Electrodeposition and Tribological Behavior of Ni-MoS₂ Composite Coatings

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Abstract

Electroplated Ni has been widely used for protection from mild corrosion and mechanical damage. The friction and wear resistance of composite coatings were improved by the incorporation of solid lubricants molybdenum disulfide (MoS₂). The electrodeposition of Ni and Ni-MoS₂ composite coatings and tribological behavior of the coatings were studied. Classified by the surfactant added in the plating bath, two series of Ni-MoS₂ composite coatings were successfully deposited on the mild steel substrate. The effect of the plating parameters (plating time and bath temperature), the MoS₂ concentration in the bath as well as the types of surfactants (anionic surfactant SDS and cationic surfactant CTAB) were investigated. The organic additive thiourea (TU) was used to control the surface roughness of the coatings. The corresponding changes in morphology and component content were discussed.

The tribological behaviors of Ni and Ni-MoS₂ composite coatings were studied by the reciprocating sliding wear test performed on a ball-on-flat tribometer. The friction coefficient of composite coatings was reduced with the incorporation of solid lubricant. The lubricity of MoS₂ diminished the plastic deformation and the abrasive wear of Ni and Ni-MoS₂ composite coatings. The tribological properties of the Ni-MoS₂ coatings changed associated with the retention of MoS₂ in the wear tracks. By modifying the morphology of the coating and the volume fraction of MoS₂ in the composite coating, the coating showed better MoS₂ retention. A lower and slightly increased friction coefficient was achieved. A transfer film was observed on the counterface after the sliding wear test. The correlation between the microstructure of the coatings, the retention capacity of MoS₂, and the wear mechanism of coatings were investigated.

Résumé

Le Ni électrodéposé est largement utilisé pour la protection contre la corrosion et les dommages mécaniques. La résistance au frottement et à l'usure des revêtements composites est améliorée par l'incorporation de lubrifiants solides, le disulfure de molybdène (MoS₂). L'électrodéposition de revêtements composites Ni et Ni-MoS₂ et le comportement tribologique des revêtements ont été étudiés. Classées par le surfactant ajouté dans le bain de placage, deux séries de revêtements composites Ni-MoS₂ ont été déposées avec succès sur un substrat en acier doux. L'effet des paramètres de placage (temps et température de placage), la concentration de MoS₂ dans le bain ainsi que les types de surfactants (surfactant anionique SDS et surfactant cationique CTAB) ont été investigués. L'additif organique thiourée (TU) a été utilisé pour contrôler la rugosité de surface des revêtements. Les changements correspondants dans la morphologie et la teneur en composants ont été discutés.

Les comportements tribologiques des revêtements composites Ni et Ni-MoS₂ ont été explorés par des tests d'usure par glissement alternatif effectués sur un tribomètre à bille sur plat. Le coefficient de friction des revêtements composites a été réduit grâce à l'incorporation d'un lubrifiant solide. Le pouvoir lubrifiant du MoS₂ a diminué la déformation plastique et l'usure abrasive du revêtement Ni et des revêtements composites Ni-MoS₂. Les propriétés tribologiques des revêtements Ni-MoS₂ ont changé en fonction de la rétention du MoS₂ dans les traces d'usure. En modifiant la morphologie du revêtement et la fraction volumique de MoS₂ dans le revêtement composite, le revêtement a montré une meilleure rétention de MoS₂. Un coefficient de frottement inférieur et légèrement supérieur a été obtenu. Un film de transfert a été observé sur la contreface après l'essai d'usure par glissement. La corrélation entre la microstructure des revêtements, la capacité de rétention du MoS₂ et le mécanisme d'usure des revêtements a été investiguée.

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Contributions of authors

The author of this thesis was responsible for most of the experimental and all the writing work. The contribution of experimental work and data analysis that was not contributed by the author is listed below:

Prof. Richard Chromik supervised the experimental and writing work of this project and reviewed this thesis.

Chapter 3: Experimental procedure

Dr. Sriraman K Rajagopalan guided the electroplating work in this chapter.

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Dr. Venkata Naga Vamsi Munagala helped plan the plating experiment and helped me during the electrodeposition process in this chapter.

Chapter 4: The development of Ni-MoS₂ composite coatings

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Chapter 5: Tribological behavior of electrodeposited Ni and Ni-MoS₂ composite coatings

Dr. Venkata Naga Vamsi Munagala helped with planning experimental and data analysis.

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Chapter 1 Introduction

1.1 Background

In modern industries, such as aerospace, automotive and marine, prolonging the working life of components is a critical design consideration related to sustainability. Research in tribology, which is focused on the surface's interaction in relative motion, provides the strategies to minimize the premature failure caused by mechanical damage of the materials, the so-called "wear".^{1, 2} It has been reported that the economic loss resulting from wear is up to 2 % of the total gross domestic product in highly industrialized countries.³ On the other hand, the improvement of tribology performance of components, like friction and wear resistance, can improve the sustainability of mechanical components and provide enormous economic and environmental benefits.⁴ As a result, lubricants and coatings on the surface of base materials are used to modify the contact and prevent the damages caused by friction and wear.^{1, 5}

For metal-to-metal contacts in engineering systems, liquid lubrication (e.g., oil) remains the primary approach to mitigate wear and control friction. However, several disadvantages, such as the instability of liquid, temperature restrictions (oxidation and degradation), and contamination caused by liquid lubrication limit the use of liquid lubricants in tribology.^{6, 7} Going forward in the next century, new approaches are being investigated that will be more environmentally friendly and still provide some acceptable level of control over friction and wear. Strategies to build up composite coatings encapsulated with reinforcement particles are extensively used to improve the tribological properties of mating surfaces.^{8, 9} Metallic matrix composite coatings (MMCs) are employed to produce coatings that exhibit superior friction and wear resistance, corrosion resistance, hardness, and high temperature performance.⁵ MMCs, proposed firstly in the 1960s, are manufactured by unifying the metallic or alloy matrix and the reinforcement, such as metallic or ceramic particles or fibers.^{10, 11} They can provide a unique combination of the properties of the matrix and the reinforcements, and various properties as well as the

production technologies.¹² Ni-based metal matrix composite coatings have been attracted interest in aerospace and automotive applications, due to their excellent corrosion resistance, wear resistance, and hardness.¹³⁻¹⁵ Ni-based MMCs with high surface qualities and high adhesion strength are used in turbine blades, rollers, engine parts, and cylinders.¹² The hard particles, such as WC and TiC, are opted as reinforcement to achieve excellent hardness, wear, and corrosion resistance.^{16, 17} Solid lubrications are used to optimize the tribological properties by minimizing the losses caused by friction.¹⁸ Encapsulating solid lubrication in MMCs effectively mitigates friction and therefore improves the sustainability of machining components.⁴

Layer-lattice compounds	
Molybdenum disulphide Tungsten diselenide Niobium diselenide Calcium fluoride	Graphite Tungsten disulphide Tantalum disulphide Graphite fluoride
Polymers	
PTFE PTFCE PVF ₂ FEP ²	Nylon Acetal Polyimide Polyphenylene sulphide
Metals	
Lead Gold Indium	Tin Silver
Other inorganics	
Molybdic oxide Lead monoxide	Boron trioxide Boron nitride

Fig. 1.1 Materials used as solid lubricants.⁸

Solid lubricants are materials that can provide lower and consistent friction on the contact surfaces during relative motion.^{19, 20} Solid lubricants are typically lamellar solids, soft metals, polymers as well as some inorganics, and could be the alternative to liquids or gases lubricants in specific working environments.^{19, 21, 22} Fig. 1.1 presented several solid lubricants that are commonly used.⁸ The lamellar solid lubricants (such as transition metal dichalcogenide or graphite) possess good lubricity owing to the low shear strength attained by their layered lattice structure. Molybdenum disulfide (MoS₂), as one of the transition metal dichalcogenides, has been extensively studied.^{22, 23} The MoS₂ solid thin film exhibits a low friction coefficient (≤ 0.2

associated with working conditions) and extremely long wear life (low wear rate lower than 1 nm/cycle), which is attributed to the easy shear of the inert basal planes.²⁴ However, the low adhesion between MoS₂ and the wear surface, the hardness of the coating, the loading capacity, and the environmental susceptibility limit its tribological applications.²⁴⁻²⁶ The production of MMC containing the solid lubricant MoS₂ effectively improves the mechanical properties and wear resistance and is proven to achieve stable and ideal tribological properties in the humid atmosphere.^{24, 27, 28} Several technologies are employed to produce solid lubricant reinforced composite coatings, including high-temperature processes, such as hot-pressing^{29, 30}, sintering³¹, ³², and electrochemical method, i.e., electro-³³⁻³⁵, electroless³⁶⁻³⁹ and electrophoretic deposition⁴⁰, ⁴¹, corresponding to the required properties of coatings and reinforcement particles. During the high-temperature process, the diffusion of Mo into the matrix optimized the mechanical properties (e.g., microhardness and tensile strength) of coatings due to the chemical reaction between MoS₂ and matrix.^{32, 42} Compared with the metallic matrix, the sintered or hot-pressed Cu or Ni-based composite coatings containing MoS₂ achieved a low friction coefficient and wear rate over a wide range of operating temperatures. The lubricity of coatings correlated with the formation of the sulfide film generated during the wear process.^{43, 44} However, the instability of MoS₂ and the production of the brittle phase under the high-temperature process could undermine the mechanical and tribological properties of coatings.^{43, 45}

In recent years, electrodeposition has been considered one of the popular techniques to manufacture composites, owing to its easy-to-implement operating environment (conducted at atmospheric pressure and ambient temperature), low cost, and high deposition efficiency.^{13, 46} The mechanical properties (microhardness or tensile strength) or tribological properties (lubricity, wear, or corrosion resistance) can be improved by the presence of the fine dispersant second phase.⁴⁷⁻⁵⁰ The volume fraction of particles and morphology of coatings can be controlled by the electroplating parameter.^{38, 50} The increase in the MoS₂ content leads to a low friction coefficient of the coating, however, affects the growth of the deposits. Due to the difficulties in dealing with porosity and modifying the microstructure of composite coatings, challenges are encountered in electroplating Ni-MoS₂ coatings with direct current.^{33, 34, 51}

1.2 Objectives and organization of the thesis

1.2.1 Objectives of the thesis

The objectives of this thesis are described as follows:

Firstly, incorporating the solid lubricant particles MoS_2 into the Ni matrix by electrodeposition and successfully fabricating the Ni-MoS₂ composite coatings; optimizing the microstructure of the composite coatings by changing the plating parameters and the additives.

Secondly, effectively reducing the friction by applying the composite coatings and investigating the tribological behavior of Ni and Ni-MoS₂ composite coatings.

1.2.2 Organization of the thesis

This thesis is organized into six chapters:

Chapter 1 introduces the general background of this project, the objectives, and an overview of the work in this thesis.

Chapter 2 gives a literature review of solid lubricant MoS_2 , the metal-based composite coatings containing MoS_2 , the principle and process of electrodeposition, the factors affecting the electrodeposition process, the principle of tribology, and the tribological behavior of composite coatings containing solid lubricants.

Chapter 3 presents the experimental process undertaken in this project. In this chapter, the characterization of the MoS_2 powder is described. The details of the electrodeposition process including the bath composition and the plating parameters, and the equipment and method of coatings' characterization are provided. The detailed parameters and test conditions of the sliding wear test carried out on the tribometer, as well as the equipment used for the wear tracks' characterizations are listed.

Chapter 4 discusses the electrodeposition of Ni and Ni-MoS₂ composite coatings. In this chapter, two types of surfactants (SDS and CTAB) are used in the plating procedure. This chapter describes the coatings electrodeposited by various parameters (plating time, bath temperature, particle concentration, and the type of surfactants). The characterizations of two series of coatings are given, including: topographic and cross-sectional microstructures, microhardness (only for pure Ni coating) surface profiling, the thickness as well as the volume fraction of reinforcement particles MoS₂, in the composite coatings. The effect of organic additive thiourea (TU) on the coatings' morphology is also discussed in this chapter.

Chapter 5 presents the tribological studies of Ni and Ni-MoS₂ composite coatings produced in chapter 4. This chapter is categorized into two sections by the types of surfactants and discusses the tribological behavior of Ni and two series of Ni-MoS₂ composite coatings. The reciprocating sliding wear tests were performed on the coatings. The friction coefficient of each coating is obtained and correlated to the MoS₂ (lubricant) content in coatings and the morphology of the coatings. The microstructural characterization of wear tracks and the phase composition in the wear tracks are shown in this chapter. The generation of third bodies and the tribological behavior of Ni and Ni-MoS₂ coatings are studied. The influence of MoS_2 particles on the coatings' wear mechanisms is investigated.

Chapter 6 contains the discussion of electrodeposition and tribology of composite coatings, the conclusions of this project, and suggested future work.

