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THE WEAR MECHANISM IN HEAVY-LOADED LUBRICATED COATED/STEEL SLIDING CONTACTS

MECHANIZMY ZUŻYWANIA WYSOKOOBCIĄŻONEGO SMAROWANEGO ŚLIZGOWEGO WĘZŁA TARCIA POWŁOKA/STAL

Key words:

coating, extreme-pressure additive, scuffing, four-ball tribosystem

Słowa kluczowe:

powłoka, dodatki przeciwzatarciowe, zacieranie, aparat czterokulowy

Abstract

The wear mechanism of the coating/steel tribosystem compared with that for conventionally used steel/steel friction contacts under sliding conditions lubricated with base oil with various concentrations of extreme-

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pressure (EP) additive is studied. A four-ball apparatus was used to determine the scuffing resistance of both tribosystems. The improvement of tribological properties in the case of coating/steel tribosystem was found to be governed by the reduction of the adhesion between rubbing surfaces of steel and coating material due to low chemical affinity (similarities) between them and by the ability of EP additive to react with steel surfaces generating a protective film preventing scuffing.

INTRODUCTION

In machine components working in a sliding contact e.g. gears, one of the dominating forms of wear is scuffing. The scuffing problem is of particular importance since it can lead to severe surface damage with rapid wear and eventually to complete deterioration and failure of the surfaces involved.

There are a number of practical ways of addressing the improving resistance to scuffing. An important way to increase the scuffing resistance of gears is to use oils with EP additives. At high contact temperature they react chemically with the rubbing surfaces and lead to the building on them a “protective” layer. However, the use of such additives has to be limited as much as possible, because they are really severe environmental pollutants. Another way of controlling scuffing is prevention of nascent metal surface by covering the sliding surfaces with coatings e.g. such as DLC (diamond-like carbon).

A low friction coefficient and high resistance to wear are features that cause low friction of coatings deposited by physical vapour deposition (PVD) methods on suitable substrate materials **[L. 1, 2, 3]** and they are predominant candidates for improving the performance of heavy-loaded machine components like gears.

Many studies have reported on the specific properties of metal-containing DLC films such as: low compressive strength (compared to non-doped and/or less hydrogenated DLC), low friction and high wear resistance of the machine components working under normal and severe contact conditions **[L. 4]**. Recently, it was also reported that tungsten doped hydrogenated DLC coatings (C:H:W coatings) exhibit excellent behaviour under heavy-loaded conditions of sliding and rolling contacts **[L. 5]**. The previous studies **[L. 4, 6]** on the effect of EP additive on performance of DLC coatings under sliding conditions have shown that in the case of DLC-steel tribosystem lubricated with synthetic base oil containing commercial EP additives, a tribofilm composed of coating material (W and C) and sulphur from the additive, is formed on contacting steel surfaces (WS_2 film) and it was found to be responsible for the improving of the tribological behaviour.

The performed investigation indicate that for WC/C coated elements working in heavy loaded EP additives are more effective than AW additives. By application of WC/C coating on steel parts of a friction pair lubricated with oil containing EP additives one can achieve increase in scuffing load and reduce the drop in pitting life caused by presence of the additive **[L. 7]**.

Furthermore, the scuffing resistance of a-C:H:W coated elements is much higher than obtained for uncoated elements lubricated with oils containing reactive additives. The mechanism of improving antiscuffing properties by chemical modification of the surface layer is replaced with the more effective antiscuffing mechanism of preventing the creation of adhesive bonds. However, a beneficial tribochemical action of lubricating additives cannot be excluded. One of the explanations of the beneficial interaction between coating and oil containing EP additives is the formation of a new class of a tribofilm **[L. 5]**.

The aim of this work was to study the effect of EP additive concentration on the mechanism responsible for improving the load-carrying capacity (scuffing resistance) of coating/steel tribosystem in comparison with their effect on steel/steel tribosystem under four-ball conditions.

