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Communication

Vacuum Tribological Properties of W-S-N Coatings Synthesized by Direct Current Magnetron Sputtering

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Abstract: This work deals with the investigation of the tribological performance of DC magnetron sputtered W-S-N coatings under vacuum atmosphere, as part of the exploration of multi-environment sliding properties of W-S-N solid lubricants. This study is part of the systematic testing of W-S-N solid lubricants in different environments, especially vacuum, which is often ignored. The trend is to test sliding properties in dry N_2 by considering it as replacement of vacuum environment testing. This approach is not appropriate. In this work, a set of coatings was synthesized with N-alloying content in the range of 0–25.5 at.%. A maximum S/W ratio of 1.47 was observed for the pure WSx coating. A maximum hardness of 8.0 GPa was observed for 23 at.% of N-alloying. The coating with the lowest N content (14.6 at.%) displayed the lowest friction, specific wear rate and wear scar depth under vacuum conditions. Despite superior sliding performance at room temperature (35% humidity), 200 °C and dry nitrogen conditions, the performance of the WSN12.5 coating deteriorated vacuum environment.

Keywords: W-S-N films; solid lubricants; friction and wear; DC magnetron sputtering

Citation: Yaqub, T.B.; Yaqoob, K.; Mukhtar, A.; Fernandes, F.; Bondarev, A.; Ferreira, F.; Al-Rjoub, A.; Cavaleiro, A. Vacuum Tribological Properties of W-S-N Coatings Synthesized by Direct Current Magnetron Sputtering. *Coatings* **2022**, *12*, 1646. https://doi.org/10.3390/coatings12111646

Academic Editor: Jose Ygnacio Pastor

Received: 16 September 2022
Accepted: 27 October 2022
Published: 30 October 2022

1. Introduction

One of the best combinations of elements for low friction solid lubricants are transition metal dichalcogenides. TMDs are made up of metal and chalcogenide atoms where, each metal atom (e.g., W or Mo) is bonded with two chalcogenide atoms (e.g., S or Se) to form a layered hexagonal crystal structure. Within the layers, there exists a strong covalent bonding while the layers are bonded by weak Van der Waals forces. This amalgam of strong and weak bonding helps the layers to slide over each other under the application of tangential forces, giving rise to the low friction characteristics [1,2]. Hence, TMDs received widespread attention as low friction coating materials in industries requiring dry lubricants, for example, in aerospace applications [1]. The most suitable and commonly adapted way of depositing low friction TMD coatings is via physical vapour deposition (PVD). Although, TMD coatings deposited by PVD displayed excellent frictional characteristics in vacuum environments, a significant decrease in the performance occurs during humid air and high temperature sliding. TMD coatings are highly porous and, thus, susceptible to moisture and oxidation attacks, leading to a swift performance degradation [1,3].

Voevodin et al. [4] introduced the concept of TMD-based nanocomposite coatings for the first time when they combined WS_2 with WC and DLC to resolve diverse environment sliding issues by a self-adaptive concept. Following this work, various studies were carried out on alloying TMDs with different metals, non-metals and compounds to enhance the sliding properties in diverse environments [3]. Although, alloying additions enhance the sliding properties in humid air and at high temperature, the literature fails to report systematic studies that compare the tribological performance in all environments (humid air, high temperature, dry N_2 and vacuum). In most of the studies, the properties of the alloyed TMD coatings are explored and reported in environments, other than vacuum, assuming the vacuum performance as granted, based on pure TMDs. Likewise, it should be noted that dry atmosphere sliding can be significantly different from vacuum testing. This means that the tribological properties in dry N_2 or dry Ar are not representative of the vacuum. Ideally, for a systematic investigation and scientific contribution, the approach should be to investigate the properties in all environments, before and after alloying.

