

MoS₂ coated with Al₂O₃ for Ni–MoS₂/Al₂O₃ composite coatings by pulse electrodeposition[☆]

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Abstract

The MoS₂ powders were coated with Al₂O₃ (5 wt.%) through controlling hydrolysis of Al(NO₃)₃·9H₂O. MoS₂ powder coated with Al₂O₃ was written as MoS₂/Al₂O₃ hereinafter. MoS₂/Al₂O₃ powders were put into Ni plating electrolyte bath. Cetyltrimethylammonium bromide (CTAB) — the surfactant was also put into the bath. The experiment proves that MoS₂/Al₂O₃ particles were absorbed onto the Ni plate. The amount of MoS₂/Al₂O₃ deposited on Ni plate rises with the increasing concentration of MoS₂/Al₂O₃ in the bath. The microhardness, micro-surface, phase and the tribological property of the MoS₂/Al₂O₃ multi-plating coating were measured and analyzed. The performances of microhardness and wear resistance of the Ni–MoS₂/Al₂O₃ composite are better than those of Ni–MoS₂ composite.

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1. Introduction

The combination of different materials could produce the improved mechanical, chemical, electrical, magnetic and optical properties. However, these properties depend upon the distribution of phase and the composition of basic phase in the composite.

One type of composite in which ceramic particles were distributed in the metal matrix has been applied widely, especially in machinery for anti-wear and anti-friction. Various cationic surfactants had been added into the plating bath in order to increase the ceramic particles in the composite since the ceramic particles in a particle-dispersed metal matrix composite can share most of the load.

Electroplating has typically been used in the surface treatment industry [1]. It is reported that the composites with ultra-fine particles have been made successfully over the past decades. These composites are combined with metallic powders,

silicon carbide powders, oxide powders, diamond powders, polymers and the multi-plating of metal or alloy. The structures and properties of the mentioned composites have been studied and confirmed [2–4].

It is well known that pulse electroplating is more effective than the traditional DC electroplating to make composite and alloy due to its independent, controllable parameters and the high instant current [5]. The structure of materials or alloys can be changed through adjusting the pulse current and the properties of materials or alloys can be controlled or improved accordingly. Electroplating is one of the most important surfaces coating technology. When there are particles among the plating bath, the particles will be absorbed onto the plate. Such kind of coating plate is called composite plating. Many researchers have confirmed that the multi coating possess of many specific properties due to the different particles in the coating [6–12].

It has been reported that low-friction composite materials such as Ni-polyethylene [13], graphite-brass [14], Ni-PTFE [15], graphite-bronze [16], Ni-P-carbon-nanotube [17] and good wear resistance composite materials such as Ni–Al₂O₃ [18], Ni–P–SiC [19], Ni–ZrO₂ [20] can be obtained via the electroplating technique.

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Table 1
Bath composition and operating conditions

Composition and operating conditions	
Nickel sulfate	330 g/l
Nickel chloride	10 g/l
Boric acid	40 g/l
Cetyltrimethylammonium bromide (CTAB)	50 ppm/l
MoS ₂ or MoS ₂ /Al ₂ O ₃ respectively	0, 5, 15, 20, 25, 30 g/l
Temperature	60 °C
PH	4.5
Pulse current condition density	15 Adm ⁻²
Duty cycle	2/3
Frequency	50 Hz
Magnetic stirring speed	600 rpm

MoS₂ has the specific property of self-lubricate. Ni–MoS₂ composite plating is obtained by adding MoS₂ particles into the Ni bath. Such kind of composite plating is called functional plating in industry. Ni–Al₂O₃ composite plating can be used as anti-friction material due to the good harness performance of Al₂O₃. The composite plating will have self-lubricate and anti-friction properties if MoS₂/Al₂O₃ was absorbed onto the plate. In this experiment, we will show you the procedure of making Ni–MoS₂/Al₂O₃ composite plating and analyze its friction property.