EXPERIMENTAL

Test method and surface analyses

Experiments were carried out using a four-ball tester, denoted T-02, designed and manufactured by ITeE – PIB, Poland. The upper ball is pressed against the three lower stationary steel balls in the presence of a lubricant at the continuously increasing load. The upper ball rotates at the constant speed. Load and friction were measured during the run.

The scuffing resistance was measured as limiting pressure of seizure (p_{oz}) according to the method described in **[L. 8]**. The tests were performed using coating/steel tribosystem (one upper ball coated/three lower uncoated) and steel/steel tribosystem (all balls uncoated). The authors performed surface analyses using Scanning Electron Microscopy/Energy

Dispersive Spectrometry (SEM/EDS), Profilolography, Glow Discharge Optical Emission Spectrometry (GDOES) and X-ray Photoelectron spectroscopy (XPS) in order to explain the antiscuffing action of the used EP additive. After the tribological tests, the specimens (coated and uncoated balls) were rinsed thoroughly with cyclohexane without using an ultrasonic bath.

Samples and lubricants

In this study a-C:H:W coating represents a-C:H:Me group of DLC deposited using PVD process by reactive sputtering **[L. 1]** on 100Cr6 chrome alloy bearing steel ball substrate. The ball diameter was 12.7 mm, surface roughness Ra = 0.032 μm and hardness 60-65 HRC. Uncoated 100Cr6 chrome alloy bearing steel balls pairs were used for comparison.
Lubricants included in the investigation comprise of pure poly-alpha-olefin base oil (PAO-8) (viscosity 7.8 mm^2/s at 100°C and viscosity index 136) mixed with a commercial EP additive concentration varied in the range of 0.1% up to 5.0% wt. (elemental composition of EP determined by Inductively Coupled Plasma Optical Emission Spectroscopy: S-29.2%,P-1.35%, Ca-0.012%, Zn-0.0004%).

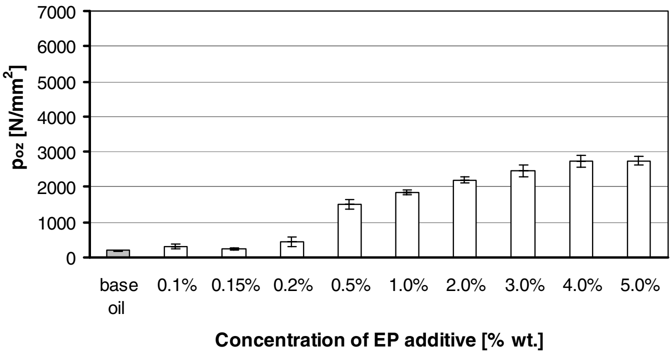
RESULTS

Tribological results

The results of the effect of EP additive concentration on the limiting pressure of seizure of coating/steel and steel/steel tribosystems are presented in **Fig. 1**.

It can be seen in the **Fig. 1** that the addition of EP additive to the base oil leads to increase the scuffing resistance of both tribosystems (steel/steel and coating/steel). The tribological results (see **Fig. 1b**) show that by the use of coating enables to significantly reduce (down to 1.0% wt.) the content of EP additive in oil. Any further increase in additive concentration does not lead to the increase of the scuffing resistance of the coating/steel tribosystem. In the case of steel/steel tribosystem, the addition of a high content (4.0–5.0% wt.) of additive to the base oil leads to an increase in the load-carrying capacity of the tribosystem compared with base oil (see **Fig. 1a**).

a)



b)