One of the most common alloying elements used to enhance the humid air and high temperature properties of TMDs is nitrogen. N-alloyed WS_2 coatings (W-S-N coatings) were introduced in 2001 [5], with extensive room temperature and dry N_2 environment studies in coming years. Despite some interesting results, the literature lacked reports on high temperature sliding until 2021 [6] while, studies on vacuum environment sliding performance are still missing. Recently, the present authors explored the industrial implementation of this W-S-N system and tested the coatings in room temperature (humid air), 200 °C and dry N_2 sliding conditions [7]. To close the loop of the systematic study and to overcome the literature gap, the properties of the W-S-N coatings under vacuum must be communicated to the scientific community as well as the industries working on dry lubricant coatings based on pure or alloyed TMDs. Thus, this study reports the vacuum sliding properties of recently studied and optimized W-S-N coatings.

2. Materials and Methods

Direct current magnetron sputtered W-S-N coatings were deposited in a dual magnetron equipped Hartec® deposition chamber (Hartec, Schleswig Holstein, Germany). One of the magnetrons was connected to a WS_2 target while the second magnetron was connected to a Cr target used for the interlayer and gradient layer depositions. The fixed WS_2 target power of 350 W coupled with varying N_2-flow rates resulted in a series of coatings with different N content, as shown in Table 1. Polished M2 steel substrates (Ø25 mm × 8 mm, (Thyssenkrupp, Leiria, Portugal) were used which were cleaned in acetone and ethanol for 15 min each before placement in the deposition chamber. The distance of the sample holder from each target and its rotation speed was fixed at 100 mm and 17 rev/min, respectively. The base pressure was ~1×10^{-5} Pa. N_2 flow rates of 0, 5, 12.5 and 20 sccm were used for depositing a total of 4 coating compositions. Despite the difference in the N_2-flow rate, all depositions were carried out at 0.3 Pa, with both Ar and N flowing inside the chamber. Further details of the deposition process are available in Ref. [7]. The chemical composition of the coatings was measured by wavelength dispersive spectroscopy (WDS) under 15 kV accelerating voltage. For hardness studies, nanoindentation was used. The applied load was 2 mN, guaranteeing that the penetration depth is less than 10% of the total coating thickness. The vacuum tribological tests of all coatings were performed in a unidirectional rotating (custom-made, Oxford instruments-model wave, Oxfordshire, UK) ball-on-disk tribometer. The tribometer was placed in a closed chamber and a vacuum of ~10^{-3} Pa was attained using a turbomolecular pump, backed by a dry scroll vacuum pump. Moreover, 100Cr6 steel ball of 10 mm radius was used as counter body, while the other testing parameters were: load = 10 N, sliding radius = 5 mm, sliding velocity = 0.1 m/s and sliding cycles = 10,000.

Table 1. Chemical composition, hardness and room temperature humid air, 200 °C and dry nitrogen friction coefficient and specific wear rates of the coatings under analysis.

Properties vs. Coatings		**WSx**	**WSN5**	**WSN12.5**	**WSN20**
Composition (at.%)	W	40.0	39.0	38.1	35.6
	S	59.0	45.6	37.9	38.1
	N	-	14.6	23.0	25.5
Hardness (GPa)		3.7	6.6	8.0	7.2
Friction Coefficients	Room Temperature (humid air)	0.09	0.15	0.09	0.11
	200 °C	0.04	0.05	0.02	0.02
	Dry Nitrogen	0.02	0.03	0.03	0.04
Specific Wear Rates (mm^3/Nm)	Room Temperature (humid air)	4.10×10^{-7}	1.00×10^{-7}	7.20×10^{-8}	6.10×10^{-7}
	200 °C	3.00×10^{-7}	1.30×10^{-7}	7.10×10^{-8}	1.60×10^{-7}
	Dry Nitrogen	5.00×10^{-8}	9.30×10^{-9}	1.20×10^{-8}	2.30×10^{-8}

3. Results and Discussion

Table 1 shows the chemical composition and hardness of all the coatings. The increase in the N_2 flow rate from 0 to 20 at.% resulted in an increase of N content from 0 to 25.5 at.% and a decrease of S/W ratio from 1.47 to 0.99. It is obvious that the increase in the N content is attributed to the increase of N flow in the deposition chamber during the coating's synthesis. Similarly, the decrements in S/W ratio are due to the sputtering effects of the lighter S atoms from the growing coatings and a probable replacement of S atoms by N atoms in the coating matrix. The WSx pure coating displayed the lowest hardness of 3.7 GPa. N additions significantly increased the hardness up to 8.0 GPa, for WSN12.5 coating, and then decreased slightly to 7.2 GPa for the WSN20 coating. A thorough discussion on the basic properties of these coatings and the underneath reasons can be found in [7].

