

**Maciej SZLICHTING<sup>\*</sup>, Dariusz M. BIELIŃSKI<sup>\*\*</sup>, Jacek GRAMS<sup>\*\*\*</sup>,  
Zbigniew PĘDZICH<sup>\*\*\*\*</sup>**

## **THE INFLUENCE OF THE KIND OF COMPOSITE FRICTION MATERIAL ON MORPHOLOGY AND COMPOSITION OF ITS SURFACE LAYER AND TRIBOLOGICAL PROPERTIES**

### **WPLYW RODZAJU KOMPOZYTOWEGO MATERIAŁU CIERNEGO NA MORFOLOGIĘ I SKŁAD JEGO WARSTWY WIERZCHNIEJ I WŁAŚCIWOŚCI TRIBOLOGICZNE**

#### **Key words:**

brake pads, friction, tribochemistry, surface modification

#### **Słowa kluczowe:**

okładziny cierne, tarcie, tribochemia, modyfikacja powierzchni

---

<sup>\*</sup> TOMEX A.J.C. Tomczyk sp. j. Budzyń, Poland.

<sup>\*\*</sup> Institute of Polymer & Dye Technology, Faculty of Chemistry, Lodz University of Technology, Lodz, Poland.

<sup>\*\*\*</sup> Institute of General and Ecological Chemistry, Faculty of Chemistry, Lodz University of Technology, Lodz, Poland.

<sup>\*\*\*\*</sup> Department of Special Ceramics, Faculty of Materials Science and Ceramics, AGH University of Science and Technology in Krakow, Poland.

## Abstract

The paper presents the characteristics of materials currently used in the construction of brake pads for passenger cars, taking into account their advantages and disadvantages. Based on this, taking into account the expectations of clients and the latest achievements in the field of polymer composites engineering and tribochemistry, the perspectives for the development of friction materials have been proposed. The discussion is illustrated by the author's study results concerning the analysis of the morphology and chemical composition of the surface of representative groups of brake pad materials. Braking test characteristics and the mechanism of the friction of the studied composites have been interpreted from the point of view of changes observed in the microstructure and chemical composition of their surface. They are related to earlier investigations by the authors devoted to the tribochemical modification of components of a polymer-metal friction pair.

## INTRODUCTION

### State of the art

Asbestos was used in friction materials as “binding” fibre. It was the perfect material because of the following characteristics:

1. It had splinters along the fibres “catching” the other components of the composite, forming a compact, homogeneous mixture.
2. It characterized itself by high thermal resistance.

When asbestos was withdrawn from use due to the suspicion of carcinogenicity (1980s/1990s), the race began in search of alternative fibres representing similar properties with regard to thermal conductivity and hardness [L. 1]. As a result of this material revolution, a number of new families of organic and metallic non-asbestos brake pads were created. each with its own unique composition. Four basic types of friction pads can be distinguished – **Table 1**:

- 1) High-steel (semi-metallic) – currently in decline,
- 2) Low-steel,
- 3) Non-asbestos organic (NAO).also known as ceramic, and
- 4) Hybrid, being a compromise between materials from groups 2 and 3.

**Table 1. Characteristics of friction materials currently used in brake pads for passenger cars**

Tabela 1. Charakterystyka materiałów ciernych stosowanych obecnie w okładzinach hamulcowych samochodów osobowych

Type of friction material	Disadvantages	Advantages
<b>Semi-metallic</b> Coefficient of friction – $\mu \leq 0.4$	<ol style="list-style-type: none"> <li>1. Wear of the friction pad dependent on the mass and speed (energy).</li> <li>2. High tendency to corrosion.</li> <li>3. High tendency to generate various types of sound during braking.</li> </ol>	<ol style="list-style-type: none"> <li>1. Low wear of the brake disk during operation.</li> <li>2. Low tendency to DTV (Disk Thickness Variation).</li> <li>3. Long service life (durability) of the friction pad.</li> </ol>
<b>Low-steel (the so-called repair pad)</b> Coefficient of friction – $\mu = 0.35-0.50$	<ol style="list-style-type: none"> <li>1. Wear of the brake disk greater than in the case of NAO.</li> <li>2. Wear of the friction pad greater than in the case of NAO.</li> <li>3. Greater tendency to irregular wear of the brake disk (DTV), dependent on the friction material and design of the brake calliper.</li> </ol>	<ol style="list-style-type: none"> <li>1. Good mechanical strength of the friction pad (ISO 6312).</li> <li>2. High braking performance at high temperatures and high speeds.</li> <li>3. Ability to regenerate the brake disk.</li> </ol>
<b>Organic - NAO</b> Coefficient of friction – $\mu = 0.3-0.4$	<ol style="list-style-type: none"> <li>1. Coefficient of friction decreases with increasing mass and speed (energy).</li> <li>2. Increased tendency to transfer the friction material onto the brake disk.</li> <li>3. Lower mechanical strength of the friction pad (according to ISO 6312).</li> </ol>	<ol style="list-style-type: none"> <li>1. Low wear of the brake disk.</li> <li>2. Low wear of the friction pad.</li> <li>3. No tendency to DTV.</li> <li>4. Reduced tendency to generate "groan-like" sounds</li> </ol>
<b>Hybrid NAO/Low-steel</b>	Combination of characteristics of the materials NAO and Low-steel.	

After asbestos had been withdrawn from the production of brake pads, it was believed that materials such as steel wool and iron powder could replace it. Thus, a new family of friction pads was born known as semi-metallic. These pads contained more than 50 wt. % of iron. However, in countries where there is no speed limit, it was quickly realized that, during braking at high speed, considerable energy is generated by semi-metallic pads, what affects their quick wear. Unlike asbestos, the thermal stability of steel wool and iron powder is much lower. As the braking temperature increases, friction pad wear increases. Semi-metallic pads survived on markets where there is a speed limit, e.g. in the USA, while, in Europe, they have not been used for a long time. The advantage of the semi-metallic pads is their low tendency to disk thickness variation - DTV, especially in favourable conditions (traveling over long distances with occasional braking, very popular for instance in the USA). However, their application seems to be decreasing, due to some problems accompanied their

exploitation, e.g. corrosion of steel fibres under winter conditions, resulting in their lower durability [L. 2].

Another milestone in restoring the properties of asbestos in the friction pad was the use of a mixture of organic fibres (aramid fibres, e.g., Kevlar, Twaron) and inorganic fibres (e.g., basalt or glass). Because these fibres cannot be used in the same amounts as asbestos fibre, a wide range of new friction components, lubricant additives, and non-ferrous metals were introduced onto the market for the production of friction pads. The development of these materials continues to this day. Strictly speaking, friction materials currently used on the European market belong to a group of friction pads called “low steel” (with low content of steel). However, it is suspected that a large number of fibres may have a carcinogenic effect, so their percentage in the material of brake pads is continuously being reduced. An alternative is the use of ceramic fibres that are capable of hydrolysis in a slightly acidic aqueous environment. Examples of such materials are fibres CerafiberR/CerachemR containing a large amount of CaO and MgO. Even if these fibres get into the lungs, they disintegrate in their aqueous environment without causing long-term irritation, as it is the case with asbestos fibres. On the European market, brake pads from the low-steel group are extremely popular because of the material’s ability to generate a DTV effect during free rotation of the brake disk, which regenerates during braking, thanks to the use of special friction materials. That is why they tend to be called “repair pads.” Their disadvantage, however, is that they increase the wear of the brake disk.