2. Experiment

Commercial MoS₂ powder was used in this study. The MoS₂ powder was suspended in a mixed mineral acid (H₂SO₄+HCl),

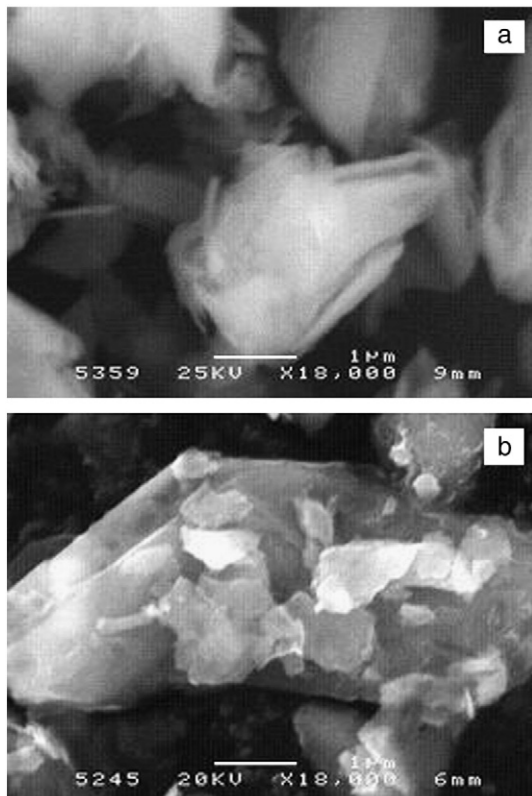


Fig. 1. SEM of powder: (a) pristine MoS₂ powder (b) 5 wt.% Al₂O₃ coated MoS₂.

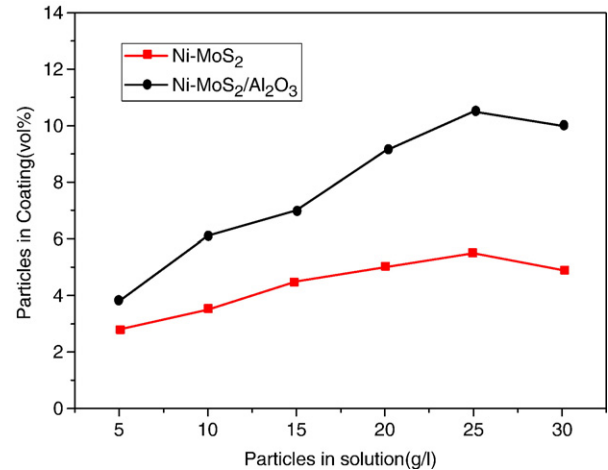


Fig. 2. Comparison of Ni–MoS₂ and Ni–MoS₂/Al₂O₃ coating.

and the acid solution was refluxed for 4 h. The MoS₂ powder treated with the mineral acid was repeatedly washed with water to remove the acid solution, and then the washed MoS₂ powder was dried in a drying oven. The MoS₂ powder 40 g, was suspended in 500 ml distilled water for experiments. Sodium acetate which was used to amortize pH of solution was added to the solution. And pH of the solution was maintained at 6. The beaker was set in a heating mantle on a magnetic stirrer to avoid settling of the MoS₂ powders during the process and subsequently by ultrasonic agitation for 20 min just prior to coating. The solution containing MoS₂ powder was heated at 80± °C for experiments. 32 g of Al(NO₃)₃·9H₂O was dissolved in 5 ml distilled water and added to the MoS₂ solution slowly. After completion of the experiment, the powder was collected by filtering and washed with hot distilled water repeatedly until the supernatant showed neutral pH. And then the powder was washed with ethanol and was collected by filtering. The MoS₂ powder treated with the Al(NO₃)₃·9H₂O reagent was heated at 300 °C for 3 h.

The MoS₂ and MoS₂/Al₂O₃ powders respectively, were suspended in the plating electrolyte bath, and CTAB, which is a surfactant. Surfactant CTAB was added to reduce the particles particle agglomeration [21]. Additionally, the adsorption of surfactant CTAB on the particles has been proven to enhance the adhesion force to the cathode, enabling larger particles to be embedded [21]. The plating electrolyte was a nickel sulfate bath. The compositions and the range of experimental operating conditions are shown in Table 1. A nickel plate of 120 mm×60 mm was used as the anode, and a low carbon steel disk of about half

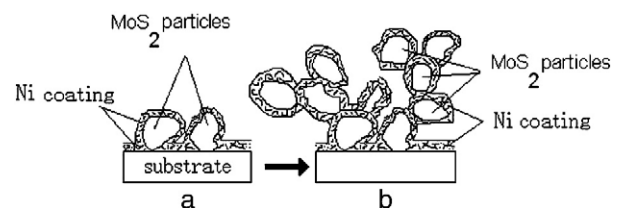


Fig. 3. Schematic of the diacritic growth of the Ni–MoS₂ coating. (a) MoS₂ was incorporated into the deposited Ni. (b) MoS₂ was adsorbed onto the protruding of the MoS₂ resulting in dendrite growth.

