ISSN 0208-7774 TRIBOLOGIA 1/2024 p. 57–66
DOI: 10.5604/01.3001.0054.4655

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STRUCTURE AND PROPERTIES OF THE NITRIDED LAYER WITH SULFIDES

STRUKTURA I WŁASNOŚCI WARSTWY AZOTOWANEJ Z SIARCZKAMI

Key words: sulfur nitriding, nitriding, T-05, dry friction, heat treatment, SEM/EDS, MoS_2.

Abstract: This study contains a brief overview of sulfur nitriding methods, i.e. a modified version of nitriding. This information is accompanied by the results of our own tests of nitrided and sulfur-nitrided coatings with the addition of MoS_2 in the scope of structure assessment by means of a scanning microscope – SEM/EDS and the results of tribological tests performed under dry friction conditions on the T-05 apparatus for four variants of thermo-chemical treatment. In tribological tests, the degree of wear was observed by measuring the weight loss of both samples and counter-samples, and the beneficial effect of sulfides on reducing wear was indicated, with the sulfur nitriding variant with MoS_2 added being the most advantageous. In this case, the lowest degree of wear was found for the friction pair with a sulfur-nitrogen coating reinforced with MoS_2, which may lead to extending the operating time.

Słowa kluczowe: azotonasiarczanie, azotowanie, T-05, tarcie suche, obróbka cieplna, SEM/EDS, MoS_2.

Streszczenie: Opracowanie zawiera krótki przegląd metod azotonasiarczania tj. zmodyfikowanej wersji azotowania. Do tych informacji dołączono wyniki własnych badań powłok azotowanych i azotonasiarczanych z dodatkiem MoS_2 w zakresie obejmującym ocenę struktury za pomocą mikroskopu skaningowego – SEM/EDS i wyniki testów tribologicznych wykonanych w warunkach tarcia suchego na aparacie T-05 dla czterech wariantów obróbki cieplno-chemicznej. W testach tribologicznych obserwowano stopień zużycia przez pomiar ubytku wagi zarówno próbek, jak i przeciwpróbek, a także wskazano na korzystny wpływ siarczków na zmniejszenie zużycia, przy czym najkorzystniejszy okazał się wariant azotonasiarczania z dodatkiem MoS_2. W tym przypadku stwierdzono najmniejszy stopień zużycia, co dla pary ciernej z powłoką azotonasiarczaną wzmocnioną dodatkiem MoS_2 oznacza możliwość wydłużenia czasu eksploatacji.

INTRODUCTION

The durability of steel parts with nitrided coatings operating in friction areas can be increased by sulfurizing the surface layer. It is where the sulfidation of nitrided surfaces working in friction nodes – which has been in use for over 70 years – originates, especially under dry friction conditions, which is a well-known method of improving wear resistance of the friction pair. The origins of sulfur nitriding can be traced to a French patent **FR942387 [L. 1]** for thermo-chemical treatment of steel in molten nitriding salts additionally containing a sulfur compound, which is the source of this element introduced into the layer of compounds.

On the surface of the nitrided layer itself, the lubricating properties can be improved by the performance of sulfidation during nitriding, which leads to a chemical reaction of iron with sulfur and the formation of iron sulfides with a hexagonal structure that facilitates sliding. In this way the resistance to seizure of two mating surfaces can be improved.

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The seizure resistance can also be improved by applying to the surface a ready-made sulfide, e.g. that of molybdenum, tungsten, or another compound revealing the characteristics of a solid lubricant. Recent attempts to improve sulfur-nitrogen coatings have been heading in this direction. In Poland, two main technologies for simultaneous nitriding and sulfidation have been developed and implemented, i.e. the "Sulfonit" technology using sulfur vapor during nitriding **[L. 2]** and the technology using SO_2 gas during nitriding as a source of sulfur (and oxygen) **[L. 3]**.

A variant of the Sulfonit technology is the process commercially trademarked NITROVAC **[L. 4],** which is known for the method of sulfur nitriding in an atmosphere of ammonia and sulfur vapors, additionally containing hydrocarbons or other compounds serving as a carbon source, and the process is also carried out at a reduced pressure ranging from 10^{-3} ÷ 750 torrs. As a result of the reduced pressure, it is easier to control the phase composition of the resulting hardened layer, and the possibility of introducing carbon extends the scope of applicability to the complex process of "nitrogen carbon sulfidation".

