Polish Society of Composite Materials
Polskie Towarzystwo Materiałów Kompozytowych

14: 1 (2014) 43-49

COMPOSITES THEORY AND PRACTICE

Bartosz Hekner[1]*, Jerzy Myalski[1], Nathalie Valle[2], Agnieszka Botor-Probierz[2]

[1] Silesian University of Technology, Department of Materials Science and Metallurgy, ul. Krasińskiego 8, 40-019 Katowice, Poland
[2] Centre de Recherche Public Gabriel Lippmann, 41 rue du Brill, L-4422 Belvaux, Luxembourg
**Corresponding author. E-mail: bartoszhekner@gmail.com*

Received (Otrzymano) 11.02.2014

INFLUENCE OF CARBON NANOTUBES AND CARBON PARTICLES ON TRIBOLOGICAL PROPERTIES IN ALUMINUM BASED COMPOSITES

This paper presents the tribological characteristics of friction materials manufactured for a high loaded friction point. Composite powders containing 1% carbon nanotubes or 5% glassy carbon particles were produced by high energy milling in planetary mills. High energy during powder preparation led to reinforcement particle fragmentation up to sizes between 0.1÷2 µm. Furthermore, mechano-chemical bonding between the reinforcement and the Al particles used as the matrix was obtained during this process. As a result of the pressing and sintering processes, composite materials with homogeneous reinforcement (SiC) or heterogeneous reinforcement (SiC with addition of 1 wt.% multiwalled carbon nanotubes (CNT) or 5 wt.% glassy carbon particles) were manufactured. The properties of the obtained composite materials were measured during tribological tests at room temperature (25°C) and high temperature (450°C). The tribological research was conducted by the *ball-on-disc* method, at a distance of 250 m, with a load of 10 N and sliding speed of 0.1 m/s. The analyses of the friction coefficient and wear results revealed the desirable influence of the carbon components especially in increasing the average value and stabilization of the friction coefficient, particularly at room temperature. Moreover, the carbon additions led to a decrease in wear in comparison to the composite reinforced with SiC particles only. The changes in the wear level and friction coefficient value are a result of the differences in the predominant wear mechanism observed between the friction surfaces of the composite materials at room and high temperatures.

Keywords: **carbon nanotubes, glassy carbon, friction coefficient, wear, wear mechanisms**

WPŁYW NANORUREK WĘGLOWYCH ORAZ CZĄSTEK WĘGLOWYCH NA WŁAŚCIWOŚCI TRIBOLOGICZNE KOMPOZYTÓW NA OSNOWIE ALUMINIUM

Przedstawiono charakterystykę tribologiczną kompozytów ciernych do zastosowań w wysokoobciążonych węzłach tarcia. Proszki kompozytowe zawierające 1% nanorurek węglowych lub 5% cząstek węgla szklistego uzyskano metodą wysokoenergetycznego mielenia w młynach planetarnych. Wysoka wartość energii towarzyszącej przygotowaniu proszku kompozytowego prowadziła do fragmentacji cząstek umacniających do wielkości ok 0,1÷2 µm. W procesie mielenia nastąpiło również mechaniczno-chemiczne połączenie cząstek zbrojenia z cząstkami Al stanowiącymi osnowę kompozytu. W wyniku procesów prasowania i spiekania uzyskano materiały kompozytowe zawierające cząstki homofazowe - SiC oraz heterofazowe - SiC z dodatkiem 1% wag. wielkościennych nanorurek węglowych oraz SiC z dodatkiem 5% wag. cząstek węgla szklistego. Właściwości uzyskanych materiałów kompozytowych określono na podstawie badań tribologicznych w temperaturze otoczenia 25°C i w temperaturze podwyższonej 450°C. Badania tribologiczne przeprowadzono metodą *ball-on-disc* na drodze tarcia 250 m, przy obciążeniu 10 N i prędkości poślizgu 0,1 m/s. Wyniki pomiaru współczynnika tarcia i zużycia wykazały korzystny wpływ komponentów węglowych powodujących podwyższenie oraz stabilizację współczynnika tarcia, szczególnie w temperaturze otoczenia. Stwierdzono, że dodatki węglowe obniżają zużycie kompozytu w porównaniu z kompozytem zawierającym tylko cząstki SiC. Zmiany zużycia i współczynnika tarcia są wynikiem różnych mechanizmów towarzyszących procesom tarcia w temperaturze otoczenia i temperaturze podwyższonej.

