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PULSED ELECTRODEPOSITION FOR PREPARING NICKEL, SILVER/GRAPHENE DOUBLE-LAYER COMPOSITE COATINGS AND STUDY ON FRICTION PROPERTIES

Nickel, silver/graphene double-layer composite coatings were prepared by pulsed electrodeposition. The composition, structure, mechanics and tribological properties of the coatings were investigated. Research shows that the Ag grains in the composite coatings decreased with the increase of graphene content. When the amount of graphene added to the bath reached 0.8 g/L, a large number of cracks were generated in the composite coating. When the amount of graphene added to the bath is 0.4 g/L, the microhardness of the composite coating is about 144 HV, much higher than that of the Ag coating (about 89 HV). Compared with Ag coating, the addition of graphene reduces the friction coefficient and wear rate of the coating. There are a lot of furrows on the Ag coating surface, and after the addition of graphene, the multilayer graphene makes the surface of the abrasion smooth, effectively reducing the friction coefficient of the coating, and the friction coefficient is more stable during the friction process.

Keywords: Pulsed electrodeposition; Composite coating; Tribological properties; Friction coefficient

1. Introduction

In practical engineering applications, friction brings huge energy consumption, and wear is also the main reason for the failure of most parts [1]. Solid lubrication materials came into being and have become the focus of scholars in the field of friction, among which solid lubrication coating technology is a material surface modification technology that effectively enhances the hardness of materials, reduces friction and anti-wear properties, and is widely used in aerospace, automotive important parts and other fields. Solid lubrication composite coating is a composite material with excellent tribological properties obtained under certain technological conditions by using metal, ceramic or non-metallic material as the matrix and adding the second phase component with lubrication or anti-wear. The composite coating has the characteristics of both the matrix material and the second phase component material, so it can meet the needs of people to a certain extent [2-13]. Graphene is a two-dimensional material with excellent physical and chemical properties. The introduction of graphene into the composite coating will greatly improve the self-lubricating properties of the composite coating and the comprehensive performance of all aspects, so the application prospect of graphene in the field of tribology is very broad [14].

Electrochemical deposition technology of metal matrix composite coating is a co-deposition technology in which one or several insoluble solid particles are embedded into metal coating to form composite coating materials on the basis of electrochemical deposition of metals [15-18]. In order to obtain a composite coating with excellent properties in electrochemical deposition, the key is how to evenly disperse the introduced second phase nanoparticles in the coating. However, the applied nanoparticles can easily agglomerate in the electrolyte, which affects the excellent performance of the nanoparticles, and then affects the performance of the composite coating. Cardinal et al. [19] studied the tribological properties of nanostructured Ni-W-MoS_2 composite coatings from Ni-W electrolyte containing suspended MoS_2 particles by pulsed electrodeposition (PED). The results show that the properties of Ni-W composite coatings are strongly affected by the codeposited solid lubrication particles. The friction coefficient of composite coating is low when MoS_2 content is low. With the increase of MoS_2 concentration, the tungsten content and microhardness of the coating

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are reduced, while the friction coefficient can remain at a low level. Therefore, codeposition of MoS_2 particles into Ni-W nanocoatings can improve the frictional properties of the coatings.

Graphene nanosheets have a regular layered structure and atomic-scale thickness, so it can be used as an additive for liquid lubricants and easily enter the contact area, preventing direct contact of the friction surface. In addition, the adjacent layers of two-dimensional graphene nanosheets are held together by weak van der waals forces, and they can easily slide against each other at extremely low shear stresses. Graphene can be used not only as an additive for liquid lubricants, but also as a high-performance solid lubrication material. Lei et al. [20] dispersed sucrose as a graphene precursor into nickel powder and grew multilayer graphene in the nickel matrix to obtain graphene-nickel composite materials. Graphene not only protects the nickel matrix from damage caused by severe oxidation, but also forms a carbon-rich friction film through a friction-induced chemical reaction. Sadoun et al. [21] prepared Cu-Al_2O_3-graphene nanocomposites by powder metallurgy. The addition of graphene improved the hardness of the composites, reduced the plastic deformation and significantly reduced the wear rate. The carbon particles exposed during the test have good lubricity, and the friction coefficient decreases with the increase of the weight fraction of graphene. A carbon-rich friction layer is formed on the surface of the composite, which improves the tribological properties of the composite.