Other local studies in the field of sulfur nitriding include such niche processes as: the technology of introducing a liquid mixture of triethanolamine with ammonium sulfide into the nitriding furnace **[L. 5]**, introducing monoethanolamine with the addition of ammonium sulfide into the nitriding furnace **[L. 6]**, cyanosulfidation by pyrolysis of ammonium thiocyanate solution NH_4CNS in ethyl alcohol **[L. 7]**, the technology of gaseous diffusion nitriding sulfidation in an alternating magnetic field **[L. 8]** and the technology of introducing molybdenum disulfide and/or tungsten onto the treated surface by spraying or by immersion in a suspension with these sulfides, after which the workpieces processed in this way are heated in the atmosphere of water vapor **[L. 9]**.

Table 1. Sulfidation methods during nitriding/nitrogen-carburizing (based on Wang et al. [L. 10])
Tabela 1. Metody nasiarczania podczas azotowania/azotonawęglania (na podstawie Wanga i in. **[L. 10]**)

Method	Name	Sulfating medium	Processing temperature, °C	Other parameters
Sulfidation in powders	Pyrolysis of solid substances	Charcoal with adsorbed H_2S	200÷600	1÷3 h
		Powder mixture of urea and sulfur **[L. 12]**	n.d.	n.d.
Gas sulfidation	Introducing gas	H_2S	250÷600	3 h
	Introducing gases	$H_2S + H_2$	200÷600	A few h
	SULFONIT **[L. 2]**	Fumes from molten sulfur	400–720	0.5–20 h
	NITROVAC + S vapors **[L. 4]**	Fumes from molten sulfur	420–700	Negative pressure 10^{-3} up to 750 torrs
	Introducing sulfur dioxide **[L. 3]**	SO_2	350–750	n.d.
	$NH_3 + NH_3$– dissoc. + magnetic field 20÷2000 Oe **[L. 8]**	0.1–2% sulfur vol.	580	0.5–15 h
Bath sulfidation	Aqueous solutions	$(NH_2)_2CS$	90÷180	1 h
	Dissolved salts	NaCN, NaCNO, Na_2SO_3	500÷600	2÷3 h
	Electrolytic method	NaSCN, KSCN, etc.	190 ±10	2.5 A/dm³
	Immersion **[L. 9]** in a sulfide suspension prior to nitriding	WS_2 and/or MoS_2 + heating in an atmosphere of water vapor	347÷647°C	0.2–6 h
Ion sulfidation	Ionization of gases	H_2S, CS_2, S vapors, etc.	160÷500	1.33 Pa, 2 h
Spraying of sulfide powders	Suspension spraying **[L. 9]** WS_2 and/or MoS_2 before nitriding	WS_2 and/or MoS_2 + heating in an atmosphere of water vapor	347÷647	0.2–6 h

n.d. – no data available (brak dostępnych danych).

Since the first patent for sulfate nitriding **[L. 1]**, a significant number of new and legally protected studies and literature have been released worldwide describing sulfides as solid lubricants **[L. 10]**, layer properties obtained **[L. 11]** and exemplary sulfur nitriding processes **[L. 12]**. The literature was expanded to include a list of selected patents from the last three decades **[L. 13–23]**, a list of selected articles on sulfur nitriding published after 2000 **[L. 24–36]** and a list of publications from the last 5 years in the field of space tribology and solid lubricants **[L. 37–47]**. Despite advanced knowledge of sulfur nitriding and solid lubricants, new solutions in the field of thermo-chemical treatment modifying anti-wear coatings applied to surfaces are constantly being sought. The aim of this search is not only to develop coatings with better functional properties but also to search for cheaper processes of their production.

The economic factor shall determine the success of new developments. Therefore, the planned experiments are focused on searching for inexpensive and easily available solutions.

Methods listed in **Table 1** are usually limited to providing "with what" sulfidation can be performed, while they hardly ever stipulate the details of "how" the sulfurization process should be carried out.

The above-mentioned list of national patents shows that none of the studies uses hydrogen sulfide for nitrosulfidation, while information in the literature indicates that there are such methods using H_2S as a source of sulfur during nitriding.

