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PHYSICOCHEMICAL ASPECTS OF THE WORK OF PASSENGER CAR BRAKE LININGS. PART II – THE EFFECT OF LUBRICATING ADDITIVES

FIZYKOCHEMICZNE ASPEKTY PRACY OKŁADZIN HAMULCOWYCH SAMOCHODÓW OSOBOWYCH. CZ. II – WPŁYW DODATKÓW SMARNYCH

Key words:

brake linings, lubricants, third body, surface, friction and wear, acoustic effects.

Abstract:

The paper presents the influence of various systems of lubricating additives which determine the performance of the friction materials of brake linings. The base hybrid friction material formulation was modified with various types of lubricating additives. These additives are divided into groups containing commonly used lubricating materials: carbons and sulphides, compounded in various proportions, influencing the formation and structure of the so-called third body layer (TBL) on the surface of the brake disc because of braking. Raman Spectroscopy (RS), time of flight Secondary Ion Mass Spectroscopy (ToF-SIMS) and high-resolution scanning electron microscopy with an X-ray analyser (SEM-EDS) equipped with a focus ion beam (FIB) were used for chemical and morphological analysis of the surface layer of brake disc after breaking tests. The results of the physicochemical analysis of TBL were correlated with the results of tribological tests (according to the SAE-J2522 procedure, commonly known as AK-Master) on a brake dynamometer adapted to the measurements of acoustic signals (NVH – noise, vibration, and harshness). The obtained results confirm the important role played by the so-called third body layer, formed on the surface of the brake disc for safety (COF), durability (wear of friction elements) and the acoustic spectrum accompanying braking.

Słowa kluczowe:

okładziny hamulcowe, dodatki smarne, trzecie ciało, powierzchnia, tarcie i zużycie, efekty akustyczne.

Streszczenie:

W pracy przedstawiono wpływ różnych układów lubrykantów, które decydują o właściwościach materiałów ciernych okładzin hamulcowych. Referencyjny hybrydowy materiał cierny zmodyfikowano różnymi rodzajami smarów stałych. Dodatki te dzielą się na grupy zawierające powszechnie stosowane materiały smarne: węgle i siarczki, mieszane w różnych proporcjach, mających wpływ na tworzenie się i strukturę tzw. warstwy trzeciego ciała (TBL) na powierzchni tarczy hamulcowej w wyniku hamowania. Do analizy chemicznej i morfologicznej powierzchni tarczy hamulcowej po testach hamowania wykorzystano odpowiednio spektroskopię Ramana (RS), spektroskopię masową jonów wtórnych (ToF-SIMS) oraz skaningową mikroskopię elektronową o wysokiej rozdzielczości z analizatorem rentgenowskim (SEM-EDS), wyposażoną w skupioną wiązkę jonów (FIB). Wyniki analizy fizykochemicznej TBL skorelowano z wynikami dynamometrycznych badań tribologicznych (zgodnie z procedurą SAE-J2522, popularnie nazywaną AK-Master) oraz widmami akustycznymi (NVH – hałas, drgania i złożoność sygnału). Uzyskane wyniki potwierdzają istotną rolę, jaką odgrywa warstwa tzw. trzeciego ciała, formująca się na powierzchni tarczy hamulcowej dla bezpieczeństwa (COF), trwałości (zużycie elementów ciernych) oraz widma akustycznego towarzyszącego hamowaniu.

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INTRODUCTION

Today's braking systems must be characterised by much greater efficiency due to the much greater power generated by the drive systems and the weight of electric vehicles. The mechanism of third body layer (TBL) formation has been reviewed in the first part of the paper, devoted to the effect of frictional additives [L. 1]. The second part focuses on the role played by lubricating additives.

The role of lubricants in the performance of brake linings and third body formation

The main task of the ingredients used in friction composites is to impart many different functional properties to brake linings. There are also known cases of the synergy effect, i.e., interactions between individual components [L. 2], which means that even a slight change in the formula of the friction material may have an influence on serious changes in the friction characteristics and braking: wear resistance, braking distance, friction stability, torque variation and noise generation [L. 3–5].

A significant group are lubricants. The main purpose of a lubricant is to stabilise the developed coefficient of friction (COF) during braking, particularly at high temperatures [L. 6]. Commonly used lubricants include various types of carbon such as natural or synthetic graphite and coke and other solid lubricants with a layered structure such as SnS_2 , MoS_2 , WS, TiS_2 or other "soft" metal sulphides, as well as other non-layered metal sulphides, e.g., Sb_2S_3 , SnS , Bi_2S_3 and CuS . Some of the latter are also considered friction modifiers, being able to eliminate copper from the composition of friction materials.

The literature review shows that the layered structure of solid lubricants is not necessary to obtain the desired brake performance [L. 6]. According to Melcher and Faullent [L. 7], such desirable properties may be related to phase changes and/or chemical reactions as well as properties of the products of chemical reactions accompanying the braking on the surface of the friction pair elements. The authors described several scenarios for the transformation of additives, demonstrating their influence on wear and COF. Matejka et al. observed a chemical reaction between Sb_2S_3 and iron at 350°C and correlated it with the observed decrease in COF [L. 8]. Research has shown that individual additives cannot meet all requirements and that

a combination of different ingredients is beneficial. Such a systematic approach to the friction of brake linings with various combinations of solid lubricants was presented by Yang et al. for graphite/ Sb_2S_3 and graphite/ $\text{Sb}_2\text{S}_3/\text{MoS}_2$ systems [L. 4, 9]. Therefore, brake linings are used to contain two or more solid lubricants, which complement each other under different braking conditions [L. 10]. Often the best choice is a combination of graphite with one soft metal sulphide. Sulphides usually oxidise at elevated temperatures during fading cycles. The resulting oxides should have a strength close to that of the original substrates, but in fact, this is only the case for Sb_2S_3 and PbS . Currently, PbS is no longer used, and Sb_2S_3 should be replaced in brake lining formulations for health reasons [L. 11]. Other "soft" metal sulphides have been extensively studied. Their oxides, such as MoO_3 , SnO , Bi_2O_3 and CuO , are harder than the corresponding sulphides, although still softer than iron oxides [L. 7]. While most brake pad manufacturers have restricted or eliminated Sb_2S_3 from their formulations, reports of systematic testing with other sulphides are very rare. Knowledge about the structure and properties of tribofilm seems to be the key to understanding the behaviour of the friction pair elements of the brake system [L. 12].

The first part of our paper already provides an introduction to the problem of the third body layer (TBL) formation was approached from the role played by frictional additives. Meanwhile, lubricants also impact the abrasion process of the brake disc and the pad itself, the composition and formation of abrasion products, and the behaviour of the so-called third body in frictional contact between the brake components [L. 13, 14]. Third body layers were comprehensively analysed by Wirth et al. [L. 15], Osterle et al. [L. 16] and most recently discussed, by Neis et al. [L. 12].

