 **DOR: 20.1001.1.2322388.2021.9.1.3.9**

Research Paper

Fabricating the Tribological Properties and Investigating of Ni₃Al-MoS₂ Composite Coating

Mahdi Mirzaaghaei^{1*}, Mohammad-Hossein Enayati², Mahdi Ahmadi³*1. Student, Department of Materials Engineering, Naghshe Jahan University, Isfahan, Iran**2. Department of Materials Engineering, Isfahan University of Technology, Isfahan, 84154, Iran**3. Department of Materials Engineering, Naghshe Jahan University, Isfahan, 77142, Iran*

ARTICLE INFO

Article history:

Received 25 April 2020

Accepted 30 July 2020

Available online 1 January 2021

Keywords:

*Ni₃Al**MoS₂**magnetron sputtering**wear*

ABSTRACT

Self-lubricant coatings are among the newly improved type of coatings to reduce the coefficient of friction and protect the substrate in various conditions. Magnetron sputtering is the best technology to fabricate coatings with good morphology. In this paper, the tribological properties of magnetron sputtered Ni₃Al-MoS₂ coating on 4340 steel are reported. For this purpose, five tablets of Ni₃Al-30 wt.% MoS₂ were prepared as the target material and were placed in a copper holder. At last, we have sputtered from the target using the best sputtering condition to get a good morphology and microstructure of the coating. The morphology and microstructure of the coatings were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The tribological properties of Ni₃Al-MoS₂ coating were investigated using a ball-on-disc tribometer at atmospheric conditions at room temperature. SEM was used to examine the morphology of the wear track after the ball-on-disc test. The Ni₃Al-MoS₂ composite coating showed lower frictions coefficient and higher wear resistance because of the hard Ni₃Al matrix and soft MoS₂ particles.

* **Corresponding author:**

E-mail address: mahdymirzaaghai@yahoo.com

1. Introduction:

Metal matrix composites with solid lubricants have attracted wide and promising applications [1-7]. Aluminides have served interesting properties such as high hardness, high-temperature stability, high creep resistance, high melting point and, low density [8,9]. A Combination of aluminides with solid lubricants particles has been considered as self-lubricating materials [10-16]. Solid lubricants have been classified into several subdivisions, such as lamellar solids (e. g., MoS₂, WS₂ and, graphite), soft metals (e. g., Ag and Pb), carbon-based solids (e. g., diamond and DLC), and organic materials/polymers (e. g., PTFE and waxes) [10-17]. MoS₂ has a lamellar structure, the bonding in the S-Mo-S sandwich is covalent and strong, but the layers of the lamellar structure are van der Waals and weak. It yields a low friction coefficient value and is mostly used in applications that need a solid lubricant [15-17]. The friction coefficient increases and the lifetime decreases when MoS₂ is used in humid air, therefore; this material can be only used in vacuum and in a water vapor-free environment [15-21]. In a previous study, composite coating of Cu-Ni₃Al-MoS₂ made using the PVD method and a complex target showed a coefficient of friction of about 0.5 after 60 minutes [16]. In this design, it is predicted that by removing copper, the coating will have a higher hardness and its tribological properties will be improved, So this

study aimed to synthesize Ni₃Al-MoS₂ coating by magnetron sputtering, and The tribological behavior of the coating was evaluated.

2. Experimental

2.1. Deposition

The Ni₃Al powder was synthesized by ball milling of elemental Ni (80-100μm, 99.9% purity) and Al (80-100μm, 99.9% purity) using planetary ball mill for 40 hours at a speed of 350rpm at room temperature under Ar atmosphere. The MA product was characterized by X-ray diffraction (Bruker X'PERT MPD diffractometer) using filtered Co K α radiation ($\lambda=0.1789\text{\AA}$), Ni₃Al-30wt.%MoS₂ composite tablets (30mm in diameter and thickness of 2mm) were made by single-axis Santam press under 350 MPa stress. Finally, five tabs were placed in a pure Cu holder which was covered by aluminum foil to prevent the copper element from penetrating into the coating. Depending on the coating conditions and the type of process used, the alumina formed on the foil acts as an insulator and the possibility of its penetration into the coating is reduced [22]. Ni₃Al-MoS₂ coating was deposited by DC magnetron sputtering on 4340 steel substrates. Fig.1 is a schematic diagram of the magnetron sputtering process with Ni₃Al-MoS₂ target tablets. Table 1 shows the coating deposition conditions.

Table 1 Shows the coating deposition parameters.

Target	Ni ₃ Al-MoS ₂
Substrate	4340
Substrate temperature	325°C
Substrate to target distance	15Cm
Voltage	850V
Current	1.2-2A
Deposition time	80min
Base pressure	10 ⁻⁷ mbar
Working pressure	1-5×10 ⁻³ mbar

The composite coatings with a thickness of 8μm were obtained by sputtering for 80 min. The Ni₃Al-MoS₂ coatings were examined by both X-ray diffraction (Philips X'PERT MPD CuK α) and scanning electron microscopy (SEM Leo 440i OXFORD).

2.2 Testing:

2.2.1. Tribological properties measurements

The tribological properties of 4340 steel substrate and composite coatings were studied by a ball-on-disc tribometer. Table 2 shows the initial conditions of the samples.

