Tribological behavior of sputter-deposited MoS_X/Ni coatings

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ABSTRACT

In this investigation, MoS_x/Ni composite coatings with Ni contents varying from 0 to 23 at. % were deposited onto steel substrate using a DC magnetron sputter process. The MoS_2/Ni ratio in the coatings was controlled by sputtering the composite targets. The composition, microstructure, and mechanical properties of the coatings were explored using an energy dispersive analysis of X-ray (EDX), X-ray diffraction (XRD), nano indentation, and scratch techniques. The tribological behavior of the coatings was investigated using the pin-on-disc test at room temperature. The results showed that adding Ni to MoS_2 coatings improved their adhesion to steel substrate and hardness as well as increased the wear performance. The films exhibited a steady state friction coefficient from 0.13 to 0.19 and the main wear mechanisms of the MoS_x/Ni coating in air were abrasive, adhesive, and oxidation wear.

1-Introduction

Sputtered MoS_2 coating has been widely used in the mechanical lubrication and the space lubricating technology [1].

Although, pure sputtered MoS_2 coating generally exhibit excellent friction and wear resistance and extended lifetime in vacuum or inert gas atmospheres, its tribological properties degrade in the presence of humidity or oxygen and high temperature environments, thereby limiting their technological applications in the Earth's atmosphere. MoS_2 generally exhibits the loose structure, low hardness and relatively high chemical reaction activity ,resulting in the Reduced wear and corrosion resistance [2, 3].

According to the recent research findings, co-sputtering MoS_2 with metal resulted in better ambient-condition tribological properties than that without sputtering metal [4].

Some of metals studied include Au, Zr, Cu, Ag, Nb, W, Ti, Ta, Cr, Al. Also mixed metal or ceramic were studied such as Mo_2N, TiAlN, TiN, WS_2, CrN or Sb_2O_3 [5-7].

It was demonstrated that co-sputtered coatings are denser, more adhesive and more oxidation-resistant than pure MoS_2 coating. These coatings showed good friction stability in ambient air with long-lasting wear durability.

Although the mechanical and tribological properties of MoS_2 with metal composite coatings have received extensive attention, it is necessary to determine the metal-doped content. In the present study the effect of adding Ni to MoS_2 contents on microstructure, mechanical properties and tribological behaviors in atmospheric environment was investigated.

2- Experimental

Samples of Ck45 (AISI 1045) plain carbon steel with a chemical composition of 0.15% C and 0.22% Si m were used as substrates.

The substrates were cleaned ultrasonically in acetone and methanol for 15 mins and

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successively rinsed with deionized water and blown with dry air.

The MoS_2 coating was fabricated in DC magnetron sputtering ion plating equipment (model DST3 – S). Prior to deposition, the chamber was pumped down to less than 3×10^{-5} Torr, and the substrates were cleaned in the argon plasma for 15 minutes. MoS_2 (purity 99.8%) and Ni (purity 99.99%) with 0, 5, 10, and 15 wt.% composite targets (50 mm diameter) fixed on a magnetron cathode were used. The composite targets were fabricated by ball milling the mixture of pure MoS_2 and Ni powders, followed by pressing the mixture under a pressure of 60 MPa in an Ar atmosphere at 850°C. After deposition, the characteristics of the coatings were evaluated by scanning electron microscopy (SEM) equipped with an energy dispersive spectroscope (EDS), atomic force microscopy (AFM, NanoScope II Version 5.12r2), X-ray diffraction (XRD, Philips X'Pert-Pro) with Cu Kα radiation. Micro hardness of the coatings was measured using a Nano test 550 nanoindenter equipped with a Berbovich diamond indenter (a three-sided pyramid), with the maximum indentation depth around 300 nm. For each sample, eight points were measured and the average hardness and standard deviation were obtained. The wear resistance and friction coefficient of samples (with dimensions of 10 mm × 10 mm × 8 mm) were investigated using a 'pin-on-disk' tester at the constant sliding speed (v=0.1 m/s) and normal load (W=2 N). The pin was made of AISI 52100 steel with diameter of 5 mm. The SEM and EDX point analysis were applied on the worn surfaces to determine wear mechanism.