While it has long been known that workpieces after nitriding alone achieve a lower friction coefficient (in addition to other advantages such as increased wear resistance, increased fatigue strength, good anti-corrosion properties), after sulfur nitriding a further reduction in the friction coefficient is observed and, above all, an increase resistance to wear and seizure. Nitrogen sulfidation technology has tremendous development potential and application possibilities wherever solid lubricants can be used in moving joints. In the conducted research, it was decided to test not only sulfur nitriding using the NH_3 + 1% H_2S atmosphere but also the effect of the addition of MoS_2 on the wear of the coatings applied in this way.

OWN RESEARCH

Research materials, aim and plan of experiments

Research materials

The samples (blocks) were made of **C45** steel following heat treatment, the counter-samples were made of **18HGT** alloy structural steel (according to PN-89/H84030/02), which was carburized to a 0.5 mm thick layer, hardened and tempered. The hardness of the counter samples was 58 HRC.

The molybdenum disulfide used to apply the coating prior to thermo-chemical treatment had a granulation of less than 0.85 μm.

Aim and scope of experiments

The aim of the experiments was to test and compare the wear resistance of nitrided coatings in the following variants:

- **A** – after nitriding,
- **AMoS$_2$** – after nitriding – with a MoS_2 layer applied before nitriding,
- **AH$_2$S** – after sulfur nitriding (nitriding in an NH atmosphere$_3$ + H_2S),
- **AH$_2$SMoS$_2$** – after sulfur nitriding (H_2S) – with an MoS_2 layer applied before nitriding.

Thermo-chemical treatments were carried out in a laboratory furnace. Nitriding (**A**) was carried out in an ammonia atmosphere, while sulfur nitriding (**AH$_2$S**) in the experimental NH_3 +1% H_2S mixture (8 h at 540°C, 2 h at 580°C, with NH_3 flow throughout the entire process – 50 ml/min, additional H_2S was administered at 580°C 0.5 ml/min).

In the modified version, both nitriding and sulfur nitriding were performed on samples covered with an MoS_2 layer before thermo-chemical treatment. Hence the designations of modified versions as **AMoS$_2$** and **AH$_2$SMoS$_2$**. The MoS_2 coating applied to the samples was 0.006 g/cm^2. The test results were compared with tests conducted on a reference sample marked as **S** – i.e. without coating.

The scope of the research included observations of the structure using a scanning microscope, roughness tests and tribological tests using a "block-roller" stand on the T-05 apparatus. In this case, the observation was limited to the loss of mass of the block (sample) and the mass of the roller (counter-sample). After the tribological tests, the abrasion places were examined and analyzed.

Research results and discussion

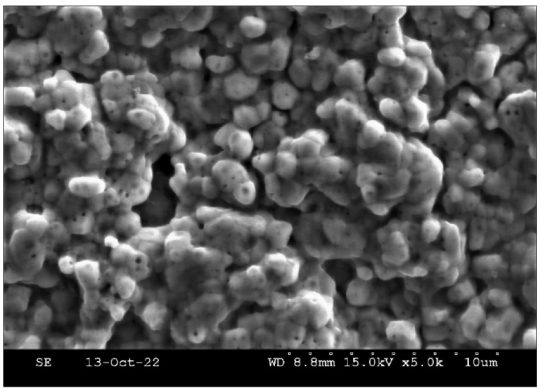
Sample surfaces after various types of heat treatment

Sample surfaces after various types of thermo-chemical treatment are shown in **Fig. 1**. The varied images are related to the presence or absence of FeS and/or MoS_2 sulfides on the surface.

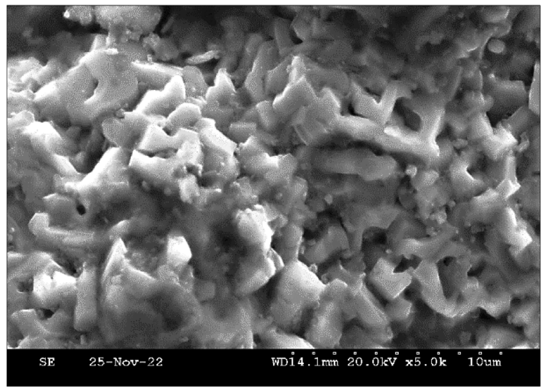
Analysis of surface stereometry depending on the type of heat treatment

Roughness measurements were carried out using Sensofar S NEOX profilographometer on **C45** steel samples and on **18HGT** steel counter-samples.