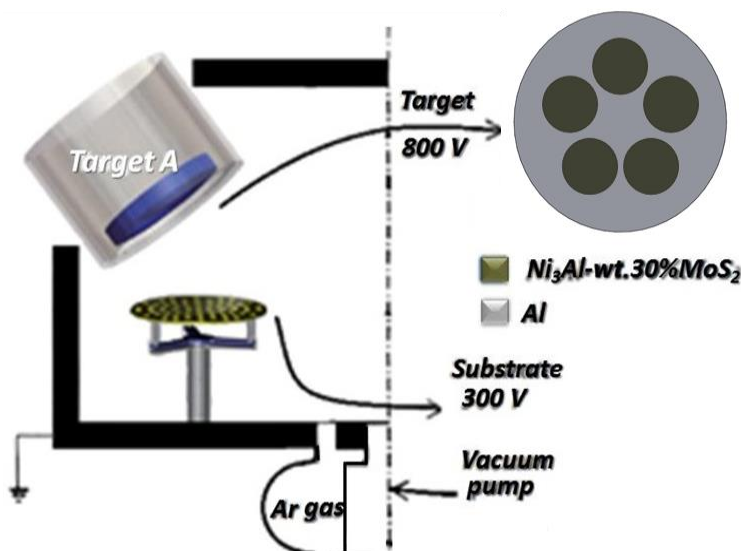


Fig.1. Schematic diagram of sputtering system for synthesizing Ni₃Al-MoS₂ composite coating.

Table 2 Different samples

Samples	Type	Hardness	Roughness (µm)
1	4340 steel	50HRC	R _a = 0/2
2	4340 steel with Ni ₃ Al-MoS ₂ coating	408HV	R _a = 0/08

All tests were carried out using a 5 mm diameter Si₃N₄ ball as the counterface. The tests were run under a load of 5 N at room temperature and a sliding speed of 0.1 m/s. The sliding load in the tribological test was monitored and recorded for 3600 seconds in order to determine the friction coefficient vs. time. The wear tracks of the coatings were examined by means of SEM.

2.2.2. Hardness measurement:

The hardness of the substrate was determined using a Rockwell C hardness with a Koopa attachment. The hardness measurements of the coatings were conducted according to ASTM 578-87 standard, using Wilson microhardness with Vickers diamond pyramid indenter under 25gr force in several points.

2.2.3. Roughness survey:

To determine the roughness of the substrate and coating surfaces was determined by a Mahr Germany device (M300C model).

2.2.4. Adhesion strength

The VDI 3198 standard specifies the well-known Rockwell C indentation test as a destructive quality test for coated compounds [23]. This technique does not give any absolute measurement of adhesion, but comparative results can be obtained with the same load for all samples. Fig. 2 gives qualitative adhesion properties considering the crack network from the indentation spot. This test also gives a qualitative measure of the toughness of the coating. The reported adhesion value ranges between HF1 to HF6 (HF is the German short form of adhesion strength) (Fig.2), with excellent adhesion property and a few crack networks in HF1 and the poorest adhesion properties indicating complete delamination of the coating in HF6 [24,25]

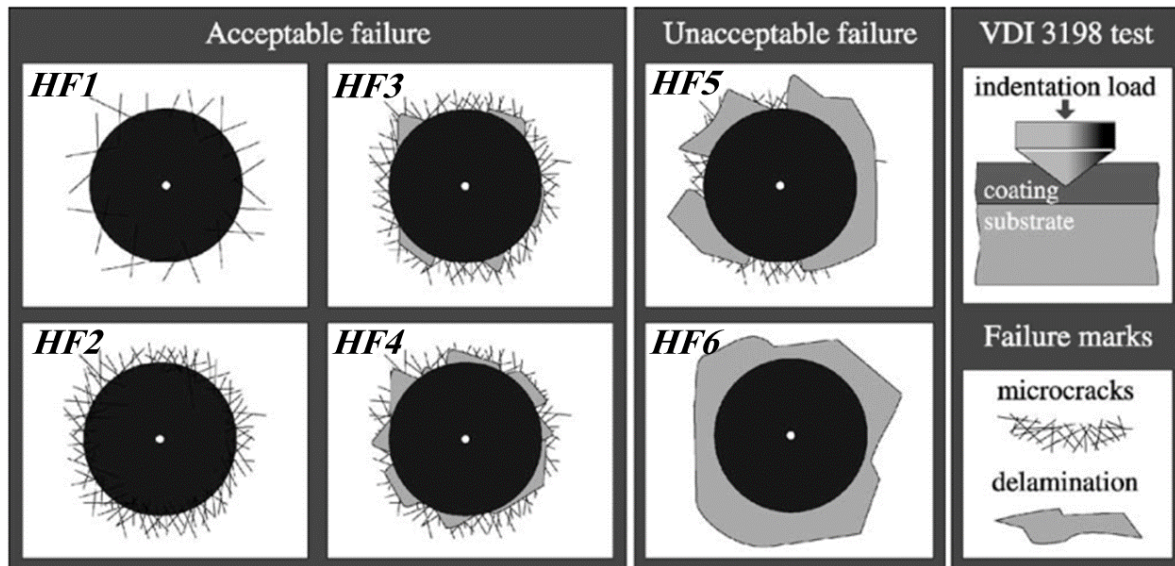


Fig.2. Adhesion strength quality based on Rockwell C indentation test [24].