Graphene not only has the advantages of good chemical inertia, high mechanical strength, easy shear and modifiable, and it can be used as both a lubricating phase and a strengthening phase in the composite material, so the graphene doped metal matrix composite can have both good anti-friction and anti-wear properties [22]. In this project, the Ag/graphene composite coating with good tribological properties was prepared by pulsed electrodeposition. The effects of different graphene additions on the mechanical and tribological properties of the composite coating were studied, and the tribological principles were analyzed.

2. Experiment details

2.1. Materials and methods

The sample base is made of 45# carbon steel. Polished step by step with emery paper. Soak in a mixture of sodium hydroxide (50 g/L) and sodium carbonate (70 g/L) at 50°C for 30 minutes, and then soak in acetone for ultrasonic cleaning for 30 minutes to remove surface grease. The composition and plating parameters for fabricating the Ni coatings of pulsed electrodeposition (PED) are given in TABLE 1, and the anode is made of pure Ni sheet. The composition and plating parameters for fabricating the Ag/graphene coatings of PED are given in TABLE 2, and the anode is made of pure Ag sheet material. The Ag/graphene composite coating is named according to the amount of graphene added to the bath, named Ag/0.4G, Ag/0.8G, Ag/1.6G respectively. Graphene was purchased directly from Shanghai Aladdin Biochemical Technology Co., Ltd.

TABLE 1

The composition and plating parameters for fabricating the Ni coating

Composition	Concentration, g/L	Parameter	Numerical value
$NiSO_4 \cdot 6H_2O$	240	Bath temperature (°C)	50
$NiCl_2 \cdot 6H_2O$	45	Forward current density (A/dm^2)	3.2
H_3BO_3	30	Reverse current density (A/dm^2)	3.2
Na_2SO_4	20	Stirring rate (rpm)	100
$C_{18}H_{29}NaO_3S$	0.1	Duration time (h)	4
		Forward pulse width (μs)	200
		Reverse pulse width (μs)	100

TABLE 2

The composition and plating parameters for fabricating the Ag/graphene coatings

Composition	Concentration, g/L	Parameter	Numerical value
$AgNO_3$	40	Bath temperature (°C)	30
$NaHSO_3$	80	Forward current density (A/dm^2)	0.8
$Na_2S_2O_3 \cdot 5H_2O$	200	Reverse current density (A/dm^2)	0.4
CH_3COONa	20	Stirring rate (rpm)	100
$C_{18}H_{29}NaO_3S$	0.1	duration time (h)	4
Graphene	0.4; 0.8; 1.6	Forward pulse width (μs)	200
		Reverse pulse width (μs)	100

2.2. Chemical analysis and performance test

The microstructure was analyzed by Quant 250FEG scanning electron microscope (SEM). The 3D surface topography was characterized by a white light interferometer apparatus (Phase Shift MicroXAM-3D). The phase compositions of the coatings were examined by Bruker-AXS D8 advance x-ray diffraction (XRD) spectrometer with Cu Ka, and the voltage is 40 kv, the current is 30 mA, the scanning step size is 0.05°, and the scanning speed is 5°/min. The variations of the phase compositions on coatings were investigated by Raman spectrometer (HORIBA, Japan). The microhardness of the coating section was tested using a microhardness tester. Vickers hardness was determined by an HXS-1000 A microhardness tester using 200 g of load for 10 s. The tribological tests were carried out by a HT-1000 ball-on-disk tribometer. The Si_3N_4 ceramic ball with diameter of 6 mm was used as the counterpart ball. The test parameters were as follows: load of 2 and 4 N; respectively; sliding speed of 0.13 m/s; and test time of 30 min. The wear volume was calculated as $V = AL$ and the wear rate as $W = V/SN$, where A is cross-sectional area of wear tracks, L is the circumference of the wear tracks, S is total sliding distance and N is applied load.