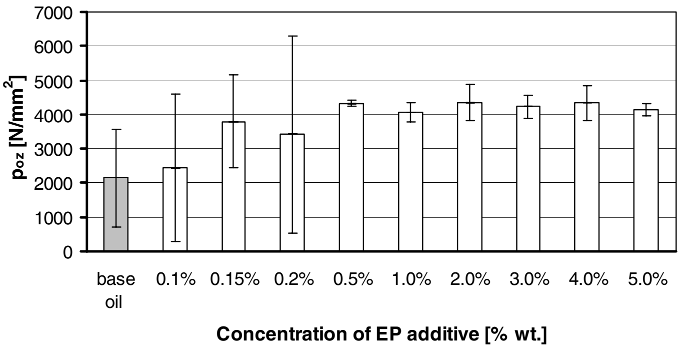


Fig. 1. Limiting pressure of seizure (p_{oz}) for EP additive at various concentrations in PAO-8 base oil: a) steel/steel and b) coating/steel tribosystems

Rys. 1. Graniczny nacisk zatarcia (p_{oz}) uzyskany dla różnych stężeń dodatku typu EP w oleju bazowym PAO-8: a) skojarzenie stal/stal, b) skojarzenie powłoka/stal

Profilolography, SEM/EDS, GDOES and XPS analyses of worn surfaces

In order to get insights on the effect of additive concentrations on the topography of steel balls (for steel/steel and coating/steel tribosystems) after tribological tests, the roughness parameter *Ra* (roughness average) has been acquired by using a Form Talysurf PGI-830 profilometer (see **Fig. 2**).

It can be seen in **Fig. 2** that by increasing the additive concentration, similar decrease of *Ra* values are obtained in the case of both tribosystems compared to pure base oil. Higher *Ra* values were obtained in the case of steel/steel tribosystem. The differences in roughness of lower steel ball surfaces from coating/steel and steel/steel tribosystems lubricated with EP additives at various concentrations are in agreement with the tribological results (scuffing resistance reflected by the limiting pressure of seizure parameter, p_{oz}) as are presented in the **Fig. 1**. High roughness in the case of steel/steel (see **Fig. 2**) indicates high wear reflected by the lower values of p_{oz} parameter compared with that one obtained for coating/steel (low roughness and less wear- higher values of p_{oz} parameter).

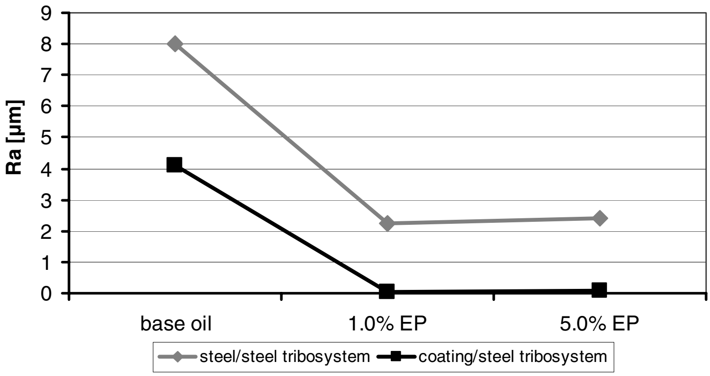


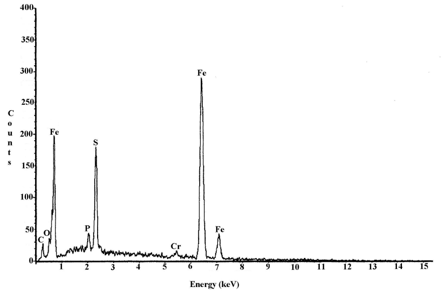
Fig. 2. Roughness average parameter (*Ra*) for steel stationary balls of steel/steel and coating/steel tribosystems lubricated with pure base oil and base oil mixed EP additive

Rys. 2. Średnia wartość parametru chropowatości Ra ze śladu tarcia stalowych kulek stacjonarnych w skojarzeniu stal/stal i powłoka/stal smarowanych czystym olejem bazowym i olejem bazowym z dodatkiem EP

In order to get information on the chemical composition of the wear scar after tribological tests SEM/EDS, GDOES and XPS analyses have been performed.