The development of non-asbestos organic pads (NAO) in Japan, in parallel to the development of semi-metallic pads in the USA and Europe, marked the end of the asbestos era. According to the Japanese philosophy, the NAO pad is a composite based on an organic binder (thermosetting carbon resin, usually rubber-modified), which does not contain steel wool or iron powders. Adding copper powder is intended to improve the efficiency of heat removal, while the hard ceramic particles ensure a braking effect, NAO pads are characterized by good resistance to wear (they generate little brake dust), a low coefficient of friction, and they provide comfortable conditions for driving. However, for European manufacturers to achieve high performance brakes in cars with powerful engines or in areas without a speed limit, these pads are inappropriate.

Therefore, more and more manufacturers of brake pads place great emphasis on the development of ceramic friction pads with high braking performance, combining the comfort of Japanese NAO pads with high braking performance of pads from the low-steel family. The research priority of European manufacturers of friction materials is to find a new friction material commonly referred to as “hybrid”.

### Prospects for progress

The concept of the new friction material for brake pads is based on the use of the phenomenon of tribochemical “regeneration” of the friction material, which provides significant benefits for both the brake pads and disks.

Phenol-formaldehyde resins commonly used as a binder are often modified by boron or phosphorus to improve their thermal stability. In contrast, the modification of resins with rubber aims to increase the flexibility of the binder and protect against brittle cracking at the phase boundary [L. 3], allowing optimum adaptation of the pad's surface to the geometry of the brake disk.

Materials such as metal sulphides, minerals, friction components, fibres, ceramic components, and various types of graphite are used in order to be able to achieve similar frictional characteristics and no worse wear resistance than pads containing copper [L. 4]. The steel wool provides high mechanical strength and protects the pads from overheating. A balanced combination of friction particles of different hardness grades and sizes, in combination with solid greases, provides an excellent braking balance and driving comfort. Recent studies have proven that the braking force is created on the small “bulges” of friction material [L. 5]. These bulges are formed by reinforcing fibres, surrounded by hardened components. Therefore, the amount of reinforcing fibres in the friction material cannot be too small. In friction composites, typically a mixture of various types of reinforcing fibres with different properties that complement each other is used. It is known that the wear of friction material increases as the content of reinforcing fibres in the composite decreases [L. 6].

The proposed new type of material for brake pads uses the energy of friction very sparingly throughout the life of the brake pads. The composition of friction material includes some components that move onto the brake disk during braking, modifying its surface layer, or at least forming a protective film, the so-called third body layer [L. 7]. As a result, we get a friction pair modified in “material” terms. The described phenomenon is common in the use of friction materials, but until recently, no one realized it. Recent studies prove conclusively the existence of tribochemical modification of the polymer - metal friction pair [L. 8–10].

During braking, the friction pad is subjected to considerable mechanical stresses and an elevated temperature is generated in its top layer, which is a consequence of the limited thermal conductivity coefficient of the material. Such conditions are conducive to the decomposition of the surface layer of the composite material of the pad, primarily (but not exclusively) the polymeric binder, releasing fragments of macromolecules in the form of active radicals, micromolecular modifiers and composite components. Some of them, in the conditions of elevated temperature and pressure associated with operation of

the pad, can react chemically ultimately leading to a modification of the surface cooperating with the brake pad of the metal disk [L. 11]. And it is not only about hydrogen wear of the disk material resulting from overtaking interstitial positions in the crystal structure of metal by hydrogen atoms originating from the polymeric decomposition of the pad binder, generating stresses damaging the surface layer of metal [L. 12], but it is also metal consumption through chemical interactions of polymer macroradicals that are generated as a result of macromolecules' scission with the surface layer of the disk [L. 13]. Proper selection of components of the friction pad not only allows the selective transfer onto the surface of the disk [L. 14], but it also allows the chemical modification of the surface layer. In an earlier paper devoted to the analysis of friction in the friction pair rubber cross-linked with a conventional sulphuric system (sulphur with accelerators in the presence of stearic acid and zinc oxide) - metal, the presence of metal sulphides at a depth of 150 nm from the surface was even confirmed [L. 8]. On the other hand, chemical interactions, e.g. hydrogen bonds between the metal surface of the disk and components, e.g. of nanometric size, or degradation products of the pad composite, being subject to permanent actions of breaking and recombination [L. 15], may as well be involved in the dissipation of energy during braking [L. 16].

## MATERIALS

Frame composition of the friction composites studied is presented in **Table 2**.

**Table 2. Frame composition [vol. %] of the composite materials for brake pads studied**  
Tabela 2. Skład ramowy [% obj.] badanych materiałów kompozytów okładzin hamulcowych

Material	Low steel	Hybrid
novolac resin	19.0	12.7
organic fibres	4.0	3.7
mineral fibres	2.1	9.9
copper/brass fibre	0.3	–
steel fibres	9.2	3.8
solid lubricant	17.6	26.3
friction dust/rubber crumbs	24.3	11.5
abrasives	3.2	7.2
calcium silicate	4.9	3.1
other fillers	15.4	21.8
Total	100.0	100.0

Components of composites for friction pads were mixed in a horizontal drum mixer equipped with plow mixers and high-speed cutter heads. Mixing was realized by mechanical mixing of the components in the form of dry, free-

flowing powders along with fibres, in order to spread them evenly throughout the volume of the friction moulding composition.

The brake pads were manufactured using the technology of hot pressing at 150°C for 4 min., at pressure of 20 MPa (hybrid pads) or 10 MPa (low-steel pads) and then heated in a chamber furnace for 3 hrs at the temperature of 180°C. The total heating time with initial heating and later cooling amounted to 7 hrs. Low-steel and hybrid pads were compared to commercial ceramic pads. The tested ceramic composite is not a material used in racing cars, which “does not work” at low temperatures, needing to obtain the adequate efficiency at temperatures unattainable for a passenger car in traffic. Therefore, to distinguish them, they are often pads made of it are called “dust-free pads”.

## **METHODOLOGY**

### **Density**

Determination of material density of composites for brake pads was carried out according to ISO 15484, based on Archimedes’ Principle (comparing the weight of the samples in the water and in the air). The test specimens were prepared by the removal of the friction pad from the pad (sheet) carrier plate and grinding them in order to reduce the risk of holding air bubbles on the surface of the specimen after immersion in water. For each of the composites, three specimens were tested. As a result, the average of three measurements was assumed.

### **Hardness**

Determination of hardness of the tested composites for brake pads was carried out according to ISO 2039-2 using a durometer TP 5006-02 (Russia), designed for determining the hardness of plastics using the Rockwell method. Two specimens of each composite were prepared in the form of flat plates with a thickness of 16.7 mm. For each sample, five measurements were made at a distance of at least 10 mm from its edge in places distant from each other by approx. 10 mm. The hardness of the composite was assumed to be the average of all 10 measurements given.

### **Shear strength**

Determination of the shear strength of the composites for brake pads was conducted according to ISO 6312. The test was performed on a testing machine for compression, tensile and bending tests under static conditions, using a type ZD20 Fritz Heckert (Germany). Four specimens of each material were prepared

for the experiments. As a result of the test for the given material, the average of the obtained values was assumed.