This paper presents the influence of various lubricating additive systems on the formation of a third body on the surface of the brake disc due to friction. The studies were carried out on the examples of two families of lubricating additives belonging to the group of sulphides and carbons (mainly graphite) added to the brake lining material of the hybrid family. Natural (NG) and/or synthetic (SG) graphite are invariably used in friction material formulations as solid lubricants due to their layered structure and thermal conductivity [L. 17–22]. The main role of graphite is to act as a friction modifier and lubricant at high temperatures [L. 23]. Its

presence on the sliding surface ensures low friction and prevents wear of the friction pair elements, eliminating undesirable friction fluctuations during braking under changing operating conditions [L. 24–26]. Gilardi et al. [L. 27] investigated the effect of graphite particles' type, texture and size distribution on thermal conductivity [L. 28] and noise generation during braking, concluding that the best results are achieved by combining synthetic graphite and the so-called thermo (conductive) graphite. Lin et al. [L. 29] investigated various carbon components: coke, carbon black, carbon fibre, NG, SG and expanded graphite (EG) for use as lubricants in friction material formulations. They showed that EG has the potential to replace Cu in copper-free friction materials because of the highest thermal conductivity, relatively low wear, and the high and stable COF of the friction materials. Cai et al. [L. 30] compared three different solid lubricants: flake graphite, PTFE and MoS₂ from the point of view of the frictional properties of phenolic resin composites.

MATERIALS

Brake linings

The frame composition of friction lining materials, broken down into families and the specification of lubricating additive systems, is presented in **Table 1**.

Table 1. Frame composition [vol. %] of the tested friction linings divided into groups of lubricating additives

Tabela 1. Skład ramowy [% obj.] badanych okładzin hamulcowych z podziałem na grupy dodatków smarnych

Material	Carbon systems	Sulfidic systems
Composition		
Organic fibres	68.5	72.3
Metallic fibres		
Mineral fibres		
Resin		
Fillers		
Abrasives		
Carbons	30.0	22.0
Sulfides	1.5	5.7

Table 2. Composition [vol. %] of lubricant systems based on graphite and coke, added to brake pad samples

Tabela 2. Składy zespołów lubrykantów [% obj.] opartych o grafity i koks, dodanych do próbek klocków hamulcowych

Sample	C1	C2	C3	C4	C5	C6	C7
Carbons							
coke	48	47	47	47	66	74	63
fine natural graphite (FNG)	31	0	0	23	21	0	22
large natural graphite (LNG)	21	0	13	0	12	12	0
synthetic graphite (SG)	0	53	40	30	0	14	15

Table 3. Composition [% obj.] of lubricant systems based on sulphides added to brake pad samples

Tabela 3. Składy zespołów lubrykantów opartych o siarczki [vol. %], dodanych do próbek klocków hamulcowych

Sample	A	C	D	F	G	H
Sulfides						
Sb ₂ S ₃	50	50			100	
SnS/FeS	50		50			100
MoS ₂		50	50	100		

Various combinations of carbon – **Table 2** and sulphide – **Table 3**, lubricants were added to the reference composition of friction linings belonging to the hybrid family.

Brake disc

The research used a highly carburised TRW DF 2804 cast iron disc (TRW, USA). Samples for microscopic examinations of the friction trace, with dimensions of 20 x 20 x 10 mm, were cut from the

brake disc using a CNC machine milling, applying a carbide milling cutter.

EXPERIMENTAL

SEM-EDS analysis

The instrument and methodology of the research are described in part I of the publication [L. 1].

Raman spectroscopy analysis

The Raman spectroscopy investigation of the brake disc surface was carried out at room temperature using a dispersive spectrometer Jobin Yvon T-64000 (Horiba Ltd., Japan), equipped with a confocal microscope Olympus BX-40 (Olympus Co., Japan). The Ar laser line (wavelength 514.5 nm, power at the sample surface ca. 300 mW) was used as a source of excitation. The acquisition time was 180 s, and two scans were averaged for the working surface brake disc samples.

Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) Analysis

The ToF-SIMS IV secondary ion mass spectrometer (ION-TOF GmbH, Germany), equipped with a bismuth ion gun (Bi^{3+}), and an ion flight time analyser with high mass resolution $m/\Delta m = 7500$ for an ion with $m/z = 29$, were used. During the measurement, the emission of secondary ions was obtained by irradiating the surface of the tested sample with a pulsed beam of primary ions with a frequency of 10 kHz. The duration of a single pulse was ca. 1 ns, and an average primary beam current was 0.2 pA at an ion energy of 25 keV. The SIMS spectra were recorded from the surface area of $100 \times 100 \mu\text{m}$ for 30 s. The same parameters of the primary ions were used for registering iconic images of the sample surfaces. Secondary ion emission profiles were made by spraying a $150\text{--}150 \mu\text{m}$ surface with 3 keV Cs⁺ ions at a spray beam current of 50 nA. The area of $50 \times 50 \mu\text{m}$ was analysed.

Performance analysis

The SAE-J2522 "AK-Master" test procedure, the most versatile tool for comparing friction materials, enabling determination of green efficiency, performance in relation to speed, fading resistance, recovery and stability of the coefficient of friction

(COF), is described in part I of the publication [L. 1].

RESULTS AND DISCUSSION

The third body layer (TBL) formation is the result of the continuous interaction of the friction material and the brake disc surface during braking. The layer created in this way, with a different composition and properties than the material of the disc or brake pad, separates the friction pair's elements, deciding the friction material's braking performance.

Analysis of the third body layer (TBL) composition and morphology

Analysis of the brake disc surface by Raman spectroscopy

The analysis of Raman spectra of the discs after braking against the pads with the addition of various systems of carbon lubricants shows that amorphous phases predominate on the disc surface. No distinct absorption bands from the crystalline phases are present in the spectra – **Figure 1**.