The chemical composition of the worn steel surfaces in case of both tribosystems was determined by EDS (see **Fig. 3**). The worn steel surfaces consist of iron, tungsten transferred from upper ball (coated) onto the steel ball (coating/steel tribosystem), oxygen, carbon, nickel (coating/steel tribosystem), phosphorus and sulphur.

a)



b)

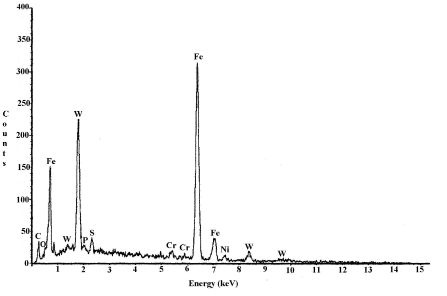


Fig. 3. EDS spectra of the wear scars of lower steel balls a) steel/steel and b) coating/steel tribosystems lubricated by PAO-8 base oil mixed with 1.0% of EP additive

Rys. 3. Widma EDS ze śladu tarcia stalowych kulek stacjonarnych w skojarzeniu stal/stal (a) i powłoka/stal (b) smarowanych czystym olejem bazowym i olejem bazowym z dodatkiem EP

The GDOES depths profile of the elements distributed in the surface layer of the wear scar of steel balls (coating/steel tribosystem) in the case of 1.0% of EP additive is presented in **Fig. 4**.

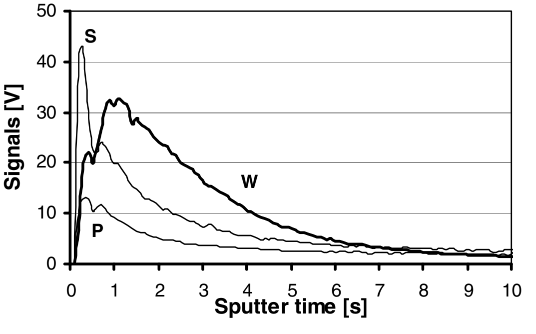


Fig. 4. GDOES depth profile of elements distributed on the steel ball surface (coating/steel tribosystem lubricated with 1.0% of EP added in PAO-8)

Rys. 4. Profile GDOES zalegania pierwiastków w głąb warstwy wierzchniej śladu tarcia kulek stalowych (skojarzenie powłoka/stal smarowane olejem PAO-8 z 1% dodatkiem EP)

It can be seen in **Fig. 4** that tungsten transferred from coated element is located beneath of the layer enriched in reaction products created by active components of lubricant.

More sensitive surface analysis XPS has been performed in order to explain the positive effect of the EP additive on tribological results. The detailed spectra of carbon *C1s*, oxygen *O1s*, phosphorus *P2p*, sulphur *S2p*, iron *Fe2p* and tungsten *W4f* were measured (see **Fig. 5**).