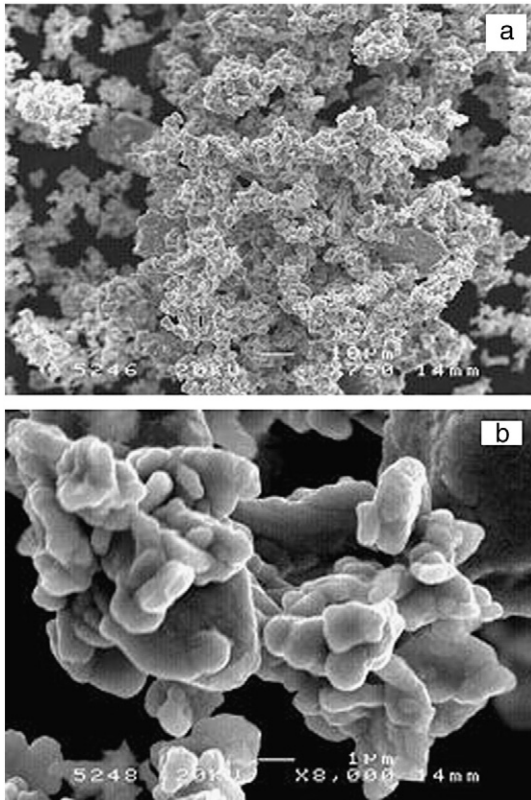


Fig. 4. SEM images of Ni-MoS₂ composites after separation from the coating.

the area of the anode was used as the cathode. The electrolyte bath was stirred by a magnetic stirrer, and heated to plating temperature at 60 °C. The magnetic stirring rate was kept constantly at 600 rpm. Each plating solution was mixed by magnetic stirring for 12 h, and subsequently by ultrasonic agitation for 20 min just prior to electroplating. The deposition condition was shown in Table 1. The PC plating had a peak current density of 15Adm⁻². The duty cycle (i.e. pulse on time divided by pulse on time plus pulse off time) was 2/3, and the frequency was 50 Hz. The composite coatings were cleaned by ultrasonic in order to remove the loosely absorbed particles on the surface after electrodeposition.

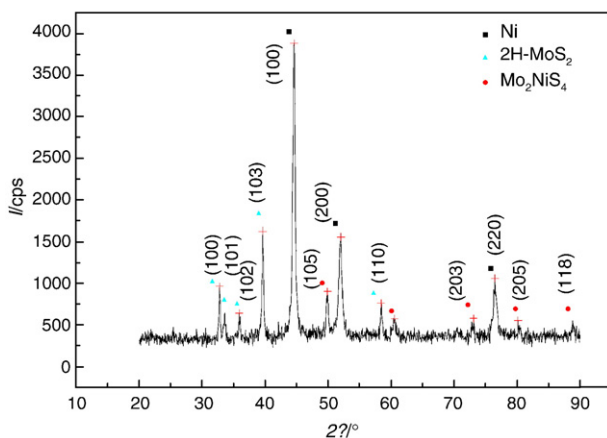


Fig. 5. The XRD pattern of MoS₂ filtered from the plating solution after electrodeposition.