3. Results and discussion

Fig. 3 indicates that the coating has a good flat surface. The observed bumps are a result of MoS₂ dots. A typical SEM image obtained from the surface and the elemental map of the Ni₃Al-MoS₂ composite coatings are shown in Fig.4. The chemical compositions which are determined by energy

dispersive spectroscopy (EDS) on SEM are given in table 3. Fig.5 shows backscatter electron (BSE) micrographs. The dark areas in the BSE image are MoS₂ because MoS₂ has a lower atomic mass. The Ni₃Al-MoS₂ composite coatings exhibit a dense structure. The thickness of the coating at the highest target current of 2A was 8µm. The measured microhardness of this coating was 408 HV.

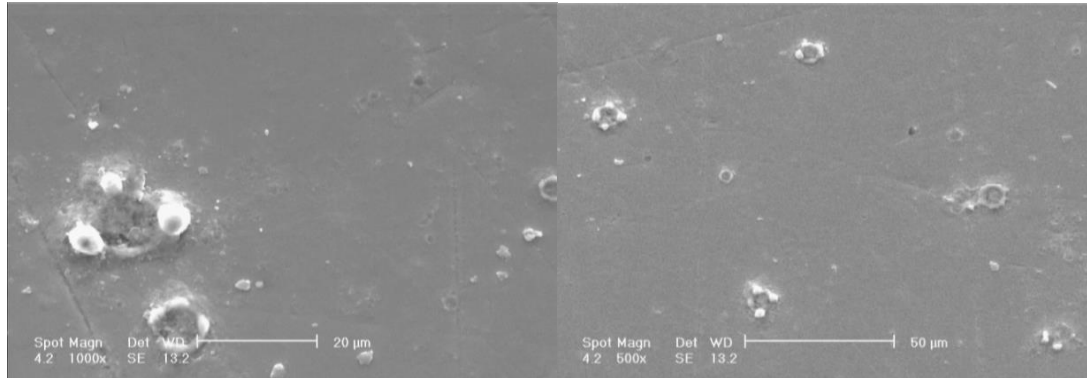


Fig.3. SEM images showing the surface of the Ni₃Al-MoS₂ composite coating.

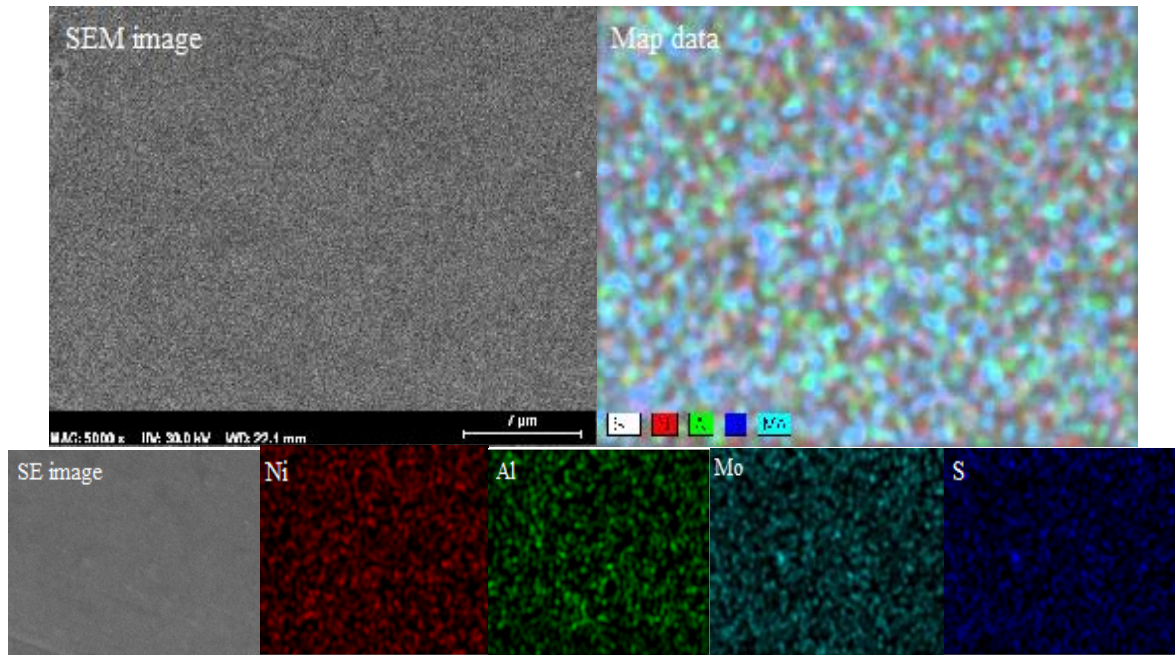


Fig. 4. SEM images showing the elemental map data of the $\text{Ni}_3\text{Al-MoS}_2$ composite coating.