Chapter 2 Literature review

2.1 Metal matrix composite coatings with solid lubricants

2.1.1 Solid lubricant particles MoS₂



Fig. 2.1 Crystal structure of MoS₂.⁵²

Molybdenum disulfide (MoS₂) is one of the most common lamellar solid lubricants, providing low friction due to its hexagonal lamellar crystal structure.¹⁹ As shown in Fig. 2.1⁵², the molybdenum (Mo) layer is sandwiched between two hexagonal layers of sulfur (S) atoms. Each Mo atom is surrounded by six S atoms and each S atom is equidistant from three Mo atoms.⁵³ The Mo and S atoms are connected by covalent bonds, while lamellar structure interacts via weak van der Waals forces, resulting in a low shear strength between S-S planes.^{54, 55} Its hexagonal closed-packed structure is crucial for lubricating properties. It shows a high loadcarrying capacity of the order of GPa with the shear strength of only about 25 MPa.²⁴ The ultralow friction coefficient of MoS₂ coatings, which is in the range of 10⁻³ to 10⁻² has been reported in high vacuum environments⁵⁶ and enhanced the wear life of components.⁵⁷ Due to the low volatility in the vacuum, good chemical stability, and sufficient wear resistance, MoS_2 has attracted attention in reducing the friction.²³

2.1.2 Metal-MoS₂ composite coatings

Considering the excellent lubricating behavior, MoS₂ has been introduced into a component to fabricate the metal matrix composite (MMC) coatings.^{29, 58-60} In the past half century, a series of metallic matrices, e.g., silver, nickel, copper, aluminum, and iron-based alloys, containing MoS₂ have been fabricated by powder metallurgy.^{54, 61, 62} The hot-pressed Ni and Au-based composite coating containing MoS_2 achieved a low friction coefficient (0.03-0.2), which can be used in the construction of bearing retainers.⁵⁴ The friction coefficient and test condition of metal-MoS₂ composite coatings studied by researchers are summarized in Table 2.1. Li et al.³⁶ studied the lubricity of MoS₂ in electroless Ni-P coating, with the friction coefficient reducing from 0.78 to 0.27. Sintered Ni-MoS₂ composite presented a low friction coefficient between 0.17-0.2, with a reduction of about 75%, compared with that of the CrNi₃MoVA steel substrate.⁶³ Pitchayyapillai et al.⁶² demonstrated the improved friction and wear resistance of MoS₂-reinforced aluminum matrix composites by studying coatings with various MoS₂ contents. Amaro et al.⁶⁰ reported that the magnetron sputtered MoS₂/Ti coating reached an extremely low friction coefficient of about 0.04. A Ni-based alloy containing MoS₂ was fabricated by powder metallurgy according to Li's study.⁴⁴ 12 % MoS₂ was added to the composite coating to achieve the lowest friction and wear rate. Decomposed soft phase (MoS₂) reacted with the matrix, thus strengthening the mechanical properties.44

In addition to high-temperature processing, such as powder metallurgy, electrodeposition has also been applied to produce metal-MoS₂ composite coatings under ambient temperature and normal pressure. Stankovic et al.⁶⁴ successfully fabricated Cu-MoS₂ by composite electrodeposition. Ma et al.⁶⁵ used electric-brush plating to produce Ni/MoS₂-C and studied its friction behavior. The author pointed out that the introduction of MoS₂ effectively reduced friction while leading to an irregular morphology. Fazel et al.⁶⁶ also confirmed that the dopant of MoS₂ reduced the friction both under room and high temperatures in an electrodeposited Ni-SiC-

 MoS_2 composite. MoS_2 effectively increased the stability of friction by preventing localized friction and detachment and reduced friction by 10-15% at elevated temperatures.⁶⁶

Coating	MoS ₂ content	Average friction coefficient	Atmosphere	Tribological test, Normal load, Test speed
Ni-P-MoS ₂ Li et al. ³⁶	Not provided	0.78 (at 25°C) - 0.27 (at 500°C) 0.33 (at 600°C)	25-600 °C in air	Unidirectional ball- on-disk, 3 N, 0.5 m/s
Ni-MoS ₂ Guo et al. 63	Not provided	0.17-0.20	Not provide	Reciprocating ball- on-flat, 20 N, 5 mm/s
Al6061/Al ₂ O ₃ /MoS ₂ Pitchayyapillai et al. ⁶²	2, 4, 6 wt.%	0.423-0.603	Room temperature (30°C), relative humidity of 60- 65%	Unidirectional pin- on-disk, 15,30,45 N, 1.25, 2.5, 3.25 m/s
MoS ₂ /Ti Amaro et al. ⁶⁰	Not provided	~0.04	Room temperature, relative humidity of 50%	Reciprocating wear test, 100 N, 150 mm/min
Ni-Cr-W-Al-Ti-MoS ₂ Li et al. ⁴⁴	6-20 wt.%	0.20-0.40 at 12 wt.%MoS ₂	RT-600 °C in dry air	Unidirectional pin- on-disk, 50-250 N, 0.4-1.6 m/s
Ni-MoS ₂ -C Ma et al. ⁶⁵	Not provided	0.3 (in humid air) ~0.07	Humid air (80 %) High vacuum/Atomic oxygen exposure /Ultraviolet irradiation	Unidirectional ball- on-disk, 12 N, 1.25 m/s
Ni-SiC-MoS ₂ Fazel et al. ⁶⁶	Not provided (non- uniform distribution of MoS ₂)	~0.4-0.55	25-300 °C	Unidirectional pin- on-disk, 15 N, 0.1 m/s

Table 2.1 Friction coefficients of metal-MoS₂ coatings reported in the literature.

2.2 Electrodeposition

2.2.1 Electroplating process

Electroplating is an effective surface modification method for developing coatings deposited on the surface of substrate materials.^{13, 46} As shown in Fig. 2.2⁶⁷, the electroplating device consists of two electrodes, an electrolyte solution, with an applied power acting on the electrodes. The anode is made of metal to be plated, and the object to be plated is used as the cathode. During the electroplating process, the electrochemical reaction takes place at the interface of electrolyte and electrodes, and ions are therefore coated onto the surface of the cathode.⁶⁸ The electrolyte contains the same ions as the anode metal to keep the concentration of the coating metal cations unchanged. The oxidation reaction occurs on the anode, and the metal ions are dissolved in the electrolyte. Under the action of the applied potential, the cations of the coating metal are attracted to the cathode and are reduced on the surface of the workpiece (cathode), to form a coating. Through electroplating, metal plating can be accomplished with improved surface characteristics, mechanical and tribological properties, and corrosion resistance.⁶⁹



Fig. 2.2 Schematic of the electrochemical process.⁶⁷

2.2.2 Mechanism of composite electrodeposition

Co-deposited particles in metallic matrices provide a strong influence on the properties of the coatings.⁷⁰ The incorporation of hard particles leads to a higher strength, microhardness, and corrosion resistance.⁷¹⁻⁷³ On the other hand, superior lubricity can be obtained by introducing the solid lubricant particles into metallic matrices, for example, MoS₂³⁸ and PTFE⁷⁴. The electrodeposition process can be considered as: the transfer of particles to the metal surface, the interaction of particles and electrodes, and the integration of particles into the coating, which can be described as the weak absorption by Van der Waals force and strong adsorption under Coulomb force in the presence of the electric field.^{35, 75} The Co-deposition process is demonstrated in Fig. 2.3, including the mechanism of particles transportation, hydrodynamic condition, and the effect of particle characteristics.^{76, 77}

The particles added in the electrolyte are surrounded by an ionic cloud composed of H⁺ and metal ions.⁷⁸ The electrically activated particles are driven through the hydrodynamic boundary layer under convective action and then continue to move towards the cathode by concentration diffusion, so-called the diffusion layer.⁷⁹ The electrokinetic potential is generated between the cathode surface and the particles' ionic cloud. Driven by the potential gradient, particles migrate through the electrical double layer with the dimensions of nanometers. As the particles reach the cathode surface, the reduction of ions cloud occurs. Metal ions are discharged, and particles are entrapped to the cathode with metal deposit.^{80, 81}



Fig. 2.3 Mechanism of particle co-deposited into a metal matrix.⁷⁹

In the case of Ni plating, for example, the nickel plating handbook offers typical operating parameters and plating compositions to obtain Ni coating with homogeneous morphology and good mechanical and physical properties.⁸² The plating electrolyte consists of nickel sulfate and nickel chloride, the current density applied to the cathode is 2-7 A/dm², and pH is controlled between 3.5-4.5, under a plating temperature of 40-60 °C.⁸²

The Ni-particles co-deposition is influenced by various plating parameters, which can modify the content of the particles entrapped in the matrix.⁸³ The influence of pH on the plating process is related to the adsorption of hydrogen and thus affects the internal stress.⁸⁴⁻⁸⁶ The volume fraction of conductive particles is maximized at pH=4-5.^{51, 87, 88} Based on the proper pH value, in most cases, the content of incorporated particles increases with the current density until it reaches a maximum value, then starts to decrease.^{87, 89-91} At lower current densities, the increased current leads to an increase in the rate at which the adsorbed nanoparticles reach the cathode, increasing

the particle content.⁹⁰ At higher current density, metal ions move faster than inert particles, and high internal stress caused by high current density eventually reduces the number of deposited particles.⁹² Meanwhile, the interaction between the current density and pH of electrolytes should be taken into consideration.⁹³

2.2.3 Metal-MoS₂ electrodeposition

Apart from the plating parameters, the morphology of composite coating can also be affected by the characteristics of co-deposited particles. The particles with different conductivity exhibit diverse growing behavior in the metal matrix. He et al.⁹⁴ demonstrated the electrolytic current distribution on the non-conductive particles and conductive particles, which is shown in Fig. 2.4. When metals are co-deposited with non-conductive particles, for example, diamond⁹⁵ and Al₂O₃⁹⁶, the electric field around the insulating particle is distorted (Fig. 2.4a); the metal ions are only attracted to the cathode and are reduced in the vicinity of the cathode, instead of being deposited on particles.⁹⁷ Fig. 2.5 shows the cross-section of nickel-Al₂O₃, which exhibits a relatively flat surface and a dense structure with fewer pores.⁹⁶



Fig. 2.4 Schematics of electrolytic current distribution on (a) non-conductive particle and (b) conductivity particle.⁹⁴



Fig. 2.5 Cross-sectional micrograph of the Ni-Al₂O₃ composite coating.⁹⁶



Fig. 2.6 (a) Cross-sectional micrograph of ion milled Cu-MoS₂ composite coating⁹⁸, (b) crosssectional micrograph of Ni-MoS₂ composite coating³⁴, and (c) schematic of the diacritic growth of the Ni-MoS₂ coating⁹⁹.

When using conductive or semi-conductive particles as reinforcements for electrodeposition $(SiC^{91}, MoS_2^{99}, WS_2^{88})$, the electric current presents another variation, which is centralized on the particle embedded in on cathode surface (Fig. 2.4b).^{94, 100} Metal ions favorably adsorb on the

particles as the effect of high electrostatic attraction (Coulomb force)^{94, 98}, as shown in Fig. 2.6a, it is obvious that Cu adsorbs on the point of MoS₂ surface.⁵³ Similarly, in the co-deposition of MoS₂ with a Ni matrix, Ni atoms are easily deposited on the MoS₂ and form protrusions (Fig. 2.6b).³⁴ In terms of MoS₂ particles, the MoS₂ in the electrolyte tends to be deposited on the nodules of the MoS₂ enveloped by Ni atoms, rather than adsorbed on Ni on the cathode surface (substrate), thus resulting in the dendritic growth and causing more defects, gaps and high porosity in the composite coating (refer to as "diacritic growth" in Fig. 2.6c).⁹⁹

2.2.4 The effect of additives

As one of the additives in the electrolyte, the surfactant provides a great contribution to the coating morphology modification.^{96, 101, 102} Depending on the electric charges of surfactant, it can be classified into: anionic, cationic, nonionic, and amphoteric. Generally, the addition of either anionic or cationic surfactants can modify the coating morphology by affecting the distribution of particles.¹⁰³ The cationic surfactant, typically, cetyltrimethyl ammonium bromide (CTAB) has been reported to be widely used in nickel-particles deposition. The addition of CTAB or TMAH¹⁰² enhances the volume fraction of the particles entrapped in the coating, meanwhile, the content of particles increases by increasing the concentration of CTAB.⁵⁰ The hydrophobic MoS₂ particles tend to agglomerate in the electrolyte, and the positive charge generated by the cationic surfactant (CTAB or BAS) on the particle surface can reduce the conductivity to prevent the agglomeration of the particles while facilitating the movement of MoS₂ toward the cathode surface, thus allowing the particles to be uniformly dispersed.^{51, 99, 101}

In the co-deposition of Ni-W-MoS₂, the anionic surfactant sodium dodecyl sulfate (SDS) is added to improve the ability of particles suspension and dispersion in the electrolyte.³³ SDS is also used to deposit Ni-SiC nanocomposite films.¹⁰⁴ As shown in Fig. 2.7, SDS increases the homogeneity and volume percentage of deposited SiC particles.^{105, 106} An improved graphene dispersion can be achieved by adding anionic surfactants and the relationship between the concentration of surfactants and the grain size reduction has been investigated by Yasin et al.¹⁰⁷ A high fluorinated anionic surfactant (SPA) is also reported to improve the dispersion of conductive particles graphene.¹⁰⁸



Fig. 2.7 Fractured surface of Ni-Co/SiC: (a) containing 0.25 g/L SDS, (b) with no surfactant.¹⁰⁶



Fig. 2.8 Cross-section of Cr-MoS₂ coating deposited with 2 g/L MoS₂ with: cationic surfactant (a) CTAB and (b) BAC; and (c) anionic surfactant SDS.¹⁰⁹

A comparison of the cationic and anionic surfactant is reported on the co-deposition of Cr-MoS₂, which is shown in Fig. 2.8.¹⁰⁹ The application of cationic surfactant promotes the incorporation of particles into the Cr metallic matrix. The addition of anionic surfactant effectively improves the suspension stability of particles by reducing the surface tension and the charge on particle surface.¹¹⁰ This, however, may reduce the attraction of particles to the cathode, and as a result, decrease the doping amount of particles.¹¹¹ For composite coatings with cationic surfactant doping, an increase or decrease in the number of doped particles has been reported, which is related to hydrophobic behavior, the surface tension, and the inhabitant of the cathodic process due to the cathodic adsorption of the surfactant.¹¹¹⁻¹¹³

The relationship between bath temperature and particle volume fraction is related to the type of surfactant in the electrolyte. Due to the absence of surfactant, changes in plating temperature do not affect the volume fraction of particles in Ni-Al₂O₃ electrodeposition.^{114, 115} The composite

coating deposited with cationic surfactant generally performs a higher number of deposited particles at a relatively low temperature, attributed to the reduction of surfactant adsorbed onto the particles at elevated temperatures.⁵¹ For coatings added with anionic surfactants, there is not a monotonic correlation between temperature and particle fraction, with a maximum particle volume fraction at an intermediate temperature.¹¹⁶ Therefore, the addition of surfactant also plays an important role during the electroplating process.