Słowa kluczowe: **nanorurki węglowe, węgiel szklisty, współczynnik tarcia, zużycie, mechanizmy zużywania**

INTRODUCTION

The implementation of new materials in the highly developed automotive industry creates several technological and material problems. Stringent requirements should be met for all new material solutions, inter alia because of work conditions that are considered as extreme. Detailed evaluation of brake pad working conditions showed that only a fractional part of the surface takes active participation in the reduction of kinetic energy [1]. Presenting the solution of particle fragmentation up to the sub-micro size led to stress distribution over a larger number of particles distributed over a larger surface pad. These effects should provide wear reduction as a result of the dispersal of the tangential forces acting on a single particle to more particles.

In the present research, an attempt to develop a multistep technology of manufacturing is presented. High energy ball milling in planetary mills was the first step. This operation was used to obtain proper bonding between the metal and ceramic particles through multiple mechanical impact during milling. The main advantage of this step is particle size reduction and the breaking down of agglomerates. Furthermore, the effect of aluminum carbide formation during production was limited. Selection of the technological parameters is the critical point in this step. Producing good quality bonding and particles fragmentation is possible only with proper milling parameters (energy, time, ball size and chamber type). The final parameters were obtained by literature data analyses and the authors' own previous experiences [2, 3].

In the next step, all the composite powders were pressed and sintered in a Degussa press. This solution allowed us to obtain a solid material with a maximum reduction in liquid phase presence which leads to the creation of undesirable aluminum carbide on the Al-SiC grain boundaries. High pressure during the process was applied for porosity reduction up to the required level.

The newest trend of construction for materials applied in high load friction nodes *t* is the manufacturing metal matrix composites (MMC) reinforced with ceramic particles [4-6]. Fulfilment of the set requirements is possible by synergic influence of the components. The high ductility of metal with high thermal conductivity led to a reduction in the growth of the work temperature and thereby extending the secure life time of the element. The high hardness and shearing resistance of the ceramic particles led to increasing the mechanical properties and decreasing the wear of the composite. Moreover, the application of ceramics with non-ferrous metals provides a reduction in degradation due to oxidation of the surface (corrosion) compared to iron alloys.

As an innovative material solution in the presented composites, carbon additions were applied. The presence of multi walled carbon nanotubes or glassy carbon was designed to increase the tribological properties. The high thermal conductivity of the carbon particles leads to decreasing the work temperature of brake pads, and thereby making it possible to apply low melting material as the matrix (melting point of aluminum – 670°C). Detailed analysis of the composites friction condition reveals the possibility of wear reduction and changing the stability and average value of friction coefficient through interference in the chemical composition. The implementation of glassy carbon as a component leads to modification of the predominant wear mechanism between friction couple materials. Glassy carbon particles are characterized by high hardness and low shear strength, which leads to the creation of a protective layer in the friction area to protect against progressive wear. Because of this property, carbon particles seem to be desirable as components in tribological materials [7-9].

The combination of innovative powder metallurgy technology with new material solutions should ensure the possibility of producing a composite material for use in a high loaded friction point, competitive with the materials currently implemented in the automotive industry [10].

EXPERIMENTAL PROCEDURE

For the analyses, aluminium based composite materials with heterogeneous reinforcement were used. As a reinforcement, silicon carbide with 1 wt.% multiwalled carbon nanotubes (CNT) or 5 wt.% glassy carbon (GC) particles were used. The detailed chemical composition is shown in Table 1. The influence of temperature on the tribological parameters (friction coefficient, wear) was tested at 25 and 450°C. The scope of the activities included both production and testing the tribological properties. The investigated materials were prepared by the powder metallurgy method. As a preliminary step of the technology high energy ball milling was conducted in a planetary mill, Planetary Micro Mill PULVERISETTE 6 classic line. The high energy of the particle impact was provided by a chamber speed rotation of 600 rpm during 3 hours in 36 intervals: 5 minutes of milling and a 30 minute break. The millings were conducted in a protective atmosphere of argon. The purity of the chemical composition was provided by using chambers with low reacting walls (silicon nitride). This step of measurement was made for a decreasing size of ceramic particles to the submicro scale and bonding between the matrix and the reinforcement particles.