3- Results and Discussion

The quantitative results of elemental analyses of coatings that were determined by EDS are presented in Table 1. Fig. 1 shows the stoichiometric ratio and Oxygen content of MoS_x/Ni composite coatings with different Ni content. Although the sputtered Target was a dense target of stoichiometric MoS_2, the deposited coatings were formed as nonstoichiometric MoS_x, which the value of x is in the range of 1.3 to 1.5. The reason of the decrease of the sulfur concentration is due to the difference of the sputtering yield of Mo and S. The sputter yield is the number of atoms ejected from the target per incident ion [8, 9]. It is also stated that the sulfur deficiency is caused by either the resputtering of sulfur atoms of the growing film though the impact of particles with high energy, or by the chemical reactions of sulfur with the residual atmosphere [9, 10].

The stoichiometric ratio and Oxygen content of MoS_x/Ni composite coatings with different Ni content are shown in Fig. 1. As can be seen with the increase of the Ni content, the Oxygen content decried and the stoichiometry ratios N_S/N_{Mo} changed from 1.1 to 1.4 . The Oxigen in the coatings probably was incorporated during the deposition as a contamination. Oxygen easily substitutes the sulfur deficient sites. Ni atoms moves into interstitial or substitution sites of MoS_2 during coating deposition and act as the barrier for oxygen diffusion, which lead to decrease of the oxygen content. also it contributes in the formation of stable MoS_2 [11].

Fig. 2 shows XRD pattern of pure MoS_X coating. In addition to the diffraction peak that arose from the substrate, peaks were evident at approximately 2θ from 14°, 32°, 33°, 35° and 39° for the pure MoS_2 coating, which was assigned respectively to the MoS_2 (002), (100), (101), (102), and (103) planes (according to JCPDS-ICDD card No 87-2416).

Table 1. Elemental composition of MoS_x/Ni coatings.

Coating	Elemental composition (at.%)				
	Ni	Fe	Mo	S	O
MoS_x	0	37	23	28	12
MoS_x/Ni 9 at.%	9	38	20	25	8
MoS_x/Ni 13 at.%	14	34	18	28	7
MoS_x/Ni 23 at.%	23	30	18	23	6

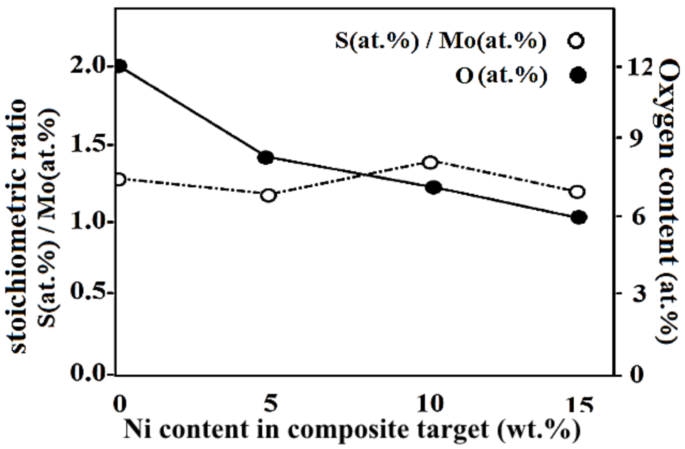


Fig. 1. The stoichiometric ratio and Oxygen content of MoS_x/Ni composite coatings with different Ni content in composite target.

Since there are very weak intensities of the peak after 60° in the MoS_X coating XRD pattern, XRD patterns of MoS_x/Ni coatings are reported only between 10° and 50° (fig. 3). XRD analyses of MoS_x/Ni coatings showed that the growth orientation of coatings depends strongly on the Ni content. With the increase of Ni content, the phase crystallite of the MoS_2-Ni composite coatings decreased, and the increased amorphous structure. When the Nickel content increases from about 14%, discrete atomic Nickel was detected.

Pursuant to chemical stability and crystallinity, The MoSx coatings are classified into three types: type I, type II and amorphous coatings. Type I films have randomly oriented basal planes, with a large proportion of the basal planes perpendicular to the substrate (edge plane orientation). Type II films have a parallel basal plane orientation. The MoS_x coatings with the basal planes parallel to the sliding direction not only supply good lubrication properties but are also more resistant to oxidation given that the edge sites are protected [12, 13]. MoS_x coating is further identified as random-oriented coating. From the Coatings XRD patterns it can be concluded that the Ni-Doped MoS_2 Composite Coatings are characterized by a very disordered microstructure consisting of randomly distributed. There is no clear evidence in the XRD patterns for existence of Ni sulphides or mixed Ni–Mo sulphides maybe due to the content of these phases too low to be detected and no considerable scattered intensity of Mo and Ni oxides were detected too.