Small amounts of organic compounds thiourea (TU) are reported to be added to the electroplating solution as a surface modifier. Many studies indicate that TU is an effective additive to modify the morphology of electrodeposited coatings by controlling the surface roughness in the electroplating process.^{117, 118} Prado et. al.⁹⁸ has reported that thiourea is used to control the roughness during the synthesis of superhydrophobic Cu-MoS₂ coating. Performing as a leveler at the macro-scale, the addition of TU to control the surface roughness is one of the keys to decreasing the void or holes in the copper electroplating.¹¹⁹ Further studies reveal the mechanism by which TU affects the quality of copper coatings. The strong inhibition of the grain growth by the complexes generated during the electrodeposition process.¹²⁰ With the increase of TU concentration, the average grain size of the deposits decreases, thereby resulting in a decreasing RMS roughness.^{121, 122}

2.3 Tribology

2.3.1 Friction and wear

Friction is a tangential resistance force when two surfaces in contact create or tend to create relative motion. Friction depends on the physical and chemical properties of materials and surface, the test and contact condition, the presence of lubricant, the test environment and many other factors, rather than an intrinsic property.^{2, 123} Friction can be expressed in terms of the friction coefficient (CoF or μ), which is defined as the ratio of frictional force (*F*) to the normal load (*L*)

$$\mu = \frac{F}{L} \tag{2-1}$$

Two bodies contact by the applied normal load, leading to the interfacial adhesion between asperities on the contact surface. when two surfaces slide relative to each other, the shearing of the adhesion bond in relative sliding results in friction. The frictional force needed to overcome the interfacial adhesion is F_a . The frictional energy required to generate micro-scale deformation is F_d .^{1, 124} The deformation takes place in the form of plastic deformation, for example, ploughing of asperities in first bodies, or caused by elastic hysteresis losses in elastomers. The total intrinsic frictional force F_i can be expressed as the sum of adhesion force and deformation force.¹

$$F_i = F_a + F_d \tag{2-2}$$

Then the friction coefficient is:

$$\mu_i = \mu_a + \mu_d \tag{2-3}$$

During the sliding process, shearing occurs at the adhesion bonds at the contact interface. Rupture occurs in the weakest regions, which can commonly be considered at the interface or in contacting bodies. After the bond is broken, new nodes are formed. The sum of each contact point area of all the contact spots constitutes the real area of the contact (*A*). Under the dry contact condition, the friction force for shearing the adhesive contacts (F_a) is given by Eq. 2-4 and 2-5¹²⁵:

$$F_a = AS \tag{2-4}$$

$$\mu_a = \frac{AS}{L} = \frac{S}{P} \tag{2-5}$$

where S is the shear strength and P is the mean contact pressure.

According to Eq. 2-5, either decreasing S or increasing P, by fabricating a coating with satisfying properties, could be the strategies to reduce the friction.²

Wear is the removal of material from the contact surface or damage to the surface that occurs when the asperities of the contact surface move relative to one another. Like friction, wear is affected by the properties of materials, contact, and environmental conditions.^{126, 127} Wear can be expressed by some common characteristics under different wear modes. The wear volume is usually proportional to the normal load and the distance traveled, and inversely proportional to

the hardness of the material.¹²⁸ The relationship between wear volume and test condition can be expressed as follows:

$$V = K' \cdot \frac{W \cdot s}{H} \tag{2-6}$$

where *V* is the worn volume, *w* is the applied normal load, *s* is the testing distance, *H* is the hardness of the material, and *K'* is a constant. To obtain a universal quantitative parameter for wear which is necessary for the development of the material, instead of the volume, a practical and general value for the amount of wear, wear rate *K*, is taken into consideration.¹²⁹ *K* equals to the constant *K'* divided by the hardness *H*, thus the wear rate can be formulated as:

$$K = \frac{V}{W \cdot s} \tag{2-7}$$

2.3.2 Wear mechanisms

Wear is manifested as surface damage and/or detachment from the surface of the material, which causes the part to lose some or all of its function. The removal of materials' surfaces can be described by several wear mechanisms, which include adhesive, abrasive, fatigue, erosion, and chemical wear.^{1, 2} Adhesion and abrasive wear commonly occur for two surfaces sliding in relative motion.¹³⁰ Adhesion occurs at the contacting asperities. As shown in Fig. 2.9, when two surfaces are in relative sliding contact, shear stress acts on the contact surface asperities and results in the detachment of material transfer from one surface to another contact surface.¹²⁹ As the relative motion continues, the transferred debris may be dislodged and transferred back to the original surface or be ejected to form the wear particles.¹

Abrasive wear occurs when one of the contact surfaces is obviously harder than another. Asperities on the hard surface are pressed into the soft surface, and, as the sliding continues, cause plastic deformation or fracture.¹²⁹ Abrasive wear induces several deformations modes, in the form of ploughing, wedge formation, cutting, or either causes crack and fracture on brittle material.¹ As shown in Fig. 2.10, it can be generally categorized into two-body abrasive wear (damaged by hard asperities) and third-body abrasive wear (caused by particles trapped between the mating surfaces).¹³¹ The two-body abrasive wear occurs when a counterbody with hard asperities (or a rough hard surface) slides on a soft surface. The asperities under the action of tangential force plough the contact surface. The worn surface morphology is typically

characterized by a series of grooves or scratches parallel to the sliding direction.^{129, 132} The thirdbody abrasive wear is caused by the sliding or rolling of wear debris on the contact surface. The wear debris generated during the sliding process can plough or abrade either one or both surfaces, if harder than the mating surface (Fig. 2.10). Those loose and free wear debris are trapped between the mating surface and abrade either one or both of them. The severity of third-body abrasive wear is regarding the size and hardness of particles. Generally, compared to two-body abrasive wear, the friction coefficient of third-body abrasive is lower by the factor of 2, and the wear rate of third-body abrasive wear is 1/3 of that of the two-body abrasive wear.^{1, 133, 134}



Fig. 2.9 Schematic of adhesive wear.¹²⁹



Fig. 2.10 Schematics of abrasive wear under two different circumstances: (a) two-body abrasive wear, (b) third-body abrasive wear.¹³¹

2.4 Tribological behavior of metal-solid lubricant composites

2.4.1 Third body behavior

In the tribology system, the contact is made up of two interacting bodies- "first bodies", and the worn material produced from the first bodies during the sliding- "third bodies". The third body is a collection of tribofilm, transfer film, and/or wear debris. The thin solid layer adhering onto the worn surface by the sliding contact of the first bodies is "tribofilm", the material transferred to the countersphere is "transfer film", and fragmented worn particles that are ejected out during sliding are "wear debris".^{135, 136} During the sliding wear test of MoS₂ or metal-MoS₂ composite coatings, wear debris are easy to be generated. The transfer behavior of wear debris was investigated by Wahl et al.²⁴ As shown in Fig. 2.11, the transfer process of wear particles is depicted as: the generation and accumulation in initial wear (stage I), rapid wear process (stage II), and depletion during the stable stage with low friction and wear (stage III).²⁴ At the initial stage of wear, a small amount of coating material is worn out and mainly concentrated in the center of contact while a small portion is transferred to the end of the wear track, referred to as a "patch". As the wear goes on, some MoS₂ wear debris remain in the contact area to provide lubricity, some of the worn materials are either ejected out of the wear track or accumulated at the "patch". Dynamic transfer of worn material takes place at the ball, the coating and the "patch". Lubricant particles that stack at "patch" replenish to the wear track and the counterface, and participant to friction and wear.²⁴ Materials exhibiting higher shear strength are prone to be ejected out. As a soft material with a low shear strength, MoS₂ tends to be trapped in the wear track.¹³⁷ The two contact surfaces are separated by third bodies, which prevent severe adhesion during the sliding.¹³⁸ The large amounts of MoS₂ facilitate the retention of the third body in the coating and lead to easier MoS₂ transfer, and the extruded and transferred MoS₂ particles build up the transfer films.¹³⁹



Fig. 2.11 Transfer processes of wear particles between the wear track, the countersphere, and patch material at turnaround points.²⁴

2.4.2 The formation of transfer film

As the friction coefficient can be expressed as the product of contact area and shear strength, it provides the strategy to reduce the friction by producing a thin, soft film covering the bulk material.¹²⁵ The solid lubricant film provides both a low area of contact and shear strength to reduce the friction coefficient. The deposition of solid lubricants, e.g., PTFE or MoS_2 , lowers the hardness of the composite coating.^{38, 39} The low shear strength is obtained from the lubricants in the coating, and the contact area is affected by the properties of the substrate, since the pressure is mainly supported by the substrate in a soft, thin coating (Fig. 2.12c).¹²⁵ The substrate with high elastic modulus and high stiffness reduces the contact area and penetration. Shear accommodation is provided by coating to reduce the interfacial bonding, thus achieving a low friction.^{140, 141}



Fig. 2.12 Schematics of the contact between two metallic materials, (a) hard metal on soft metal, (b) hard metal on hard metal, and (c) hard metal on soft thin film covered on hard metal.¹²⁵

As relative motion goes, the transfer of material occurs between the contact surfaces. The low friction of solid lubricant particles is related to the formation of transfer film during the sliding process^{54, 142-144}, which is shown in Fig. 2.13.¹⁴⁴ When the asperities on the contact surface strongly adhere to the contact surface, or the debris are generated and transferred to the counterface, a transfer layer is formed in the wear process. Owing to the different tribological properties of the transfer film, new tribological pairs are generated. In the early stages of the sliding process, the transfer occurs in the form of loose wear particles.¹⁴³ After the run-in period, the formation of transfer film prohibits the contact between surfaces prone to high friction, e.g., metal-metal contact.¹⁴⁵ Lamellar MoS₂ or WS₂ exhibits low interfacial shear strength. Intracrystalline slip leads to the formation of transfer film on the counterface, resulting in low friction of composite coatings containing solid lubricant particles.^{23, 125}



Fig. 2.13 Schematic of the formation of transfer layer.¹⁴⁴

The lubricity of MoS₂ in composite coatings has been investigated by many studies.^{54, 63, 146} Zhang et al.¹⁴⁶ obtained low friction of 0.014 for brush plated Ni-MoS₂ composite coating as the MoS₂ content increased from 31.6 % to 78 %. The author concluded that most of the MoS₂ grains show a preferred orientation of (0001), which is parallel to the sliding direction, and therefore the coating provides excellent lubrication properties.¹⁴⁶ Later, Wang et al.²⁹ also observed a (0001) orientation of MoS₂ after the sliding wear test. In recent studies, it is further confirmed that during the sliding wear process, disordered MoS₂ particles in the coating can be reoriented to the (0002) plane.^{23, 147} The transfer film generated on the counterface is also oriented to (0002) planes, the self-mating between basal planes results in a low friction of the composite coating.²⁸ The formation of transfer film is usually considered to be the partial sintering of wear material (transition-metal dichalcogenide) and its adherence to the countersphere, which covers the contact area.¹³⁷