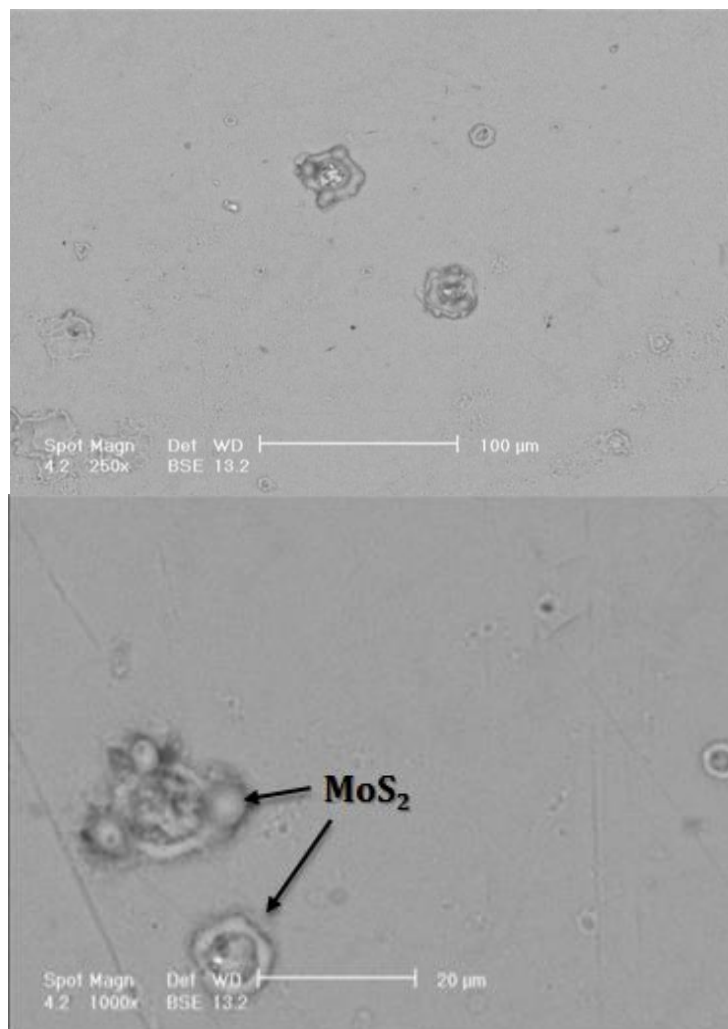
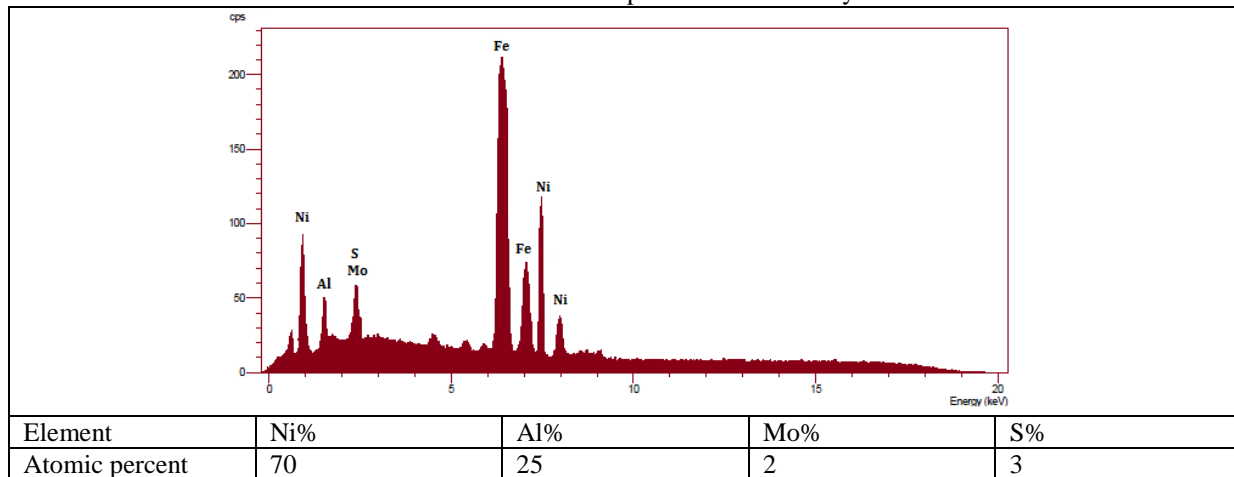


Fig. 5. BSE image of the $\text{Ni}_3\text{Al-MoS}_2$ composite coating.

Table 3 The chemical composition measured by EDS



3.1. XRD analyses

The X-ray diffraction pattern of Ni₃Al-MoS₂ composite coating is shown in Fig.6. The X-ray diffraction profile revealed that the coatings were mainly consisted of Ni₃Al and MoS₂ phases, with no preferred orientation. Diffraction peaks of AlNi can be observed besides Ni₃Al. One definition can be the Al foil, which has covered the target surface.