3. Results and discussion

3.1. Characteristics of raw materials

The microstructure and raman spectra of graphene is shown in Fig. 1. As can be seen from the figure, the graphene used is a multilayer structure.

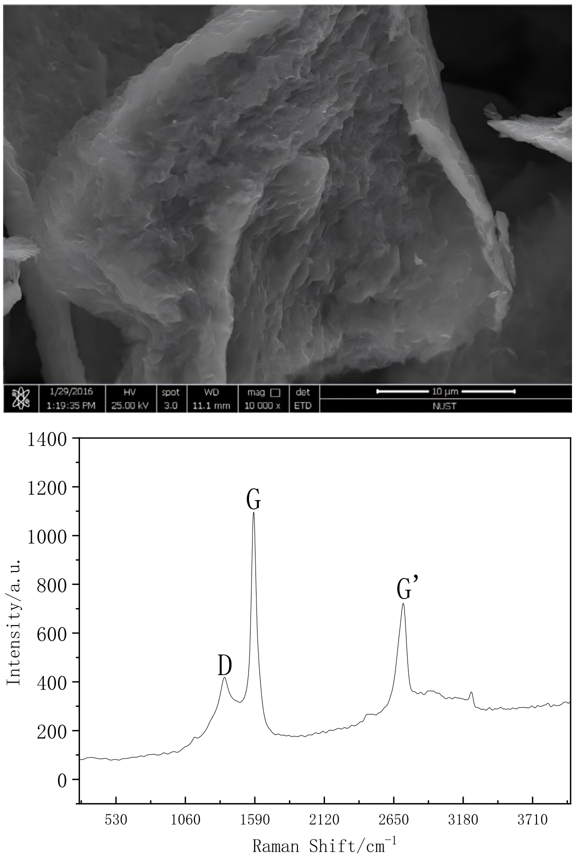

Fig. 1. Microstructure diagram and raman spectra of graphene

3.2. Microstructure and chemical composition of composite coatings

The surface microstructure and EDS element diagram of composite coating are shown in Fig. 2. It can be seen from the figure that the grain size of the composite coating gradually increases with the increase of graphene addition. The surface elements of the coating show that the composite coating is composed of two substances, Ag and graphene. The principle of electrodeposition coating is that the cation in the solution absorbs electrons and deposits them on the surface of the sample. Graphene is a layered structure, with the increase of the concentration, the agglomeration phenomenon is gradually serious, the agglomeration of graphene wrapped Ag adsorbed on the surface of the sample, making the surface a large particle rough surface. TABLE 3 lists the element contents of the four composite coatings. It can be seen that as the amount of multi-layer graphene added to the bath increases, the mass fraction of carbon elements in the composite coatings is 6.11%, 7.15%, and 9.9% respectively. With the increase in the amount of graphene added to the bath, the content of graphene in the composite coatings also increases.