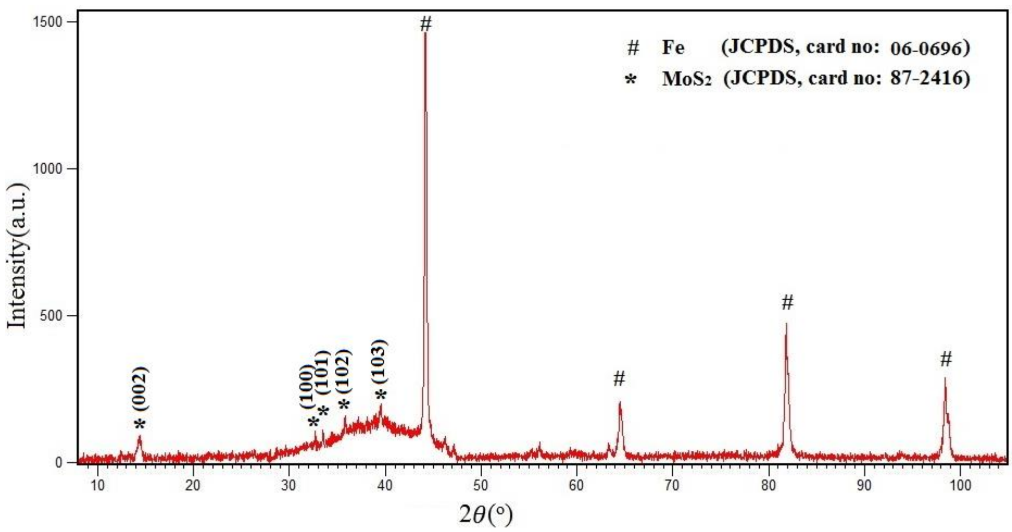


Fig. 2. XRD pattern of MoS_2 coating.

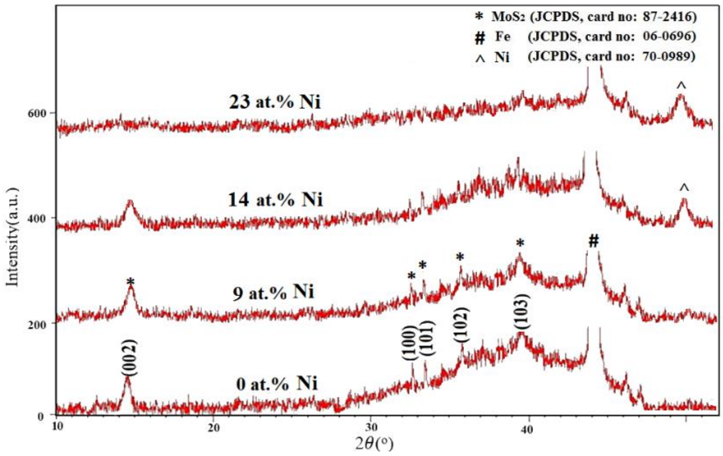


Fig. 3. XRD patterns of MoS_2/Ni composite coatings with different Ni content.