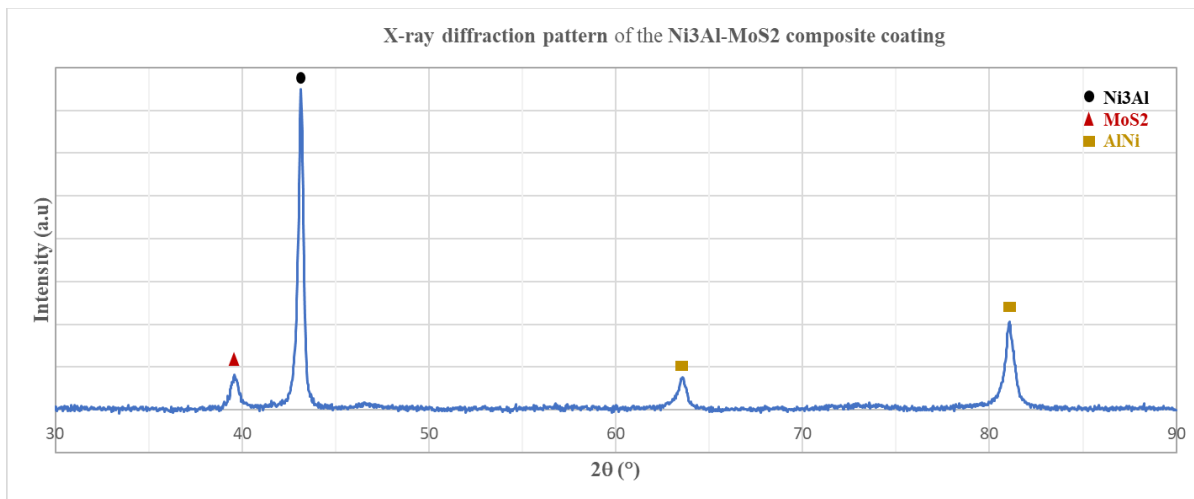


Fig. 6. XRD pattern of Ni₃Al-MoS₂ Composite Coating.

3.2. Adhesion strength

Fig.7 shows the optical micrographs of Rockwell-C indentation on Ni₃Al-MoS₂ coating. The Rockwell-C indentation test showed an acceptable adhesion.

According to the standards presented in the previous section [23-25], coating adhesion strength was evaluated to be HF3, which represents good adhesion and strength to the substrate.

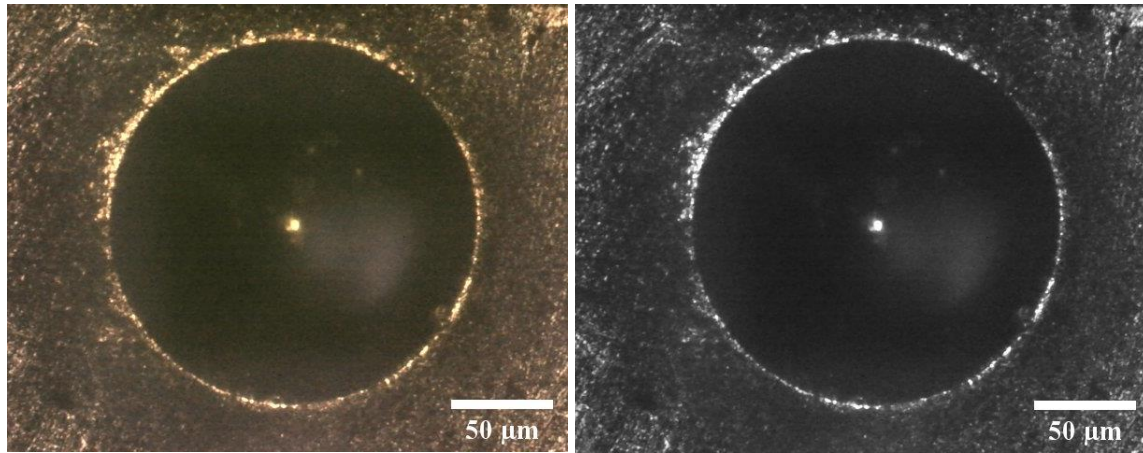


Fig. 7. Rockwell C adhesion test of Ni₃Al-MoS₂ coating (load 150kg).

3.3. Tribological properties measurements

Fig.8 (a) illustrates the evolution of the friction coefficient of the composite coating under dry sliding for the duration of 1 h at a sliding speed 0.1 m/s and an applied load of 5 N. The friction coefficients of the coating were approximately 0.2 in 25 °C. In comparison, the friction coefficients of the 4340-steel substrate were much higher (above 0.9) than that of the coating. These results prove that the Ni₃Al-MoS₂

coating exhibits excellent self-lubricating properties. Fig.8 (b) shows the mass loss results. The mass losses of substrate and coating were 0.02 and 0.005 gr, respectively. Humidity has a positive effect on friction coefficient, and decreases wear life which is probably because of dangling unsaturated bonds on the edge of basal plans reacting with moisture and oxygen in the environment to form tribooxidation products, such as MoO₃ [26-28].