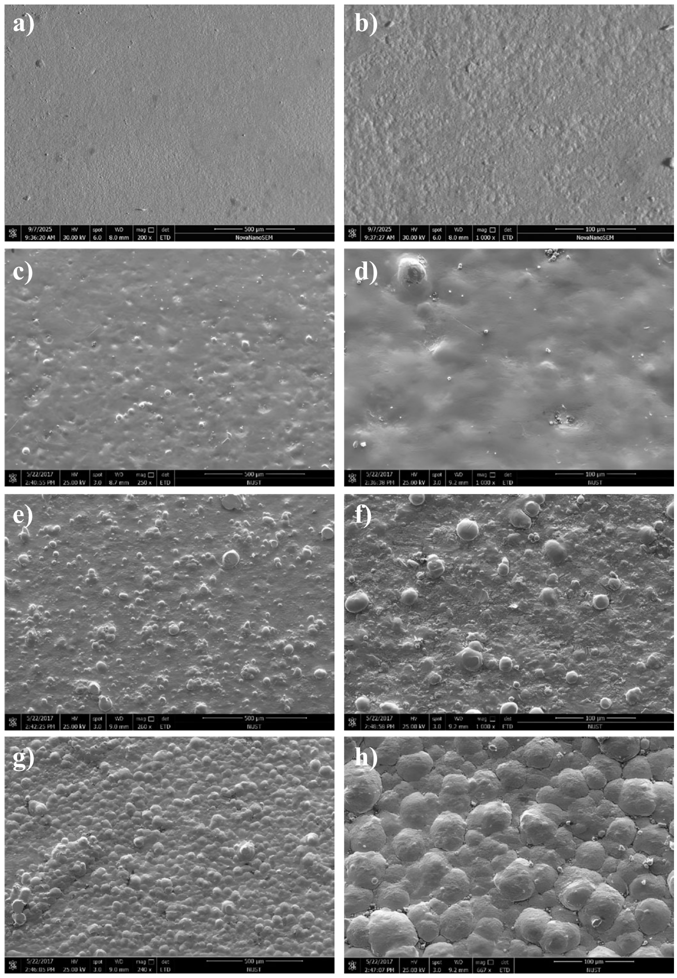

Fig. 2. Surface microstructure and EDS element diagram of composite coating : (a, b) Ag coating (c, d) Ag/0.4G coating; (e, f) Ag/0.8G coating; (g, h) Ag/1.6G coating

TABLE 3

Composition content table of composite coating

Element	Ag	0.4 g/L	0.8 g/L	1.6 g/L
C	2.77 (wt.%)	6.11 (wt.%)	7.15 (wt.%)	9.90 (wt.%)
O	2.69 (wt.%)	6.24 (wt.%)	8.37 (wt.%)	10.17 (wt.%)
Fe	0.10 (wt.%)	0.39 (wt.%)	0.58 (wt.%)	0.91 (wt.%)
Ag	94.44 (wt.%)	87.26 (wt.%)	83.90 (wt.%)	79.02 (wt.%)
	100.00 (wt.%)	100.00 (wt.%)	100.00 (wt.%)	100.00 (wt.%)

Through the X-ray diffraction of composite coatings (Fig. 3). It can be seen from the figure that Ag in the coating is a face-centered cubic structure. With the increase of graphene content, the diffraction peak slightly shifted to the right, which may be due to the incorporation of carbon atoms to reduce the unit cell parameters. The grain size can be determined by the X-ray diffraction pattern combined with Scherrer's formula. The grain size of Ag coating is 38.1 nm; Ag/0.4G coating is 31.1 nm; Ag/0.8G coating is 27 nm; Ag/1.6G coating is 20.8 nm. It shows that the addition of graphene can refine the silver grains, probably because graphene is multilayer, which separates the grains and makes the grains finer.

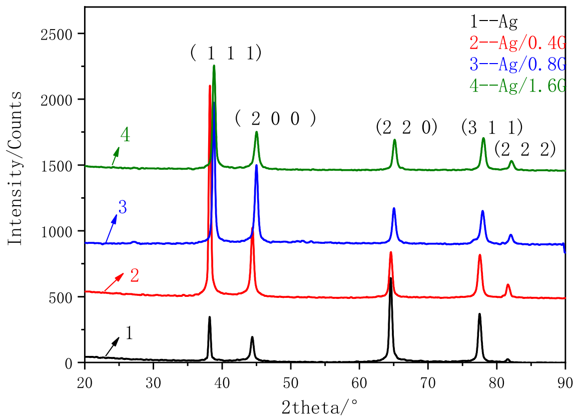

Fig. 3. X-ray diffraction of composite coatings

Scherrer's formula is:

$$d = K\lambda/\beta\cos\theta$$

In the formula:

d – Mean grain diameter;

K – The constant is 0.89;

λ – Cu target incident wavelength 0.154060 nm;

β – Half-height width (radian) of the diffraction peak;

θ – Diffraction Angle (°).