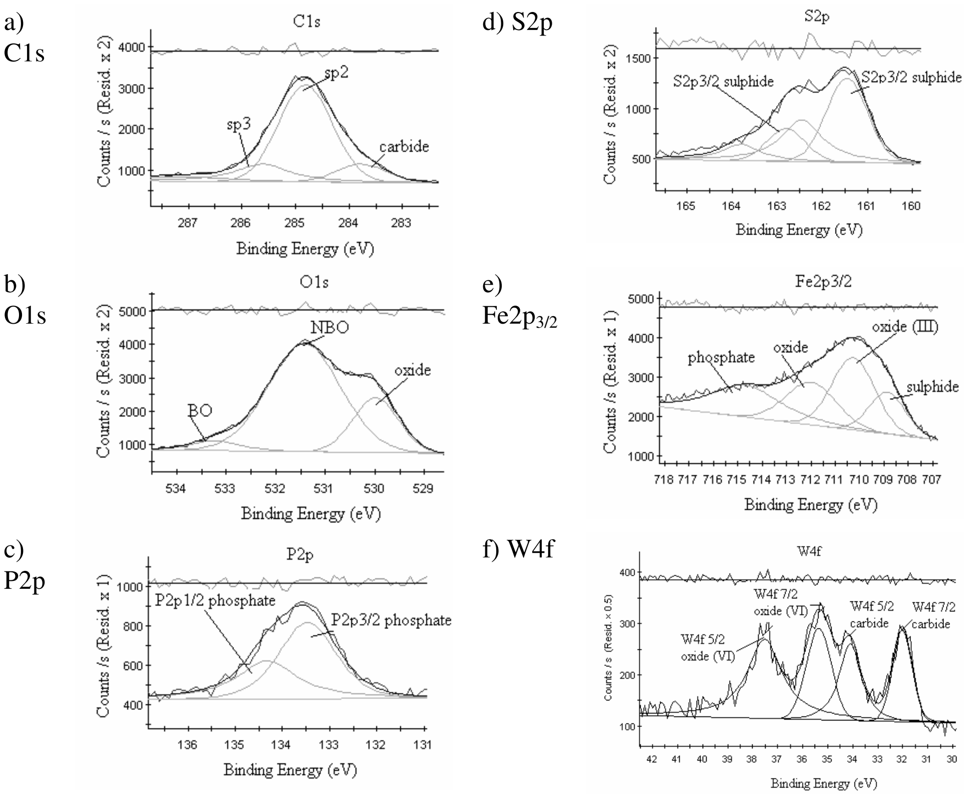


Fig. 5. XPS detail spectra of: a) C1s, b) O1s, c) P2p, d) S2p, e) $Fe2p_{3/2}$ and f) W4f of the worn steel surfaces (coating/steel tribosystem) lubricated by the base oil mixed with 1.0% wt. of EP additive

Rys. 5. Widma XPS z warstwy wierzchniej śladu tarcia kulek stalowych (skojarzenie powłoka/stal smarowane olejem PAO-8 z 1% dodatkiem EP): a) C1s, b) O1s, c) P2p, d) S2p, e) $Fe2p_{3/2}$ i f) W4f

The binding energy values and chemical states of the elements (C, O, P, S, Fe and W) on the surface are listed in **Table 1**.

The results of quantitative XPS elemental analysis measured on steel balls (coating/steel tribosystem) lubricated with 1.0 and 5.0% of EP additive are presented in **Fig. 6**.

Table 1. The identification of XPS peaks
Tabela 1. Identyfikacja pików z widm XPS

Peaks	Binding energy (eV)	Chemical bond	Reference
C1s	283.7	carbide (WC)	**[L. 9]**
	284.8	sp^2-hybridised graphite-like carbon atoms	**[L. 10]**
	285.6	sp^3-hybridised graphite-like carbon atoms	**[L. 10]**
	286.6	C-O	**[L. 11]**
O1s	530.0	oxide	**[L. 12]**
	531.4	non-bridging oxygen (NBO) in phosphates	**[L. 13]**
	532.2	bridging oxygen (BO) in the phosphate group	**[L. 13]**
$P2p_{3/2}$	133.5	phosphate	**[L. 13]**
$S2p_{3/2}$	161.5	monosulphides (S^{2-})	**[L. 14]**
	162.8	disulphides (S_2^{2-})	**[L. 14]**
$Fe2p_{3/2}$	708.7	iron sulphide	**[L. 15]**
	710.8	iron oxide	**[L. 15]**
	712.4	iron phosphate	**[L. 16]**
	714.3	iron phosphate	**[L. 16]**
W4f	31.8	Tungsten carbide	**[L. 17, 18]**
	35.3	Tungsten oxide	**[L. 19]**