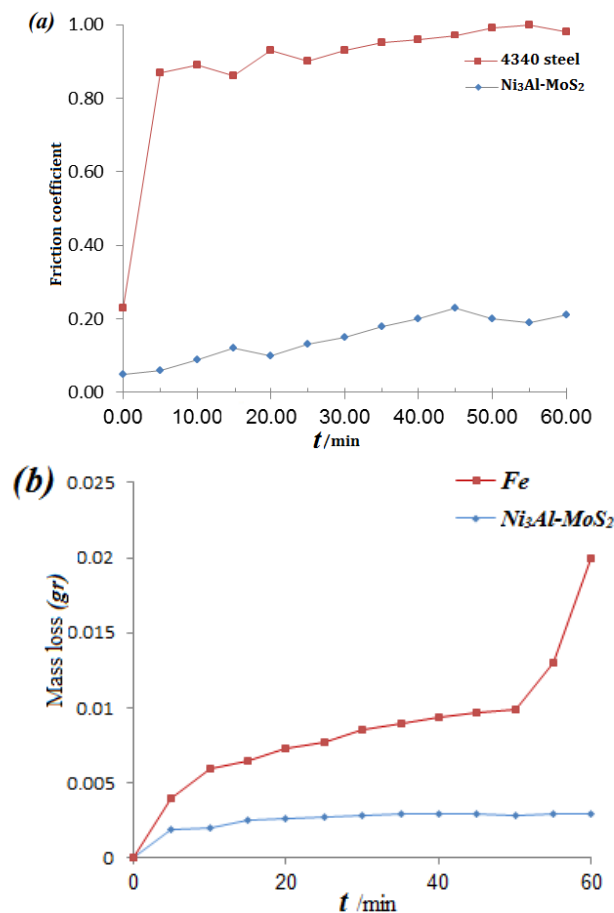


Fig. 8. (a)The friction coefficients and (b) mass loss of the coating at room temperature

Fig. 9 (a) shows the worn surfaces of the coating after wearing for 1 h at a load of 5 N and sliding speed of 0.1 m/s at room temperatures. The parallel furrows and spallation are observed, which reveal that the wear mechanism is abrasive. Fig. 9(b) given the EDS data taken from the wear area. EDS analysis was performed to determine the surface composition in the wear track. EDS confirmed the presence of Ni, Al, Mo and, S within the composite coating (Table 4). The worn area on the film counter body is smooth with patchy and powdery debris. Some worn debris piled up at both sides of the wear track with no abrasive wear effect. This is the reason why the friction coefficient remained very stable during the 1

h sliding test. The overall aspects of this worn surface image are typical for all coating studied here. The wear resistance of coatings depends on several factors, including the hardness, thickness, plastic deformation behavior, roughness and, lubricating properties. By properly adjusting these parameters, the wear behavior can be improved [29]. The microhardness test on the coating indicates that the coating hardness was 408 HV; due to the lower hardness of coating in comparison with the substrate, the coating half-life is low. However, the amount of lubricant material MoS₂ provides the condition for improving the lubrication.

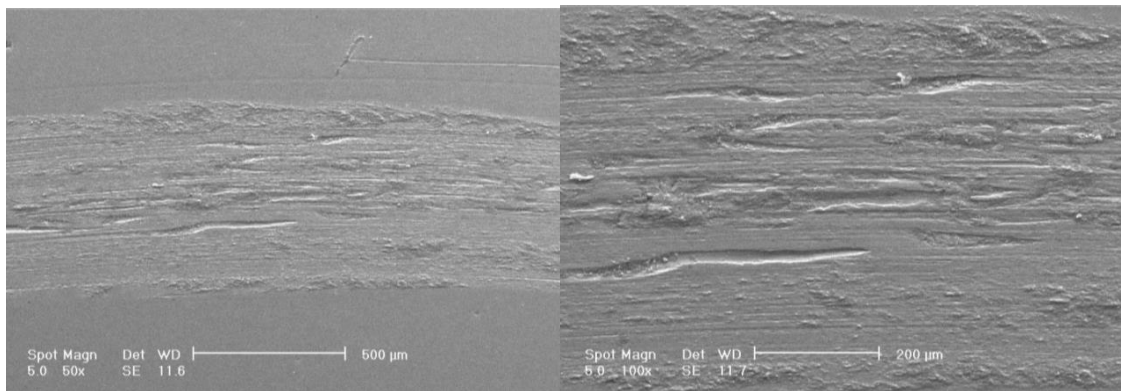
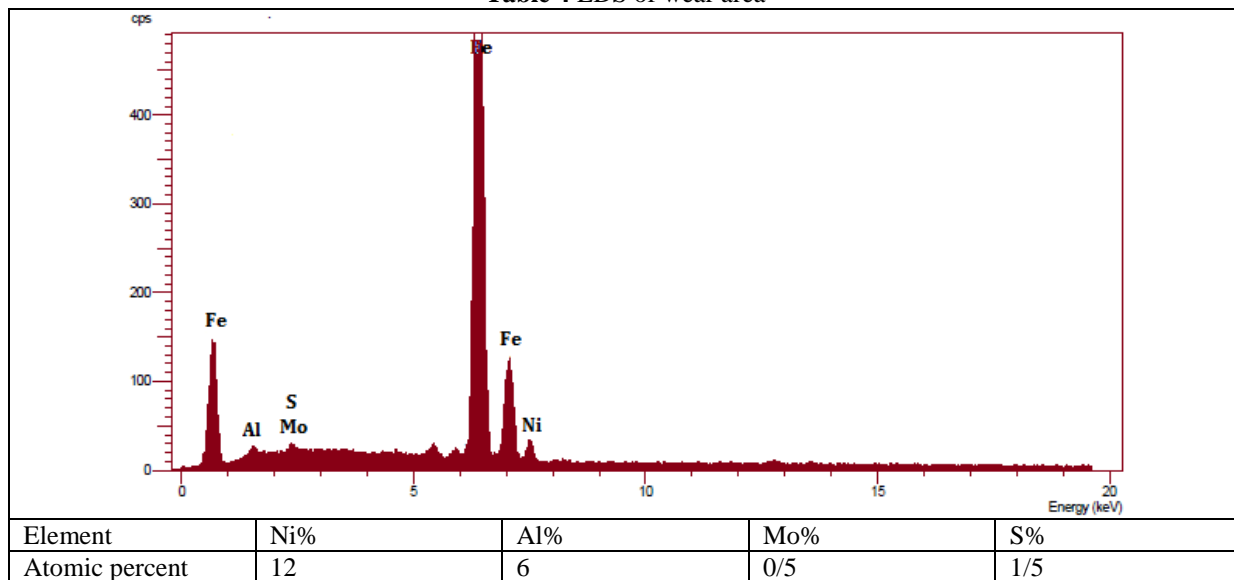