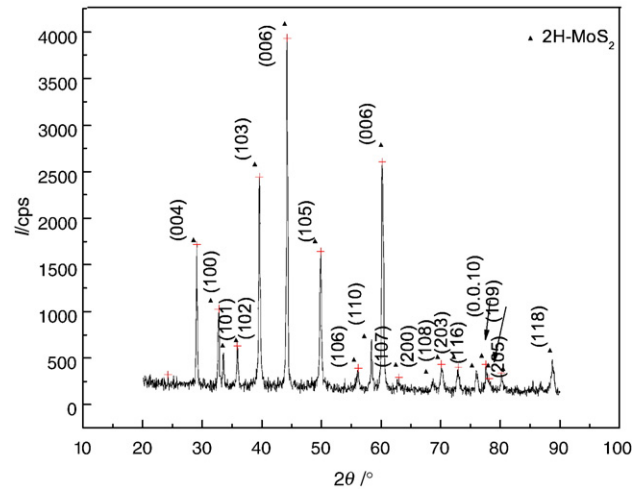


Fig. 6. The XRD pattern of MoS₂/Al₂O₃ filtered from the plating solution after electrodeposition.

The morphology of MoS₂/Al₂O₃ powder and the deposited plating were characterized by SEM. The volume fraction of particles in composite coatings (denoted by V_p) was determined by gravimetric analysis. The phase of coating was determined by XRD method. The hardness of the composite coatings, which were about 50 μm thick, was measured on a Vickers' microhardness instrument at an applied load of 200 g for 10 s. Measurements were conducted five times on each sample and the results were averaged.

The wear tests were performed on circumrotating ball-on-disk MG2000 high-temperature tribometer at room temperature with a relative humidity of 65–85% under dry sliding wear conditions. The coating was deposited on steel disk (d: 48 mm×8 mm) and was used as a wearing sample. A ceramic ball (Ø 12.7 mm, Ra 0.2 μm), which was made of Al₂O₃, was used as the counter body. The ceramic ball was sliding on the disk and the diameter of wear scar was 31.4 mm. Dry sliding wear tests were performed under a load of 20 N with a sliding speed of 355 mm s⁻¹. Wear rates of all coatings were calculated on the basis of the weight loss. The wear resistance of the composite coatings was characterized by weight loss after a sliding distance of 1000 m. It was obtained by

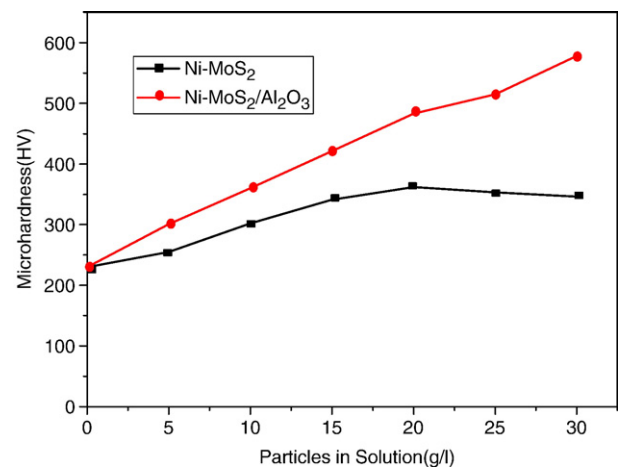


Fig. 7. The relationship between microhardness and particles in solution.

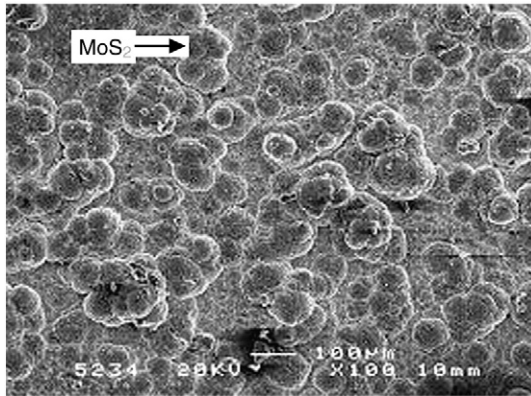


Fig. 8. SEM images of the surface of composite coating containing approximately 3 vol.% MoS₂.

weighing the specimen before and after each cycle of wear test. A balance with a precision of 0.1 mg was used to weigh the wearing mass loss. The samples were cleaned with acetone after each test. The morphology of wear scar was characterized by an optical microscope.