2.4.3 MoS₂ effects on tribological behavior

The high MoS₂ content in the coating is key to reducing the friction coefficient, however, the friction is not always proportional to the particle concentration.^{29, 41} The concentration of MoS₂ dominates the morphology of the coating, and morphology is another factor that determines the tribological behavior of the coating.^{99, 100} The typical morphology of wear tracks is shown in Fig. 2.13. Zhang et al.⁴¹ studied the tribological behavior of Ni-Co-Al₂O₃-MoS₂ coatings with various MoS₂ contents. The coating with 0.5 g/L MoS₂ reinforcement exhibited good lubricity. Adhesive wear was observed on the coating deposited with 1 g/L MoS₂. The formation of transfer film on this smooth, dense coating resulted in the lowest friction and wear. In the case of coating with MoS₂ concentrations of 1.5 and 2 g/L, particles were easily pulled out and formed the wear particles. Cracks and grooving marks appeared on the worn surface, indicating severe abrasive wear. According to He's study^{94, 100}, the composite coatings with 7.9 wt.% and 7.1 wt.% MoS₂ were produced by depositing 10 g/L and 20 g/L MoS₂ in the plating bath, respectively. The relatively smooth coating (Ni-P-7.9 MoS_2) surface exhibited a constant friction coefficient, while rough coatings (Ni-P-7.1MoS₂) showed a linear increase in the friction coefficient, a wider wear track, and a raised oxidation.¹⁰⁰ The saturation of particles caused a decrease in the percentage of MoS₂ in the coating. Meanwhile, the addition of excessive particles in the electrolyte led to the aggregation of MoS₂. Therefore, the coating quality was deteriorated by the high surface roughness and a low percentage of lubricant particles.^{41, 100} The coating achieved a low surface roughness with a guaranteed particle content, and thus showed a minimum and constant friction coefficient value of 0.05. The compact and continuous transfer film was detected on the counterface, which provided a stable friction coefficient in the entire sliding process.¹⁰⁰


Fig. 2.14 Wear track image of Ni-Co-Al₂O₃ composites: (a) without MoS₂ particles, (b, c, d, e) with MoS₂ concentration of 0.5, 1.0, 1.5 and 2.0 g/L, respectively.⁴¹

As shown in Fig. 2.14, with the addition of MoS_2 , the friction is effectively decreased. At a low level of MoS_2 content, which ranged from 1-4 wt.%, the rise of MoS_2 led to the decrease of wear rate (indicated in micrometer) from around 55 to about 17 μ m.¹⁴⁸ However, the high content of MoS_2 reduced the friction coefficient but caused high wear; as a relatively soft phase, MoS_2 would have a negative effect on the mechanical properties of coatings.^{31, 54} The effect of MoS_2 deposited in the coating. Wu et al.³⁰ hot-pressed Ni composite coatings with various MoS_2 concentrations. The Ni/MoS₂ composite coating reached a low friction coefficient of about 0.08 as increasing the MoS_2 content to 60%. With an optimized concentration of MoS_2 , the composite coating presented as a homogeneous and lubricating film, whereas remarkable weakened mechanical properties can be found when further increases the content of MoS_2 .⁴⁸

Mechanical properties of the co-deposited composite coatings can be modified by adjusting the plating conditions, for example, agitating the electrolyte by ultrasonic oscillation instead of magnetic stir³⁴, or depositing the coating through pulse current to provide more nucleation sites during plating.⁴⁸ For the metal-MoS₂ coatings which have relatively low hardness, one strategy to improve the wear resistance is to increase the microhardness of the coating by either introducing a hard phase or modifying the manufacturing process. Due to the incorporation of Al₂O₃-coated MoS₂ particles, the pulse electrodeposited Ni-MoS₂/Al₂O₃ coating was reported to have higher microhardness and lower weight loss.⁹⁹ According to Eq. 2-5, the reduction of contact area could decrease the friction coefficient. As discussed in section 2.2.3, due to the conductivity of MoS₂, coatings grow dendritically, and irregular protrusions exhibit on the coating surface. The protrusions on the coating surface provide a low contact area during sliding contact, resulting in lower friction coefficients.⁹⁹ The protrusions are subject to the normal load and undergo plastic deformation. As the coating materials are worn out, the friction coefficient was increased on account of the expansion of the contact area and the loss of lubricnats.³⁴ In terms of the relatively soft composite coating, although the surface of the composite coating is fractured, the wear debris are lubricant-rich and are transferred to the contact area continuously.⁶⁵ The third-body behavior provided by the solid lubricant MoS₂ contributes to the reduction of friction and wear. Increasing the amount of MoS2 could enhance the ability of the third bodies (e.g., transfer film and wear debris) to remain in the contact zone between the parent material (first bodies).¹⁴⁹ The MoS₂ particles also facilitate the development of the dense transfer film that strongly adheres to the counterface. The dense, stable transfer film isolates the direct contact between the two first bodies and causes low friction and wear.^{65, 149} It is necessary to optimize the plating parameters, which can balance the lubricity and mechanical properties, to fabricate coating with desirable tribological properties, meanwhile, to gain a better understanding of the tribology behavior of electrodeposited Ni-MoS₂ coatings.

Chapter 3 Experimental procedure

3.1 MoS₂ powder characterization

The as-received MoS₂ powder (NanoChemaZone, Edmonton) was imaged by scanning electron microscope (SEM) (SU-3500, Hitachi, Japan) and is shown in Fig. 3.1. The low-magnification micrograph (Fig. 3.1a) shows irregular clusters of agglomerated powder. The high magnification micrograph in Fig. 3.1b shows that the powders making up the cluster are a flake-like morphology. The size distribution of MoS₂ powder was obtained by the laser scattering particle size distribution analyzer (LA-920, Horiba, Japan). The as-received powders were dispersed in water to avoid agglomeration before the analysis. The size distribution histogram of individual MoS₂ particles is shown in Fig. 3.1c, with an average particle size of $1.42 \pm 0.71 \mu$ m. The phases in the powder were analyzed by an X-ray diffractometer (Bruker D2 PHASER, USA) with Co-K α radiation. The diffraction peaks (Fig. 3.1d) were all indexed to MoS₂ with the hexagonal structure. The Miller indices were demarcated according to the PDF card (00-004-0850).



Fig. 3.1 SEM images of MoS₂ powder in (a) low magnification and (b) high magnification; (c) particle size distribution, and (d) XRD pattern of MoS₂ powder.

3.2 Electroplating procedure

The pure Ni and Ni-MoS₂ composite coatings were deposited on a mild steel substrate by direct current. Two series of coatings were produced. The Ni-MoS₂ coatings were classified by the type of additional surfactants, i.e., coatings deposited with anionic surfactant SDS (Ni-MoS₂-SDS) and cationic surfactant CTAB (Ni-MoS₂-CTAB). For the Ni-MoS₂-SDS coatings, the steel substrates were pre-polished using 320-1200 grit silicon carbide papers and 9, 3, and 1 µm diamond pastes. The received substrates for Ni-MoS₂-CTAB were grit-blasted according to the standard MIL-STD-1504. The substrates were blasted by 80 to 120 grit aluminum oxide particles. The compressed air at 40 to 60 psi was used to propel and suspend the particles before the impact. The blasting was proceeded in the blast cabinet, with the blast angle varying between 45 and 90 degrees, and the distance between the substrate and blast gun 5 to 10 cm. The acid-activated process was conducted on the pre-polished steel substrates and the received grit-blasted steel substrates by immersing the substrate into a 10 % HCl solution for 1 minute before the electrodeposition process. The pure Ni plate (99.0 %) was placed in the plating solution as the anode. The pre-treated mild steel substrate with a dimension of $25 \times 25 \times 1 \text{ mm}^3$ was installed parallel to the pure Ni anode in the plating solution as the cathode.⁸² The plating solution was a Watts bath. It was composed of nickel sulfate (NiSO₄·6H₂O), nickel chloride (NiCl₂·6H₂O), and Boric acid (H₃BO₃).

Bath composition	Parameter
NiSO ₄ .6H ₂ O	300 g/L
NiCl ₂ .6H ₂ O	90 g /L
H ₃ BO ₃	45 g/L
pH	4
Current density	5 A/dm^2
Agitation speed	200 rpm

Table 3.1 The Watts bath composition and processing parameters for all coatings in this thesis.

	MoS ₂	MoS2 in	Additives			Bath temperature (°C)	Plating time (min)
Sample in coatings bath (g/L) (vol.%)	SDS	СТАВ	TU				
Ni	-	-	-	-	-		
Ni-MoS ₂ -0.5 g/L	0.5	-		-	-		
Ni-MoS ₂ -1 g/L	1	-		-	-	45	40
Ni-MoS ₂ -1.5 g/L	1.5	-	0.1 g/L	-	-		
Ni-2MoS ₂	15	2.1 ± 0.6		-	-	30	40
Ni-18MoS ₂	15	18 ± 4		-	-	45	40
Ni-16MoS ₂	15	16 ± 3		-	-	60	40
Ni-18MoS ₂	1	18 ± 5	-	- 1/10 - 0f	0	50	30
Ni-9MoS ₂	1	8.6 ± 0.9	-		1/10 of MoS ₂		40
Ni-24MoS ₂	2	24 ± 4	-	WIOS ₂			30
Ni-27MoS ₂	2	27 ± 3	-				40

Table 3.2 Coatings and plating parameters corresponding to each coating in this thesis.

The Watts bath was agitated by a polytetrafluoroethylene (PTFE)-coated rod-shaped magnetic stirrer (12 mm in length \times 4 mm in diameter) for 30 mins before plating. The MoS₂ powders and other additives were added, while the magnetic stirrer kept working at 200 rpm during the deposition process. The bath temperature was controlled by a hot plate and the temperatures corresponding to the different Watts baths are listed in Table 3.1. The bath temperatures were kept constant during the plating. The constant current was provided by a potentiostat/galvanostat (EG&G PAR Model 363, USA). A plating current density of 5 A/dm² was used to generate pure Ni and composite coatings. Based on the study of the effect of pH value on the Ni and MoS₂ deposition, the deposition fraction of MoS₂ was insensitive to variations in pH.⁵¹ According to the literature, the pH value was selected at the value of 4, considering the optimization of morphology and the mechanical properties of the composite coatings (see section 2.2.2).^{87, 88, 99, 103} Therefore, in this project, the pH of all plating solutions was constant at 4.

The bath composition and general plating parameters are listed in Table 3.1, and the specific bath temperature, plating time, and additive content for each plating system are summarized in Table 3.2. The composite coatings are named simplified based on the MoS₂ volume fraction in coatings (e.g., Ni-2MoS₂), and those coatings for which the volume percentage of MoS₂ could not be calculated are named by the concentration of MoS₂ added into the Watts bath (e.g., Ni-MoS₂-0.5 g/L). For Ni-MoS₂-SDS, four different concentrations of MoS₂ (0.5, 1, 1.5, and 15 g/L) were added to the Watts bath. Three different plating temperatures of 30, 45, and 60 °C were selected, the temperatures were kept constant during the plating process along with an agitation speed of 200 rpm for 40 mins. In terms of the Ni-MoS₂-CTAB, 1 and 2 g/L MoS₂ were added in the Watts bath, and coatings were obtained by plating for 30 and 40 mins corresponding to each MoS₂ concentration.

3.3 Characterization techniques

3.3.1 Microstructure analysis

The morphology of the electrodeposited coating was investigated by a non-contact optical profilometer (Zygo Corporation, USA). The surface roughness was obtained in terms of the arithmetic mean deviation (R_a) of 10 locations (square with a side length of 1660.6 µm). The coating was also cross-sectioned by an abrasive cutter (Delta AbrasiMet, Buehler, USA) and cold mounted in an epoxy-containing conductive copper filler. The mounted cross-section sample was mechanically ground by 320, 400, 600, 800, and 1200 grit papers in sequence, followed by fine polishing with 9, 3, and 1 µm diamond suspensions.

The phase identifications of Ni and Ni-MoS₂ composite coatings were analyzed by the XRD with Co K α radiation. Fig. 3.2 shows the diffraction peaks produced on Ni and Ni-MoS₂-SDS and Ni-MoS₂-CTAB, with the Miller indices demarcated based on PDF card. In the pure Ni coating, Ni and Fe were detected; the trace amounts of Fe were from the dissolved steel substrate. The phases of Ni, a limited amount of Fe, and MoS₂ with hexagonal crystal lattice were observed in the composite coatings. The morphology and the composition of the deposited Ni and composite coatings were studied by SEM equipped with backscattered electrons (BSE) detector. Fig. 3.3 shows an example of the topography and cross-sectional characterization of the Ni-MoS₂ coating.

The topography of the coating was observed by the secondary electrons (SE) imaging of SEM, and the composition of the sample was provided by BSE with an accelerating voltage at 15 keV. The working distance was around 10 mm. For the cross-section of the sample, the accelerating voltage was set at 30 keV. The BSE mode of SEM is sensitive to atomic numbers and provides element information through brightness and contrast. The MoS_2 powder appears as a dark flake due to its lower mean atomic number, while the Ni which has a higher atomic number appears as a bright gray matrix. The chemical analysis of the coatings was provided by energy-dispersive X-ray spectroscopy (EDX). The element mapping and point ID analysis were acquired on the top surface and cross-section of the coating by the EDX detector. The thickness of the coating and MoS_2 volume fraction in the composite coatings were measured by the ImageJ software. Twenty different locations were selected to obtain the thickness of the coating by pixel count. The area fraction of MoS₂ particles was obtained by dark contrast in the BSE images, and cross-sectional images of 15 random locations were taken for each composite coating and processed with ImageJ software. The MoS₂ area fraction was considered to be the volume fraction of MoS₂ in the coating. The MoS₂ content is presented in Table 3.2 and the details will be indicated in sections 4.1 and 4.2.



Fig. 3.2 XRD diffraction peaks of: (a) Pure Ni, (b) Ni-MoS₂-SDS, (c) Ni-MoS₂-CTAB.