Fig. 9. SEM micrographs of worn surface of the coating (0.1 m/s, 5 N and 1 h).

Table 4 EDS of wear area



3.4. Investigation wear rate of the coating and substrate

Fig. 10 shows the wear rate of the as-received substrate and Ni₃Al-MoS₂ coating. The presence of the soft MoS₂ particles within the hard Ni₃Al matrix

and the smoothness of the surface, and the good adhesion strength of the coating to the substrate all contribute to the improvement of the substrate tribological properties reduces the wear rates. The wear rate of the coating was 50% smaller than that for the substrate.

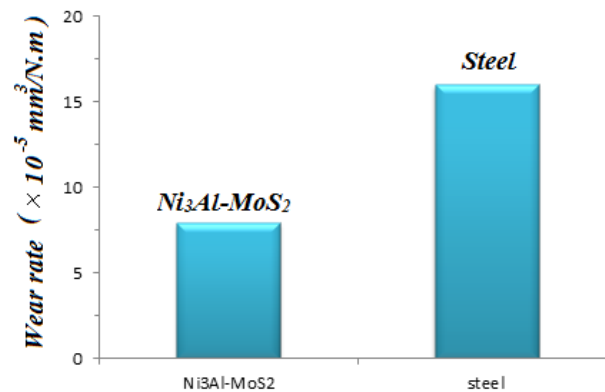


Fig.10. Wear rate of coating and substrate

4. Conclusions

XRD analysis indicated that the composite coating had no preferred orientation. In the BSE image, the dark area is the MoS₂ phase observed. The first coefficient of friction at room temperature is 0.24. These results prove that the coating provides a stable and low friction coefficient in stable conditions; in other words, it proves the coating exhibits self-lubricating properties. The main reason for the low coefficient of friction seems to be the presence of a composite structure containing hard matrix Ni₃Al with solid lubricant MoS₂. In addition, no failure(s) were observed during the wear test.

Acknowledgments

The authors are profoundly grateful to Freshte Surani for her generous help in this work.

References

- [1] S. Sun, J. Chen, Y. Wang, L. Wang, and Z. Sun, "Structural sensitivity of MoS₂-based films in solid space lubrication," *Surface Engineering*, vol. 36, pp. 106-113, 2020/01/02 2020.
- [2] Freschi, M., Di Virgilio, M., Zanardi, G., Mariani, M., Lecis, N., and Dotelli, G., 2021, "Employment of Micro- and Nano-WS₂ Structures to Enhance the Tribological Properties of Copper Matrix Composites," *Lubricants*, 9(5).
- [3] H. Torres, H. Rojacz, L. Čoga, M. Kalin, and M. Rodríguez Ripoll, "Local mechanical and frictional properties of Ag/MoS₂-doped self-lubricating Ni-based laser claddings and resulting high temperature vacuum performance," *Materials & Design*, vol. 186, p. 108296, 2020/01/15/ 2020.
- [4] M. S. Libório, G. B. Praxedes, L. L. F. Lima, I. G. Nascimento, R. R. M. Sousa, M. Naeem, et al., "Surface modification of M2 steel by combination of cathodic cage plasma deposition and magnetron sputtered MoS₂-TiN multilayer coatings," *Surface and Coatings Technology*, vol. 384, p. 125327, 2020/02/25/ 2020.
- [5] H. Du, C. Sun, W. Hua, T. Wang, J. Gong, X. Jiang, et al., "Structure, mechanical and sliding wear properties of WC-Co/MoS₂-Ni coatings by detonation gun spray," *J. Mater. Sci. Eng: A*. 445-446 (2007) 122-134.
- [6] Rajesh Kumar, L., Saravanakumar, A., Bhuvanewari, V., Jithin Karunan, M. P., Karthick Raja, N., and Karthi, P., 2020, "Tribological Behaviour of AA2219/MoS₂ Metal Matrix Composites under Lubrication," *AIP Conf. Proc.*, 2207(February).
- [7] Devaganesh, S., Kumar, P. K. D., Venkatesh, N., and Balaji, R., 2020, "Study on the Mechanical and Tribological Performances of Hybrid SiC-Al7075 Metal Matrix Composites," *J. Mater. Res. Technol.*, 9(3), pp. 3759-3766.
- [8] Liu, C., Chen, Y., Qiu, L., Liu, H., Bai, M., and Xiao, P., 2020, "The Al-Enriched γ' -Ni₃Al-Base Bond Coat for Thermal Barrier Coating Applications," *Corros. Sci.*, 167(2517), p. 108523.
- [9] Yang, Z. W., Lian, J., Wang, J., Cai, X. Q., Wang, Y., Wang, D. P., Wang, Z. M., and Liu, Y. C., 2020, "Diffusion Bonding of Ni₃Al-Based Alloy Using a Ni Interlayer," *J. Alloys Compd.*, 819, p. 153324.
- [10] K. P. Furlan, J. D. B. de Mello, and A. N. Klein, "Self-lubricating composites containing MoS₂: A review," *Tribology International*, vol. 120, pp. 280-298, 2018/04/01/ 2018.
- [11] S. Zhu, J. Cheng, Z. Qiao, and J. Yang, "High temperature solid-lubricating materials: A review," *Tribology International*, vol. 133, pp. 206-223, 2019/05/01/ 2019.
- [12] Yuan, J., Ph, D., Wang, Q., Liu, X., Lou, S., Li, Q., and Wang, Z., 2020, "Microstructures and High-Temperature Wear Behavior of NiAl / WC-Fe x Coatings on Carbon Steel by Plasma Cladding," *J. Alloys Compd.*, 842, p. 155850.
- [13] Shi, X., Song, S., Zhai, W., Wang, M., Xu, Z., Yao, J., Qamar ud Din, A., and Zhang, Q., 2014,