3. Results and discussion

3.1. MoS₂ coated with Al₂O₃

Fig. 1 a and b shows the SEM micrographs of the pristine MoS₂ and 5 wt.% Al₂O₃ coated MoS₂ powder, respectively. From Fig. 1 a and b, it was observed that the surface of the pristine particles is distinctly changed upon coated particles. The increase in brightness of the material observed for the coated sample compared to the pristine sample is associated with the accumulation of charge on the non-conducting coating material (Al₂O₃) as the electron beam impinges on it.

3.2. Content of the particles embedded in coating

Fig. 2 shows the content of MoS₂ and MoS₂/Al₂O₃ particles incorporated into the Ni composite coatings as a function of the bath in the PC plating. The figure shows that the MoS₂/Al₂O₃ content in the deposit rises sharply with increasing MoS₂/Al₂O₃

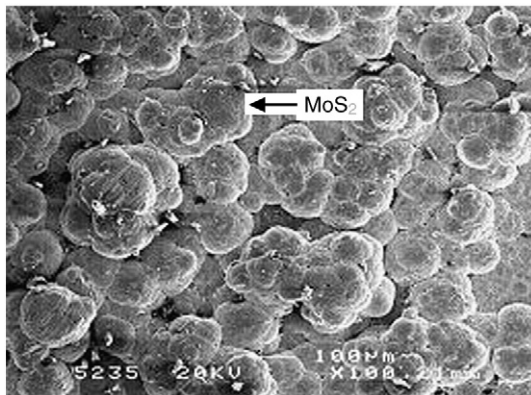


Fig. 9. SEM images of the surface of composite coating containing approximately 5 vol.% MoS₂.

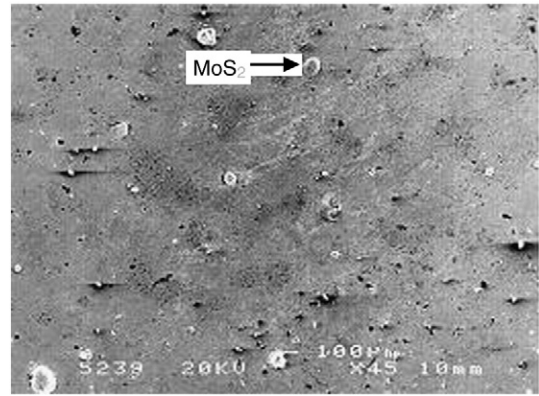


Fig. 10. Surface of composite coating containing approximately 4 vol.% MoS₂/Al₂O₃.

concentration in the bath at PC plating. Additionally, at the same average current density, the MoS₂/Al₂O₃ content in the coatings is higher than the content of MoS₂ particles. When the MoS₂ particles in the solution reach to 25 g/l, MoS₂ content in coating reaches to 6 vol.%, which is in agreement with Straffellini [22]. But MoS₂/Al₂O₃ content in coating reaches to 12 vol.%, when the MoS₂/Al₂O₃ particles in the solution reach to 25 g/l. This can be attributed to the dendrite growth structure that makes MoS₂ particles hard to be incorporated in Ni electroplating.

The proposed dendrite growth process of the Ni-deposited MoS₂ is sketched in Fig. 3. At first, MoS₂ are incorporated into the deposited Ni film (Fig. 3 (a)). Because the MoS₂ possess high electrical conductivity, Ni is electrodeposited both on the substrate and on the incorporated MoS₂; electrodeposited Ni particles on the outer MoS₂ surface grew to surround the MoS₂. The protruding ends of the MoS₂ incorporated into electrodeposited Ni have lower resistance than those in other sites and the substrate. Therefore, Ni²⁺ ions easily accept electrons and electrodeposits selectively on the ends of the MoS₂. At the same time, MoS₂ more easily adsorbed on protruding ends of the MoS₂ incorporated into electrodeposited Ni than the substrate, resulting in a dendrite growth of Ni–MoS₂ composite (Fig. 3 (b)).