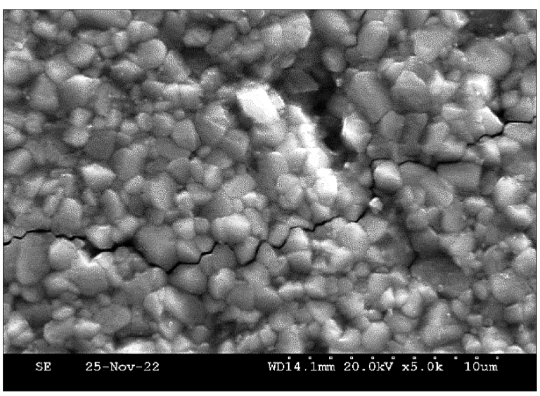
The results of measurements of the Ra parameter on the test surfaces of samples (blocks) after various variants of thermo-chemical treatment and counter-samples are summarized in **Table 2** and in **Fig. 2**.



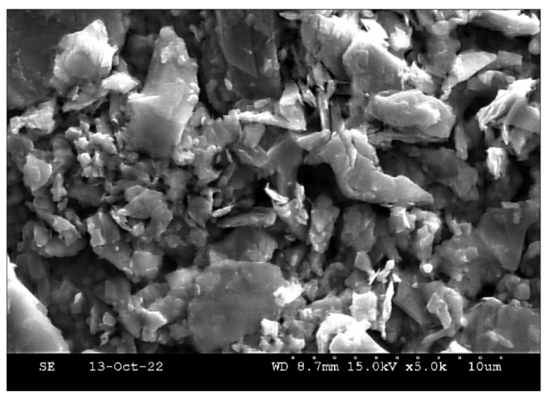
A sample (without the addition of MoS_2)
Próbka **A** (bez dodatku MoS_2)



The **$AMoS_2$** sample (i.e. with the addition of MoS_2)
Próbka **$AMoS_2$** (tj. z dodatkiem MoS_2)



The **AH_2S** sample (i.e. without the addition of MoS_2)
Próbka **AH_2S** (tj. bez dodatku MoS_2)



AH_2SMoS_2 sample (i.e. with the addition of MoS_2)
Próbka **AH_2SMoS_2** (tj. z dodatkiem MoS_2)

Fig. 1. List of surface structures after various types of heat treatment. SEM
Rys. 1. Zestawienie struktur powierzchni po różnych wariantach obróbki cieplnej. SEM

The Ra parameter on all rollers was very similar, while the Ra values for the samples reveal significant differences depending on the coating applied to the surface. The reference point is the **(S)** sample and its surface before thermo-chemical treatment. After processing, the Ra parameter is higher in each case. Comparison of the Ra parameter for the nitrided sample **(A)** with the Ra parameter for a sample without thermo-chemical treatment **(S)** indicates a clear increase in the parameter by approx. 67% after nitriding. Increase in roughness after nitriding the **$AMoS_2$** sample i.e. with MoS_2 powder was lower and amounted to 42%. The sulfur nitriding process itself had a stronger impact on the increase in the Ra parameter **(AH_2S)** and the highest increase in roughness was found on the nitrosulfated sample with the presence of MoS_2 powder **(AH_2SMoS_2)**.

Table 2. Tested parameters of workpieces before the test on the T-05 apparatus (the given values are arithmetic means of three measurements)

Tabela 2. Badane parametry detali przed testem na aparacie T-05 (podane wartości są średnimi arytmetycznymi z trzech pomiarów)

Workpiece	Parameter	Thermo-chemical treatment variant				
		S	**A**	**$AMoS_2$**	**AH_2S**	**AH_2SMoS_2**
Roller (counter sample)	HRC	58	58	58	58	58
	Ra, µm	0.780	0.795	0.775	0.783	0.788
Block (sample)	Ra, µm	0.269	0.449	0.382	0.584	1.055

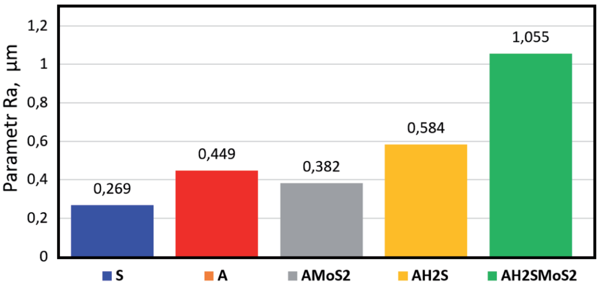


Fig. 2. Change in sample surface roughness depending on the heat treatment applied