### Characteristics of braking

Determinations were performed on an inertia test bench type Krauss AB-791 (Germany). The tests were performed according to ECE ONZ R-90 regulations, appendix 9 point 2.2.2.1.1. Brake disc material was a commercial product, made of grey iron. This is a test with constant braking pressure, which is determined by the following formula:

$$p = \frac{M_d}{0.57 \times r_w \times A_k}$$

where

$M_d$  – torque (braking) moment

$M_d = 150 \text{ Nm}$  for  $A_k \leq 18.1 \text{ cm}^2$

$M_d = 300 \text{ Nm}$  for  $A_k > 18.1 \text{ cm}^2$

$A_k$  – area of piston(s) of the caliper

$r_w$  – effective radius of the disk.

The friction characteristics of the pad material were determined based on the value of the braking moment, recorded at selected points of the test program. When the braking pressure ( $p$ ) is constant (e.g. disk brake), the braking moment can be translated directly on the coefficient of friction. The test consists of 7 steps. Each braking lasted 5 s. The pause between brakings was a minimum of 10 s. The value of the “practical coefficient of friction” ( $\mu_{op}$ ) is equal to the average of values of the coefficient of friction recorded during cycles 2–7, and the measurements were carried out after 1 s from the start of the first braking in every cycle. During the test, the maximum coefficient of friction –  $\mu_{max}$  was also determined (the highest value recorded during all cycles) and the minimum coefficient of friction –  $\mu_{min}$  (the lowest value recorded during all cycles). The order and parameters at which the individual cycles of the test were performed are shown in **Table 3**.

**Table 3. Program of test with constant brake pressure**

Tabela 3. Program badania ze stałym ciśnieniem hamowania

No. of cycle	Number of brakings	Initial temp. of brake disk (°C)	Maximum temp. of brake disk (°C)	Forced cooling
1	1 × 10	≤ 60	Unspecified	no
2–6	5 × 10	100	unspecified	no
7	1 × 10	100	unspecified	yes

## Friction wear

After each braking test described above, the value of linear and weight loss was determined for each friction material. Each brake pad was weighed before and after the test with an accuracy of 0.01g and its thickness was measured at three different points with an accuracy of 0.01mm and averaged.

## Analysis of the surface layer

### *Scanning electron microscopy with chemical microanalysis (SEM-EDS)*

In order to compare the morphology of the surface of specimens of composite materials of brake pads and to identify their components, as well as to analyse what happened on the surface of the materials after friction, a scanning electron microscopy was used, equipped with an adapter for X-rays diffraction analysis (SEM-EDS). The tests were carried out using an electron microscope FEI NovaNano SEM 200 (USA), operating in the mode of low vacuum detection. The specimens before the test were not covered with any layer that improves conductivity. Chemical analyses were performed using an EDS detector from the company EDAX Int. (USA). The results of chemical analyses should be treated as qualitative, due to the topography of the sample surface and the minimum volume from which the analysed signal derives. Both factors significantly affect the signal intensity. In the case of simple compounds such as  $\text{CaCO}_3$ , oxides or metal alloys like brass, this identification is accurate, but deciding on the type of silicate phase is based primarily on the knowledge of the composition of the composites tested. In addition, published reports have been taken into account, indicating, e.g. the method of distinguishing mineral fibres from calcium silicate [L. 17].

### *Time-of-flight secondary ion mass spectrometry (ToF-SIMS)*

To compare the chemical composition of the surface layer of specimens of composite materials for brake pads and to analyse changes associated with friction of pads, time-of-flight secondary ion mass spectrometry was used (ToF-SIMS). The tests were carried out with a spectrometer TOF-SIMS IV, from the company ION-TOF (Germany). As a source of primary ions, ion beam  $\text{Bi}^+$  with an energy of 25 keV was used. For each specimen, 3 spectra were collected from various locations on the surface of the sample, averaging the sizes of the signals. The size of the analysed areas was  $500 \times 500 \mu\text{m}$ . The charge accumulating during the measurement was neutralized with the use of electron beam of low energy, called a "flood gun." Ions  $\text{CH}_3^+$  and  $\text{C}_2\text{H}_5^+$  were selected as representatives of ions containing carbon. Ions  $\text{S}^+\text{O}^-$  were treated together because the resolution of signals was not the best, which did not allow

the separation of signals from sulphur and oxygen. The intensities of selected secondary ions were subjected to the normalization process. The obtained quantitative data should be interpreted in a comparative manner.

## RESULTS AND DISCUSSION

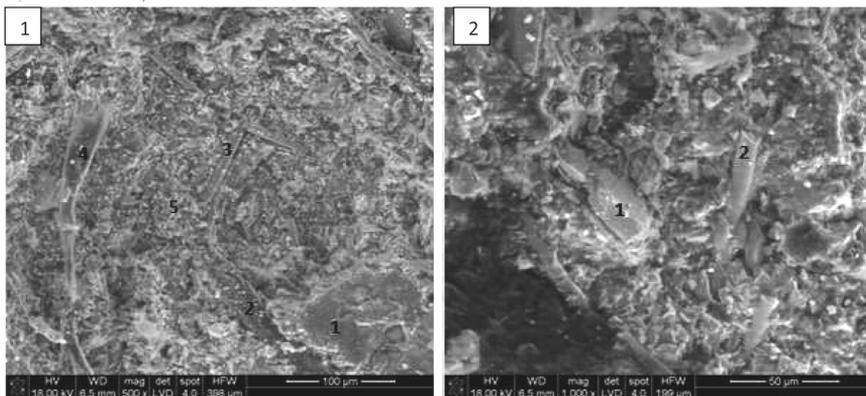
### SEM-EDS

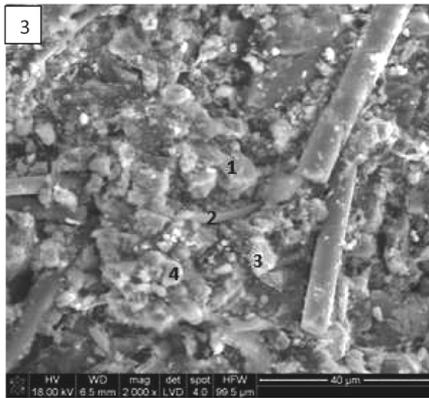
Microscope pictures (SEM) confirm a very complex, macroheterogenous surface morphology of composite materials for brake pads – **Fig. 1**.

The surface of the material of a ceramic pad has a much finer microstructure than the surface of low steel or hybrid material. In microscopic pictures of the surface of the latter, very large objects can be found, which are absent in the other two materials. In contrast, the low-steel material differs from the others with much lower electrical conductivity (which has a negative effect on the contrast of the image obtained by SEM), which is caused by its phase composition, which is different from ceramic or hybrid composite – containing more non-conductive components, e.g. rubber crumbs or powder rubbers. The lower electrical conductivity may also be caused by a much larger content of the resin binder.