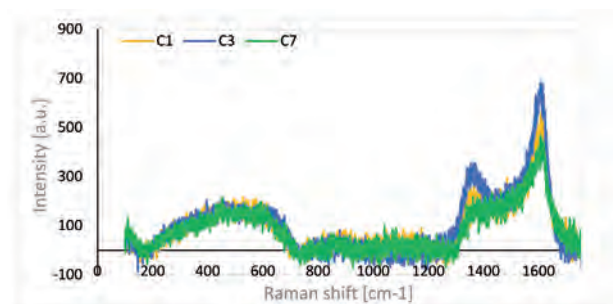


Fig. 1. Raman spectra of the brake disc surfaces after braking against brake pads containing different carbon lubricant systems. Due to the overlapping of spectra for C3 and C4 specimens, the latter spectrum was omitted

Rys. 1. Widma Ramana powierzchni tarcz hamulcowych po hamowaniu względem klocków hamulcowych zawierających lubrykanty węglowe. Z powodu zachodzenia na siebie widm dla próbek C3 i C4, ostatnie widmo zostało pominięte

In the examined spectra of the disc surfaces after braking with pads containing various sets of carbon lubricants, the absorption bands from amorphous carbon in the range of $1250\text{--}1750 \text{ cm}^{-1}$ are mostly visible [L. 31, 32]. The samples differ in the intensity of IG (1600 cm^{-1}) to ID (1375 cm^{-1}) bands and, at first glance, in their half-

widths, which are quite large, which also confirms the amorphous nature of these phases. In the spectrum of the disc surface after braking against the brake pad containing the C1 lubricant system, there is a distinct narrow band of about 1580 cm^{-1} , which may come from crystalline graphite [L. 32]. In the other samples (after braking against pads with the addition of C3, C4 and C7 lubricant systems), the carbon is rather in an amorphous form. A wide band can be seen in all analysed samples, most likely consisting of several peaks overlapping each other, coming from iron oxides, mainly iron III [L. 33], and amorphous carbon [L. 34] in the Raman shift range $200\text{--}700\text{ cm}^{-1}$. The high-resolution Raman spectrum of the brake disc after braking against a pad containing the C4 lubricant system additionally reveals distinct absorption bands at ca. 220 and 280 cm^{-1} , most likely derived from Fe_2O_3 .

The analysis carried out by the Raman spectroscopy method shows that the composition of the group of carbon lubricants added to the friction materials does not have a significant influence on the phase composition of the films formed on the brake disc surface. Only in the case of the brake disc sample spectrum after braking against a pad containing the C1 lubricant system, which contains the most graphite compared to coke, a faint band can be seen that can be attributed to crystalline graphite (1580 cm^{-1}) [L. 32]. However, this does not result in a high coefficient of friction (COF) between the pad and disc during braking. This is only the case if the graphite in the lubricant set is of natural origin, or the latter contains 50–65% coke content in the mixture with graphite.

Similarly, to the Raman spectra of the of brake disc surfaces after braking tests against friction materials containing carbon lubricants, also in the spectra of the disc surfaces after friction against pads with the addition of sulfidic lubricants, bands of crystalline iron oxides dominate, as confirmed by our previous X-ray scattering (XRD) tests [L. 35]. Friction materials with lubricants, which contain a mixture of tin and iron sulphides and/or molybdenum disulphide (D, F and H), generate tribofilm on the brake disc surface, the main components of which are magnetite and quartz or cristobalite. Contrary to expectations, no crystalline sulphides were found in the XRD spectra from the brake disc surfaces after the braking tests. Lubricants containing antimony sulphide (A and C) are much more effective. In their case, X-ray analysis of tribofilms formed on the brake disc surfaces after braking tests did not

show the presence of magnetite, indicating the disc material's oxidation and abrasive wear. Instead, tin sulphide appeared in their composition, but contrary to expectations, no trace of crystalline antimony was found.

Analysis of the brake disc surface using the SEM-EDS method

Wear particles, formed due to fragmentation of the surface layer of the friction pair elements, mix and react chemically with each other and with the atmosphere, leading to the formation of TBL with a different phase and elemental composition. SEM BSC analyses of the cross-sections of TBL layers, cut from brake disc samples after braking tests against brake pads containing representative lubricants, reveal the elemental composition presented in **Table 4**.

Table 4. Elemental composition of TBL formed on the surface of the brake disc after braking against brake pads containing representative sulphide and carbon lubricants

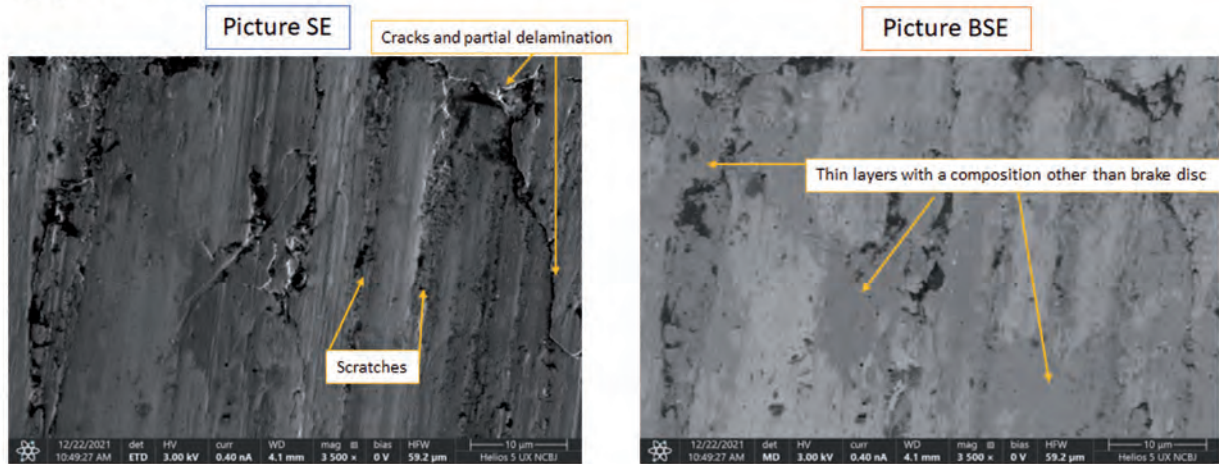
Tabela 4. Skład pierwiastkowy TBL powstającej na powierzchni tarczy hamulcowej po hamowaniu względem klocków hamulcowych zawierających reprezentatywne lubrykanty siarczkowe i węglowe

Samples	Elementary composition
C	Fe, Mn, Cr, Si, Ti, S, Ca, Ba, Sb , Al, O, Mg, C
H	Fe, Mn, Cr, Al, Ba, Sn , Ca, S, Si, Mg, O, C
C4	C, O, Si, Al, S, Sb , Mn, Fe, Cr, Ti, Ba, Ca, Mg
C7	C, O, Si, Al, S, Sb , Mn, Fe, Cr, Ba, Ca, Mg

It differs only in the metal atom present in the used sulphide lubricant (highlighted in the table above). Qualitative identification of Mo with the EDS method is impossible due to the overlapping of the signal by the signal of S, occupying the same place of the X-ray scattering spectrum [L. 36]. The microscopic images of TBL formed on the surface of the brake disc after braking are presented in **Figure 2**.