Rys. 2. Zmiana chropowatości powierzchni próbki w zależności od zastosowanej obróbki cieplnej

Microstructure of coatings in cross-section

The microstructures of the coatings observed in cross-sections after nitriding and sulfur nitriding are very similar, with the difference that the types with the addition of MoS_2 applied before thermo-chemical treatment have a clearly marked presence of the MoS_2 layer on the surface. Such image of the structure proves that the MoS_2 layer present on the surface before nitriding does not interfere with the formation of the coating.

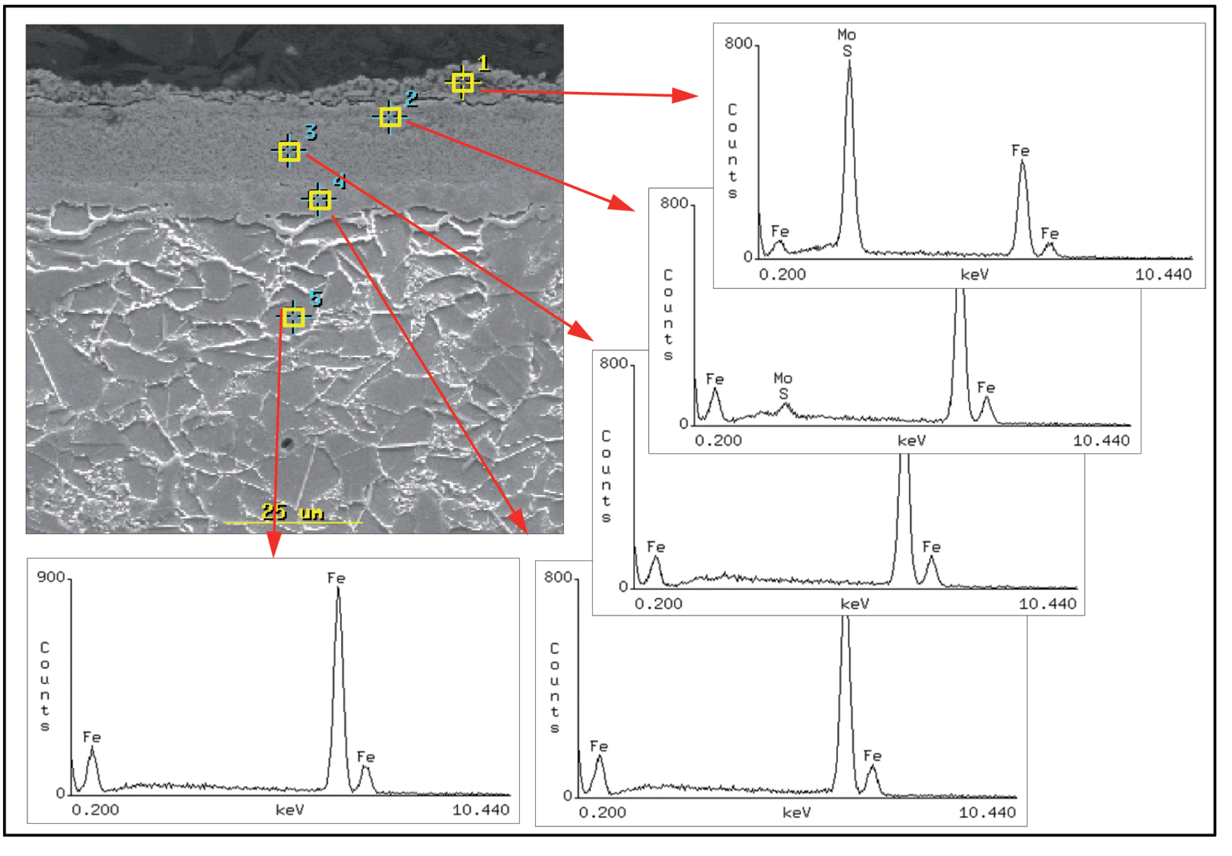


Fig. 3. Microstructure of the coating after sulfur nitriding with the addition of MoS_2 – AH_2SMoS_2. Spot analyses from the coating locations indicated by squares were performed using an EDS spectrometer at a scanning microscope

Rys. 3. Mikrostruktura powłoki po azotonasiarczaniu z dodatkiem MoS_2 – AH_2SMoS_2. Analizy punktowe z miejsc powłoki wskazanych kwadratami wykonano za pomocą spektrometru EDS przy mikroskopie skaningowym

Mass loss in tribological test

The following parameters of the test runs were adopted in the tests on the T-05 apparatus:

- counter sample rotation speed – 180 rpm,
- friction node load – 300 N,
- test run time – 600 s,
- method of lubricating the friction pair – dry.