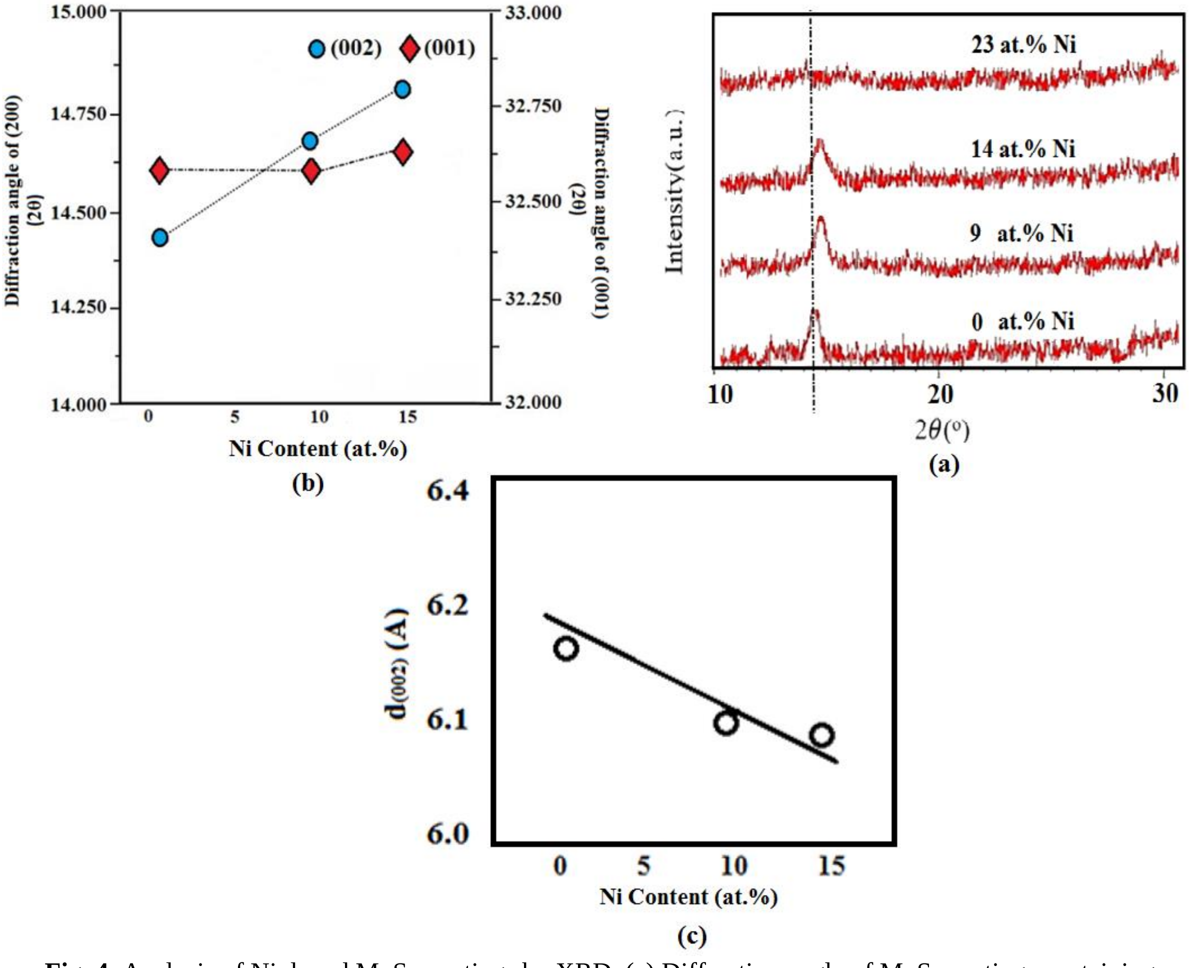


Fig. 4. Analysis of Ni doped MoS_X coatings by XRD. (a) Diffraction angle of MoS_2 coatings containing varying amounts of nickel deposited at at the diffraction angle of about 14.5°, (b) The diffraction angle value of 2θ for the (002) plane vs. nickel dopant, (c) Changes in d-spacing for the (002) plane vs. nickel dopant.

Fig. 4-a shows the XRD patterns of Ni-Doped MoS_2 Composite Coatings at at the diffraction angle of about 14.5°, also Changes in diffraction angle value for the (002) plane vs. Nickel dopant and changes in d-spacing for the (002) plane vs. nickel dopant presented in Fig. 4-b and 4-c., respectively. As can be seen, the peak position of the (002) reflection was observed to shift to

higher 2θ values as the nickel content increased (Fig.4-a). This show that the doping of nickel into the MoS_2 structure tends to shrink the structure in the z-direction, so the distance between (002) planes decease.

Fig. 5 shows the hardness and Young's modulus of the MoS_2/Ni composite coatings as a function of the Ni content. Increasing the Ni content led to the significant increase of the hardness of the coatings. For the pure MoS_2 coating, the hardness was only about 8 GPa, while it increased to 11.5 GPa with the Ni content of 14 at.%. Beyond of this threshold value of 14 at.% Ni, the over rich doped soft Ni atoms in turn caused the structure deterioration and led to the constant of hardness of 11.5 GPa.

The structure densification dependence on the Ni. The hardness increase of the MoS_2/Ni composite coating could be understood by the solid solution hardening effect and can be attributed to their dense structure. When the Ni doping content increased beyond the threshold value of 14 at.% Ni, the coating hardness remains constant. This could be due to either the structure deterioration or the possible formation of discrete metallic particles. The hardness firstly increased and reached to the maximum value due to the structure densification with a certain of saturation value of Ni content. Critical load played the crucial role in the tribological property of the coating. Fig. 6 shows the critical load of the MoS_x/Ni composite coatings as a function of the Ni. The normal displacement and lateral force displayed in the data are explained as critical load (P_{crit}) and critical depth (h_{crit}), respectively.

3-D in-situ SPM image of MoS_x coating after a 4000 μN ramping force nanoscratch test is shown in Fig. 7 since the scratch groove depth is less than 1 μm the strength of adhesion is higher than coating cohesion. It can thus be deduced that Ni concentration seemed to play a significant role in coating cohesion.