The high degree of complexity of the analysis of TBLs formed on the brake disc surfaces after braking tests against brake pads containing sulfidic lubricants caused that it was decided to focus on the analysis of films produced in the case of braking against friction materials containing

Sample C



Sample H

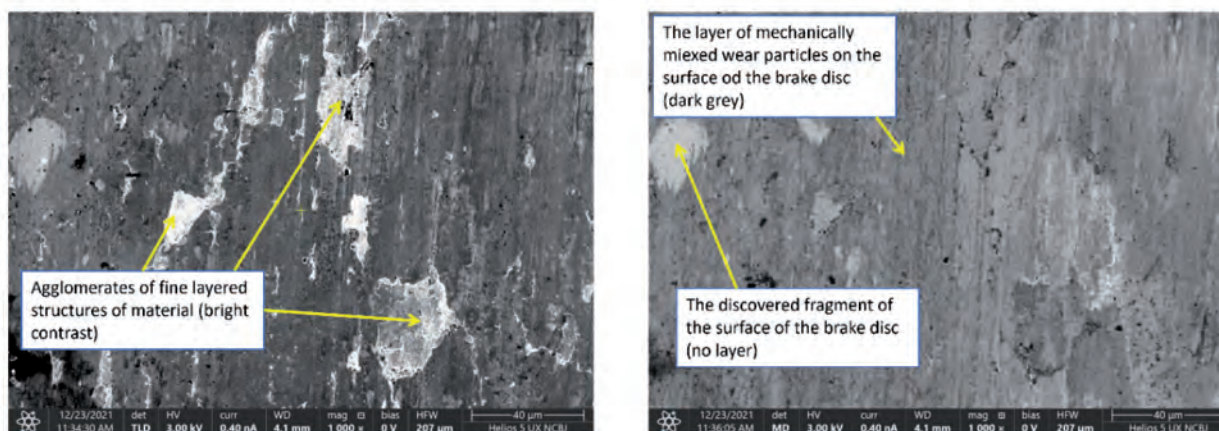


Fig. 2. SEM-EDS analysis of the films created on the surface of brake discs after braking against brake pads containing different sulphides

Rys. 2. Analiza SEM-EDS filmów powstałych na powierzchni tarcz hamulcowych w wyniku hamowania względem klocków zawierających różne siarczki

carbon lubricant systems. The microscopic images obtained by scanning electron microscopy (SEM) – **Figure 3** show that the films formed on the disc surface in the case of samples after braking against brake pads with the addition of C4 and C7 carbon lubricant systems are single-layer, have different morphology and significantly different from each other in thickness and chemical composition (C, O, Fe). The BSE images additionally revealed a few microns and submicron-sized objects, most likely originating from the pad material.

When imaging the surface of the brake discs after braking in the topographic contrast, numerous scratches and cracks, as well as a discontinuous layer of mixed wear products on the surface, were

detected. The compositional contrast revealed numerous thin discontinuous layers of material enriched with those light elements (e.g., O, C), which differed in composition from the base material of the disc (dark streaks in BSE images). On the brake disc surface after braking against a brake pad containing a set of C7 carbon lubricants, a tribofilm is formed in the form of thin (300-900 nm) trails, while when braking against a pad with the addition of the C4 lubricant system, it is much thicker (600-1900 nm). Both films show clear traces of cracks and the detachment of the film (the third body – TBL) from the brake disc surface – **Figure 4**.

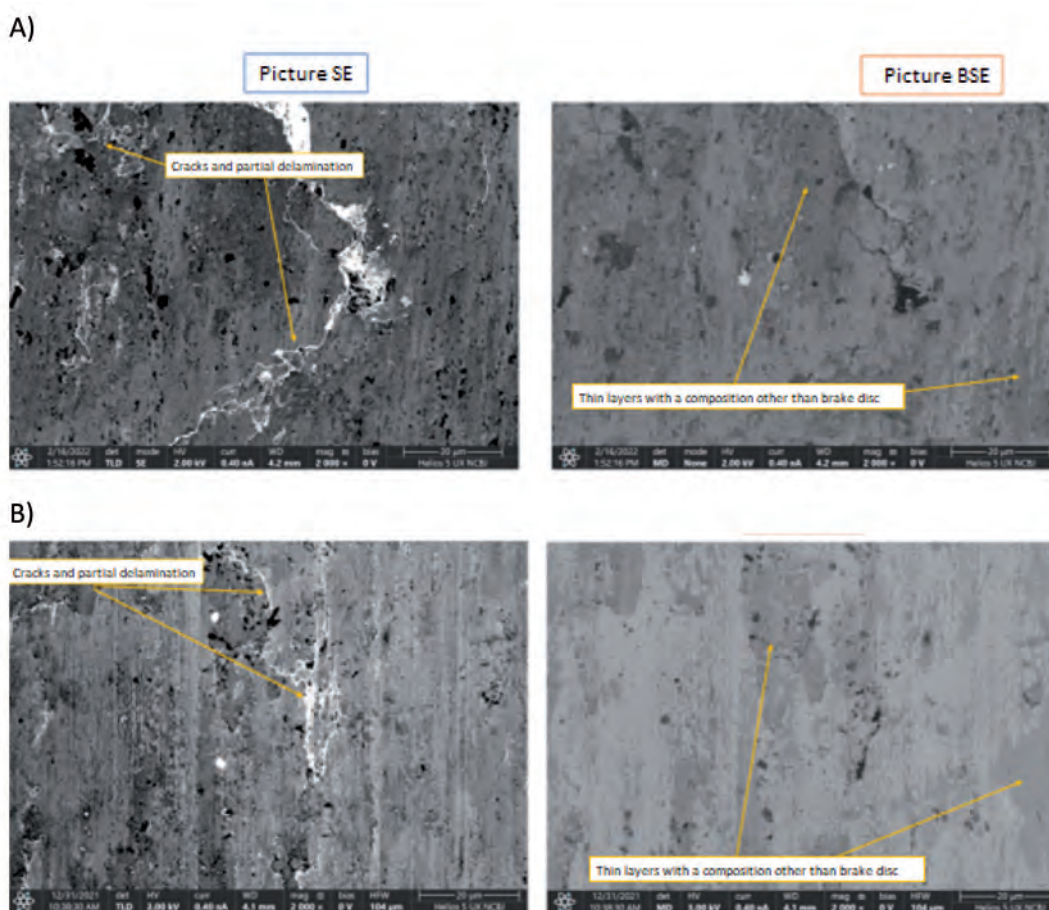


Fig. 3. SEM-EDS analysis of the films created on the surface of brake discs after braking against brake pads containing carbon lubricant systems C4 (A) and C7 (B)

Rys. 3. Analiza SEM-EDS filmów powstałych na powierzchni tarcz hamulcowych w wyniku hamowania względem klocków zawierających układy lubrykantów węglowych C4 (A) i C7 (B)

Analysis of the brake disc surface using the ToF-SIMS method

The content of a given element from the surface of the brake disc (atomic profile) illustrates the secondary ion emission profiles as a function of the time of sputtering of the disc surface – **Figure 5**.