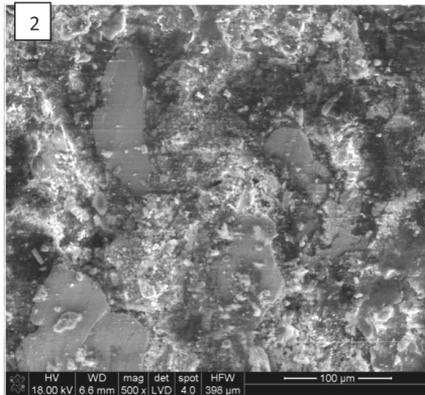
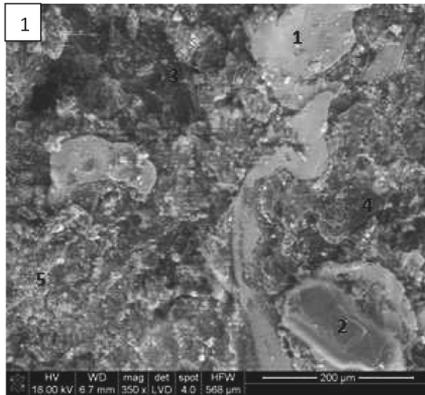
The most characteristic components present in the microscopic pictures of the surfaces of the composites tested, in the form of grains, flakes, crystals, or fibres (**Fig. 1**), can be identified by their chemical composition, determined by X-ray analysis (EDS) – **Table 4**. Other elements present in the spectra originate from the immediate environment of characteristic objects. In all point analyses, carbon and oxygen are recorded, even when the tested object is pure graphite or aluminium silicate.

#### A) Ceramic composite

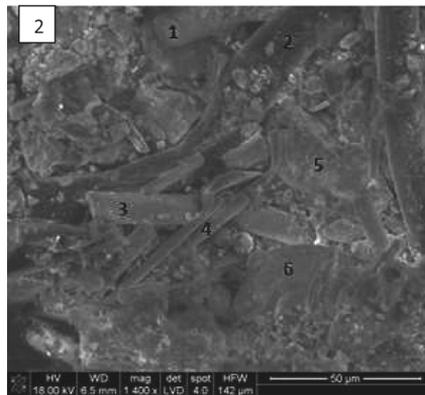
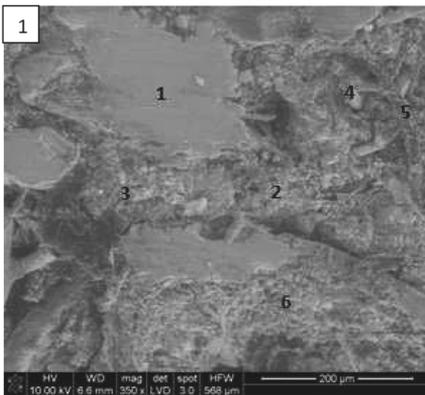


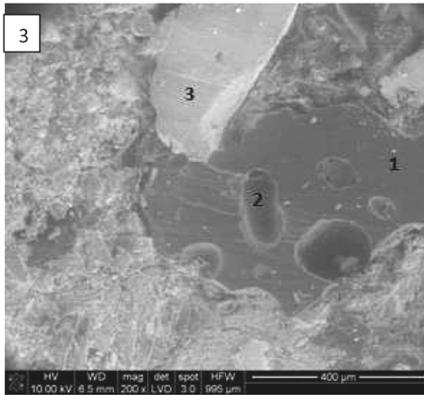


B) Low-steel composite



C) Hybrid composite





**Fig. 1. Morphology of the surface of the tested composite materials for brake pads before tests (SEM)**

Rys. 1. Morfologia powierzchni badanych kompozytowych materiałów okładzin hamulcowych (SEM)

**Table 4. Main components [at.%] of objects present on the surface of the tested composite materials for brake pads (EDS) marked in Fig. 1**

Tabela 4. Główne składniki [% at.] obiektów obecnych na powierzchni badanych kompozytowych materiałów okładzin hamulcowych (EDX), zaznaczonych na Rys. 1

A) Ceramic composite

		C	O	Ca	Si	Al	Mg	S	Ba	K	Ti	Fe	Zn
1.1	ground grains of calcium carbonate with high granulation	–	42.5	14.2	–	–	–	–	–	–	–	–	–
1.2	graphite	81.9	–	–	–	–	–	–	–	–	–	–	–
1.3	mineral (aluminosilicate) fibre	25.8	46.4	5.8	10.8	5.5	2.5	–	–	–	–	–	–
1.4	"smeared" organic fibre (e.g. cellulose, aramid or polyacrylonitrile)	64.4	27.3	4.0	–	–	–	–	–	–	–	–	–
1.5	grains of calcium carbonate with low granulation	39.3	45.0	12.2	–	–	–	–	–	–	–	–	–
2.1	grains of iron oxide with a bit of brass/copper powder	35.4	36.3	22.9	–	–	–	–	–	–	–	–	–
2.2	mineral fibre (aluminium silicate)/calcium silicate	34.6	38.0	6.0	10.4	5.2	–	–	–	–	–	–	–
3.1	grains of calcium carbonate	41.9	47.7	7.8	–	–	–	–	–	–	–	–	–
3.2	calcium silicate	34.7	45.9	4.1	7.1	–	1.8	–	–	–	–	–	–
3.3	mixture of calcium carbonate, barium sulphate and a small amount of brass powder	56.5	22.3	4.9	1.2	–	–	4.7	6.5	–	–	–	–
3.4	mixture of titanium oxide, magnesium oxide, and potassium titanate	27.6	46.6	–	–	–	4.0	–	–	5.5	12.6	–	–

## B) Low-steel composite

		C	O	Ca	Si	Al	Mg	S	Ba	K	Ti	Fe	Zn
1.1	ground grains of iron oxide/steel wool	41.0	8.7	-	-	-	-	-	-	-	-	43.1	-
1.2	magnesium silicate	24.1	50.5	-	9.8	-	12.0	-	-	-	-	-	-
1.3	graphite	89.4	6.8	-	-	-	-	-	-	-	-	-	-
1.4	graphite	89.2	6.1	-	-	-	-	-	-	-	-	-	-
1.5	ground organic fibre with a small amount of barium sulphate	81.4	13.0	-	-	-	-	1.2	0.9	-	-	-	-

## C) Hybrid composite

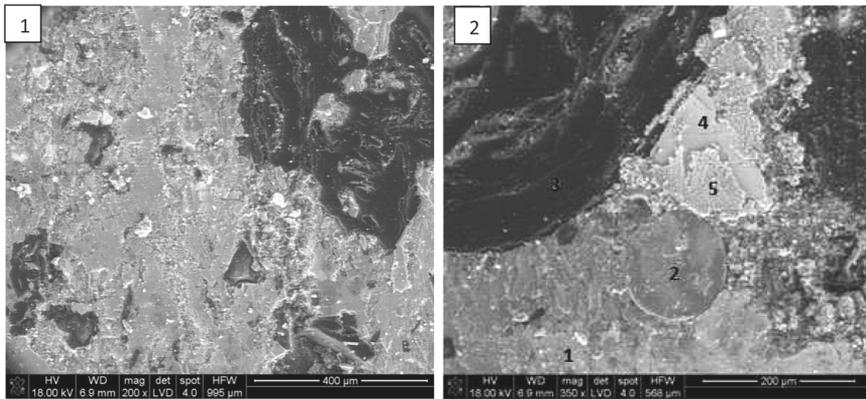
		C	O	Ca	Si	Al	Mg	S	Ba	K	Ti	Fe	Zn
1.1	large grain of iron oxide or ground steel wool	46.7	8.1	-	-	-	-	-	-	-	-	40.5	-
1.2	mixture of powders of barium sulphate, aluminium silicate, iron oxide and zinc	38.2	36.7	-	-	9.1	-	4.4	3.7	-	-	2.6	1.4
1.3	mixture of powders of barium sulphate, aluminium silicate and calcium silicate and iron oxide	64	27.2	-	-	-	-	1.7	1.6	-	-	1.9	-
1.4	mixture of powders of barium sulphate, aluminium silicate, and calcium silicate	38.7	45	-	7	6.6	-	-	-	-	-	-	-
1.5	organic fibre (e.g. cellulose, aramid, or polyacrylonitrile)	80.3	14.2	-	1.1	1.4	-	-	-	-	-	-	-
1.6	mixture of powders of barium sulphate (fine fraction), aluminium silicate and calcium silicate, iron oxide and zinc	36.7	34.2	4	7	8.5	-	2.3	1.5	-	-	2	2.4
2.1	mixture of powders of barium sulphate, iron/steel oxide, thick mineral fibre, and calcium silicate	44	29.2	5.9	7.5	4.8	1.6	-	-	-	-	3.9	-
2.2	carbon or organic fibre	84.5	12.1	-	-	-	-	-	-	-	-	-	-
2.3	thick mineral fibre (aluminosilicate) with the addition of iron	25.5	47.3	-	11.4	4.8	-	-	-	-	-	1.6	-
2.4	thin mineral fibre (aluminosilicate) with the addition of iron and calcium silicate	33.9	37.8	5.2	10.6	5.5	2.1	-	-	-	-	2.5	-
2.5	flake of barium sulphate	28.5	43.4	-	-	-	-	10.5	10	-	-	-	-
2.6	flake of barium sulphate	31.3	39.8	-	-	-	-	9.4	9.8	-	-	-	-