Figure 1a shows the COF under vacuum environment sliding. The average COF is calculated from the steady state region which varied with changes in the N-alloying. The WSx pure coating displayed the highest COF of 0.04. The steady state region considered during this average calculation is from 5000 to 10,000 cycles. The coating with the lowest nitrogen concentration i.e., WSN5 coating, displayed the lowest friction coefficient. The average steady state COF is 0.02, with the steady state region lying between 1000 and 10,000 cycles. The WSN12.5 coating that displayed the best sliding properties in room temperature humid air, 200 °C and dry nitrogen sliding displayed the worst frictional properties in vacuum. From 500 to 5000 cycles, the COF was ~0.02 but after 5000 cycles, a sudden increase to ~0.05 was observed. The final steady state average COF of this coating was 0.05 (considered between 5000 and 10,000 cycles). The highest N content coating's steady state region lied between 4000 and10,000 cycles with an average COF of 0.03.

Unlike the COF, the specific wear rate of the W-S-N coatings displayed a linear increase with increasing N concentration (Figure 1b). The pure coating displayed the highest wear rate of 1.1×10^{-6} mm^3/Nm. After N introduction, the specific wear rate suddenly drops one order of magnitude, showing the beneficial influence of N-alloying. From the lowest to the highest N content, the specific wear rate progressively increased with the highest value of 2.4×10^{-7} mm^3/Nm being achieved by WSN20. The lowest value of 3.7×10^{-8} mm^3/Nm was observed for the WSN5 coating. The values of the specific wear rates corroborate the 2D cross-section profiles of the wear tracks, as shown in Figure 2. The evolution of the 2D profiles depicts an abrasive wear mode for all the coatings. Additionally, the accumulation of the wear debris on the sides of the wear tracks is also visible. This wear debris accumulation is a common feature shown by alloyed-TMD coatings.

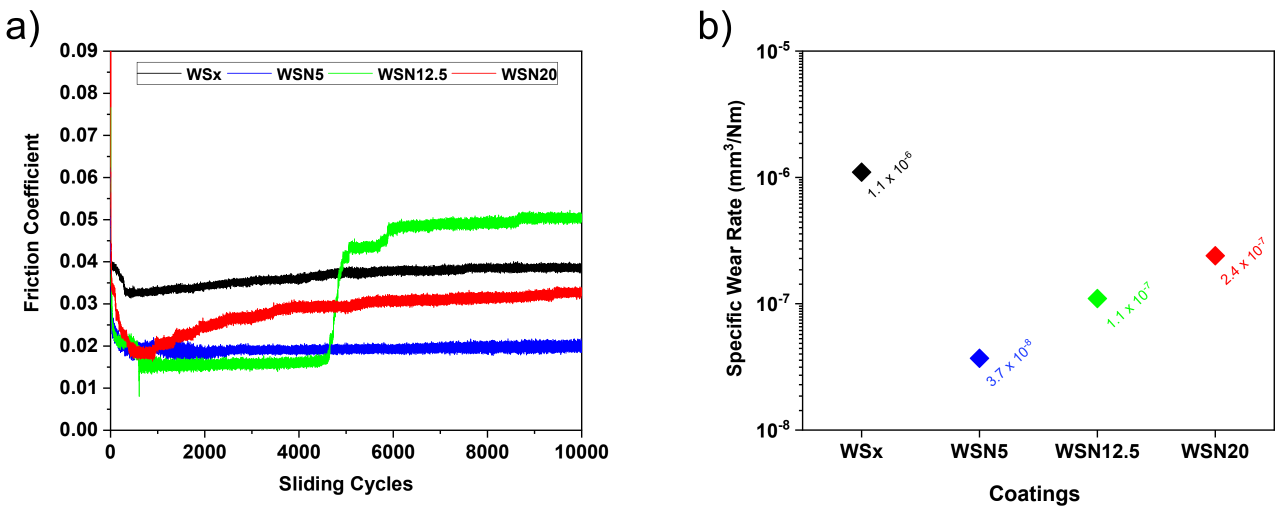

Figure 1. (**a**) Friction coefficient and (**b**) Specific wear rate of the coatings.