Due to the micro-roughness of the disc surface, which increases additionally after braking, it is impossible to analyse the content of elements directly as a function of depth.

The obtained results indicate a relatively high sulphur content in all samples of brake discs after braking compared to the virgin ones, which confirms the effective transfer of sulphur compounds from the surface layer of the brake pad to the brake disc, accompanying friction, noted by us earlier [L. 37]. This is most evident in the case of the brake disc surfaces after braking against friction

materials containing D, H and G sulfidic lubricants. After braking against a pad containing H lubricant for the disc, a sulphur-enriched surface layer was observed, reaching a depth corresponding to 800 s of ion sputtering. The beneficial effect of sulphur and iron compounds formed as a result of friction on the braking performance cannot be ruled out because of the emission of FeS^- ions from the disc surface after braking against friction materials with sulfidic lubricants – **Figure 6**.

The highest emission of Sb^- ions from the brake disc surface was found for brake disc samples after braking against friction materials containing A, C and G sulfidic lubricants, which were characterised by the highest braking efficiency [L. 4, 7, 20]. Much higher carbon content was found in the surface layer of brake discs after braking against friction materials containing G and H lubricants

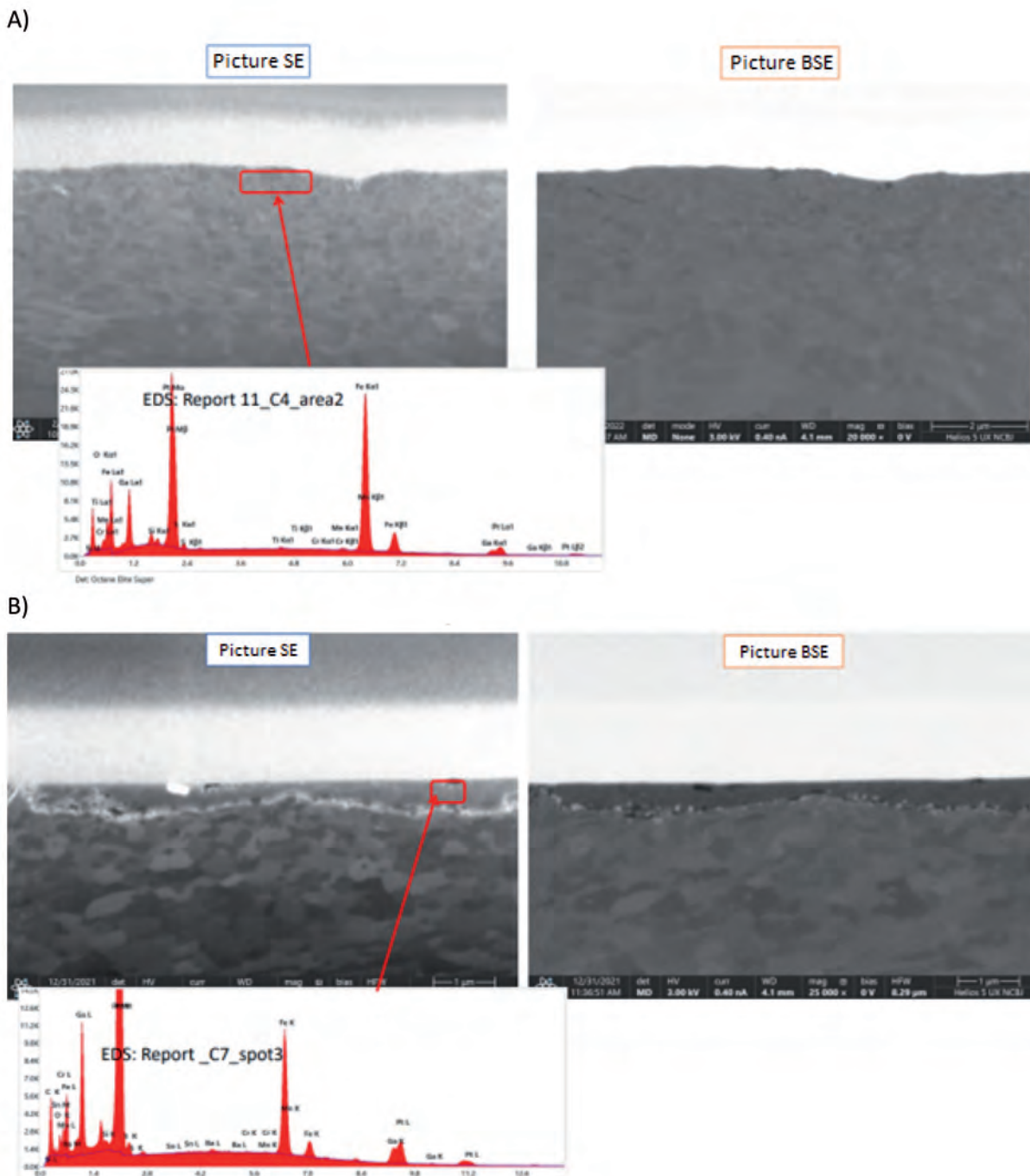


Fig. 4. Thickness, morphology and EDS analysis of the film formed on the disc surface after braking with the pad containing the carbon lubricant system C4 (A) or C7 (B)

Rys. 4. Grubość, morfologia i analiza EDS filmu powstającego na powierzchni tarczy hamulcowej po hamowaniu klockiem zawierającym układ lubrykantów węglowych C4 (A) oraz C7 (B)

compared to the disc before the braking test. In the case of the disc surface after braking against the pad with the addition of lubricant H, on the basis of the recorded TOF-SIMS depth profiles, the existence of a carbon-enriched disc surface layer up to a depth corresponding to approx. 800 s of ion sputtering

was found. The shallowest carbon penetrates deep into the brake disc after braking against a brake pad material with the addition of sulfidic lubricant C. An important observation is also the finding of a thicker, compared to other samples, tribofilm with high oxygen content formed on the brake discs after