3.1	large particle of graphite with visible pores	96	2.7	-	-	-	-	-	-	-	-	-
3.2	large particle of graphite with visible pores	84	11.8	-	-	-	-	-	-	-	-	-
3.3	iron powder/steel wool	33.6 0	17.3 0									40.2

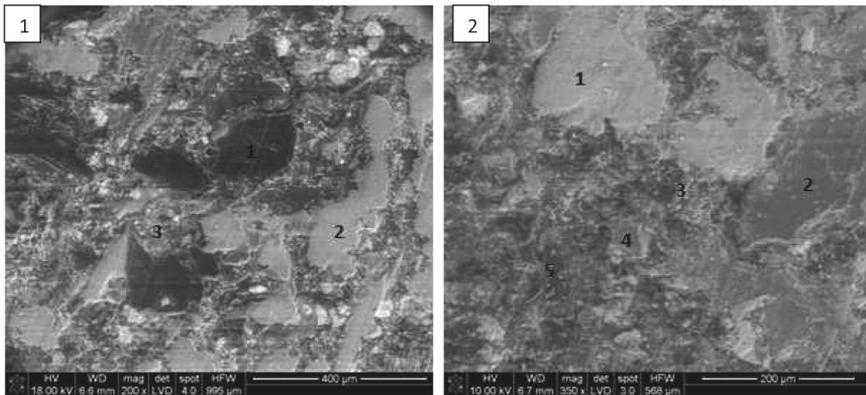
Differences in the surface morphology of the tested composites before friction are responsible for their different microstructure also after the braking test (see point 3.4) – **Fig. 2**.

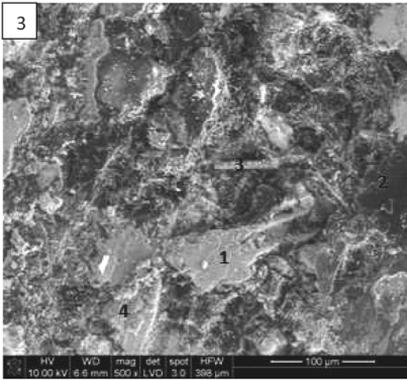
X-ray analysis (EDS) of characteristic objects in the SEM photographs of composite materials of brake pads subjected to braking test (**Fig. 2**) – **Table 5**. allows one to propose friction mechanisms and friction wear of the pads accompanying their operation.

A) Ceramic composite

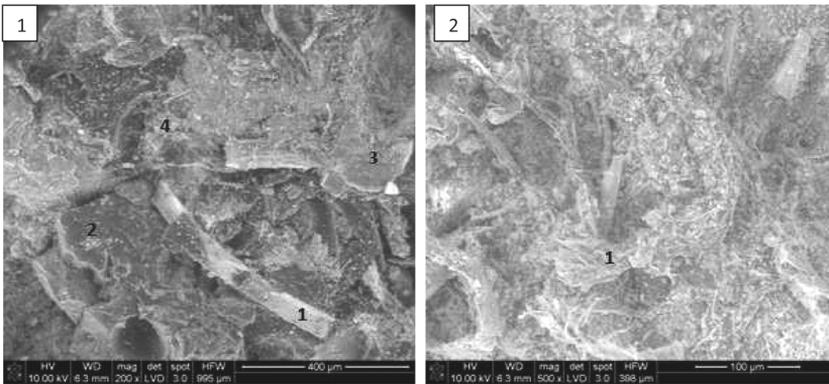


B) Low-steel composite





C) Hybrid composite



**Fig. 2. Morphology of the surface of the tested composite materials of brake pads (SEM) after braking tests**

Rys. 2. Morfologia powierzchni badanych kompozytowych materiałów okładzin hamulcowych (SEM) po testach hamowania

Tribological properties of ceramic composites are affected by particles of copper or brass, barium sulphate, graphite and calcium carbonate, which, as a result of the braking process, react with each other and the products of this reaction are then “smeared” on the surface of the material. In the case of low-steel composites, primarily very large grains of graphite and steel wool are “smeared.” In contrast, the friction of hybrid composite is accompanied by “smearing” of large organic fibres present on the surface of the composite. Folded “film” which is formed in their place is able to absorb the energy generated during braking. Another morphological feature of the surface of the hybrid composite after friction is the presence of fine particles of wear products which unlike the other tested materials, are not removed from the friction zone reducing “dusting” of pads. Their presence certainly also affects the tribological properties of the brake pads. In addition to this the formation of the

layer of the third body is greatly affected by mineral and organic fibres, which, if selected in appropriate proportions, serve as mechanical reinforcement, stopping primary components and secondary products of friction – forming the actual friction contact surface of the pad with the brake disk.

**Table 5. Atomic composition [% at.] of objects present on the surface of the tested composite materials of brake pads (EDX) after braking tests, marked in Fig. 2**

Tabela 5. Skład atomowy [% at.] obiektów obecnych na powierzchni badanych kompozytowych materiałów okładzin hamulcowych (EDX) po testach hamowania, zaznaczonych na **Rys. 2**

A) Ceramic composite

		C	O	Ca	Si	Al	Mg	S	Ba	Fe	Zn	Cu
2.1	brass powder	43.3	18.1	–	–	–	–	–	–	–	13.4	16.2
2.2	mixture of aluminium silicate, calcium and magnesium carbonate/silicate and brass	26.8	40.7	6.6	12.3	6.0	2.3	–	–	–	0.6	0.6
2.4	product of tribochemical reaction of graphite with copper oxide and metal sulphides	46.6	11.8	1.5	–	–	–	2.0	–	3.1	1.2	21.3
2.5	product of tribochemical reaction of copper and sulphur/copper sulphide	49.4	11.1	1.4	1.4	–	–	18.4	–	1.2	0.5	17.6