The results of mass loss measurements for samples after various variants of thermo-chemical treatment and counter-samples are summarized in **Table 3** and in **Fig. 4** and **5**.

Table 3. Mass loss of samples and counter-samples in the block-roller test on the T-05 apparatus
Tabela 3. Zużycie wagowe próbek i przeciwpróbek w teście klocek-rolka na aparacie T-05

Workpiece	Mass loss [g]				
	S	**A**	**$AMoS_2$**	**AH_2S**	**AH_2SMoS_2**
Sample (block)	0.0717	0.0613	0.0496	0.0381	0.0167
Counter sample (Roller)	1.1399	0.8652	0.5140	0.2632	0.1675

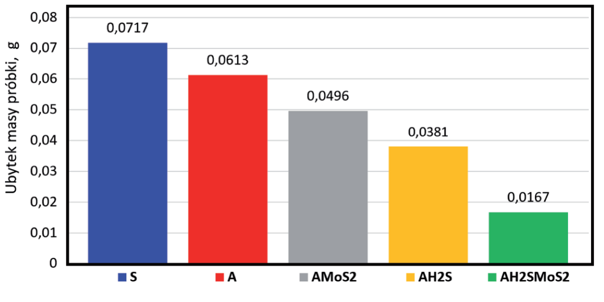


Fig. 4. Mass loss of the cube in the tribological test – T-05 tester
Rys. 4. Zużycie wagowe kostki w teście tribologicznym – tester T-05

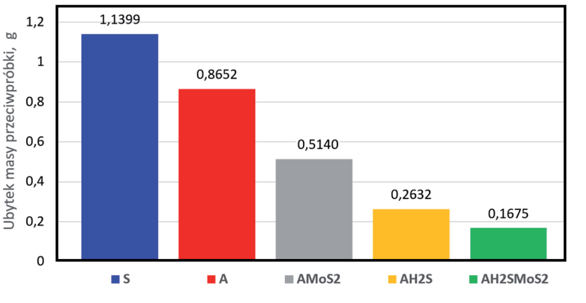


Fig. 5. Mass loss of the roller in the tribological test – T-05 tester
Rys. 5. Zużycie wagowe rolki w teście tribologicznym – tester T-05

Surface microstructure after friction

The examination of abrasion places provides important information about the process of wear and tear. In **Fig. 6** the effects of wear and tear produced during test are clearly visible on the T-05 device. The wear of the mating elements of the friction pairs during operation will *in fact* result in the destruction of the surface layer.

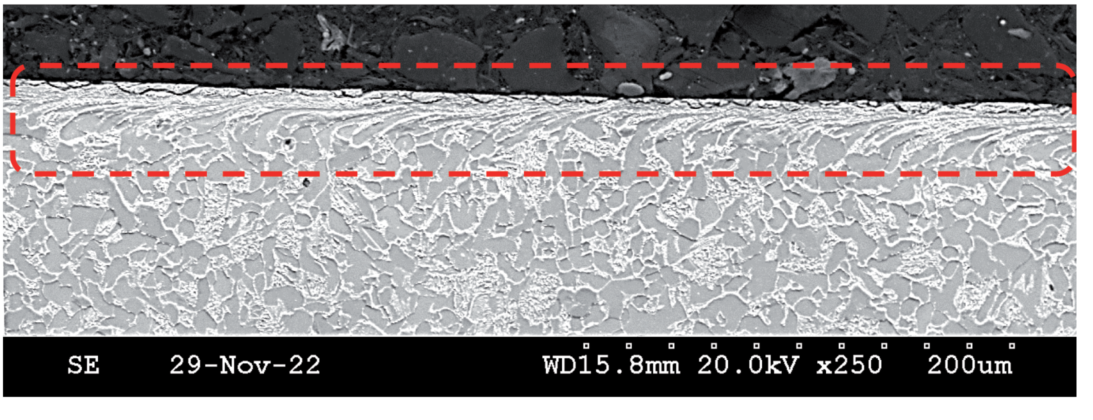


Fig. 6. The abrasion surface examined under the microscope in cross-section reveals numerous particles pressed into the deformed subsurface layer. SEM
Rys. 6. Powierzchnia wytarcia badana pod mikroskopem na przekroju poprzecznym posiada liczne cząstki wprasowane w odkształconą warstwę podpowierzchniową. SEM