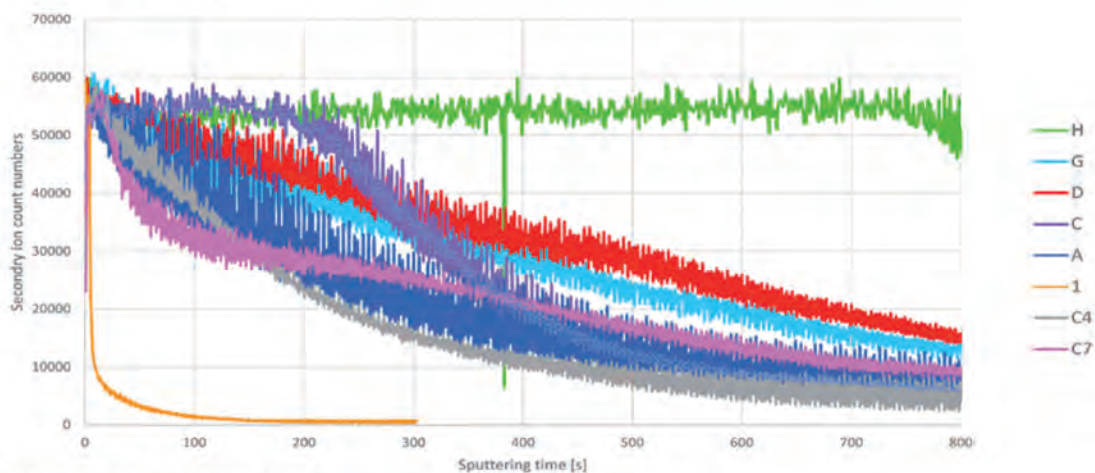
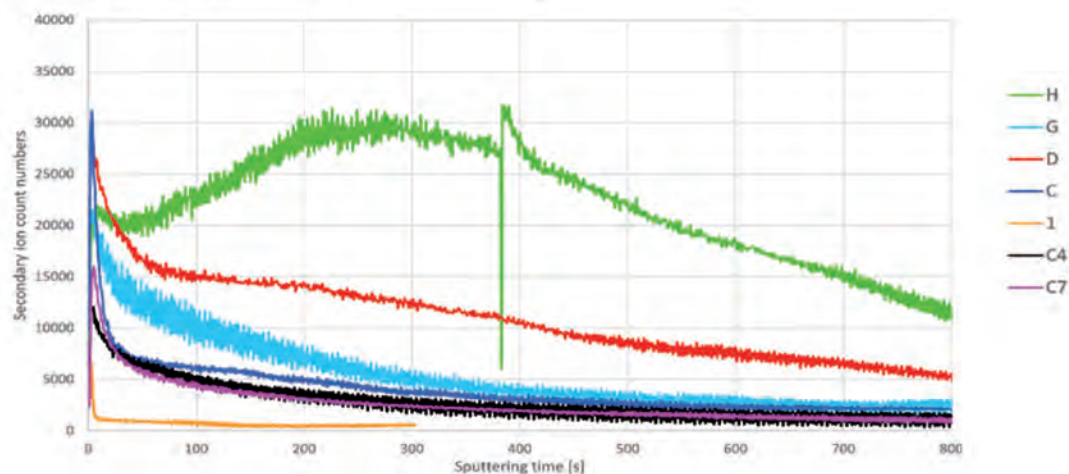
A) profiles of O⁻ ions emissionB) profiles of S⁻ ions emission

Fig. 5. Emission profiles of selected secondary ions: O⁻ (A) and S⁻ (B) from the top layer of brake discs after braking against brake pads containing various lubricant systems

Rys. 5. Profile emisji wybranych jonów wtórnych: O⁻ (A) i S⁻ (B) z warstwy wierzchniej tarcz hamulcowych po hamowaniu względem klocków zawierających różne układy lubrykantów

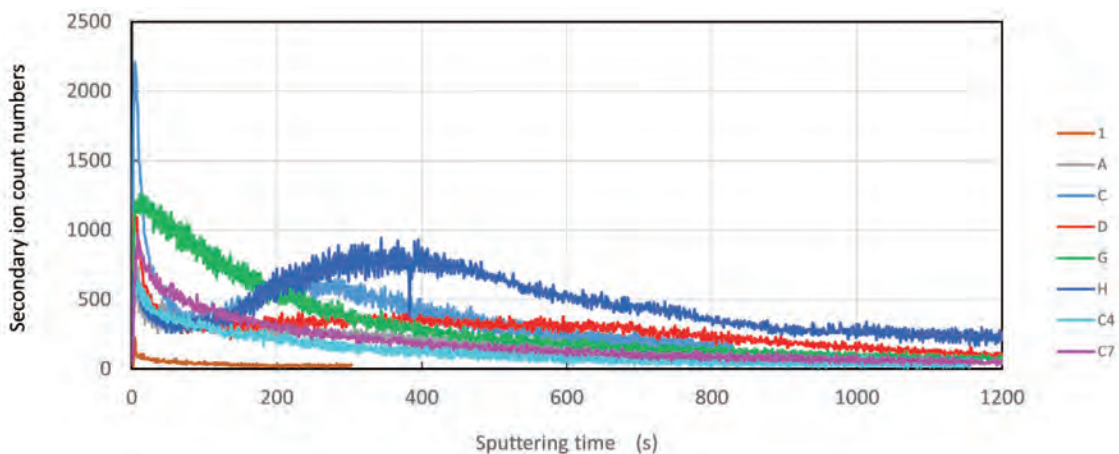


Fig. 6. Emission profiles of FeS⁻ ions from the surface of brake discs after braking against brake pads containing various sulfidic lubricants

Rys. 6. Profile emisji jonów FeS⁻ z powierzchni tarcz hamulcowych po hamowaniu względem klocków hamulcowych zawierających różne lubrykanty siarczkowe

braking against friction materials containing C and H lubricants, which indicates significant oxidation of the disc surface in these cases.

Performance analysis of the frictional materials

Brake effectiveness (SAE J 2522)

The performance of the brake and the phenomena occurring in the area of contact between the pad and the brake disc are of physical, thermomechanical and chemical nature. Kinetic energy is converted into heat, plastic deformation, chemical reactions, and wear debris formation [L. 38], influencing the friction coefficient and the wear of the friction pair.

The tests for the brake pad materials containing lubricants from the sulfidic group were similar either to the friction material with the addition of lubricant C – for materials containing Sb_2S_3 or to the friction material with the addition of lubricant H – for materials not containing Sb_2S_3 . This component is oxidised in two stages. The first stage begins at $380^\circ C$, and then Sb_2O_3 and Sb_2O_5 are formed, while the second stage takes place at $570^\circ C$ and is accompanied by the formation of Sb_2O_4 . Oxides are characterised by a higher coefficient of friction than sulphides, and thus, in the desired temperature range (when the decomposition of organic compounds takes place), the COF of friction linings against brake discs increases. Oxides also play a lubricating role; therefore, the transformation is not accompanied by a sharp increase in wear, and the stability of COF increases [L. 4].

On the other hand, for the carbon group of lubricants, the changes in the braking performance for brake pad materials containing the C2, C5 and C6 lubricant systems were small compared to the friction materials with the addition of the C7 system, while the C1, C3 systems were similar to the C4 one. Therefore, the performance analysis of pads with added carbon lubricant systems has been limited to the most representative friction materials containing C4 and C7 lubricant systems.