As can be seen, the addition of Ni content from 0 to 14 % led to the significant increase of the cohesion of the coatings. Thus, it can be reasoned that the addition of Ni has a significant role in coating cohesion. The further increase of Ni content from 14 to 23 % results in the densification deterioration of the coating, which in turn leads to lowering the coating hardness and cohesion of the coating.

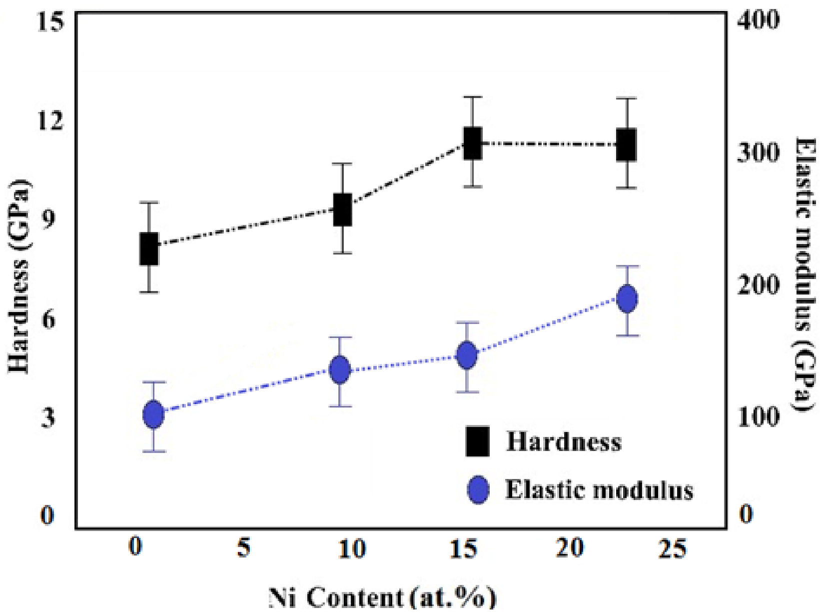


Fig. 5. The hardness and elastic modulus results of the MoS_x/Ni composite coatings as a function of Ni content.

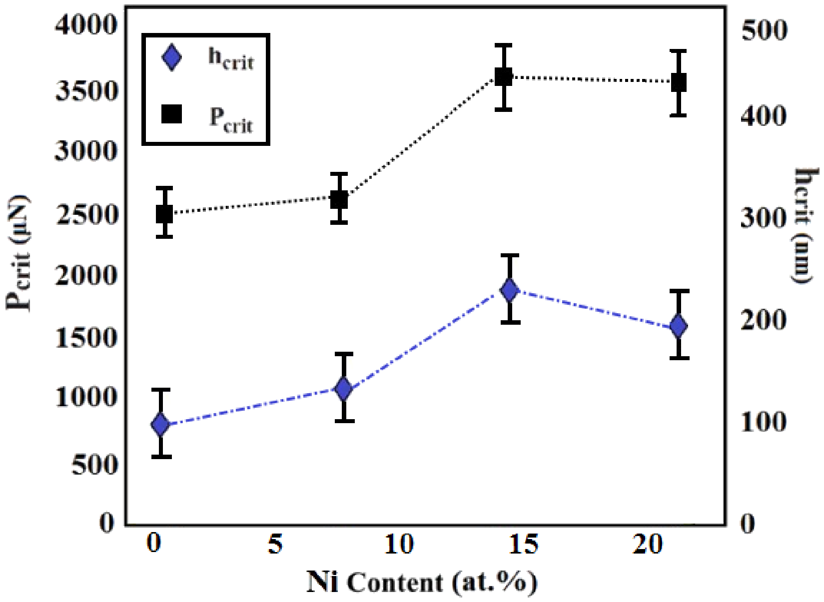


Fig. 6. the P_{crit} and h_{crit} results of the MoS_x/Ni composite coatings as a function of Ni content.