“Tribological Behavior of Ni3Al Matrix Self-Lubricating Composites Containing WS₂, Ag and HBN Tested from Room Temperature to 800°C,” *Mater. Des.*, 55, pp. 75–84.

[14] Yao, Q., Jia, J., Chen, T., Xin, H., Shi, Y., He, N., Feng, X., Shi, P., and Lu, C., 2020, “High Temperature Tribological Behaviors and Wear Mechanisms of NiAl-MoO₃/CuO Composite Coatings,” *Surf. Coatings Technol.*, 395(March), p. 125910.

[15] Dong, C., Cui, Q., Gao, X., Jiang, D., Fu, Y., Wang, D., Weng, L., Hu, M., and Sun, J., 2020, “Tribological Property of MoS₂-Cr₃O₄ Nanocomposite Films Prepared by PVD and Liquid Phase Synthesis,” *Surf. Coatings Technol.*, 403(July), p. 126382.

[16] Mirzaaghaei, M., Enayati, M. H., and Ahmadi, M., 2016, “The Tribological Properties of Cu-Ni 3 Al-MoS₂ Composite Coating Deposited by Magnetron Sputtering,” 4(4), pp. 37–45.

[17] A. Erdemir, in: B. Bhushan (Eds.), *Modern Tribology Handbook*, vol. II, CRC Press, Boca Raton, FL, 2001, p. 736.

[18] E. Arslan, F. Bülbül, A. Alsaran, A. Celik, and I. Efeoglu, The effect of deposition parameters and Ti content on structural and wear properties of MoS₂Ti coatings, *Wear* 259 (2005) 814-819.

[19] F. Bülbül, İ. Efeoglu, E. Arslan, The effect of bias voltage and working pressure on S/Mo ratio at MoS₂-Ti composite films, *Appl. Surf. Sci.* 253 (2007) 4415-4419.

[20] N. M. Renevier, V. C. Fox, D. G. Teer, J. Hampshire, Coating characteristics and tribological properties of sputter-deposited MoS₂/metal composite coatings deposited by closed field

unbalanced magnetron sputter ion plating, *Surf. Coat. Technol.* 127 (2000) 24-37.

[21] W. Heinke, A. Leyland, A. Matthews, G. Berg, C. Friedrich, E. Broszeit, Evaluation of PVD nitride coatings, using impact, scratch and Rockwell-C adhesion tests, *Thin Solid Films* 270 (1995) 431-438.

[22] S. Tokumaru and M. Hashimoto, "High resistivity AlO_x thin films deposited by a novel two-step sputtering process," *Surface and Coatings Technology*, vol. 54-55, pp. 303-307, 1992/11/16/1992.

[23] Verein Deutscher Ingenieure Normen, VDI 3198, VDI-Verlag, Dusseldorf, 1991.

[24] Vidakis N., Antoniadis A., and Bilalis N., The VDI 3198 in dentationtest evaluation of areliable qualitative control for layered compounds. *J. Mater. Proc. Technol.*, pp. 143-144, 2003.

[25] Heinke W., Leyland A., Matthews A., Berg G., Friedrich C., and Broszeit E., Evaluation of PVD nitrid ecoatings, using impact, scratch and Rockwell-C adhesion tests. *Thin Solid Films.*, pp. 431-270, 1995.

[26] Brainard, W.A. (1969) The thermal stability and friction of the disulfides, diselenides and ditellurides of molybdenum and tungsten in vacuum (10⁻⁹ to 10⁻⁶ torr). NASA TN D-5141.

[27] H. E. Sliney, Solid lubricant materials for high temperatures—a review, *Tribol. Int.* 15 (1982) 303-315.

[28] S. V. Prasad, J. S. Zabinski, Tribology of tungsten disulphide (WS₂): characterization of wear-induced transfer films, *J. Mater. Sci. Lett.* 12 (1993) 1413-1415.

[29] T. W. Scharf, S. V. Prasad, Solid lubricants: a review, *J. Mater. Sci.* 48 (2010) 511-513.