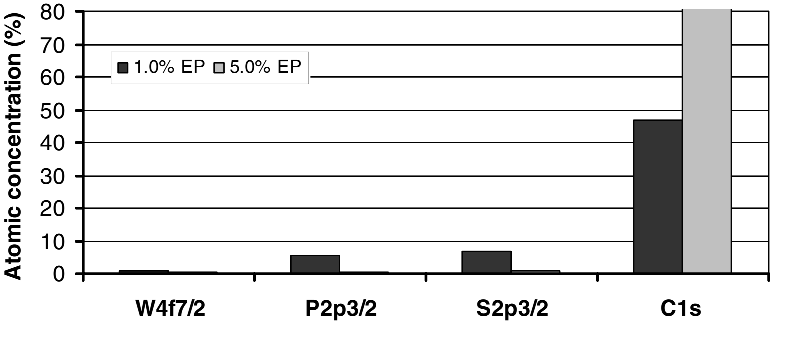


Fig. 6. The results of quantitative XPS analysis of the elements found on the steel surfaces (coating/steel tribosystem) lubricated with 1.0 and 5.0% of EP additive

Rys. 6. Wyniki ilościowej analizy XPS pierwiastków zidentyfikowanych w obrębie śladu zużycia elementu stalowego (skojarzenie powłoka/stal) smarowanego olejem z 1% i 5% dodatkiem EP

In the surface layer of steel (coating/steel tribosystem) wear scar phosphorus and sulphur are present in a higher content for lower concentration of EP additive and also, a higher amount of carbon on the steel surface was detected for higher concentration of EP additive (see **Fig. 6**).

In the *W4f* spectra (see **Fig. 5f**) measured on the steel and coated balls it was found that is no any additional peak in the region ($4f_{7/2}$ – $4f_{5/2}$) =32.8-35.0eV specific for tungsten bounded to sulphur (WS_2) **[L. 19, 20]**. The results evidenced that no reaction occurred between tungsten and sulphur on the steel and coated balls. Only transfer of coating material to the steel counter-surface was found, showed by the presence of the tungsten carbide on the wear scar of steel ball and also by the presence of sulphides, phosphates and oxides.

DISSCUSSION

On the basis of the tribological results on scuffing resistance (p_{oz} values) the synergy between the additive effect and the coating material effect for base oil (PAO-8) tribosystems was obtained (see **Fig. 7**). The synergy effect of coating and additive (C > A + B) is higher than the sum of two single actions of additive and coating.

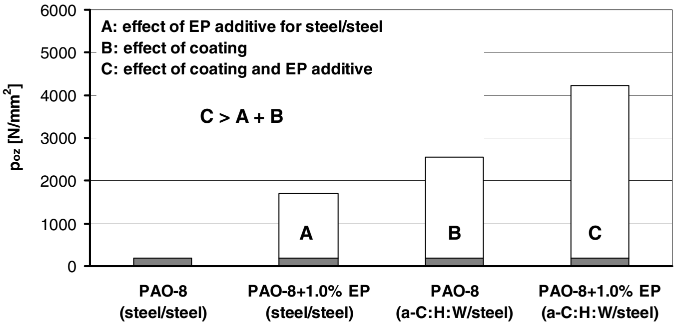


Fig. 7. A synergy between EP additive and coating material effects

Rys. 7. Synergetyczny efekt pomiędzy przeciwzatarciowym działaniem dodatku EP I materiału powłoki

In order to describe the wear mechanism for the coating/steel tribosystem compared with that one of steel/steel tribosystem, the worn surfaces were examined by using SEM and optical microscope which are used for observation of material transformation, also by EDS, GDOES and XPS analysis which give information regarding the formation of the surface layer.

In the case of steel/steel tribosystem the additive is initially adsorbed (physisorption) on the iron surfaces and the surfaces are separated by the lubricant oil. By the increasing in loads, the temperature contact is increased and causes the adsorbed additive to be decomposed on the worn surface leaving the sulphur atom (or any other active element from lubricant) to react with the iron of the worn surface. At higher loads the thin lubricant film formed is broken down, and the removal of tribofilm layers in microareas of contact leads to direct metal-metal contacts and further increasing in load leads to severe destruction of the surface layer which causes seizure.