Fig. 3.3 EDX analysis of the Ni-MoS₂ coating: (a) topography, (b) cross-section, and EDX maps of the rectangles in a and b, respectively; MoS_2 flakes and porous are indicated by arrows.

3.3.2 Microhardness testing

The microhardness measurement of electrodeposited coatings was carried out on a Vickers microhardness tester (Buehler, USA). The microhardness test was taken on the top surface of electroplated pure Ni coating under a 50 gf load with a dwell time of 15 s. More than 10 indentations were taken on pure Ni coating to determine the average microhardness. Each indentation was spaced at least with a distance of 5 times the diagonal of the previous indent. Considering the low thickness of the electrodeposited coatings, the thickness of coatings should be at least ten times the indentation depth. Due to the high roughness and the fluffy structure of Ni-MoS₂ coatings, regular rhomboidal indentation on the coating surface could not be obtained, therefore the hardness of the Ni-MoS₂ coating was not measured.

3.4 Sliding wear test

3.4.1 Sliding wear test setup

The sliding wear test was performed by a custom-built ball-on-flat reciprocating tribometer. Fig. 3.4 shows the schematic of the tribotest system.¹⁵⁰ The normal load was applied to each coating during the sliding test by placing weights on the loading arm. The counterface was held on the cantilever arm and the specimen was fixed on the stage which was equipped with a motorized stage to provide the reciprocating motion in the tribological test. A piezoelectric sensor, mounted under the sample stage, was used to measure the friction force with a sampling frequency of 800 to 2800 Hz. The tribometer was enclosed in a high-density polyethylene enclosure (HDPE) bag and the humidity was monitored by a thermohygrometer. The sliding wear test was carried out in dry air condition under a room temperature of 25 °C. During the sliding test, the HDPE bag was filled up with dry air from the designed hole. The relative humidity was kept below 3%, which was indicated by the thermohygrometer. The AISI-440C stainless steel ball with a diameter of 6.35 mm was used as the counter body, conducted with normal loads of 1 N and 5 N and a sliding speed of 3 mm/s. All the tests were run for 1000 cycles, with a track length of 10 mm and a sliding distance of 20 m in total.



Fig. 3.4 Schematic of the ball on flat tribometer.¹⁵⁰

3.4.2 Wear track characterization

After the sliding wear test, the morphology of the wear track was studied by a non-contact optical profilometer (Zygo Corporation, USA). 2D and 3D profiles of the entire wear track and counterface were generated by the software. The unworn surface of the coating was assumed as the reference plane (marked as the red dotted line in Fig. 3.5). The line profiles were extracted perpendicular to the wear track. Thirty to forty cross-sectional profiles were generated at different locations and then uploaded to Origin 2018 (OriginLab, USA) software. The cross-sectional area was determined by integrating the height profiles across the wear track over the baseline (Fig. 3.5). Similarly, the profile of the countersphere was also obtained by the profilometer and fitted to a sphere with the same diameter as the unworn countersphere (6.35 mm) to obtain a flattened surface (Fig. 3.6). The flattened unworn surface was considered as the reference plane, and the volume below the reference plane provided the information of worn volume.



Fig. 3.5 The scan profile of the wear track.



Fig. 3.6 The profile of the worn countersphere.

SEM was used to characterize the morphology of worn surface, counterface and third bodies in order to understand the wear mechanism. The material transfer and chemical element distribution inside the wear track after the sliding test were revealed by BSE mode and EDX mapping. To perform a further identification of phase, an inVia Raman microscope (Renishaw, UK) equipped with an Ar⁺ ion ($\lambda = 514.5$ nm) laser source was used to characterize the wear track and counterface. Three trials were acquired on each feature in the localized area. Combined with the result of EDX mapping, this provided a better understanding of the phase transformation and tribo-chemical reaction during the sliding wear test.

Chapter 4 The development of Ni-MoS₂ composite coatings

4.1 The development of Ni-MoS₂ coatings with anionic surfactant

4.1.1 The effect of MoS₂ concentration

The pure Ni coating and Ni-MoS₂-SDS coatings were fabricated by electrodeposition as outlined in section 3.2. Fig. 4.1 shows the topography and cross-section of the electroplated pure Ni coating. The Ni coating showed a uniform surface with a roughness of $0.092 \pm 0.008 \mu m$. According to the cross-section micrograph, a dense and smooth Ni coating with a thickness of $13.5 \pm 1.5 \mu m$ was deposited after a 40-minute plating.



Fig. 4.1 SEM images of electroplated pure Ni coating: (a) topography, (b) cross-section.

The Ni-MoS₂ coatings plated with different initial concentrations of MoS₂ particles are shown in Fig. 4.2. With the addition of solid lubricant particles MoS₂, the morphologies of electrodeposited Ni-MoS₂ composited coatings switched to a nodular structure. In the BSE images of the coatings' cross-section, the MoS₂ particle appeared as a dark gray flake. Under the MoS₂ concentration of 0.5 g/L (Fig. 4.2a and b), nearly no MoS₂ particles were deposited into the coating. With the increase of MoS₂ concentration to 1 and 1.5 g/L (Fig. 4.2c-f), only a few MoS₂ particles were encapsulated in the Ni matrix. The increasing concentration of MoS₂ in the bath led to an increase in the content of MoS₂ incorporated into coatings. The increased MoS₂ volume fraction resulted in the increase in both the number and the volume of the nodules.



Fig. 4.2 Ni-MoS₂-SDS coatings with different MoS₂ concentrations in the initial bath, (a, c, e, g) are the top surface of the coating with 0.5, 1, 1.5, 15 g/L MoS₂ concentration; (b, d, f, h) are cross-sectional BSE images of coatings in each particle concentration, respectively; the arrow in (h) is the Ni layer in the composite coating.

As increasing the MoS₂ particle concentration to 15 g/L, the morphology of the coating changed from a single nodular morphology to clustered nodules, as shown in Fig. 4.2g and h. The introduction of MoS₂ particles increased the surface roughness, from $1.6 \pm 0.1 \,\mu\text{m}$ (Ni-MoS₂-0.5 g/L) to $4.0 \pm 1.0 \,\mu\text{m}$ (Ni-MoS₂-15 g/L). Although the MoS₂ content increased, the bond between the loose nodules and the Ni matrix was weak. As the concentration of MoS₂ in the bath increased, the thickness of Ni that adhered to the substrate (arrow in Fig. 4.2h) decreased extremely. This could be the result of the increased collision between the cathode and MoS₂ particles, which decreased the plating efficiency of Ni.^{33, 87} Meanwhile, the agglomeration of MoS₂ particles was also aggravated, which resulted in a coating with a porous, fluffy morphology.

4.1.2 The effect of plating temperature

The plating temperature is known to have an effect on the morphology of $Ni-MoS_2$ composite coatings.^{84, 92} The Ni-MoS₂-SDS coatings electrodeposited at different plating temperatures are shown in Fig. 4.3. The composite coating deposited at 30 °C was composed of a relatively flat surface of Ni matrix and individual nodules growing on the top surface (Fig. 4.3a). When the plating temperature raised to 45 °C, the protrusions grew significantly into large clusters. The MoS_2 particles were loosely deposited on the substrate as shown in Fig. 4.3c. Compared with the coating deposited at 45 °C, the volume of nodules further increased when the temperature elevated to 60 °C; and finally, a continuous fluffy cluster was formed, as shown in Fig. 4.3e. According to the cross-sectional micrograph, Ni-2MoS₂ (plated at 30 °C) was a dense coating with a few gaps between the nodules (Fig. 4.3b). Ni-18MoS₂ (plated at 45°C) showed a discontinuous microstructure with weak bonding between protrusions and between protrusions to flat Ni deposition close to the substrate. A thicker coating was deposited at 60 °C. The Ni-16MoS₂ (plated at 60 °C) coating exhibited a continuous top surface and a porous subsurface with a porosity of 18.1 ± 5.57 %. The porous coating was generated due to the dendritic growth of the deposited MoS₂. As the temperature went higher, the thickness of the coatings increased significantly. The elevated plating temperature also increased the surface roughness from $1.91 \pm$ 0.05 μ m at 30 °C, to 4.0 \pm 1.0 μ m at 45 °C, and reached the maximum surface roughness of 9.7 \pm 1.3 µm at 60 °C. The coating thickness and surface roughness are listed in Table.4.1.

Bath temperature also influenced the MoS_2 volume fraction of the coatings. The volume fractions of MoS₂ particles are listed in Table 4.1. The MoS₂ content in the coating increased from 2.1 \pm 0.6 % to 18 \pm 4 % when the bath temperature was 45 °C. This can be attributed to the effect of temperature on conductivity; i.e., the increase in the bath temperature improved the conductivity of the semiconductor MoS₂ particles, thus more MoS₂ can be driven to the cathode surface.⁹⁹ The MoS₂ content slightly decreased to 16 ± 3 % when increasing the plating temperature to 60 °C. There was a non-monotonic correlation between bath temperature and particle volume fraction, with a maximum particle volume fraction at an intermediate temperature. This is suspected to be the result of the enhanced electrical conductivity of the MoS₂ particles leading to strong agglomeration, which dominated at temperatures up to 60°C.⁹⁹ The Ni ions moved to the cathode surface rapidly and fewer Ni ions were able to adsorb onto the protrusion of MoS_2 at a high-temperature plating bath. The cross-sectional image of Ni-16MoS₂ coating (plated at 60 °C) is shown in Fig. 4.3f. MoS₂ particles were more concentrated in the head of the nodules rather than deposited in the Ni matrix near the cathode. This could be an explanation for the reduced MoS₂ content incorporated in the Ni-MoS₂ composite coatings at a high temperature. A similar phenomenon has been observed in the study of the effect of temperature on nickel graphene composite coatings.¹¹⁶ It is noted that the effect of bath temperature is related to the type of surfactant added in the Watts bath. This non-linear correlation between temperature and content of deposited particles is only reported in the deposition with anionic surfactant.¹¹⁶

	Ni-2MoS ₂	Ni-18MoS ₂	Ni-16MoS ₂
Plating temperature	30 °C	45 °C	60 °C
Coating thickness	$11.4\pm2.1~\mu m$	$18.6\pm7.5~\mu m$	$64.2\pm20.6~\mu m$
Surface roughness	$1.91\pm0.05\mu m$	$4.0\pm1.0\mu m$	$9.7\pm1.3\mu m$
MoS ₂ vol. fraction	$2.1\pm0.6~\%$	18 ± 4 %	16 ± 3 %

Table 4.1 Thickness, surface roughness, and MoS₂ volume fraction of Ni-MoS₂-SDS composite coatings with different plating temperatures.



Fig. 4.3 SEM images of Ni-MoS₂-SDS coatings deposited at different temperatures: (a, b) at 30 °C, (c, d) at 45 °C, (e, f) at 60 °C; (a, c, e) are the top surface, (b, d, f) are cross-sectional images of the coatings.

4.2 The development of Ni-MoS₂ coatings with cationic surfactant

In the previous section, the Ni-MoS₂ coatings were deposited with the anionic surfactant SDS. In this section, the additive in the electrolyte was switched to the cationic surfactant CTAB. The concentration of CTAB was 1/10 of that of the MoS₂ in the initial plating bath, the specific plating parameters are listed in Tables 3.1 and 3.2. The morphologies of Ni-MoS₂ coatings deposited at different particle concentrations and plating times are presented in Fig. 4.4. With the addition of 1 g/L MoS₂ in the bath, the Ni-MoS₂ coating had a surface with loosely clustered nodules, similar to that of the composite coating containing SDS. Comparing four coatings in Fig. 4.4, it can be seen that adjusting the plating time (from 30 to 40 mins) and MoS₂ particle concentration (from 1 to 2 g/L) in the plating solution had no distinct effect on the morphology of the top surface.



Fig. 4.4 The top surface of Ni-MoS₂-CTAB composite coatings deposited by different plating parameters: (a, b) 1 g/L and (c, d) 2 g/L MoS₂ in the bath; (a, c) plated in 30 mins, (b, d) plated in 40 mins; (b, c, d) with the addition of TU. (C_{CTAB}: 1/10 MoS₂ concentration, C_{TU}: 1/10 MoS₂ concentration).



Fig. 4.5 Cross-sectional BSE images of Ni-MoS₂-CTAB coatings with 1 g/L MoS₂ in bath, (a) plated in 30 mins, (b) plated in 40 mins with the addition of TU. (C_{CTAB}: 1/10 MoS₂ concentration, C_{TU}: 1/10 MoS₂ concentration).

Due to the high conductivity of MoS₂, the MoS₂ particles incorporated with Ni were deposited on the substrate in the form of dendrites. To modify the surface morphology of the composite coating, the organic additive thiourea (TU) was added to the plating bath. TU has been reported to be an effective additive to control surface roughness in the electroplating process.^{117, 151-153} The addition of TU was 1/10 of the concentration of MoS₂ in the bath. The morphology of the surface and cross-section of modified composite coating are shown in Fig. 4.4b and Fig. 4.5b. According to the cross-sectional image, the thickness of flat surface in modified Ni-MoS₂ coating increased from $7.3 \pm 0.72 \ \mu m$ to $16.5 \pm 2.9 \ \mu m$. A more compact coating was achieved compared to the coating deposited in the TU-free electrolyte.