The experiment conducted a raman spectra test on the composite coating. It can be seen from the Fig. 4 that with the increase of the amount of graphene added in the plating solution, the peaks of D and G become more and more obvious and sharp, indicating that the actual graphene content in the coating increases with the increase of the amount added in the plating solution.

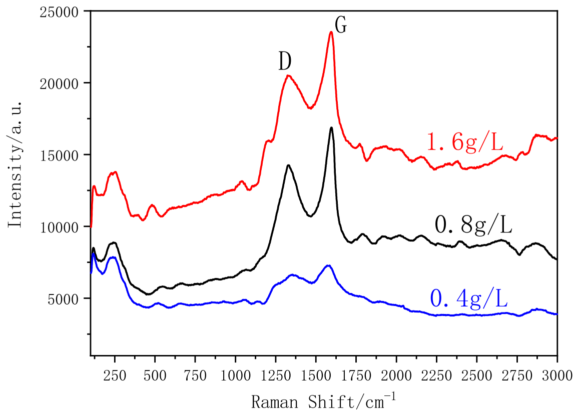

Fig. 4. Raman spectra of composite coatings

Fig. 5 shows the microstructure cross-section of composite coating. It can be seen from the figure that the thickness of Ag coating is about 48 μm; Ag/0.4G coating is about 32 μm; Ag/0.8G coating is about 24 μm; Ag/1.6G coating is about 22 μm. That is with the increase of graphene concentration in the bath, the thickness of its composite coating shows a decreasing trend. This may be because with the addition of graphene, more and more graphene adsorbed on the nickel coating substrate affects the deposition of silver on the nickel coating, resulting in a gradual reduction in the thickness of the deposited layer. Large scale cracks appeared at the interface between Ag/0.8G coating and matrix, and at the interface between Ag/1.6G coating and matrix. This may be due to a large number of multilayer graphene cutting matrix stress concentration generated cracks, during the coating growth process caused by external forces to further crack propagation.

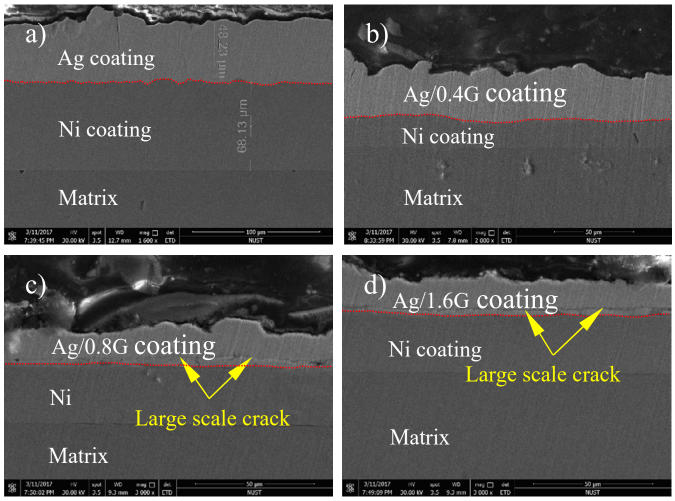

Fig. 5. Microstructure cross-section of composite coating: (a) Ag coating; (b) Ag/0.4G coating; (c) Ag/0.8G coating; (d) Ag/1.6G coating

3.3. Mechanical and tribological properties of composite coatings

It can be seen from the microhardness values of coatings in Fig. 6 that the microhardness of Ag coating is about 89 HV; Ag/0.4G coating is about 144 HV; Ag/0.8G coating is about 129 HV; Ag/1.6G coating is about 131 HV. The data show that the surface hardness of silver coating can be significantly increased by adding graphene. The reason may be that the multilayer graphene cuts off the silver crystal and refines the grain to improve the strength. The graphene layer itself has a high strength and can disperse the load, which is equivalent to supporting the silver matrix. For the composite coating, due to the agglomeration phenomenon caused by the increase of the amount of graphene added to the bath and the occurrence of cracks in the coating, the microhardness of the composite coating decreased slightly with the increase of the amount of graphene added to the silver coating.