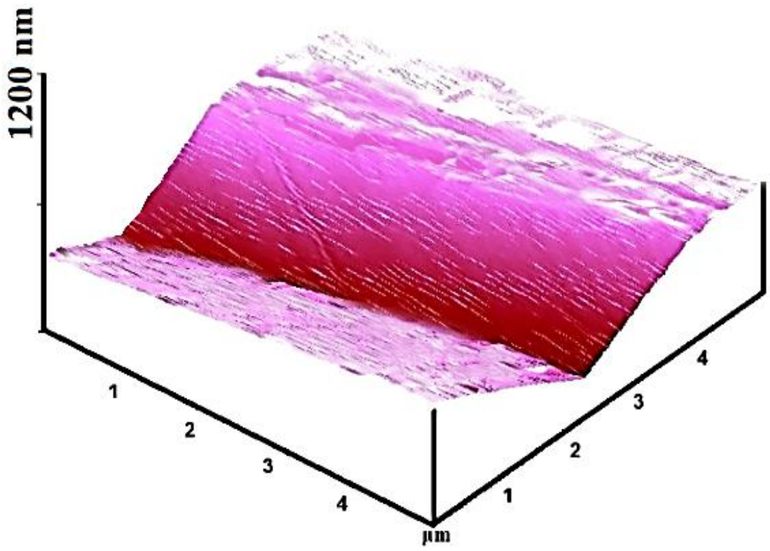


Fig. 7. 3-D in-situ SPM image of MoS_x coating after a 4000 µN ramping force nanoscratch test.

In order to investigate the effect of doped Ni content on the wear resistance of the MoS_2/Ni composite coatings, pin-on-disc friction tests were performed under ambient air. Friction coefficients were continuously recorded during the wear tests. Fig. 8 shows typical pin-on-disk measured friction coefficient vs. sliding distance .The friction coefficient curves can be divided into two sections. The first one is a smooth curve with a low friction coefficient. The second section is a fluctuating curve with a high friction coefficient. These results are summarized in Fig. 9. The durability lifetime (L) is defined as the duration of Section 1, i.e. the time from the starting of the testing until the friction coefficient increases and fluctuates.

The frictional 'noise' of the MoS_x/Ni coating was much lower than in relation to the MoS_x coating. Fig. 8 shows the average friction coefficient of MoS_2/Ni composite coatings with different Ni contents.

As can be seen, with the increase of the Ni content, the average friction coefficient of the coating reduced from 1.85 (pure MoS_2) to 1.55

(MoS_2-Ni, 13 at.% Ni). doping Ni (13 at.%) into the MoS_x coatings presented a relatively steady and low friction coefficient that was lower than for the pure MoS_x. The addition of Ni to MoSx/Ni (<13 at.% Ni) increased the endurance of MoS_2 coatings. The MoS_2 coatings failed after approximately 900 cycles during the pin-on-disc wear tests. The loss of endurance of MoSx is believed to be related to the reaction with oxygen and counter-face materials, which change the wear mode of the coating and no longer provide a lubrication effect [14].

Fig. 8 shows specific wear rate of MoS_x/Ni composite coatings as a function of Ni content. The results are x typical of those obtained for the composite coatings with a performance better than the pure MoS_x coating. In contrast, despite its high hardness and good coating Cohision, the MoS_2–Ni 22 at.% coating shows a high friction coefficient and poor wear resistance.

Fig. 9 shows the wear coefficients of MoS_x/Ni composite coatings. Within the Ni content region of 0–14 at.%, increasing the Ni content led to a significant decrease of the coating' s wear coefficient. This indicates that the doped Ni improved the tribological properties of pure MoS_2 in the atmospheric environment. The optimum composition of coatings are MoS_2/Ni_x% with x = 14% level. A reasonable explanation is due to the increase of both hardness and adhesion of the MoS_2/Ni coatings with the increase of nickel content to 14 at.%.