The concentration of MoS₂ in the plating bath had a significant effect on the cross-sectional morphology of the coating, by affecting the content of particles incorporated into the coating. While the particle volume fraction was affected by the additives in the Watts bath. The addition of CTAB effectively increased the deposition efficiency of MoS₂ particles compared with the coating added SDS. Table 4.2 presents the volume fraction of MoS₂ and surface roughness of Ni-MoS₂-CTAB and Ni-MoS₂-SDS. Considering coatings of Ni-MoS₂-SDS, nearly no MoS₂ particle was successfully deposited into coating in the Watts bath containing 1 g/L MoS₂ (Fig. 4.2d). The coating Ni-MoS₂-CTAB was plated by the same MoS₂ concentration in the bath, i.e., 1 g/L. However, the volume fraction in this coating was 18 ± 5 % (Fig. 4.5a), which was far

more than that of the coating Ni-MoS₂-1 g/L (SDS). In terms of the Watts bath with 15 g/L MoS₂, 16 vol.% MoS₂ was deposited in coating Ni-MoS₂-SDS (Fig. 4.3f). While, when changing the surfactant to CTAB, a large number of MoS₂ particles were driven to the substrate and prohibited the deposit of Ni. This resulted in the lack of bonding between the MoS₂ and the nickel matrix, and excessive MoS₂ led to the failure of the coating deposition. It is noted that the addition of CTAB led to a huge improvement in MoS₂ plating efficiency. Therefore, it is easy to acquire a coating with similar MoS₂ volume fraction and surface roughness to that of Ni-MoS₂-SDS, even though only less than 1/10 of MoS₂ was involved in the plating bath.

Table 4.2 Comparison of the Ni-MoS₂ coatings with SDS and CTAB.

	MoS ₂ concentration in bath	MoS ₂ vol. fraction	Surface roughness
Ni-MoS ₂ -SDS	1 g/L	-	$1.9\pm0.7~\mu m$
Ni-MoS ₂ -SDS	15 g/L	$16 \pm 3 \%$	$9.7\pm1.3\mu m$
Ni-MoS ₂ -CTAB	1 g/L	18 ± 5 %	$10.3\pm0.5~\mu m$

The addition of TU, on the other hand, decreased the volume fraction of MoS₂ particles (from 18 \pm 5 % to 8.6 \pm 0.9 %, in Fig. 4.5). The MoS₂ content in the coating was limited, which was associated with the inhibition effect of TU during the electrodeposition process.¹⁵⁴ In order to generate a coating with both good morphology and reinforcement particle content, a further increase of the MoS₂ concentration (2 g/L) and TU (1/10 of MoS₂ concentration) was processed in the plating bath. The morphology of the coatings is illustrated in Fig. 4.4c and d. Under the synergistic effect of TU and increased particles content, the nodules of the coating grew into a relatively continuous microstructure. As shown in the previous section, a high concentration of MoS₂ in the bath produced a high volume fraction of particles in coatings, meanwhile, causing a rough surface. The addition of TU can effectively control the roughness of the coating but inhibit the electroplating process. The roughness of the coating and the content of particles deposited in the coating were mutually restricted. The surface roughness of Ni-MoS₂ composite coatings with CTAB and the volume fraction of reinforcements MoS₂ are shown in Fig. 4.6.



Fig. 4.6 (a) Surface roughness and (b) MoS₂ volume fraction of Ni-MoS₂-CTAB coatings corresponding to different plating parameters.



Fig. 4.7 Cross-sectional BSE images of Ni-MoS₂-CTAB coatings with 2 g/L MoS₂ in bath, (a) plated in 30 mins, (b) plated in 40 mins. (C_{CTAB}: 1/10 MoS₂ concentration, C_{TU}: 1/10 MoS₂ concentration).

The increased efficiency of the MoS_2 plating caused an increase in the volume fraction of MoS_2 reinforcement in the coating, which consequently affected the surface roughness. It was approved in section 4.1 that as the particle volume fraction increased, the surface roughness increased. The combination of TU and CTAB could help to produce a coating with high content of particles and relatively dense morphology. With the increase in the plating time and MoS_2 concentration in the plating solution, the surface roughness tended to increase. When increasing the MoS_2 to 2 g/L under a 30-minute plating time, the particles incorporated into coatings

increased greatly from 8.6 % to 24 %, while the roughness remained in the same range. It can be inferred that the TU presented an excellent modification of the coating morphology under such a plating condition. The fluffy protrusions were reduced, the nodules were flattened and elongated, and the coating thus showed displayed a relatively dense structure, as shown in Fig. 4.7a. When further increasing the plating time to 40 mins, the surface roughness raised significantly while the MoS₂ content in the coating increased slightly (from 24 % to 27 %, in Fig. 4.7). The agglomeration of particles on the top surface led to a loosening of the nodules. Ni was preferably deposited around those particles. The inhibitory effect of TU was weak, and the morphology of the coating was dominated by the MoS_2 fraction in the coating. As a consequence, a porous coating with a fluffy nodules head was produced as demonstrated in Fig. 4.7b.

Chapter 5 Tribological behavior of electrodeposited Ni and Ni-MoS₂ composite coatings

The tribological behavior of the composite coatings can be influenced by the volume fraction of the reinforcement and the surface morphology. The friction behavior and wear mechanisms of the composite coating will be demonstrated in this section. Sliding wear tests on composite coatings deposited with anionic and cationic surfactant were used to evaluate the tribological behavior. The sliding test parameters were illustrated in section 3.4. Tests under each parameter were performed 2-3 times for each sample, and the test results were reproducible.

5.1 Coatings deposited with anionic surfactant SDS

5.1.1 Sliding wear tests

Sliding wear tests were carried out on Ni and Ni-MoS₂-SDS coatings with different content of MoS₂ volume fractions. The friction coefficient (CoF) versus cycle numbers is shown in Fig. 5.1. The friction coefficient of pure Ni coating started at a high level around 0.9 then decreased slightly to reach a steady level at 0.79. Spikes exhibited on the friction coefficient curve could be related to the adhesion of the smooth contact surface.¹⁷ The Ni-2MoS₂ showed a slightly lower average friction coefficient and a different friction behavior compared with pure Ni coating. The friction coefficient value of Ni-2MoS₂ started at a relatively low value around 0.37 and then increased to 0.67, with the curve fluctuating between 0.6 and 0.75. Due to the significant increase in the MoS₂ content, the Ni-16MoS₂ coating showed a distinctly lower friction coefficient that stabilized at 0.09 and continued to the end of the test. With the introduction of MoS₂ particles, the solid lubricant phase effectively reduced the friction coefficient of electroplated Ni coatings. The higher number of solid lubricant particles provided a lower and more stable friction coefficient.



Fig. 5.1 Friction coefficient (CoF) versus cycle numbers of Ni and Ni-MoS₂-SDS coatings under 1N normal load.

5.1.2 Worn surface characterization

After 1000 cycles of the sliding wear test, SEM was used to characterize the worn surface to understand the friction and wear mechanisms of pure Ni and composite coatings. The worn surface of the pure Ni coatings is shown in Fig. 5.2. The localized adhesive wear caused the high friction of Ni coating. According to Fig. 5.2a, scoring marks were observed in the wear track along the sliding direction. Large amounts of wear debris were generated during the sliding test. A part of debris flowed aside from the wear track and the rest of the wear particles that remained in the wear track moved cyclically between the countersphere and coating. The wear debris abraded the coating surface and therefore caused the third-body abrasive wear.



Fig. 5.2 Wear track morphology of pure Ni coating: (a) SEM image of wear track surface, (b) wear track profile.



Fig. 5.3 Wear track of Ni-2MoS₂: (a) SEM image of wear track surface, (b) EDX maps of Fe, Ni, Mo, and O distribution in the rectangle of (a), (c) wear track profile, the red dashed line indicates the reference plane, the distance between the arrows refers to the wear depth.

Fig. 5.3 shows the morphology of the worn surface of $Ni-2MoS_2$ after the 1000 cycles test. According to the topographic profile (Fig. 5.3c), large amounts of wear debris were ejected out and piled up on the side of the wear track. Few wear debris was displayed in the center of the wear track, which resulted in fewer ploughing marks compared with Ni coating. EDX maps displayed in Fig. 5.3b show the distribution of different elements on the worn surface. After a 1000-cycle test, the selected area was covered with Fe and a little Ni. The wear depth can be obtained in the profile of the wear track. As shown by the arrows in Fig. 5.3c, the depth of the wear track was 5-7 μ m, which was smaller than the thickness of the coating. This indicated that Fe in the substrate was not exposed to the worn surface, so the source of Fe was only from the countersphere. The distribution of Mo was difficult to tell since a low amount of Mo was left after the wear test. Fe was likely transferred from the countersphere (steel ball) so that the contact surface of the two bodies was "Fe and Ni" against the steel ball. The tribo-oxide of Ni and a few of Fe took place at the contact surface. The distribution of oxygen was presented in the place where rich in Ni and a part of Fe (Fig. 5.3b). The average friction coefficient value of Ni-2MoS₂ coating was around 0.67, which was close to the friction coefficient of steel versus steel (around 0.6).⁹⁴



Fig. 5.4 Raman spectra of the wear track: (a) pure Ni, (b) Ni-2MoS₂.

Raman spectra were carried out on the worn surface of both Ni and Ni-2MoS₂ coatings, as shown in Fig. 5.4a and b respectively. According to the peaks identified, the peaks of NiO, Fe₂O₃ and Fe₃O₄ were detected by Raman, and were thought to be the result of the oxidation of the counterface. No MoS₂ was detected in the wear track of Ni-2MoS₂ coating, even though MoS₂ is a Raman-sensitive compound. This was supported by the results of EDX maps (Fig. 5.3a and b), indicating that a trace amount of MoS₂ has limited effects on the friction behavior of the coating.



Fig. 5.5 Wear track of Ni-16MoS₂: (a) morphology, white arrow shows the Raman test location;(b) Raman spectra of the worn surface, and (c) topography and profile of the worn surface, the red arrow indicates the worn nodules.

Fig. 5.5 shows the wear track morphology of Ni-16MoS₂ and the Raman spectra of the worn surface. The wear surface morphology of the rough coating after the sliding friction test was completely different from that of the Ni-2MoS₂ coating. Due to the high roughness, at the initial stage, only a few heads of nodules on the coating were in contact with the countersphere. After the 1000-cycle reciprocating test, slight wear occurred. As shown in Fig. 5.4c, in the profile of the worn surface, by the red arrow, only the head of nodules was "polished" and rough unworn regions can be found below the worn surface. Nearly no wear debris could be observed in the

image of topography and cross-sectional profile (Fig. 5.5a and c). MoS_2 in the coating provided easy shear, thus the worn surface was smooth with only a few microcracks, and no ploughing marks or scores were observed throughout the wear track. At the point indicated by the white arrow, Raman analysis showed the presence of both MoS_2 and oxidation of Ni and Fe, indicating the persistence of MoS_2 after the sliding wear test.

5.2 Coatings deposited with cationic surfactant CTAB



5.2.1 Sliding wear tests

Fig. 5.6 Friction coefficient (CoF) curve of Ni and Ni-MoS₂-CTAB coatings under 5N normal load.

The sliding wear tests were carried out on Ni-MoS₂-CTAB coatings deposited with various plating parameters. The friction coefficient of the composite coatings versus the sliding cycle numbers is plotted in Fig. 5.6. The coatings incorporated with solid lubricant particles MoS_2 presented different friction behavior. The MoS_2 volume fraction and average friction coefficient

of coatings according to various plating parameters are listed in Table 5.1. The friction coefficient of pure Ni coating reached the maximum value of 0.88, then gradually decreased and stayed around 0.7. The friction coefficient of Ni-9MoS₂ started at around 0.22 and rapidly rose to about 0.65 after a short run-in period, and then gradually rose to 0.77. After a few run-in cycles, the friction of Ni-18MoS₂ went into a steady state till around 400 cycles, then increased almost linearly to around 0.43 at the end of the test. The coatings Ni-24MoS₂ and Ni-27MoS₂ exhibited similar friction behavior. The friction coefficient stayed at a low value for the entire test but did increase gradually reaching 0.23-0.25 by the end of the test. The coating containing a higher MoS₂ volume fraction presented a longer "stable worn out" stage over 600 cycles with less oscillation of the curve over 600 cycles.

Table 5.1 The average friction coefficient values of Ni-MoS₂-CTAB coatings.