Fig. 4 shows the appearance of the electrodeposits separated from the cathode by ultrasonic irradiation in acetone bath. The separated electrodeposits were powdery (Fig. 4) and the MoS₂

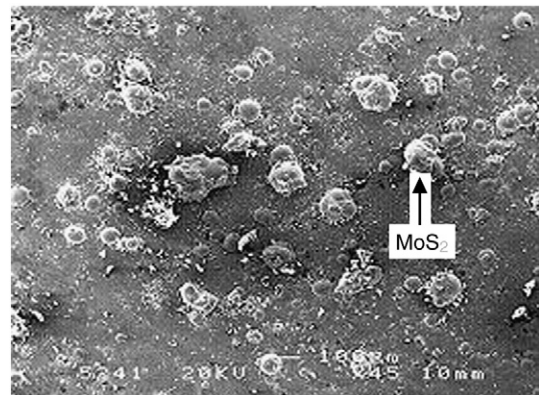


Fig. 11. Surface of composite coating containing approximately 11 vol.% MoS₂/Al₂O₃.

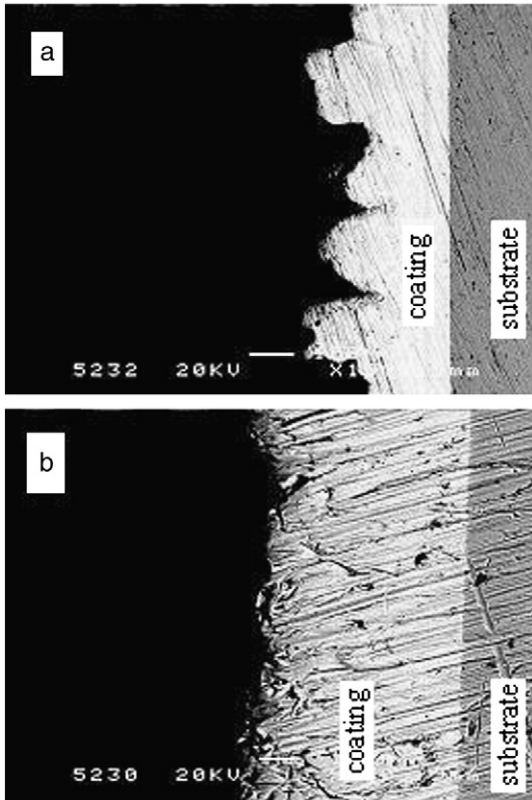


Fig. 12. Cross-sectional profiles (a) Ni–MoS₂ coating and (b) Ni–MoS₂/Al₂O₃.

securely incorporated or coated by the electrodeposited Ni, resulting in an MoS₂ powder hard to be incorporated in the Ni deposited. Most of the Ni–MoS₂ composites were separated from the cathode, only a little of the MoS₂ particles firmly adhered to the deposited Ni film remained on the substrate.

Figs. 5 and 6 show the XRD pattern of the powder which was collected by filtering from the plating solution after electrodeposited and washed with hot distilled water. Fig. 5 shows that the MoS₂ powder has been coated with nickel and forms a new Mo₂NiS₄ phase. Fig. 6 shows that the MoS₂/Al₂O₃ powder has

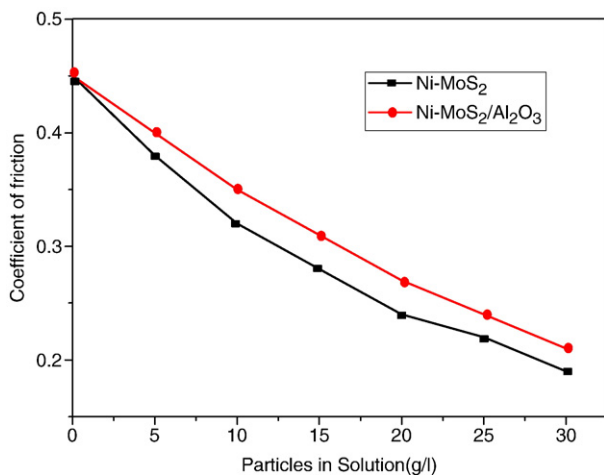


Fig. 13. The effect of particles in the solution on the friction coefficient of the coating.