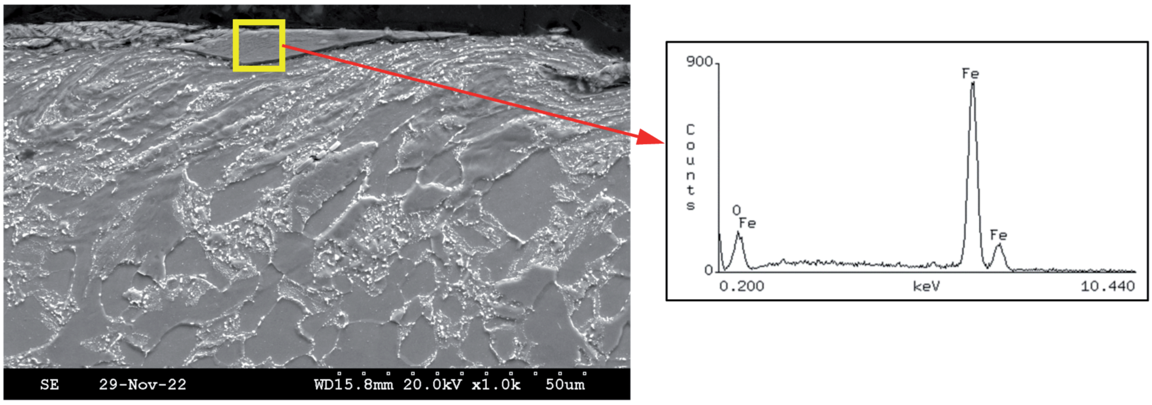


Fig. 7. An example of an oxide pressed into the abrasion surface. SEM/EDS
Rys. 7. Przykład tlenku wprasowanego w powierzchnię wytarcia. SEM/EDS

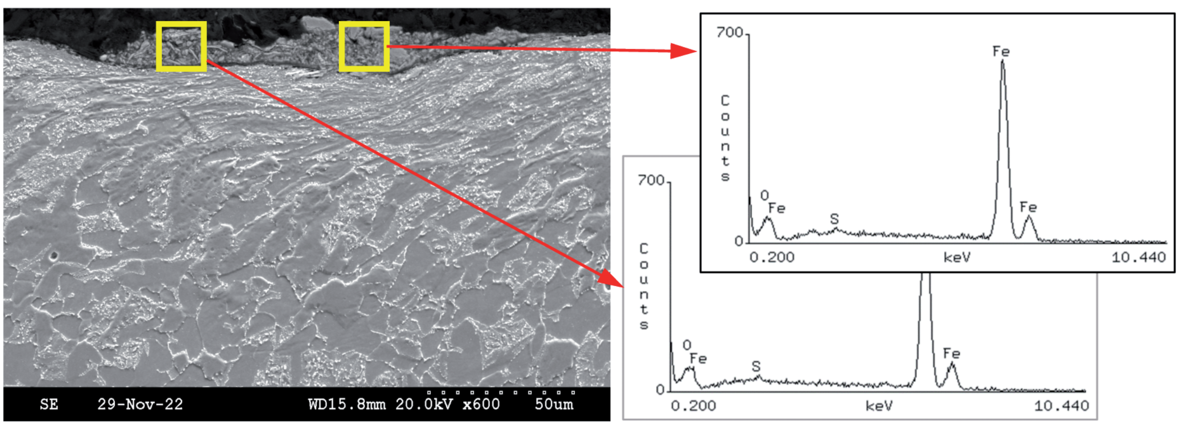


Fig. 8. An example of a mixture of oxides and sulfides pressed into the abrasion surface. SEM/EDS
Rys. 8. Przykład mieszaniny tlenków i siarczków wprasowanych w powierzchnię wytarcia. SEM/EDS

DISCUSSION OF RESULTS

The dissociation of ammonia on the steel surface within the ferritic range is possible due to the catalytic effect that iron has on the adsorbed ammonia molecules. Monatomic nitrogen formed from ammonia *in statu nascendi* can thus be captured by the steel and used to develop a hardened coating.