Most of the tested friction materials are characterised by similar changes in COF during the braking cycles. The registered COF increased after the lapping of the brake pads and then decreased slightly during the speed sensitivity testing stage at different brake system pressure. After that, the COF of the materials increased during the regeneration stage, decreased during fading braking, and finally stabilised at the end of the test. Only materials

with H and F lubricants, without Sb_2S_3 in their composition, behaved slightly differently. After the first fading braking, their COF dropped drastically to a level unacceptable in commercial applications. During the further course of the test, these materials could no longer "rebuild" themselves and return to the expected level of COF value. Similar, but only a bit better, performed the friction material with the addition of lubricant D, in which Sb_2S_3 was replaced with SnS / FeS and MoS_2 .

On the other hand, the friction material with the addition of lubricant C, containing Sb_2S_3 , achieved the highest COF. Additionally, the introduction of more MoS_2 resulted in higher resistance of the friction material to fading braking. The friction material with the addition of lubricant G, containing only Sb_2S_3 , showed slightly lower resistance to fading braking but braked at a similar level as friction materials containing A and C lubricants. Taking into account the results obtained for friction materials with sulfidic lubricants, and in order to ensure braking at an acceptable level, all of them should contain Sb_2S_3 in their composition.

Friction materials achieved the highest COF values within the group of carbon lubricants with the addition of C5, C6 and C7 systems, in which the ratio of coke to graphite was higher, and the material sample with a C2 lubricant system, in which apart from coke, only synthetic graphite was used. According to Kolluri et al., Synthetic graphite is superior to natural graphite in terms of the stability of COF and the resulting wear [L. 20]. In the case of the friction material containing the C4 lubricant system, in which natural (GN) and synthetic (GS) graphite were used, and their total share in relation to coke has increased, the COF is slightly lower. Compared to samples containing a more favourable – lower ratio of graphite to coke, the velocity and temperature fading are more visible for this material. Despite this, the material exhibits good regenerative properties, stabilising its COF at the level required for commercial applications. The friction materials containing C1 and C3 lubricant systems achieved only slightly better performance.

The coefficient of friction (COF) and wear

The reasons for the higher level of COF in the initial phase of the test, until the first fading, in the case of friction materials containing the system of C lubricants, can be subscribed to the lower adhesion of mechanically detached particles from the brake pad material to the brake disc surface [L. 39].

The friction material achieved the highest level of friction in this test phase with the addition of the C lubricant containing MoS_2 , which increases the friction coefficient even at low temperatures (100°C). At approx. 450°C , it is oxidised to MoO_3 , and further heating causes its evaporation at 700°C [L. 7, 15, 40, 41]. Additionally, MoS_2 probably also counteracts the formation of the tribofilm [L. 39]. The obtained effect is consistent with literature reports that the friction coefficient is reduced due to the creation of the TBL [L. 42]. The high and stable average COF of the friction material containing the C7 lubricating system is due to its higher content of graphite and petroleum coke, which improve the wear resistance of the friction pair elements, lowering the braking temperature, stabilising friction, reducing fading and noise generated during braking, thanks to the porosity and compressibility of the components [L. 43–45].

The highest changes in COF, differentiating the friction materials tested and the effectiveness of lubricants, take place only during the first fading, at an increased temperature, the increase of which is a key factor for the formation of TBL [L. 46, 47]. At this stage of the test, the temperature reaches over 650°C , which causes the decomposition of parts of the friction lining components that mix with the nanocrystalline iron oxide formed as a result of tribo-oxidation of the brake disc surface, which is the main component of the TBL nanostructure being formed. The strong plastic deformation and temperature increase, especially on the graphite plates, favours the local mixing and chemical reaction of magnetite with exfoliated graphite flakes [L. 48]. At this stage of the test, the lowest decrease in COF was achieved by friction materials containing C and C7 lubricants, for which the TBL film formed on the brake disc surface is much thinner than in the samples when C4 and H lubricants were used to modify the brake pad material. TBL formed on the disc surface after friction against a brake pad containing lubricant, C also has the highest oxygen and the lowest carbon content among the samples tested (refer to the ToF-SIMS analysis). This suggests that the higher stability of COF, in this case, maybe the result in an increase in the proportion of iron particles formed due to tribooxidation of the cast iron disc in relation to graphite particles and other wear products. This is the key stage of the test, after which the COF should stabilise at an average level of 0.3–0.5. This condition was met by three of the

friction materials tested – containing C, C2 and C7 lubricants. The composition of system H, which did not contain Sb_2S_3 but the SnS / FeS substitute, did not stabilise COF at the expected level. With its addition, the COF of the friction material dropped well below 0.2 and was no longer able to build up to the desired level during the recovery phase of the test. In this case, the abrasive wear products of the brake pad were mechanically pressed into the plastically mixed and deformed layer, previously formed on the disc surface, creating a film with a total thickness of up to $3\ \mu\text{m}$. The results of ToF-SIMS analysis may indicate that in the case of the friction material containing the H lubricant additive, the SnS lubricant used in the material H did not oxidise and therefore remained unchanged throughout the entire test run. SnS is oxidised only at a temperature of approx. 700°C [L. 7], while the maximum temperature during the test was even below 650°C . Therefore, oxides reflected by a higher coefficient of friction could not be formed, disabling the development of a TBL of the structure similar to the film generated by the friction of brake pads containing C or C7 lubricants. The friction material with the addition of lubricant F, in which Sb_2S_3 was replaced with MoS_2 , behaved similarly. Despite the fact that this component oxidises at a temperature of approx. 450°C , the formed oxides most probably did not manage to develop the TBL film's appropriate structure, making COF remain at the same level after the first fading [L. 49]. The COF values at various stages of the ISO SAE J2522 – AK Master test and the amount of wear of the friction pairs tested elements are summarised in **Tables 5 and 6**, respectively.