B) Low-steel composite

		C	O	Ca	Si	Al	Mg	S	Ba	Fe	Zn	Cu	Cr
1.2	iron oxide and sulphide in the powder form	45.9	14.6	–	1.7	–	–	18.4	–	32.1	–	–	–
1.3	ground product of tribochemical reaction of graphite with iron oxide/steel	60.3	27.2	–	–	–	–	–	–	7.2	–	–	–
2.1	ground product of tribochemical reaction of graphite with iron oxide/steel, in which aluminosilicate fibre plays a role	42.6	14.6	–	1.6	2.2	–	–	–	36.2	–	–	–
2.2	ground grains of aluminium silicate and magnesium silicate with the addition of iron	25.0	45.2	–	12.6	2.1	10.9	–	–	2.9	–	–	–
2.3	product of tribochemical reaction in the form of steel wool modified with graphite with the addition of barium and iron compounds	50.7	25.7	3.0	2.8	1.2	–	–	1.2	13.3	–	–	–
2.4	graphite flake modified with the addition of aluminium silicate, calcium and iron silicate	73.9	16.0	1.5	1.7	1.4	–	–	–	3.1	–	–	–
2.5	graphite modified as above	69.8	17.3	2.4	2.4	3.4	–	–	v	1.9	–	–	–
3.1:	ground grains of steel powder/iron oxide	42.3	25.1	v	1.5	2.3	1.0	v	–	24.8	–	–	1.0

3.2	flake graphite	95.1	3.5	-	-	-	-	-	-	-	-	-
3.3	fine carbon/organic fibre	90.8	6.2	-	-	-	-	-	-	-	-	-
3.4	ground grains of iron oxide/steel powder	35.6	44.2	-	-	-	-	-	-	15.6	-	-

### C) Hybrid composite

		C	O	Ca	Si	Al	Mg	S	Ba	Fe	Zn
1.1	steel wool	46.3	8.6							39.0	
1.3	steel powder modified with aluminium and magnesium silicates and zinc sulphide	46.1	26.7	-	3.0	6.1	2.3	2.3	-	9.8	1.3
1.4	mixture of powders of aluminium silicate, calcium, iron silicate, barium and zinc sulphate	63.6	17.0	3.8	3.3	3.4	1.1	1.4	1.4	1.9	2.3
2.1	stratified carbon/organic fibre	78.9	16.9	-	-	-	-	-	-	-	-

### ToF-SIMS

When analysing the differences in the chemical composition of the surface layer of specimens of composite material for brake pads, it should be noted that only the ceramic specimen contains molybdenum and lead, elements absent in the other composites. Unlike the ceramic composite, the “low steel” composite and hybrid material specimens contain much more barium and smaller amounts of copper and zinc. Titanium is present in the two latter samples only in trace amounts. **Tables 6–8** show the normalized intensities of the selected secondary ions present in the specimens before and after the braking test.

**Table 6. Normalized ion intensities calculated based on secondary ion mass spectra obtained from the surface layer of ceramic composite**

Tabela 6. Znormalizowane intensywności jonów obliczone na podstawie widm mas jonów wtórnych otrzymanych z warstwy wierzchniej kompozytu ceramicznego

Ion	Virgin sample	Sample after friction
CH <sub>3</sub> <sup>+</sup>	0.0054	0.0082
Na <sup>+</sup>	0.012	0.018
Mg <sup>+</sup>	0.015	0.012
Al <sup>+</sup>	0.0094	0.0068
Si <sup>+</sup>	0.0083	0.0148
C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	0.0034	0.0198
K <sup>+</sup>	0.41	0.31
Ca <sup>+</sup>	0.13	0.16
Ti <sup>+</sup>	0.0130	0.0056
Fe <sup>+</sup>	0.021	0.032
Cu <sup>+</sup>	0.054	0.017
Zn <sup>+</sup>	0.0065	0.0017
Mo <sup>+</sup>	0.0159	0.0015
Pb <sup>+</sup>	0.0014	0.0001
S+O <sup>+</sup>	0.026	0.025
Cl <sup>-</sup>	0.0160	0.0077

**Table 7. Normalized ion intensities calculated based on secondary ion mass spectra obtained from the surface layer of low-steel composite**

Tabela 7. Znormalizowane intensywności jonów obliczone na podstawie widm mas jonów wtórnych otrzymanych z warstwy wierzchniej kompozytu low-steel

Ion	Virgin sample	Sample after friction
CH <sub>3</sub> <sup>+</sup>	0.0085	0.0096
Na <sup>+</sup>	0.047	0.051
Mg <sup>+</sup>	0.013	0.015
Al <sup>+</sup>	0.0134	0.0079
Si <sup>+</sup>	0.042	0.024
C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	0.017	0.024
K <sup>+</sup>	0.050	0.059
Ca <sup>+</sup>	0.069	0.065
Ti <sup>+</sup>	0.0007	0.0003
Fe <sup>+</sup>	0.025	0.090
Cu <sup>+</sup>	0.0010	0.0075
Zn <sup>+</sup>	0.0006	0.0003
Mo <sup>+</sup>	–	–
Ba <sup>+</sup>	0.045	0.028
Pb <sup>+</sup>	–	–
S+O <sup>-</sup>	0.0054	0.0058
Cl <sup>-</sup>	0.0096	0.0049

**Table 8. Normalized ion intensities calculated based on secondary ion mass spectra obtained from the surface layer of hybrid composite**

Tabela 8. Znormalizowane intensywności jonów obliczone na podstawie widm mas jonów wtórnych otrzymanych z warstwy wierzchniej kompozytu hybrydowego

Ion	Virgin sample	Sample after friction
CH <sub>3</sub> <sup>+</sup>	0.0065	0.0094
Na <sup>+</sup>	0.043	0.037
Mg <sup>+</sup>	0.027	0.044
Al <sup>+</sup>	0.031	0.045
Si <sup>+</sup>	0.020	0.082
C <sub>2</sub> H <sub>5</sub> <sup>+</sup>	0.024	0.016
K <sup>+</sup>	0.041	0.034
Ca <sup>+</sup>	0.038	0.122
Ti <sup>+</sup>	0.0004	0.0006
Fe <sup>+</sup>	0.015	0.016
Cu <sup>+</sup>	–	–
Zn <sup>+</sup>	0.0018	0.0043
Mo <sup>+</sup>	–	–
Ba <sup>+</sup>	0.029	0.031
Pb <sup>+</sup>	–	–
S+O <sup>-</sup>	0.0118	0.0066
Cl <sup>-</sup>	0.0067	0.0027

Significant changes in the signal coming from iron ions was observed for specimens of ceramic and low-steel pads, in the surface layer of which, after braking, the amount of iron significantly increases by 50% and 3.6 times, respectively. Such a tendency may indicate the transmission of the products of wear of the brake disk onto the pad, but it was not observed in the case of pad made of hybrid material that contains the least amount of iron. When comparing the size of the signal from copper in ceramic and low-steel pads,

a significant discrepancy in its size before and after the braking test can be observed. Before the test, the content of copper ions in the surface layer of the ceramic composite is 5.4 times higher, while after the braking test, 4.4 times more copper is found in the surface layer of low-steel material than ceramic material. This indicates the important role of copper compounds in the operation of these pads, although their mechanism of action in ceramic composites is different from the behaviour in the friction of low-steel material. A comparison of compositions of the surface layer of the ceramic and hybrid material after the test indicates a large difference in the quantity of aluminium ions, the presence of which is most likely connected with the wear of the disk. This explains the low wear of the brake disk by the ceramic pads, where the size of the signal from aluminium ions is the smallest and the greatest wear of the brake disc which cooperated with the hybrid pad, in which case, the aluminium content in the surface layer is the greatest, increasing after the braking test by as much as 45%. Perhaps silicon and iron in the form of steel wool are also responsible for the disk wear. Tests have confirmed the highest iron content in the low-steel composite. In the ceramic material, iron was added most probably in the form of oxides or sulphides; therefore, 50% more iron ions were found in the surface layer of the ceramic material than in the hybrid material. This confirms that the good tribological properties of ceramic pads are provided by copper, which will be very difficult to replace. In this context, it would be interesting to supplement the conducted tests with ceramic composite containing no copper, the so-called “eco friction” ones.