In the experiments, there was concern about the effect of "poisoning" of the catalyst known in petrochemistry – in our case: steel – by sulfur, so the process of sulfurization of the surface layer with H_2S was set at the end of the heat treatment cycle after nitriding for 8 h. The second problem might have been the presence of MoS_2 particles before heat treatment on the surface, the practice of nitriding requires great discipline in the preparation of the charge and the need to thoroughly clean the surfaces before processing. The presence of MoS_2 was unknown in the cases studied on the surface before heat treatment will not interfere with nitriding.

The tests showed, however, that in the case of samples with a layer of molybdenum disulfide, the nitrided coating would increase unhindered under the layer of powdered MoS_2 applied before thermo-chemical treatment. After the heat treatment, a layer of MoS_2 remained on the very top incorporated into the surface structure both in the case of the nitrided layer and in the case of the sulfur-nitrided layer.

The most important result, however, concerns the useful properties of the coatings measured by the amount of wear as part of the dry friction test on the T-05 device. The outstanding result indicating very low consumption on sulfur-nitrogen samples reinforced with MoS_2 powder is the result of the synergistic interaction of the two sulfides with a hexagonal structure, i.e. FeS and MoS_2 on the **AH_2SMoS_2** sample.

It should be borne in mind that in the course of use, the applied layer is not indestructible and will gradually wear out. Still, a low friction coefficient and low wear will be observed as long as sulfides are present on the surface. Removing the sulfides-rich surface layer will result in increased and accelerated wear in the deeper parts of the layer of compounds composed only of nitrides. It can therefore be assumed that in the case of an ideal composite structure consisting of a layer of nitride compounds with sulfides incorporated throughout the thickness, the life of the workpiece treated in this way will be further improved compared to a layer with sulfides present only on the surface.

It should be assumed that research on the use of sulfides to improve nitrided layers will probably continue its driving force being the excessive requirements for space technologies. The importance of these issues is evidenced by the dynamically developing new branch of tribology known as “space tribology”, dealing mainly with solid lubricants.

SUMMARY

The conducted tribological experiments enable the assessment and comparison of the impact on wear of friction pairs with different surface layers after thermo-chemical treatment. The influence of the type of surface layer on the amount of wear is best captured in: **Fig. 4 and Fig. 5** where the gradation of wear improvement by measuring the mass loss of samples can be set in the following order in relation to the raw sample – **S** (without coating):

- nitrided coating (**A**) compared to non-nitrided material (**S**) shows less wear,
- applying an MoS_2 layer (**$AMoS_2$** variant) results in the reduction of the wear of the layer compared to the layer obtained after nitriding (**A**),
- the type of sulfur nitriding alone (**AH_2S**type) demonstrates even less wear than the **$AMoS_2$** type,
- and the combination of sulfur nitriding with the addition of MoS_2 (**AH_2SMoS_2** type) offers the best result.

The above summary of wear test results shows that the mere application of the MoS_2 layer to the nitrided coating only is not a very attractive solution. However, the combined effect of sulfur nitriding and the MoS_2 layer applied before heat treatment results in a synergy effect and in this way the wear resistance of the coating can be significantly improved.

Comments regarding the amount of wear apply to both changes in the weight of samples and counter-samples. Even the surface roughness of the processed samples had no significant effect on the obtained gradation of the influence of the type of coating on wear, which was the highest for sulfur nitride samples reinforced with the addition of molybdenum disulfide.

Microstructure tests on cross-sections perpendicular to the wear surface showed that under conditions of heavy load – which is visible in the form of a deformed subsurface layer after the tribological test (**Fig. 6**, **7** and **8**) – both sulfides and oxides pressed into the surface are present. Sulfides are the very factor facilitating slippage during friction, which accounts for the research results obtained.

To sum up – the positive effect on reducing the wear of the sulfate nitriding coating with the addition of molybdenum disulfide is due to the presence of sulfides on the surface, which are known for their directional properties and are often used as a solid lubricant.

However, it must be remembered that the considered tribological processes always refer to a specific pair of interacting elements. Therefore, depending on the combination of friction surfaces, the intensity of wear and even its mechanism may be different.

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