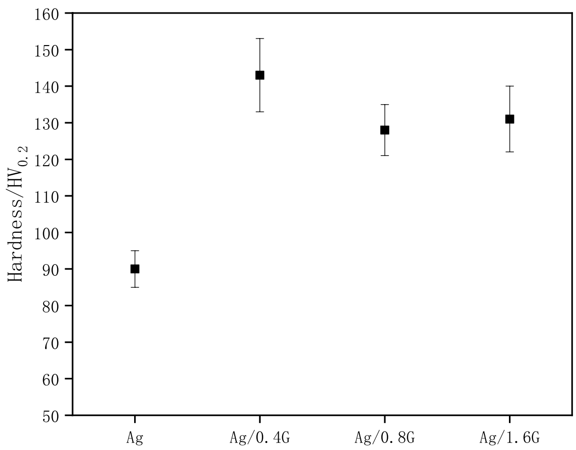

Fig. 6. Microhardness diagram of composite coating

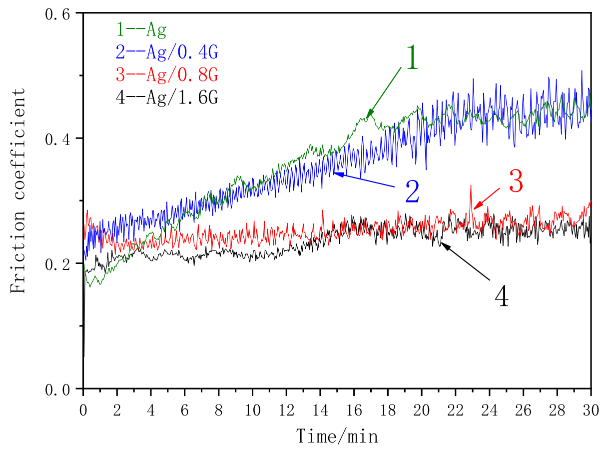

Fig. 8. Friction coefficient diagram of composite coating under 4 N load

The friction coefficient diagram of composite coatings under 2 N load are shown in Fig. 7. As can be seen from the figure, the friction coefficient of the composite coating with graphene added to the silver coating is lower than that of the Ag coating, and the friction coefficient is between 0.15 and 0.3. With the increase of graphene addition, the friction coefficient of the composite coating decreases and becomes more stable. Fig. 8 shows the friction coefficient diagram of composite coating under 4 N load. It can be seen from the figure that when the friction load rises to 4 N, the friction coefficient curves of Ag coating and Ag/0.4G composite coating are similar. The friction coefficient curve of the Ag/0.8G composite coating is similar to that of the Ag/1.6G composite coating. The overall friction coefficient is distributed between 0.2 and 0.4. As the load increases, the friction coefficient of the Ag/0.4G coating shows a slight increase of about 0.1. As can be seen from Fig. 6, compared with the other three coatings, the Ag/0.4G coating has the highest microhardness. Meanwhile, as shown in Fig. 10, the wear spots on the wear surface of the Ag/0.4G coating are wider, indicating some abrasive wear. During the high-load friction process, the hard abrasive particles have caused damage to the lubricating film formed by the synergy of silver and graphene, resulting in a slight upward trend of the friction coefficient.