Sample	Average friction coefficient
Ni-18MoS ₂	0.27 ± 0.07
Ni-9MoS ₂	0.77 ± 0.05
Ni-24MoS ₂	0.22 ± 0.03
Ni-27MoS ₂	0.22 ± 0.02

5.2.2 Worn surface characterization

Fig. 5.7 shows the wear track morphologies of Ni and Ni-9MoS₂ coating, which presented high friction coefficient at the last hundreds of cycles. Pure Ni coating was subject to plastic deformation. Continuous abrasion marks induced by wear debris were observed throughout the surface of the wear track parallel to the sliding direction as shown in the higher magnification image (Fig. 5.7b). Wear debris abraded the coating's surface. As indicated by the arrow in Fig. 5.7b, a few fine debris agglomerated to a scale of tens micrometer and ploughed the coating surface. The worn surface of the coating containing 8.6 vol.% MoS₂ is displayed in Fig. 5.7c. EDX maps carried out in the wear track center indicated the presence of Fe, which was transferred from the countersphere. The dark patch was the tribo-oxidation of Fe and Ni which was evidenced in Fig. 5.7e (EDX maps). However, a trace of MoS₂ was retained in the wear track surface, Mo was concentrated in the location of the bright patch, while only a very small

amount of Mo was detected in the center of the EDX test region (also the center of the wear track). Since less MoS_2 was deposited into the coating and was easy to be worn out during the run-in period of the sliding test, the adhesion wear started to dominate, resulting in high friction. It is evidenced by the tongue-shaped microstructure as the arrow shown in Fig. 5.7d.



Fig. 5.7 Wear track characterization of coating exhibiting high friction coefficient: (a, b) Ni coating, (b) high magnification of (a), arrow in (b) indicates the agglomerated wear debris; (c, d) Ni-9MoS₂ coating, (d) high magnification of (c), (e) BSE image and EDX maps of the rectangle in (e), arrow in (d) indicates tongue-shape microstructure.

The worn surface morphologies of Ni-18MoS₂ and Ni-24MoS₂ coatings are shown in Fig. 5.8.

Scoring marks along the sliding direction were observed in both coatings, while less wear debris was found along the side of the wear track of Ni-24MoS₂ coating. Abrasive wear was more intense in Ni-18MoS₂ (Fig. 5.8a) compared with Ni-24MoS₂ (Fig. 5.8d). After the sliding test, the Ni-18MoS₂ coating showed a non-uniform morphology with a quite few tribo-oxide layers. The dendritic grown MoS₂ in Ni-18MoS₂ was easily fragmented and dislodged from the wear track surface. According to the EDX analysis (Fig. 5.8c), only 0.7-1.1 wt.% Mo can be detected, and the patch of Fe oxidation on the surface of the wear track was the evidence of the material transfer between the counterface. Comparing the worn surface of two coatings tested under the same condition, the effect of lubricant MoS₂ particles was more pronounced on Ni-24MoS₂ since it showed a smoother worn surface and quite fine scratch marks (Fig. 5.8d and e). Wear debris were retained in the wear track, and nearly no debris was ejected out of the wear track.



Fig. 5.8 Wear track morphology: (a, b) Ni-18MoS₂ and (c) BSE image of Ni-18MoS₂ and EDX maps of rectangle area, (d, e) SEM images of Ni-24MoS₂, (e) high magnification of (d).

Raman analyses (Fig. 5.9-5.11) were conducted on the worn surface of Ni, Ni-18MoS₂, and Ni-24MoS₂ coatings. In pure Ni coating, as shown in Fig. 5.9, no Raman sensitive phase was detected in most areas of the wear track, e.g., arrow1, indicating that the wear track was mainly metallic phases. Strong peaks corresponding to the oxide of Ni were only detected in a specific region, i.e., arrow2, which showed a darker contrast in the patch area. A detachment of coating material was observed in the center of the wear track, where the fine wear debris were concentrated on the edge of the cavity, i.e., arrow3. Raman spectra carried out on arrow3 identified the peak of the Ni and Fe oxide, revealing that the bright regions were composed of Ni and Fe oxide.



Fig. 5.9 Raman spectra of Ni coating at different locations in the wear track; arrow1: wear track, arrow2: dark patch, arrow3: edge of the cavity.

For Ni-18MoS₂ coating, Fig. 5.10 shows the Raman spectra and the micrograph of the wear track corresponded. In the wear track (arrow1) mostly no Raman active phase was detected, only a weak MoS₂ peak was identified in the specific area. At the location of arrow2, fine debris were adhered to the wear track and smeared during sliding of the counterface. Chemical analysis was conducted in the area of arrow2, indicating the peaks of NiO and a relatively weak peak of Fe₃O₄. The dark patch (arrow3), similarly, exhibited the peaks of NiO, Fe₂O₃, and Fe₃O₄. The peak at around 856 cm⁻¹ was identified as CrO₃, where Fe and Cr were transferred from the worn countersphere. MoS₂ was not present in the wear debris adhering to the wear track (arrow2) and dark patches (oxide film) (arrow3). This was consistent with the results of EDX maps, i.e., most of the MoS₂ particles were smeared out during the sliding.



Fig. 5.10 Raman spectra of Ni-18MoS₂ coating at different locations in the wear track; arrow1: wear track, arrow2: wear debris adhering to the wear track, arrow3: dark patch.



Fig. 5.11 Raman spectra of Ni-24MoS₂ coating at different locations in the wear track; arrow1: pores, arrow2: wear track, arrow3: free wear debris.

Fig. 5.11 shows the micrographs of wear track and Raman analysis on different features of Ni-24MoS₂ coating. Different morphologies in the worn surface: pores (arrow1), fine main wear track (arrow2), and free wear debris (arrow3), were analyzed. Similar Raman spectra were obtained at three test locations, with the relatively weak Fe oxide peaks found on Ni-24MoS₂ coating. This is aligned with the previous results that nearly no Fe was found in EDX maps. Due to the low friction coefficient of the Ni-24MoS₂ coating and the relatively rough surface, the countersphere contacted the head of the nodules initially. Therefore, a cavity morphology was formed probably at the initial cycles and was not worn out during the sliding process (e.g., arrow 1). After the sliding wear test, the pores were filled with wear debris (arrow1). It can be assumed

that the wear debris moved driven by the counterpshere and fell into the pores when encountering the cavity morphology. During the sliding process, a part of the wear debris moved along the sliding direction and circulated between the two first bodies. The hypothesis can be checked by the Raman spectra of the pore which presented a chemical composition similar to that of the free wear debris particles (arrow3). Sharp peaks of MoS_2 were identified on each test spot of the wear track, indicating the retention of MoS_2 lubricant particles. Since the coating contained a higher amount of MoS_2 , the amounts of wear debris consisting of adequate MoS_2 particles were trapped in the wear track. The lubricants provided low shear stress and reduced the friction coefficient. This facilitated the reservation of MoS_2 in the wear track. Nearly no debris was ejected out of the wear track; instead, these fine particles containing MoS_2 were compacted together on the wear track during the sliding process.

5.2.3 Counterface analysis



Fig. 5.12 (a) SE, and (b) BSE image of counterface mating with Ni-18MoS₂ coating and EDX maps of the rectangle in (b), arrow1 indicates the wear scar.



Fig. 5.13 (a) SE, and (b) BSE image of counterface mating with Ni-24MoS₂ coating and EDX maps of the rectangle in (b), arrow2 indicates the transfer film.

The micrographs of the counterface mating with Ni-18MoS₂ coating after 1000 cycles test are shown in Fig. 5.12. A bright contrast patch was observed on the worn surface, surrounded by wear debris. To understand the distribution of different elements of the transferred material, EDX maps were produced on the worn counterface. The presence of coating materials (Ni and Mo) on the worn surface of countershpere provided evidence of the formation of transfer film. However, a circular wear scar was observed in the center of the counterface (arrow1), with the absence of Ni and Mo. The center of wear scar was a Fe-rich region, the transfer film was worn out during the sliding process and Fe was exposed to the contact. Due to the lack of lubricant phase in this unstable transfer film, the contact between countersphere and coating was "steel versus Ni-MoS₂", which contributed to a relatively high friction coefficient (Fig. 5.6).

For Ni-24MoS₂ coating, as shown in Fig. 5.13, the Ni and MoS₂ were transferred from the coating surface, similar to the case of Ni-18MoS₂. However, the morphology of the transfer film was different, with Fe mainly distributed at the periphery of the contact region. At the contact region, the fine transferred materials were compacted onto the worn counterface and smeared along the sliding direction. MoS₂ remained in the center of the wear scar (arrow2), which highly coincided with the area containing Ni. As sliding continued, the transferred Ni and MoS₂ developed a relatively stable transfer film. The appearance of the stable transfer film containing MoS₂ indicated that the contact mechanism was switched from "steel versus Ni-MoS₂" to "Ni-MoS₂ versus Ni-MoS₂ self-lubricating".
Chapter 6 Discussion

6.1 Fabrication of Ni-MoS₂ composite coatings

As reported in the studies of MoS₂ lubricated composite coatings, the tribological properties of coatings are strongly correlated to the bath composition and coatings' morphology.^{41, 99, 100} Anionic and cationic surfactants have been reported to contribute to the co-deposition of metal and reinforced particles, e.g., MoS₂^{33, 101}or SiC¹⁰⁶. In this project, two series of Ni-MoS₂ composite coatings with the addition of different surfactants were produced by electrodeposition, i.e., Ni-MoS₂-SDS (anionic surfactant) and Ni-MoS₂-CTAB (cationic surfactant).

In the study of Ni-MoS₂-SDS, the effect of particle concentration was investigated by adding 4 different concentrations of MoS₂ particles in the Watts bath, i.e., 0.5, 1.0, 1.5, 15 g/L. According to the works in literature, the production of metal-MoS₂ composite coatings with 0-2 g/L MoS₂ has been reported by the addition of anionic surfactant SDS.^{33, 109} In this work, however, due to the low bath concentration of MoS₂ particles (0.5-1.5 g/L) and the low plating efficiency, nearly no MoS₂ particles were successfully deposited into coatings. As increasing the MoS₂ content to 15 g/L, a coating containing 18 vol.% MoS₂ was produced. The increase in the volume fraction of MoS₂ in the coating led to significant changes in the surface morphology of the coatings.^{33, 34}

The plating temperature was adjusted in order to modify the particle fraction in the composite coatings. The effect of temperature was studied by adjusting the plating temperature to 30, 45, and 60 °C, based on the MoS₂ bath concentration of 15 g/L. The volume fraction of MoS₂ in the deposited coating was maximized at intermediate temperatures of 45 °C, which is in agreement with Wang's study.⁵¹ However, the increase in the MoS₂ volume percentage in coatings deteriorated the coating quality. As the maximum MoS₂ volume fraction was reached, the Ni-MoS₂ coating deposited at 45 °C became porous and fluffy. The higher temperature (60 °C) promoted the movement of Ni ions towards the cathode while limiting the deposition of MoS₂ particles and the adsorption of Ni on MoS₂.^{99, 116} This is evidenced by the slight decrease in the volume percentage of MoS₂.

Researchers have deposited composite coatings with different surfactants and either increases or

decreases in the percentage of reinforcing particles have been reported in the case of SiC codeposited coatings.¹⁰⁹⁻¹¹¹ To investigate the effect of the type of surfactant on Ni-MoS₂ coatings, the cationic surfactant CTAB was used in place of SDS. The addition of CTAB effectively improved the plating efficiency of MoS₂. The Ni-MoS₂-CTAB coating plated with the MoS₂ bath concentration of 1 g/L showed a similar surface roughness and MoS₂ volume fraction as the Ni-MoS₂-SDS coating plated in the bath containing 15 g/L MoS₂ particles. The Ni-MoS₂-CTAB coatings achieved a higher MoS₂ volume fraction. Analogous to the coating deposited with SDS, the dendritic microstructure of deposited materials correlated with the increment of MoS_2 was observed.^{34, 99} Therefore, the composite coatings exhibited a rough and loose morphology. The addition of TU further modified the morphology of the coatings but had a negative impact on the deposition process.^{98, 119} The inhibition of deposition by TU was evidenced by a reduction in the amount of MoS₂ deposited in the coating. However, the inhibitory effect of TU failed in the case of a considerable increase in the deposited reinforced particles, e.g., by increasing the plating time or MoS₂ concentration in the plating bath. By compromising the concentrations of TU and MoS₂, the coating approached a relatively dense microstructure with a slight decrease in the percentage of MoS₂ (but still around 20 vol.%).

6.2 Tribology of Ni and Ni-MoS₂ coatings

The sliding wear tests were performed on pure Ni coating, Ni-MoS₂-SDS coatings (Ni-2MoS₂ and Ni-16MoS₂,) and Ni-MoS₂-CTAB coatings (Ni-9MoS₂, Ni-18MoS₂, Ni-24MoS₂, and Ni-27MoS₂). The wear mechanisms of Ni and Ni-MoS₂ composite coatings are described in Fig. 6.1-6.3.

The pure Ni coating underwent plastic deformation during the sliding wear test and presented a high friction coefficient under the normal load of 1N and 5N. As shown in Fig. 6.1-left, the Ni coating had a flat surface. After the wear test, amounts of wear debris were observed in the wear track and the rest of them were ejected outside the wear track (Fig. 6.1-right). The wear debris abraded the surface of the coating and produced scoring marks (Fig. 5.2). Under a higher normal load of 5N, abrasion and scoring marks caused by wear debris were observed on the surface of the wear track. Furthermore, delamination occurred at the specific region in the wear track. The

coating materials were detached from the coating surface and left a concavity on the worn surface (Fig. 5.9). The Raman spectra showed that Fe was transferred from the countersphere to the worn surface, and therefore the "metal versus metal" contact appeared at the contact surface. (Fig. 5.7a, b, and Fig. 5.9). It was indicated that without the lubricants, the Ni coating showed mainly adhesion and third-body abrasive wear.