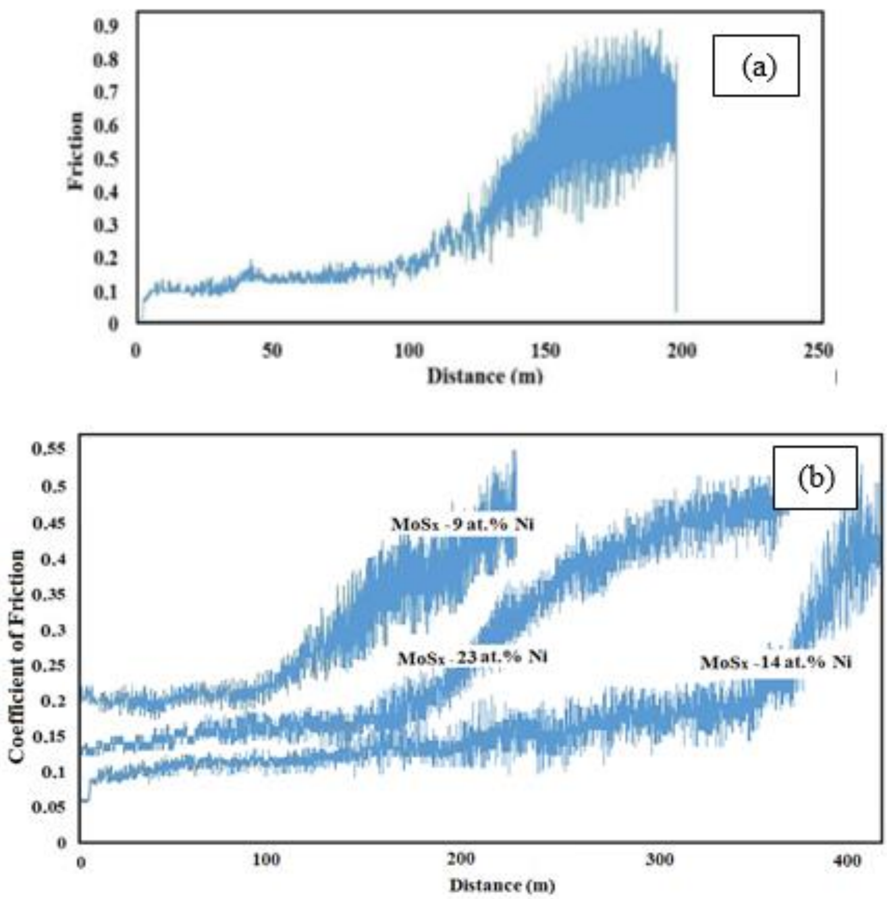


Fig. 9. Variation of the friction coefficient as a function of wear distances for (a) Pour MoS_x and (b) MoS_x/Ni composite coatings during the pin-on-disc wear test.

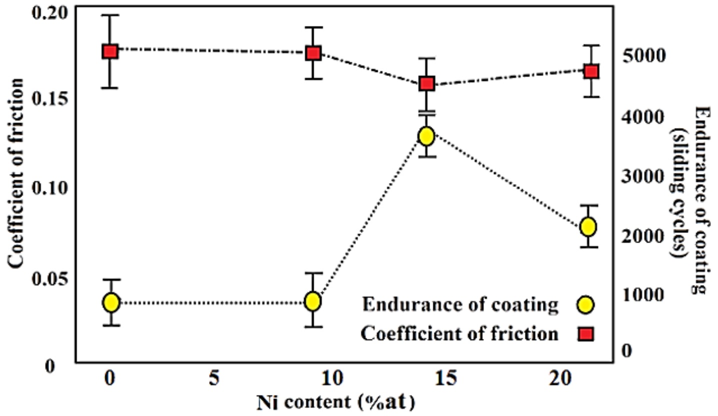


Fig. 10. Average friction coefficient and endurance of coatings test results of MoS_2/Ni composite coatings with different Ni contents.