Fig. 9 shows the wear rate of composite coating. It can be seen from the figure that the wear rate of Ag coating and Ag/0.4G composite coating is about 7×10^{-5} mm^3/Nm. The wear rate of Ag/0.8G composite coating and Ag/1.6G composite coating is about 1×10^{-5} mm^3/Nm. In general, the addition of graphene has improved the anti-wear performance of composite coatings. Fig. 10 shows the three-dimensional morphology of composite coating wear marks. It can be seen from the figure that the wear spot width of Ag/0.4G composite coating is larger than that of Ag/0.8G and Ag/1.6G composite coatings. It can be seen from the figure that the wear spot width of Ag/0.4G composite coating is larger than that of Ag/0.8G and Ag/1.6G composite coating. The wear spot width of Ag/0.8G and Ag/1.6G composite coatings is basically the same. This result is basically consistent with the coating wear rate shown in Fig. 9. Fig. 11 shows the original microstructure of composite coating and morphology of wear marks. As can be seen from the figure, Ag coating and graphene added to the silver coating wear marks are significantly different. The Ag coating has a certain amount of furrows on the scratched surface, while the Ag/0.8G surface with graphene added is smooth and flat. This is because the graphene in the composite coating is a layered structure, which can be spread on the friction surface during the friction process, thereby reducing the damage of friction to the coating surface.