The analysis of the amount of abrasive wear of friction materials with the addition of carbon lubricants and the influence of the tested material on the brake disc shows that the wear of the friction linings is similar (the range of 7.5–9.6 g), while the wear of the brake discs varies significantly – **Table 6**. The distinct effect of synthetic graphite (SG) is visible; the addition of which to the pad material significantly reduces the wear of the brake disc, even by half. On the other hand, the friction materials containing NG turned out to be the most "aggressive" in relation to the brake discs. Friction materials with a mixed composition of SG and NG abraded the brake discs to an intermediate degree, depending on the proportion of SG to NG. By analysing the amount of abrasive wear of brake pads with the addition of sulfidic lubricants, and

Table 5. ISO SAE J2522 – AK Master COF of the friction materials tested

Tabela 5. ISO SAE J2522 AK Master – Wartości współczynnika tarcia badanych materiałów ciernych

Material with lubricants		COF	Nominal	Fade	Min.	Max.
Carbon lubricants system	C1	0.39	0.34	0.29	0.45	
	C2	0.41	0.38	0.31	0.47	
	C3	0.38	0.33	0.29	0.44	
	C4	0.38	0.29	0.25	0.43	
	C5	0.42	0.37	0.32	0.48	
	C6	0.41	0.38	0.31	0.47	
	C7	0.44	0.38	0.31	0.50	
Sulfidic lubricants system	A	0.45	0.38	0.34	0.61	
	C	0.41	0.37	0.34	0.60	
	D	0.30	0.26	0.21	0.54	
	F	0.27	0.20	0.14	0.42	
	G	0.44	0.36	0.29	0.57	
	H	0.26	0.20	0.12	0.40	

Table 6. Wear of the friction pair elements after ISO SAE J2522 – AK Master test

Tabela 6. Zużycie elementów pary cierniej po teście ISO SAE J2522 – AK Master

Material with lubricants		Wear [g]	Brake pad	Brake disc
Carbon lubricants system	C1	9.4	4.9	
	C2	7.5	2.1	
	C3	8.9	3.2	
	C4	9.6	1.3	
	C5	8.3	5.4	
	C6	7.8	3.3	
	C7	8.3	3.3	
Sulfidic lubricants system	A	7.0	4.3	
	C	7.9	5.3	
	D	10.8	3.7	
	F	12.6	3.7	
	G	9.0	5.2	
	H	16.9	2.5	

their impact on the wear of brake discs, a clear difference can be observed between the friction materials that contained Sb_2S_3 and the others – without this solid lubricant. The friction linings, including Sb_2S_3 in their composition, were wearing at a similar level as were the brake discs paired with them, whereas friction materials containing sulfidic lubricant systems: D, F and H abraded much more while being less "aggressive" to brake discs, wearing inversely proportional to paired friction linings.

Noise-Vibration-Harshness (NVH) analysis

Unstable operation of the brakes resulting from the occurrence of vibrations on the friction surfaces leads to a reduction in the efficiency of the brake and the durability of its components and may also cause vibrations of the vehicle as a whole. The wear mechanism used to be considered somehow related to noise, as proposed by Lee et al. [L. 32]. The noise accompanied by braking of the brake linings materials studied during AK Master tests is characterised (by NVH) in **Table 7**.

Table 7. Noise-Vibration-Harshness (NVH) analysis of the elected brake lining materials tested

Tabela 7. Analiza hałasu-wibracji-złożoności sygnału akustycznego (NVH) wybranych materiałów okładzin hamulcowych

Material with lubricants	Parameters	Noise [%]	Frequency [kHz]	
			Band 1	Band 2
Carbon lubricants system	C1	3.2	3	–
	C2	12.1	3	11–17
	C3	17.2	3	16–18
	C4	10.1	3	12–14
	C5	19.5	3	–
	C6	21.9	3	16–18
	C7	34	3	–
Sulfidic lubricants system	A	2.5	3	–
	C	9.4	3	–
	D	3.7	3	–
	F	4.7	3	–
	G	2.2	3	–
	H	5.4	3	–

The type of lubricants added to the friction materials generally significantly affects the acoustic spectrum of brake lining materials with their addition. Despite a few differences in the amount of the so-called "loud" braking and their intensity, the main frequency in each analysed spectrum of friction material is at 3 kHz. Loud braking of all friction materials with sulfidic lubricants occurred only at this one frequency. The lowest percentage of squeaking braking was recorded by friction materials with the addition of the G lubricant system, containing Sb_2S_3 in its composition, and the A system – with the addition of Sb_2S_3 and SnS/Fe, which are characterised by very good friction parameters. The addition of SnS/FeS slightly increased the COF value, with almost no effect on the noise of the friction linings. The friction material with the addition of the C system, containing MoS_2 and Sb_2S_3 , exhibited the best COF stabilisation but the highest percentage of squeaking braking.

Carbon lubricants can be divided into two groups when evaluating the acoustic behaviour of friction materials. Those that generated squeaks during braking at one frequency band (3 kHz) and those that "made noise" at two bands. Friction materials with the addition of C1, C5 – C7 lubricant systems, which were characterised by the best parameters of frictional resistance, made noise at

one frequency band. Noisy, "two frequency bands" friction materials containing C2-C4 lubricant systems characterise themselves by the lowest COF values and the highest per cent of inhibiting squeaks.

SUMMARY & CONCLUSIONS

SEM BSC and ToF SIMS analyses of tribofilms formed on the surface of brake discs reveal their diverse morphology and chemical composition, which depend on the composition of the lubricant group used in the friction lining material. Based on the obtained results, the following facts accompanying braking have been revealed:

1. The sulfidic group of lubricants were characterised by the fact that the braking performance and the wear of the friction materials with their addition were determined by the use of Sb_2S_3 . This is likely due to the oxidation of antimony sulphide accompanying braking, producing a material with a greater COF but softer than the magnetite tribofilm (TBL) matrix. As a result, it can also act as a lubricant, stabilising friction, not leading to a sharp increase in wear and noisy braking. The replacement of Sb_2S_3 in the composition of sulfidic lubricant systems with SnS/FeS or MoS_2 causes that in the TBL composition appear hard SnS/FeS or MoO_3 inclusions, which makes the friction material unable to create stable TBL structures on the brake disc surface, noting the worst acoustic behaviour. The thick layers of tribofilm formed in this case make them slide over each other, leading to a drastic decrease in COF. Over time, TBL stratified and detached from the brake disc surface, translating into the highest noisy braking percentage. The highest wear of friction linings but the lowest wear of brake discs were recorded for materials F and H, which did not contain Sb_2S_3 .
2. The carbon group of lubricants tested (coke, LNG, FNG, SG) characterised itself by the fact that the wear of brake discs was determined by the use of synthetic graphite (SG). The lower wear of the brake disc after friction against brake pads containing SG in their composition, which is characterised by a much greater purity, porosity and thermal conductivity compared to NG, is probably related to the formation of a diffusion barrier of the transfer film, being a mixture of oxidised wear particles and SG,

protecting the surface of the brake disc. The increased wear of brake pads containing NG can be subscribed to contamination of the lubricant [L. 50]. The addition of coke to the carbon lubricant system increased the braking performance. As for the acoustic behaviour, the

higher coke content caused an increase in noisy braking, which most likely can be attributed to its roughness and higher impurity level compared to SG, whereas LNG addition made unwanted sounds reduced, shifting the vibration frequency towards lower values, beyond the area of human hearing.

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