a circle with many shallow and smooth grooves. It was found that the diameter of the wear scar sliding with the pure Ni coating is 685.63 μm, which is smaller than the wear scar sliding with the Ni/UHMWPE coating deposited at the concentration of 10 g/L (742.05 μm). The increased wear scar may be related to the deformation of the composite coating due to its lower hardness (see in Fig. 5). However, although the coating deposited by two-step method exhibits the lowest hardness, the wear scar on the counter ball decreased to 605.33 μm. As is known, a large amount of UHMWPE particles on the surface of Ni matrix may shorten the distance between particles, which contributes to form a relatively continuous and effective UHMWPE self-lubricating film. Consequently, the wear on the coating and count ball decreased both.

To figure out the anti-wear mechanism of the coating fabricated by the two-step method, the evolution of the worn surfaces on the coating and upper ball were observed at the different stages of the sliding process (see in Fig. 10). Due to the highest roughness of the surface, one can imagine that the real area of contact is small at the running in stage (see Fig. 10, initial morphology of the coating) and only micro-bulges of UHMWPE particles are in contact with the upper ball. At a certain load, these micro-bulges deform plastically along the direction of the normal load and it was confirmed as shown in Fig. 10 (5 min later). Thus, the contact area between the micro-bulges and the upper ball increases obviously. During the friction process, subjected to the shearing stress, the deformed micro-bulges gradually develop a discontinuous UHMWPE solid lubrication film, which then spreads along the sliding direction (see Fig. 10, 10 min later). Ultimately, the tribo-pairs transits slowly from the UHMWPE-bulges/ball to UHMWPE-film/ball dominantly and the corresponding wear mechanism changes from the abrasive to adhesive wear in the steady-state sliding condition. Thus, the decreased wear loss is mainly because of the scuffing and the higher lubrication prevailing of UHMWPE.

Besides, the adhesion performance of UHMWPE also needs to be considered. When metals sliding against UHMWPE films, a transfer film can usually be formed on the wear tracks [15–17]. In our experiments, as the ball sliding on the coating, the transfer film was also found on the wear scar of the ball (see in Fig. 10). Thus, the contact of polymer/polymer is formed, which will lead to a slight increment in the friction coefficients [16]. And similar phenomenon was found in our