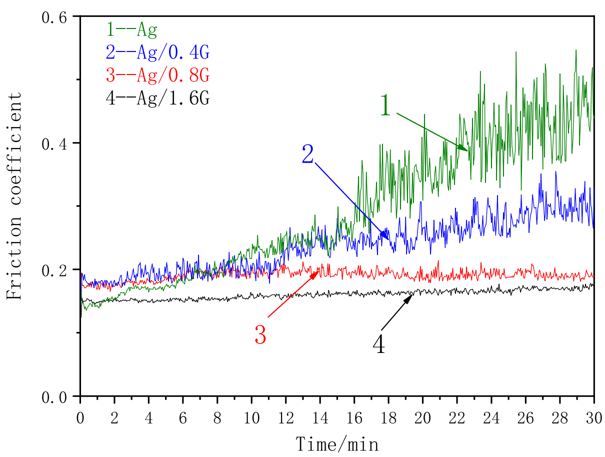

Fig. 7. Friction coefficient diagram of composite coating under 2 N load

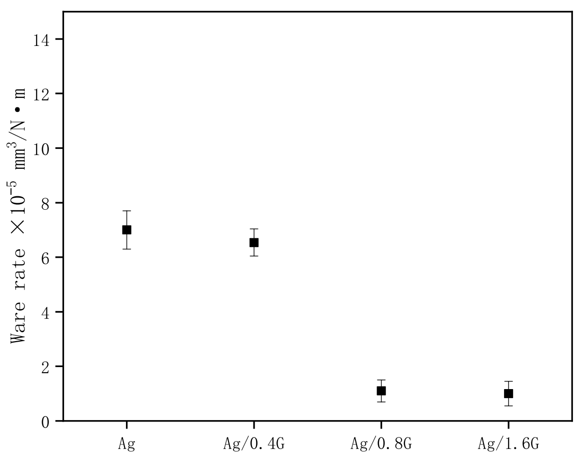

Fig. 9. Wear rate of composite coating

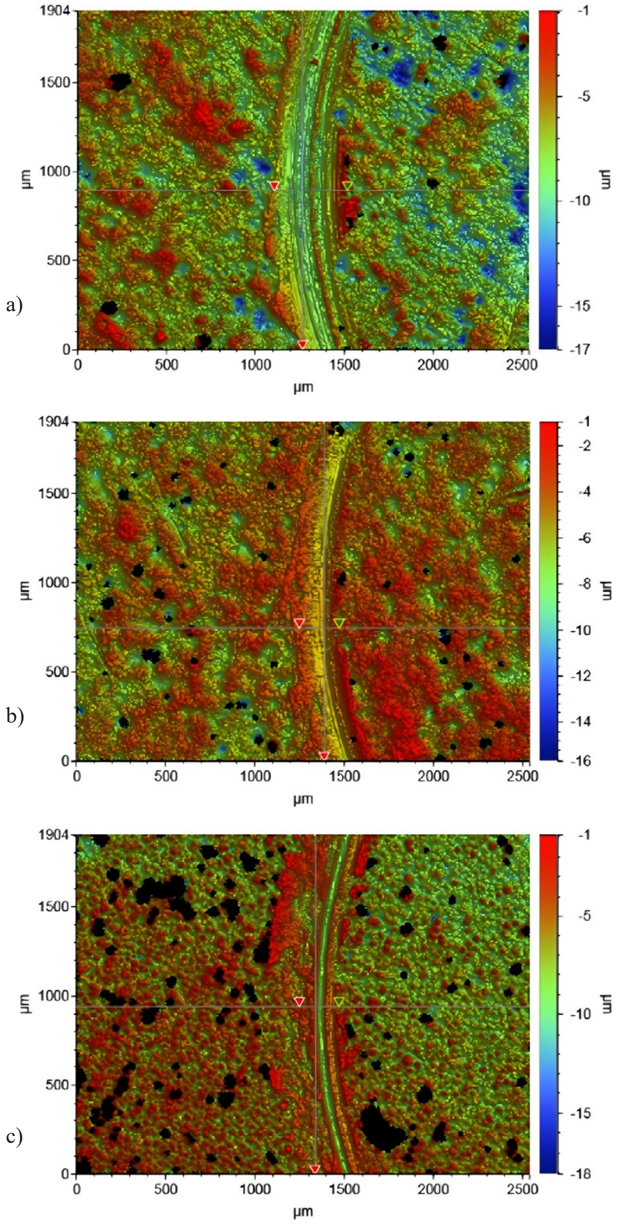

Fig. 10. Three-dimensional morphology of composite coating wear marks: (a) Ag/0.4G coating; (b) Ag/0.8G coating; (c) Ag/1.6G coating

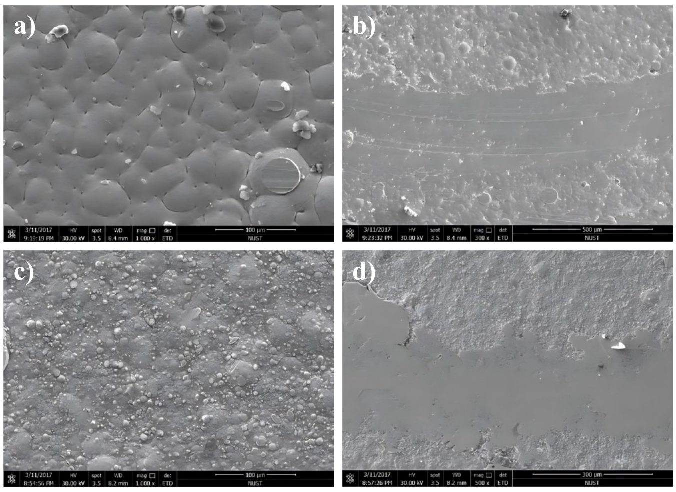

Fig. 11. Original microstructure of composite coating and morphology of wear marks: (a, b) Ag coating; (c, d) Ag/0.8G coating

4. Conclusions

(1) A series of Ag/graphene composite coatings were successfully prepared by electrodeposition. The Ag grains in the composite coatings decreased with the increase of graphene content.

(2) The addition of graphene in the composite coating improves the microhardness of the composite coating. The Ag coating is about 89 HV; Ag/0.4G coating is about 144 HV; Ag/0.8G coating is about 129 HV; Ag/1.6G coating is about 131 HV. When the amount of graphene added to the bath reached 0.8 g/L, a large number of cracks were generated in the composite coating.

(3) Compared with Ag coating, the friction coefficient and wear rate of composite coating are reduced to some extent. The addition of graphene improved the furrow phenomenon on the surface of the coating.

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