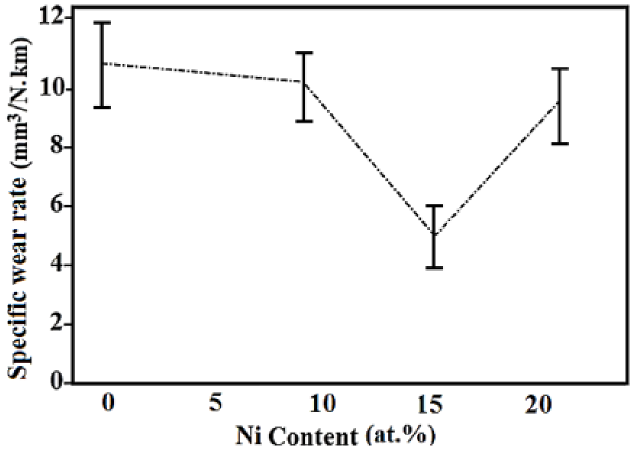
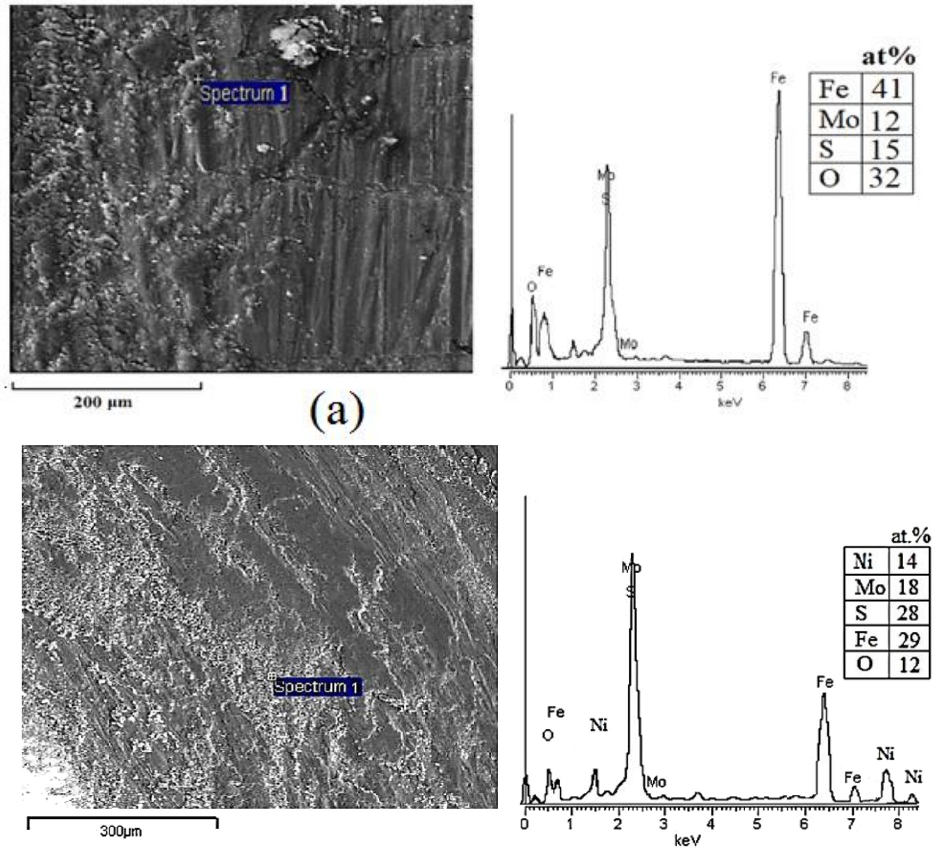


Fig. 11. Wear rate of MoS_x/Ni composite coatings as a function of Ni content.

In order to determine dominant wear mechanisms, the wear tracks of pure MoS_2 and MoS_2/Ni 14% coatings at the normal load of 5 N and after 800 wear cycles were examined by SEM and EDX. As can be seen in Fig. 11(a), many wide and deep grooves in the direction of slip were found. These grooves parallels are also typical features associated with abrasive wear. In addition of grooving, some locally plastic deformation can be seen in Fig. 11(b). Worn surface of the MoS_2/Ni coating is smoother and shows fine grooves and significant plastic flow. However, severe plastic deformations were present in MoS_x/14 at.% Ni coating. The main wear mechanisms in the MoS_x and MoS_x/Ni coatings were therefore abrasive and adhesive, respectively.

The EDS analysis of the wear tracks showed that there is a high level of oxygen, which indicates tribochemical wear happened. The formation of oxidation products led to an increase of coefficient friction and a decrease of wear life in the MoS_2 composite coatings. The presence of nickel atoms within the MoS_2 structure prevented the erosion of the water vapor and oxygen. With increasing Ni content, more MoS_2 was protected and less MoO_3 formation existed. The formation of oxidation products led to an increase of coefficient of friction and decrease of wear life, thus creating a corrosive and abrasive effect on the contrary.

The major wear mechanism in MoS_x coatings is generally a mixture of abrasive and oxidation reaction.



(b)

Fig. 12. Worn morphologies and EDX analysis of the (a) pour MoS_x (b) MoS_2/Ni, 14 at.% Ni after 800 wear cycles.

4- Conclusion

In this investigation, MoS_x/Ni composite coatings with Ni contents varying from 0 to 23 at.% were deposited onto steel substrate using a DC magnetron sputter process. The following conclusions can be drawn from the results:

1. The properties of MoS_2 coatings can be significantly improved through the co-deposition of an appropriate amount of nickel.
2. A Ni metal atomic percentage at 14% in the MoS_2/Nix% coating was found to possess the optimum wear resistance and durability.
3. The degree of crystallization of the Ni-Doped MoS_2 Composite Coatings decreased with the increase of Ni content, and the structure of the MoSx/Ni composite coatings turned into the amorphous structure.
4. The degree of crystallization of the MoS_2/Ni coatings decreases with the increase of nickel content.
5. Appropriate doped Ni (14 at.%) led to high coating hardness and adhesion combined with the densification and compaction of the coating.
6. The MoS_x/Ni coatings exhibited a steady state friction coefficient from 0.15 to 0.19.
7. The main wear mechanisms in the MoS_x and MoS_x/Ni coatings were therefore abrasive and adhesive, respectively.

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