Fig. 6.1 The wear mechanism schematic of the pure Ni coating; left is the unworn coating, right is the coating after wear test; 440C steel ball contacts the surface of coatings, with an applied normal load shown in red arrow, SD indicates the sliding direction.

It has been proved that the introduction of lubricant MoS_2 can effectively reduce the friction coefficient. The friction coefficient of MoS_2 reinforced composite coatings can be reduced to a level of about one-fifth of that of unmodified coatings.^{39, 41-43, 87} So far, few researchers have explored the worn surface morphology and the mechanisms of electrodeposited Ni-MoS₂ coatings. The wear mechanism of the composite coatings associated with the MoS_2 content, the bath composition and the morphology of the coatings are discussed in detail.

The wear mechanisms of Ni-MoS₂-SDS coatings are shown in Fig. 6.2. Ni-2MoS₂ and Ni-16MoS₂ coatings presented different mechanisms, which were correlated to the difference in MoS₂ volume fraction. For the coating containing a low amount of MoS₂, the addition of MoS₂ provided lubricity and made the smoother worn surface (Fig. 5.3a) compared with the pure Ni coating (Fig. 5.2a). However, the low amounts of MoS₂ showed a limited effect on the tribological behavior, which resulted in a relatively high friction coefficient (Fig. 5.1). Similarly, a slight decrease in friction coefficient is reported in several works, with the MoS₂ in deposit around 1-4 wt.%.^{100, 148} The Ni-2MoS₂ (Fig. 6.2a-right) coating showed abrasive wear, as evidenced by the ploughing marks of the wear debris (Fig. 5.3a). The nodules on the coating were worn out and the wear debris were generated. Driven by the countersphere, the wear debris abraded the wear track surface and leave the fine furrows.¹⁴⁸ After the test (Fig. 6.2a-right), a part of the wear debris remained in the wear track and others were pulled out, which was proved by the pileup along the wear track (Fig. 5.3c). Raman analysis showed that the surface of the wear track was predominantly NiO and Fe₃O₄. Fe transferred from the countersphere onto the wear track surface (Fig. 6.2a-right, Fig. 5.3a, b and Fig.5.4b). Due to the absence of MoS₂ remaining in the wear track, the Ni-2MoS₂ coating was subject to adhesion and third-body abrasive wear under the metallic contact (steel versus steel) between the coating surface and the countersphere.



Fig. 6.2 The wear mechanism schematics of the Ni-MoS₂-SDS coatings: (a) Ni-2MoS₂, (b) Ni-16MoS₂ coating; left is the unworn coating, right is the coating after wear test; 440C steel ball contacts the surface of coatings, with an applied normal load shown in red arrow, SD indicates the sliding direction.

In the case of Ni-16MoS₂ coating, it showed a constant low friction coefficient throughout the sliding wear test compared with Ni-2MoS₂ (Fig. 5.1). According to the works in literature, lower friction coefficients have tended to be found in composite coatings containing large amounts of MoS₂, but the negative effect on microstructure caused by the conductivity of MoS₂ deteriorated the wear resistance of the coatings.^{33, 34} However, in the Ni-16MoS₂ coating, only minimal wear occurred on the top surface of the coating. This could be explained by the significant increase in MoS₂ incorporated in the coating (Fig. 4.3 and Table 4.1). The large amount of MoS₂ provided easy shear, meanwhile, the Ni-16MoS₂ coating exhibited a porous structure, with a high surface roughness (Fig. 4.3f and Fig. 6.2b-left). The presence of the nodules decreased the contact area and further reduced friction.⁹⁹ After the sliding wear test, the counterface was rich in MoS₂ which was evidenced by Raman spectra (Fig. 5.5b). The lubricating tribofilm was formed on the rough surface and prevented the third-body abrasion (Fig. 6.2b-right). This reduced the plastic deformation on the coating surface and therefore only a small amount of coating material was removed, as evidenced by the fact that no debris was observed either on the surface of the wear track or ejected out of the wear track (Fig. 6.2b-right and Fig. 5.5a). As a result, the MoS₂-rich lubricating film maintained a low and constant friction coefficient.

In terms of Ni-MoS₂-CTAB coatings, the friction coefficient and wear behavior are related to the MoS₂ volume fraction and the retention ability of MoS₂. Fig. 6.3 describes the wear mechanisms of three Ni-MoS₂-CTAB coatings. Ni-9MoS₂ showed a nodular structure, with the MoS₂ concentrated mainly on the head of nodules (Fig. 6.3a-left and Fig. 4.5b). As the sliding wear test proceeded, the plastic deformation occurred on the nodules, causing the embedded MoS₂ to be pulled out of the wear track, and the ejected wear debris were observed on the side of the wear track (Fig. 6.3a-right and Fig. 5.7c). Though the coating contained a higher amount of lubricant, the negative influence of the microstructure on the tribological behavior was dominant, hence the coating underwent adhesive wear and presented a high coefficient of friction.⁸⁷ Meanwhile, the adhesive transfer of Fe occurred, and tribo-oxidations of Fe and Ni were presented on the wear track surface. A similar phenomenon of the Fe transformation was observed in He's work and was confirmed by a friction coefficient close to that of "steel against steel".⁹⁴ This coincided with the trend of its friction coefficient curve (Fig. 5.6), the rapid increase of which corresponded to

the "MoS₂ worn-out stage"; the fluctuation at a high level was associated with the adhesion wear (Fig. 5.7d).

A higher amount of MoS_2 in Ni-18MoS_2 coating reduced the friction. Similar to Ni-16MoS_2 coating (deposited with SDS), Ni-18MoS₂ coating exhibited high surface roughness. Chen reported a low and stable friction coefficient, although the coating came with a rough surface.³⁴ However, in terms of Ni-18MoS₂ coating, a linear increase in the friction coefficient revealed the failure in the lubricating properties of the composite coating. The Ni-18MoS₂ coating showed a dendritic nodular structure, in which the majority of the MoS₂ contained in the coating was concentrated (Fig. 6.3b-left and Fig. 4.5a). At the initial stage of the sliding test, the low contact area enabled the coating to achieve a low coefficient of friction.⁹⁹ The subsequent increase in the friction coefficient indicated that the loose structure was detrimental to the retention of MoS₂, and the dendrites were easy to smear.³⁴ Fragmented debris were generated and either maintained in the wear track or ejected out. The Ni-18MoS₂ coating was subject to third-body abrasive wear and presented the ploughing marks on the surface of the wear track (Fig. 6.3b-right and Fig. 5.8a and b). Tribo-oxidation films, consisting of Ni, Fe₂O₃, and Fe₃O₄, were observed in localized areas on the surface of the wear track (Fig. 6.3b-right and Fig. 5.10). The "MoS₂ smeared out" was revealed by Raman analysis, and this can be the explanation for the gradual increase in the friction coefficient (Fig. 5.10 and Fig. 5.6).

Lower friction coefficients have been observed in coatings with higher lubricant content, however, high wear has also been reported due to the introduction of the soft phase (MoS_2) .^{31, 54, 87} In contrast, the Ni-24MoS₂ coating (Ni-27MoS₂ is similar) presented a good retention capacity of MoS₂, correlated to the high MoS₂ volume percentage and the relatively dense structure with elongated nodules (Fig. 6.3c-left and Fig. 4.7a). With a comparable lubricant content, coatings with a lower roughness could achieve a more stable friction coefficient.¹⁰⁰ The leveled nodules and the gap (or void) between nodules in Ni-24MoS₂ coating were conducive to the preservation of MoS₂ particles (Fig. 6.3c-left). The head of nodules fractured during the sliding test, and the fragmented wear particles were observed in the wear track (Fig. 5.8e), however, nearly no wear debris was ejected out of the wear track (Fig. 6.3c-right and Fig. 5.8d). The wear debris composed of Ni and MoS₂ filled in the voids between nodules. Those particles were compacted during the reciprocating sliding process and preserved the lubricants in the wear track. MoS₂

reduced the third-body abrasion caused by wear debris, which resulted in a smooth wear track (Fig. 6.3c-right and Fig. 5.8d). Meanwhile, a compact transfer film of Ni and MoS₂ was developed on the countersphere (Fig. 5.13). The well-established transfer film could prevent the metallic contact between the coating and countersphere.^{29, 100, 146} The third body behavior, i.e., the retention and circuit of wear debris and the development of transfer film facilitated the retention of lubricant.^{30, 65} The "Ni-MoS₂ versus Ni-MoS₂" contact on the counterface ensured the endurance of the low friction coefficient throughout the sliding test.



Fig. 6.3 The wear mechanism schematics of the Ni-MoS₂-CTAB coatings: (a) Ni-9MoS₂, (b) Ni-18MoS₂, (c) Ni-24MoS₂ coating; left is the unworn coating, right is the coating after wear test; 440C steel ball contacts the surface of coatings, with an applied normal load shown in red arrow, SD indicates the sliding direction.

MoS₂ can effectively decrease the friction coefficient in the initial stage of wear since the friction coefficient of all Ni-MoS₂ coatings started at a low value (Fig. 5.1 and Fig. 5.6). However, for all the Ni-MoS₂ coatings, the lubricant particles and Ni matrix was bonded mechanically, and particles were not always tightly embedded in the matrix. The wear debris were easy to be produced during the sliding test and caused third-body abrasive wear. The morphology of the coating and the content of lubricant particles both affected the friction behavior. For the coatings containing low MoS₂ content, MoS₂ can provide limited lubricity manifested as reduced friction coefficient oscillations, but no obvious decrease in the friction coefficient value (Ni-2MoS₂ and Ni-9MoS₂). Even if the coating contained a higher volume fraction of MoS_2 , without a uniform and dense structure, MoS₂ was still susceptible to being worn out (Ni-18MoS₂). With the absence of MoS₂, the materials with higher shear strength tended to be ejected out of the wear track¹³⁷, and the wear debris composed of metals abraded and grooved the surface of the coating. This was evidenced by the continuously increasing friction coefficient in the Ni-18MoS₂ coatings (Fig. 5.6). For the coatings exhibiting adequate MoS_2 reinforcement as well as the flattened and dense nodules (Ni-24MoS₂), the wear caused by third body abrasion can be mitigated due to the presence of lubricant in the wear debris. Large amounts of wear debris containing MoS₂ were engaged in the circulation during the test, and the transfer film developed on the contact surface modified the metallic contact and provided low shear strength. Therefore, the coating showed a low and consistent friction coefficient and good wear resistance.

Chapter 7 Conclusions and future works

7.1 Conclusions

- 1. The Ni-MoS₂ composite coatings with two types of surfactants (SDS and CTAB) have been successfully developed by direct current electrodeposition. The MoS₂ volume fraction in coatings was increased by the MoS₂ concentration in the Watts bath. The increase in bath temperature exhibited a non-monotonic effect on the MoS₂ volume fraction in the coatings. The composite coating plated at 45 °C showed the highest MoS₂ volume fraction, after which the MoS₂ depositing process was limited due to the particle agglomeration caused by the elevated plating temperature.
- 2. The addition of CTAB increased the plating efficiency of MoS₂. The volume fraction of MoS₂ achieved in this coating was similar to that of the coating plated with SDS, but the concentration of MoS₂ in the plating solution was only about 1/10 of that in the Ni-MoS₂-SDS coating. The coating surface roughness was controlled by TU. However, the addition of TU showed a restriction on the plating process and was regulated with MoS₂ deposition.
- 3. The friction coefficients of Ni-MoS₂ composite coatings were reduced compared with pure Ni coating, which was attributed to the incorporation of easily sheared MoS₂. As the volume fraction of the solid lubricant increased, the composite coating showed a lower friction coefficient. The friction coefficients of composite coatings depended on the preservation of MoS₂ in the wear track. The MoS₂ retained in the wear track reduced the plastic deformation and the third-body abrasive wear of coatings. Ni-16MoS₂-SDS and Ni-24MoS₂-CTAB coatings possessed high MoS₂ retention and therefore presented a consistently low friction coefficient.
- 4. For the Ni-18MoS₂-CTAB and Ni-24MoS₂-CTAB coatings, the transfer films composed of Ni and MoS₂ were developed on the counterface. The Ni-24MoS₂ coating showed a better retention ability of MoS₂ corresponding to the morphology of the coating. The

formation of transfer film delayed the increase in the friction coefficient. The lower friction coefficient was attributed to the "Ni-MoS₂ versus Ni-MoS₂" contact on the counterface.

7.2 Future works

- 1. Ni-24MoS₂-CTAB coating provided a low friction coefficient; however, the friction coefficient value still increased slightly in the last few hundred cycles. There is a certain amount of lubricant loss in the sliding wear test. Therefore, the self-lubrication properties of Ni-24MoS₂-CTAB coating need to be optimized. The retention capacity of MoS₂ could be further studied and the transfer film formed during the wear process may need further characterization.
- 2. The Ni-MoS₂ coatings in this thesis exhibited high surface roughness, caused by the high electrical conductivity of MoS₂. The pulse current electrodeposition can be used to reduce the surface roughness and optimized the morphology of composite coatings. The tribological behavior of composite coatings obtained by pulse current electrodeposition can be investigated and compared with the coatings deposited by direct current.

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