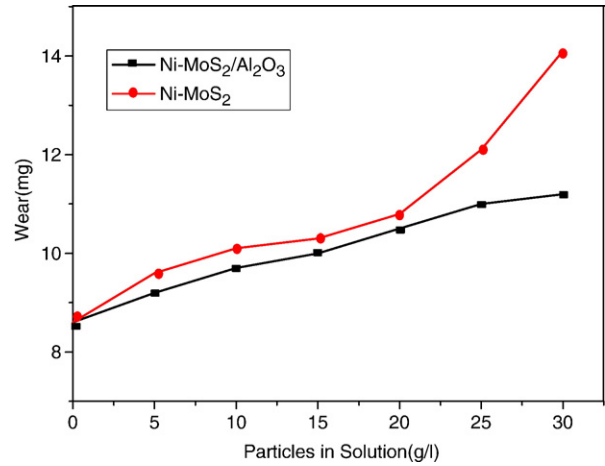


Fig. 14. The effect of particles in the solution on wear loss of the coating.

not been coated with nickel or forms the Mo₂NiS₄ phase. This is because the MoS₂ was coated with Al₂O₃. But the absence of diffraction patterns corresponding to Al₂O₃ may be due to a thin coating layer on the surface of the core material [23] and the Al₂O₃ thin coating layer on the surface of the core material is amorphous [24].

The MoS₂/Al₂O₃ possesses low electrical conductivity, this can be attributed to the dielectric Al₂O₃ particles coated onto the MoS₂ surface, Ni only electrodeposited on the substrate but not electrodeposited on the MoS₂/Al₂O₃, avoiding the dendrite growth of Ni–MoS₂/Al₂O₃ composite. The MoS₂/Al₂O₃

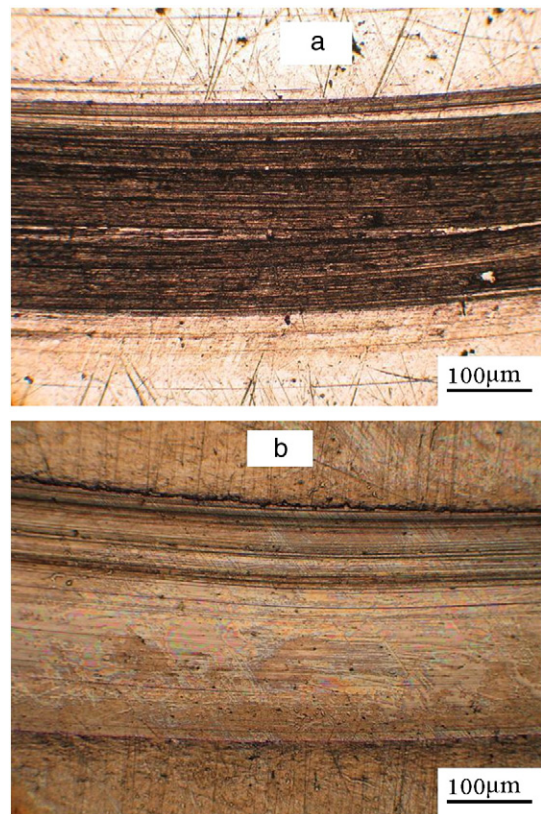


Fig. 15. Worn surface morphology of the deposit after a sliding distance of 1000 m (a) Ni–6 vol.% MoS₂/Al₂O₃ coating (b) Ni–6 vol.% MoS₂ coating.

particle can be incorporated in Ni electroplating more easily than the MoS₂ particle.

3.3. Microhardness

It is evident from Fig. 7 that the typical value for nickel is 230 VHN, microhardness increase with increasing concentration of the MoS₂ particles in the solution from 0 to 20 g/l, this can be attributed to the dispersion strengthening. But it decrease with an increase in the amount of MoS₂ from 20 g/l to 30 g/l, this can be attributed to the soft nature of the lubricating particles. On the other hand, microhardness increases with an increase concentration of the MoS₂/Al₂O₃ particles in the solution from 0 to 30 g/l. Due to the hard nature of the Al₂O₃ particles, microhardness of Ni–MoS₂/Al₂O₃ coating is higher than those of Ni–MoS₂ coating. The hardness of a plated metal depends upon many factors and the most important is the composition of the plating bath. The greater hardness is produced due to the dispersion hardening effect of the particles and also as a result of the fine-grained structure of the deposit. The hardening effect can be associated with the dispersion strengthening, where in the matrix carries the load and the particles impede the motion of dislocations.