### Functional characteristics of pads

Results of the tests for commercial composite materials of pads from the low-steel group (**Fig. 3**) and ceramic group (**Fig. 4**) were compared with the prototype hybrid material (**Fig. 5**). Functional parameters of the tested materials for brake pads are summarized in **Table 9**.

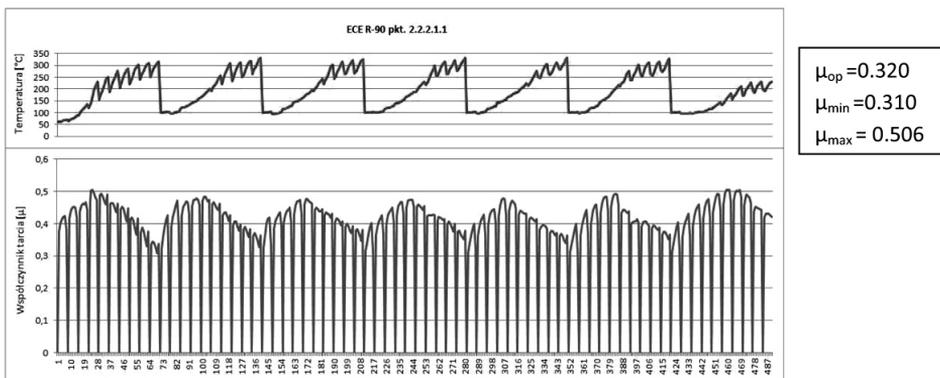
The obtained braking characteristics have confirmed the advantages of the developed material, such as the following:

- 1) A higher value of the “cold” coefficient of friction, and
- 2) A high value of the “hot” coefficient of friction at little fading.

The undoubted advantage of the new material is also its fast hot bedding.

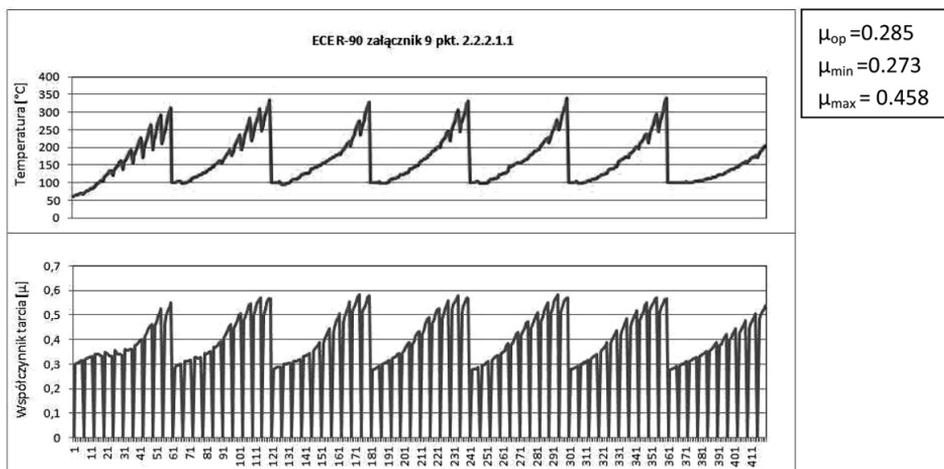
The program of running in for the prototype hybrid material was identical to the one for commercial materials (ceramic and low steel). The friction characteristics obtained (**Figs. 3–5**) show that the pads made of hybrid material behave more “aggressively” in relation to the brake disk than the ones made of ceramic composite or low-steel one. The values of “cold” coefficients of friction for “hybrid” pads are also higher, resulting in generating slightly higher temperatures during brakings. Consequently, an increase in the coefficient of friction is observed during brakings, which occurs with the increase in

temperature up to about 300°C. In contrast to ceramic pads, where at this temperature stabilization of the coefficient of friction occurs, a reversal of trend to increase the coefficient of friction occurs, and fading brakings appear. The greatest resistance to this phenomenon was shown by ceramic pads, for which brakings of this type appeared at the end of fading steps of the test (2–7). For low-steel pads, fading brakings appear as early as in the middle of these steps. Weight wear of the pads after the test is similar for ceramic and hybrid pads. but it is significantly different, and to their benefit, from low-steel pads, characterized by two-times higher friction wear. However, in terms of linear wear, ceramic pads showed their superiority over the other tested pads, for which the value of thus measured wear turned out to be two times higher.



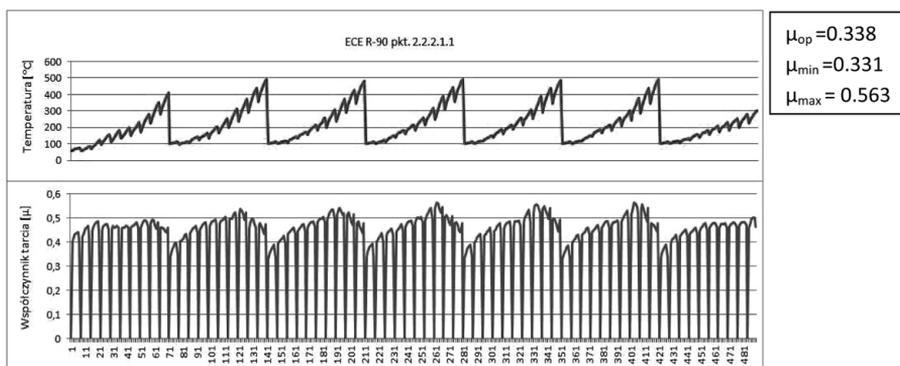
**Fig. 3. Friction characteristics (ECE ONZ R-90) of commercial low-steel material**

Rys. 3. Charakterystyka tarcia (ECE ONZ R-90) komercyjnego materiału low-steel



**Fig. 4. Friction characteristics (ECE ONZ R-90) of commercial ceramic material**

Rys. 4. Charakterystyka tarcia (ECE ONZ R-90) komercyjnego materiału ceramicznego



**Fig. 5. Friction characteristics (ECE ONZ R-90) of prototype pad made of hybrid material**  
 Rys. 5. Charakterystyka tarcia (ECE ONZ R) prototypowej okładziny z materiału hybrydowego

**Table 9. Summary of functional parameters of the brake pads tested**

Tabela 9. Zestawienie parametrów użytkowych badanych okładzin hamulcowych

Parameter	Unit	Norm / method	Composite		
			Ceramic	low-steel	hybrid
$\mu_{op}$	–	ECE R-90 appendix 9 p. 2.2.2.1.1	0.285	0.320	0.338
$\mu_{min}$	–	ECE R-90 appendix 9 p. 2.2.2.1.1	0.273	0.310	0.331
$\mu_{max}$	–	ECE R-90 appendix 9 p. 2.2.2.1.1	0.458	0.506	0.563
Wear av.(brake pad)	[g]	–	-0.27	-0.72	-0.23
Wear av.(brake pad)	[mm]	–	-0.03	-0.07	-0.06
Shear stress	MPa	ISO 6312	4.0	4.7	4.5
Shear stress after test (Krauss)	MPa	ISO 6312	3.1	3.0	4.1
Density	[g/cm <sup>3</sup> ]	ISO 15484	2.14	2.19	2.18
Hardness	HRR	ISO 2039-2	60	38	47