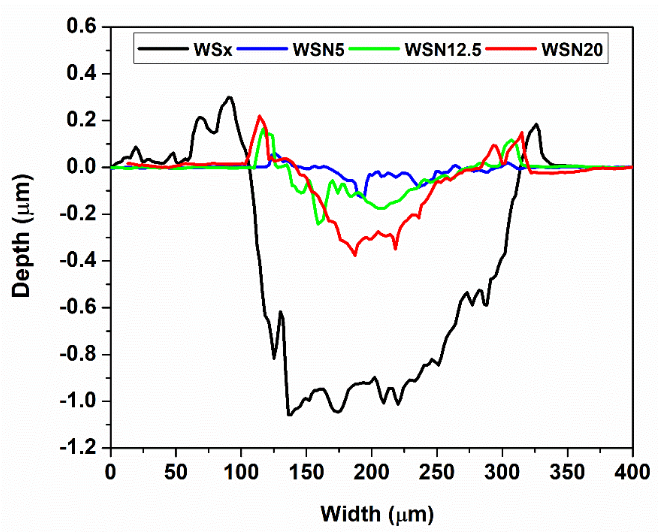

Figure 2. 2D wear tack profiles of the wear tracks vacuum sliding tests.

In summary, WSN5 displayed superior vacuum sliding properties contrarily to the results of tribological testing in other environments (see our previous study [7]), as summarized in Table 1. WSN12.5 coating is the one which displayed superior sliding properties in all three previously studied environments (room temperature humid air, 200 °C and dry N_2) while, in vacuum, its performance is the worst. Additionally, the COFs and the specific wear rates of the dry N_2 testing (which is normally used for replicating dry atmospheres) were slightly different from the vacuum sliding tests. Thus, the analysis in vacuum environments must always be performed before deciding coatings for diverse environment sliding. This should also be carried out to report properties of dry lubricants in a systematic and organized manner.

4. Conclusions

In this work, the vacuum tribological properties of the DC magnetron sputtered W-S-N coatings were studied to overcome a literature gap. From this work where testing W-S-N coatings was carried out for the first time in vacuum, it can be concluded that TMD lubricant coatings can show a different tribological performance when tested in different dry multi-environments. The approach of taking the vacuum environment performance of TMDs as representative of dry sliding is not ideal, since one coating/composition displaying the best properties in this environment does not mean that it will be ideal for others. This factor is sometimes missing in literature on alloyed-TMD coatings from which WSN coating system is a good example.

Author Contributions: T.B.Y.: writing-original draft, conceptualization, investigation, validation, data curation, methodology; K.Y.: investigation and draft editing; A.M.: investigation and draft preparation; F.F. (Fabio Ferreira): writing-review and editing, conceptualization, validation; A.B.: writing-review and editing, investigation, analysis, data curation, validation; F.F. (Filipe Fernandes): data curation and investigation; A.A.-R.: draft preparation, investigation; A.C.: writing-review and editing, results analysis, funding acquisition, supervision. All authors have read and agreed to the published version of the manuscript.

Funding: This work is sponsored by FEDER National funds FCT under the projects: SMARTLUB ref. "POCI-01-0145-FEDER-031807", CEMMPRE ref. "UIDB/00285/2020", On-SURF ref. "POCI-01-0247-FEDER-024521", "LA/P/0112/2020" and Atrito-0 ref. "POCI-01-0145-FEDER-030446". Andrey Bondarev acknowledges the support of the project "International Mobility of the scientific workers MSCA-IF IV at Czech Technical University in Prague, Grant No: CZ.02.2.69/0.0/0.0/20_079/0017983".

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: In this section, you can acknowledge any support given which is not covered by the author contribution or funding sections. This may include administrative and technical support, or donations in kind (e.g., materials used for experiments).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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