3.4. Study of morphology

Figs. 8 and 9 show the morphology of the surface of Ni–MoS₂ coating containing approximately 3 vol.% of MoS₂ and 5 vol.% of MoS₂ respectively. Both morphologies of the Ni–3 vol.% MoS₂ and Ni–5 vol.% MoS₂ composite coatings are irregular, the protruding points are clearly visible on the surface with a homogeneous distribution. With MoS₂ content in bath increases, the morphology of surface is more irregular. The micro MoS₂ particles show the presence and distribution of MoS₂ particles which appear as protruding points in the metal matrix. Figs. 10 and 11 show surface of Ni–MoS₂/Al₂O₃ composite coating containing approximately 4 vol.% of MoS₂/Al₂O₃ and 11 vol.% of MoS₂/Al₂O₃ respectively. The morphology of the Ni–4 vol.% MoS₂/Al₂O₃ composite coating is uniform and the deposit has a regular surface. But the morphology of the Ni–11 vol.% MoS₂/Al₂O₃ composite coating is irregular and the protruding points are clearly visible on the surface when MoS₂/Al₂O₃ content in bath increases. Compare Fig. 10 with Fig. 11, the morphology of the Ni–4 vol.% MoS₂/Al₂O₃ is more regular and smooth than those of Ni–4 vol.% MoS₂ coating. The morphology presented allows comparison between the Ni–MoS₂ (Figs. 8 and 9) composite coating and the Ni–MoS₂/Al₂O₃ composite coating (Figs. 10 and 11) at different content of the particles. The morphology of the Ni–MoS₂/Al₂O₃ composite coating (Figs. 10 and 11) is uniform. And the surface of Ni–4 vol.% MoS₂/Al₂O₃ composite coating is much smoother than those of the Ni–11 vol.% MoS₂/Al₂O₃ coating.

Fig. 12 (a) illustrates a cross-section of the Ni–MoS₂ deposit coating. It shows the dendritic growth of Ni–MoS₂ coating. MoS₂ particles that were added to the bath collided to the cathode and conditions for growth are dendritic. Fig. 12 (b) illustrates a cross-section of the Ni–MoS₂/Al₂O₃ deposit

coating. It shows the uniform thickness and completely smooth surface of Ni–MoS₂/Al₂O₃ coating.

3.5. Tribological properties

Figs. 13 and 14 indicate the tribology behavior both of the Ni–MoS₂ and Ni–MoS₂/Al₂O₃ coating. An increase in the amount of both MoS₂ and MoS₂/Al₂O₃ particles in the solution led to a decrease of the coefficient of friction (see Fig. 13), and increase weight loss in wear test (see Fig. 14). Both MoS₂ and MoS₂/Al₂O₃ particles concentration in solution reaches to 30 g/l, friction coefficient of Ni–MoS₂ coating lower than that of Ni–MoS₂/Al₂O₃ coating. The MoS₂ particles concentration in solution reaches to 20 g/l, weight loss increase sharply with the increase of concentration. This can be attributed to the soft nature of the MoS₂ particles. By contrast, weight loss increases slowly when the MoS₂/Al₂O₃ particles increase, due to the hard nature of the Al₂O₃ particles which were coated on the MoS₂ particles. The wear morphology is shown in Fig. 15 a and b, which demonstrates that the worn scars of the Ni–6 vol.% MoS₂/Al₂O₃ coating are much shallower and the surface is smoother than the Ni–6 vol.% MoS₂ coating.

4. Conclusions

The MoS₂ powders were coated with 5 wt.% of Al₂O₃ successfully through controlling the hydrolysis of Al(NO₃)₃·9H₂O aqueous solution. Ni–MoS₂/Al₂O₃ composite electroplating was synthesized by pulse current electroplating technique. The MoS₂/Al₂O₃ particle can be incorporated in Ni electroplating more easily than the MoS₂ particle. Morphology of deposits obtained from Ni–MoS₂ coating is irregular, because the MoS₂ that was coated with nickel appears as protruding points. The introduction of MoS₂ particles into the solution caused dendritic growth. The deposit with MoS₂/Al₂O₃ particles has a smooth surface and uniform thickness. The microhardness and wear resistance of the Ni–MoS₂/Al₂O₃ composite were better than those of Ni–MoS₂ deposits.

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