The friction torque curve and applied load during a test run for coating/steel tribosystem lubricated with PAO-8 base oil mixed with 1.0% wt. of EP additive and wear stages are presented in the **Fig. 8**. The point *0* in the friction torque curve and applied load (see **Fig. 8**) represents conditions where the surfaces are separated by the lubricant oil and corresponds to the hydrodynamic regime of lubrication.

In the case of coating/steel tribosystem the improvement of tribological properties of a-C:H:W/steel tribosystem (see **Fig. 7**) under sliding conditions in comparison with steel/steel tribosystem it is found to be due to some transfer of coating material and carbon transfer layer to the steel counter-face (see **Fig. 8**, Stage *1a*) which has low friction and wear behaviour and by chemical reaction due to high temperatures in micro-contacts during sliding process **[L. 21]** which can lead to tribochemical reactions of the lubricating additive with the steel counter surface (**Fig. 9**, Stage *1b*).

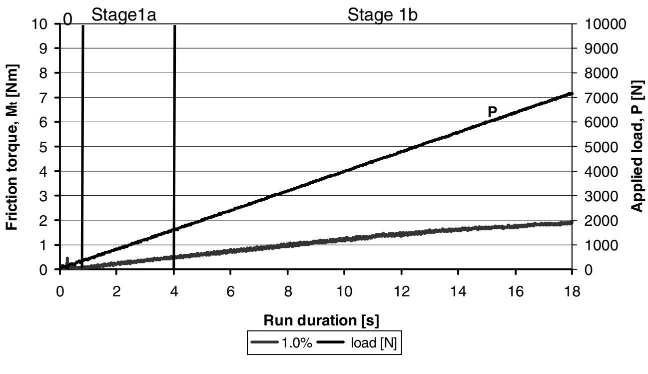


Fig. 8. The friction torque curve and wear stages for coating/steel tribosystem lubricated with PAO-8 base oil mixed with 1.0% wt. EP

Rys. 8. Przebieg momentu tarcia z wyróżnionymi etapami – skojarzenie powłoka/stal smarowane olejem PAO-8 z 1% dodatku EP

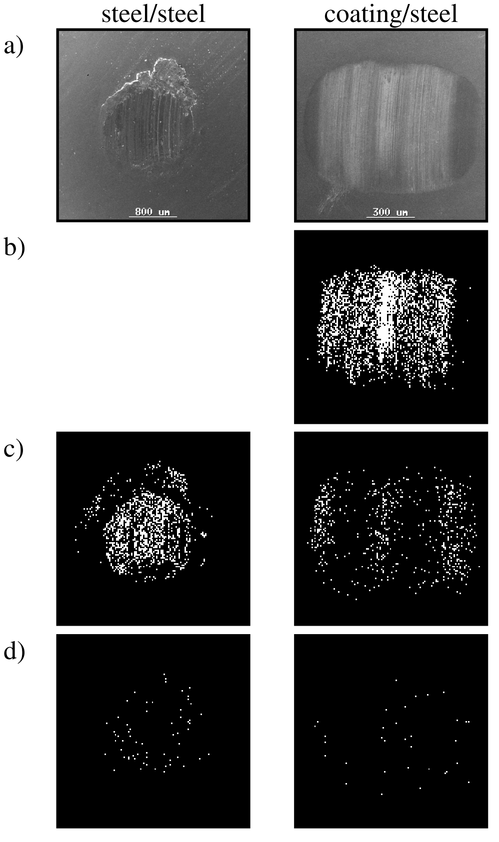


Fig. 9. SEM images (a) of the wear scars of steel surfaces (steel/steel and coating/steel tribosystems) lubricated with 1.0% EP additive and EDS maps for: b) W, c) S and d) P

Rys. 9. Obrazy SEM (a) śladów zużycia kulki stalowej (skojarzenia stal/stal i powłoka/stal) smarowane olejem z 1% dodatku EP oraz wyniki analizy EDS: b) W, c) S i d) P

The SEM images and EDS maps of distribution of elements present in the wear scar of the steel stationary ball surface (steel/steel and coating/steel tribosystems) lubricated with 1.0% of EP additive added in PAO-8 are presented in **Fig. 9**.