## SUMMARY

In this paper, we wanted to draw the reader's attention to the tribochemical phenomena undervalued in the design of brake pads materials. Their rational use opens up a wide field of possibilities for material engineering, surface engineering, and tribology. An additional benefit created by tribochemical phenomena is the possibility of reducing the wear of brake pads cooperating with surface of the disk modified during friction. Other possibilities open with the creation of a friction film on the surface of the disk, which could cause the friction grains released during braking to gather, settling on the surface of the brake disk. So, some of the friction particles, taking part in the braking process would not be irretrievably lost but could participate in subsequent brakings. For the longest possible persistence of the transmitted friction particles on the surface of the brake disk, one could, e.g., use a combination of carefully

selected sulphide greases, which introduced into the composite are able to significantly extend the life of the disk, limit the "dusting" of pads and will allow the elimination of environmentally harmful antimony sulphide, which has been used so far.

1. The new concept of the material of friction composites presented in the paper, the "hybrid material" developed for the needs of all markets, connects the highest requirements concerning safety, comfort, design life, and braking efficiency in the best possible way. It can be an effective compromise between quite divergent requirements for high braking efficiency (Europe) and driving comfort (Japan and North America) due to the composition of the composite.
2. The new approach in designing the composition of hybrid materials of brake pads also takes into account and even effectively uses the chemical reactivity of the disk material.
3. The prototype hybrid material is very promising. Its advantage is a lower price than in the case of ceramic pads, low weight wear, and greater resistance to fading compared to low-steel pads. Further work on its development will aim towards reducing the "aggressiveness" in relation to the brake disk and stabilizing the coefficient of friction of brakings at lower temperatures (approx. 300°C). They will be accompanied by efforts to further reduce the cost of materials (expensive ingredients) while maintaining the current operating parameters. For this purpose, it is planned to use to a greater extent cheaper mineral-layered fillers (e.g., halloysite) and to take advantage of tribochemical phenomena occurring in the friction contact. The proposed concept should take into account both elements of the friction pair: brake pad and disk.

### Acknowledgement

The authors would like to thank Ms Magdalena Ziąbka, PhD Eng. from the Department of Ceramics and Refractory Materials of the Faculty of Materials Science and Ceramics, AGH University of Science and Technology for help with microscopic observations.

### REFERENCES

1. Breuer B., Bill K.H.: Brake Technology Handbook.SAE International. Warrendale. USA 2007.
2. Ścieszka S.F.: Friction Brakes. Design and Tribological Problems. ITeE, Radom, Poland 1998.
3. Dobrowolski O., Bieliński D.M., Dul J., Mandryk R., Nyszko G.: Zastosowanie analizy termicznej i termowizji w badaniach materiałów okładzin hamulcowych.Tribologia. 2008. 218. 145–152.

4. Nosal S., Orłowski T.: Ustalanie receptury kompozytowego ciernego materiału hamulcowego. *Tribologia*. 2010. 220. 75–84.
5. Eriksson M., Bergman F., Jacobson S.: On the nature of tribological contact in automotive brakes. *Wear*. 2002. 252. 26–36.
6. Gudmand-Hoyer. L., Bach. A., Nielsen. G. T., Morgen. P.: Tribological properties of automotive disc brakes with solid lubricants. *Wear*. 1999. 232. 168–175.
7. Lu Y.: A combinatorial approach for automotive friction materials. Effects of ingredients on friction performance. *Composites Sci.Technol*. 2006. 66. 591–598.
8. Bieliński D.M., Grams J., Paryjczak T., Wiatrowski M.: Tribological modification of metal counterface by rubber. *Tribol.Lett*. 2006. 24. 115–118.
9. Bieliński D.M., Siciński M., Grams J., Wiatrowski M. (60%. concept of the paper. performing part of the research. development of results. preparing the text for publication). Wpływ budowy węzłów sieci przestrzennej gumy na stopień modyfikacji warstwy wierzchniej żelaza w węźle ciernym elastomer-metal. *Tribologia* 2007. 212 (2). 55–64.
10. Siciński M., Bieliński D.M., Grams J., Wiatrowski M. (60%. concept of the paper. performing part of the research. development of results. preparing the text for publication). Modyfikacja warstwy wierzchniej przeciwpróbki żelaznej współpracującej z polimerem zawierającym siarkę. *Tribologia*. 2008. 220 (4). 69–76.
11. Płaza S.: *Chemia Procesów Tribologicznych*. Wydawnictwo Naukowe Uniwersytetu Łódzkiego. Łódź 1997.
12. Starczewski L.: Wodorowe zużywanie ciernych elementów maszyn. *Problemy Eksploatacji*. 2003. no. 4. 47–57.
13. Gent A.N., Pulford C.T.R.: Wear of metal by rubber. *J. Mater.Sci.*. 1979. 14. 1301–1307.
14. Pogosian A., Hovhannisyan K., Isajanyan A.: Polymer friction transfer w *Encyclopedia of Tribology*. Springer. 2013. p. 2585–2592.
15. Zhang J., Wang N., Liu W., Zhao X., Lu W.: Intermolecular hydrogen bonding strategy to fabricate mechanically strong hydrogels with high elasticity and fatigue resistance. *Soft Matter*. 2013. 9. 6331–6337.
16. Shi F-K., Wang X-P., Guo R-H., Zhong M., Xie X-M.: Highly stretchable and super tough nanocomposite physical hydrogels facilitated by the coupling of intermolecular hydrogen bonds and analogous chemical crosslinking of nanoparticles. *J. Mater.Chem.B*. 2015. 3. 1187–1192.
17. Razo S., Adolfo D., Fernao P., Decrock J., Opsommer A., Fabre M.: PROMAXON-D in NAO non steel disc pad formulations. The importance in the third body layer and its effect on brake noise. *Proc. of the SAE Brake Colloquium*. Charleston. SC. USA. 26–28-01-2015. p. 3–13.

## Streszczenie

**Praca przedstawia charakterystykę materiałów stosowanych aktualnie w budowie okładzin hamulcowych samochodów osobowych, zwracając uwagę na ich wady i zalety. Na tym tle, kierując się oczekiwaniami ze**

---

strony klientów oraz biorąc pod uwagę najnowsze osiągnięcia w obszarze inżynierii kompozytów polimerowych i tribochemii. zaproponowano perspektywy postępu w obszarze materiałów ciernych. Rozważania zostały zilustrowane wynikami badań własnych dotyczących analizy morfologii i składu chemicznego powierzchni reprezentatywnych grup materiałów okładzin hamulcowych. Charakterystyki hamowania oraz mechanizm tarcia badanych kompozytów zostały zinterpretowane z punktu widzenia zmian zaobserwowanych w mikrostrukturze i składzie chemicznym ich powierzchni. Nawiązują one do wcześniejszych badań autorów związanych z tribochemiczną modyfikacją elementów węzła ciernego polimer-metal.