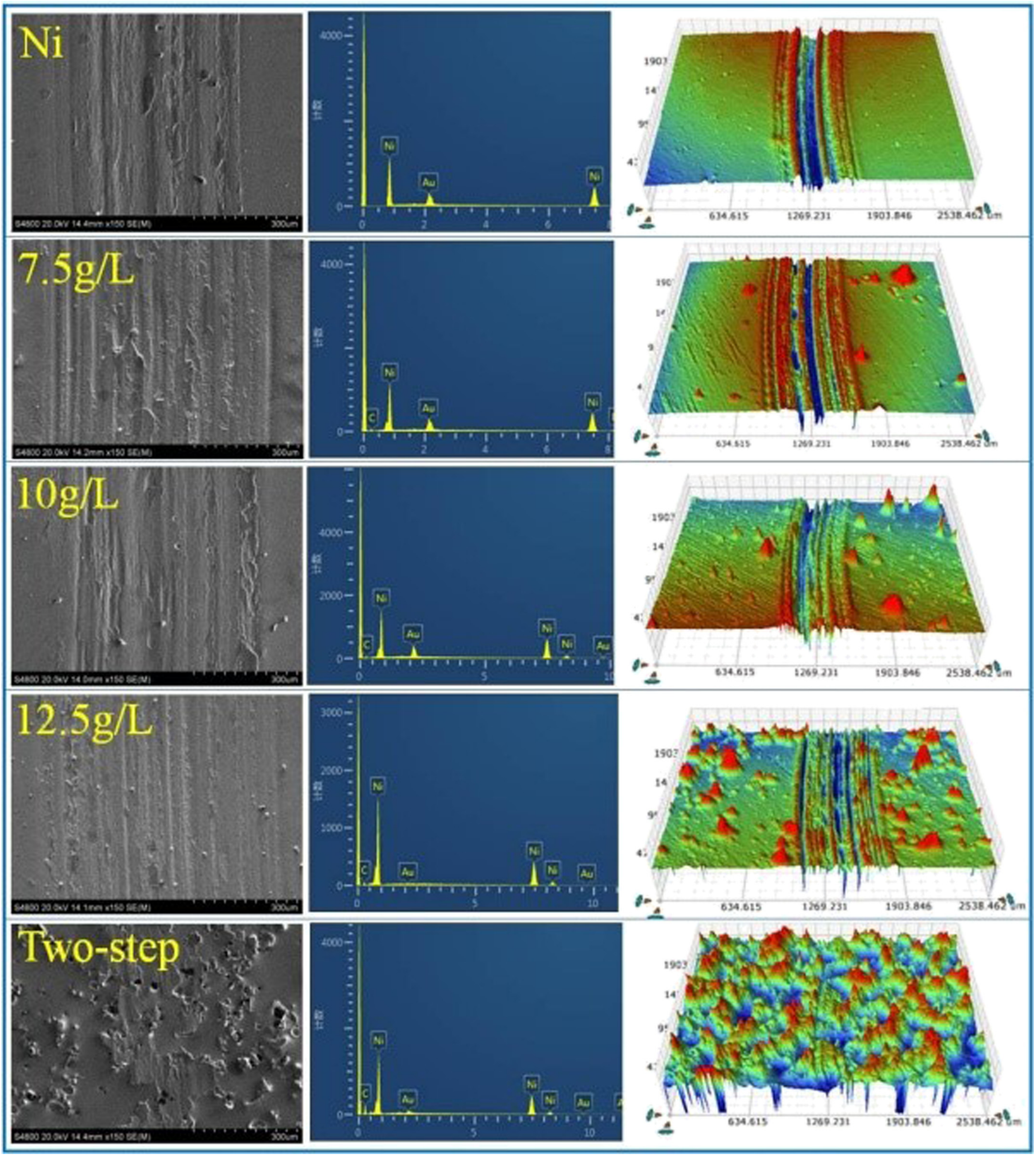

Fig. 8. SEM images of wear tracks and corresponding EDS and 3D profiles.

experiment (see in Fig. 7, two-step). From the wear point of view, the mode is always adhesive wear due to the transfer film, which contributes to lubricate the surface [16]. Compared with other coating samples, diameter of the wear scar sliding with coating deposited by two-step method is the smallest, which may also result from the transfer film, although the chemical composition on the wear scar should be further explored.

4. Conclusion

In this paper, Ni/UHMWPE composite coating was fabricated by traditional composite electroplating and electrophoretic deposition combined with electrodeposition (two-step method), respectively. The main results are summarized as follows:

(1) Compared with traditional co-depositing, the two-step method is an

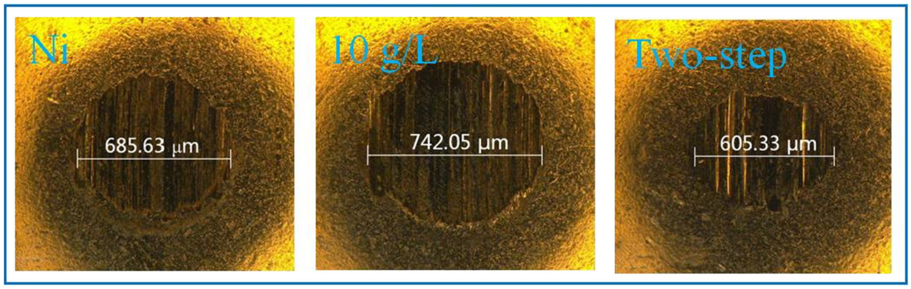

Fig. 9. Images of wear scar on the counter ball.

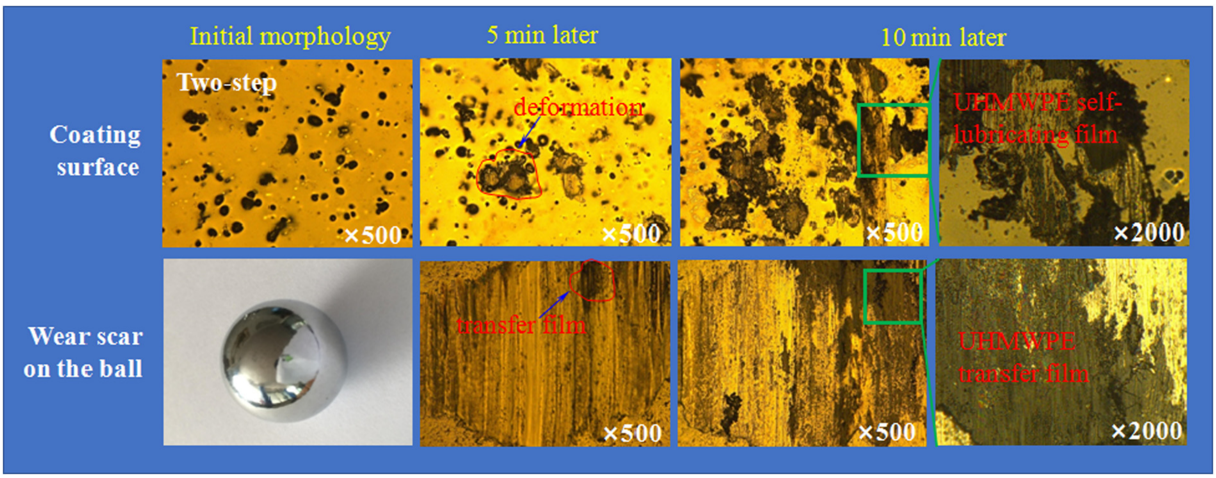

Fig. 10. Evolution of the worn surfaces on the coating and upper ball.

effective technique to produce coatings with higher particle content while using low particles concentration of ethanol solution.

(2) The surface roughness and residual stress increase with enhancing amount of UHMWPE in the Ni/UHMWPE coatings, but the contrary tendency is discovered for the hardness and adhesive strength.

(3) Coatings with the higher UHMWPE particle content present better antifriction and anti-wear capacities in general. In comparison to the co-deposited coatings, tribological performance of the coating produced via the two-step method was improved obviously. Meanwhile, the wear of the counter ball decreased also.

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