It can be seen in **Fig. 9** that the transfer of coating onto the steel surface occurred (see **Fig. 8**, Stage *1a*) and by increasing the load, adsorption of the additive to the steel surface takes place (see **Fig. 8**, Stage *1b*) as is indicated by the presence of chemical active elements (S, P) from additive (see **Fig. 9 c-d**). Also, it can be noticed in the **Fig. 9** that tungsten is present on the wear scar in zones where the sulphur is not present.

This might indicate that the chemical reactions are not taking place between the tungsten and sulphur. This observation is in agreement with the results confirmed by XPS analyses (see caption 3.2).

The results of surface analyses showed that the cause of the improvement of the tribological properties of coating/steel tribosystem is due to the low chemical affinity (similarities) between steel and coating material leading to the reduction of the adhesion between rubbing surfaces and also by the reaction of additive with steel surfaces generating a protective film enables to prevent scuffing initiation.

Based on the tribological and surface analyses results obtained, a schematic presentation of the main wear stages of tribological coating/steel tribosystem behaviour lubricated with base oil mixed with EP additive during the scuffing test is proposed in the **Fig. 10**.

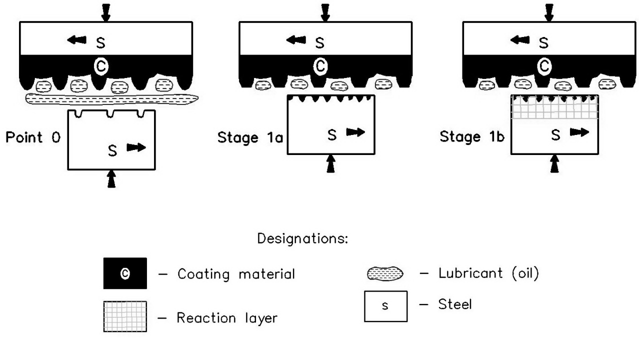


Fig. 10. The wear stages of tribological coating/steel tribosystem behaviour lubricated with base oil mixed with EP additive during the scuffing test

Rys. 10. Modele przebiegu zużywania skojarzenia powłoka/stal smarowanego olejem z dodatkiem EP

CONCLUSIONS

The tribological results had shown that the scuffing resistance of coating/steel tribosystem is two times higher than that of steel/steel tribosystem. For the coating/steel tribosystem the content of additives can be lowered down to 1.0% that reflects a positive effect from an ecological point of view while, for steel/steel tribosystem the best antiscuffing properties were obtained with 5.0% of additive.

A synergistic effect between additive and coating material for base oil (PAO-8) tribosystem has been observed. The main difference between the wear mechanisms of the tribosystems is caused by the difference in chemical affinity between steel and coating material surfaces and by the ability of EP additive to react with steel surfaces generating a protective film preventing scuffing.

Aknoledgements

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Streszczenie

W pracy dokonano porównania mechanizmów zużywania skojarzenia powłoka/stal w warunkach zacierania smarowanego olejem z różnymi stężeniami dodatku przeciwzatarciowego typu EP (extreme pressure) do mechanizmu zużywania skojarzenia stal/stal. Badania odporności na zacieranie przeprowadzono z wykorzystaniem aparatu czterokulowego w warunkach ciągłego narastania obciążenia. Na podstawie wyników badań tribologicznych i analiz powierzchni zaproponowano opis mechanizmu zużywania w warunkach zacierania skojarzenia powłoka/stal smarowanego olejem bazowym z dodatkiem EP. Wyjaśnia on poprawę charakterystyk tribologicznych skojarzenia powłoka/stal w stosunku poprzez: ograniczenie adhezji wynikające ze zmiany powinowactwa materiałów trących, transfer materiału powłoki na element stalowy i powstawanie produktów reakcji dodatków ze stalą, które tworzą warstewkę chroniącą przed inicjacją zacierania.