TABLE 1. **Chemical composition of produced materials**
TABELA 1. **Skład chemiczny wytworzonych kompozytów**

Composite	Al [wt.%]	SiC [wt.%]	CNT [wt.%]	GC [wt.%]
Al-SiC	84.2	15.8	-	-
Al-SiC-CNT	83.4	15.6	1.0	-
Al-SiC-GC	80.0	15.0	-	5.0

Subsequently, all the obtained powders were pressed and sintered in a Degussa press with a10 MPa load. The sintering was conducted in two steps: first, the materials were heated up to 480°C and held for 20 minutes, next they were heated to the target value of 700°C. The whole sintering process was conducted in vacuum (10^{-3} Tor).

Afterwards, the tribological characteristics for the obtained materials were analysed using a CSM High Temperature Tribometer with Instrum X software. The tribological characterisations were conducted in friction in air conditions, using the *ball-on-disc* method, with a 0.1 m/s sliding speed and a 10 N load. The counterpart was produced from 100Cr6 bearing steel in the form of a 6 mm ball. The analyses were carried out at 25 and 450°C respectively at distances of 100 m and 250 m. For a comprehensive description of the tribological properties, the stability of the friction coefficient on the distance, mass loss and the predominant wear mechanism were observed.

All the obtained powders, solid materials and wear tracks were observed by means of a Scanning Electron Microscope HITACHI SU-70 with INCA software.

RESULTS

Microstructure observations of composite

As a result of the conducted actions, composites reinforced with different types of carbon were manufactured. During microstructure observation with a Scanning Electron Microscope, similar effects of ceramic particle fragmentation and proper homogeneity in the whole volume of the composites were found. The size of the silicon carbide particles were reduced to the range of 0.1÷1 μm. Such high crushing of particles justified a high energy milling process as part of the presented technology. However, breaking of the glassy carbon (GC) particles was not as high as the SiC particles. In the case of the GC particles, a wide range of size distribution (between 2 up to 100 μm) was observed. The described results are shown in Figure 1 as an example of composite microstructure with GC particles addition.

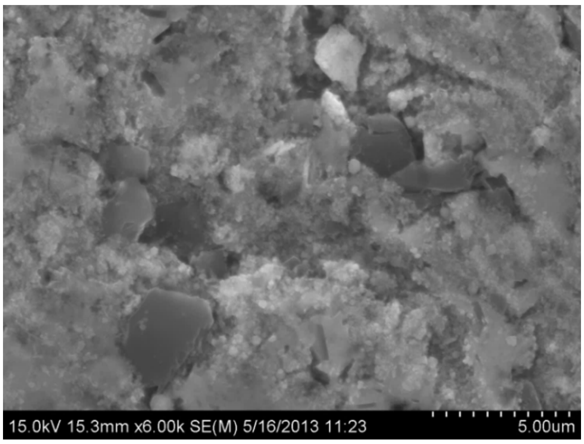

Fig. 1. Microstructure of aluminum based composite reinforced with SiC particles with GC addition

Rys. 1. Mikrostruktura kompozytu aluminiowego zbrojonego cząstkami SiC z dodatkiem GC

Tribological investigations

As the next step of properties evaluation, tribological tests at 25°C were conducted for all the materials. Among the analysed materials, the lowest friction coefficient (0.5) was obtained for the Al-SiC composite. The carbon components (CNT and GC) led to an increase in the average friction coefficient value (up to 0.63 and up to 0.68 accordingly). Therefore direct influence of the type of carbon particles on the friction properties was detected. However, in this case the quantity and size of particles (different chemical compositions) are of importance. The application of carbon nanotubes resulted in decreasing the tribological properties on the analysed distance. After slight variations at the beginning of the friction test (about 25 m), further periodic changes in the value between 0.53÷0.69 with a growing tendency were observed. The composite without the carbon addition showed high stability of properties during friction without a lapping effect of the characteristics for materials in the friction couple. However, the lowest variance of friction coefficient on the analysed distance was observed for the Al-SiC-GC composite. After initial lapping (about 10 m), this composite showed high stability during the whole friction distance test (Table 2).

TABLE 2. **Results of friction tests at 25°C**
TABELA 2. **Wyniki testu ciernego w 25°C**

Composite	Parameter	
	Friction coefficient	Mass loss [g]
Al-SiC	0.48÷0.51	0.004
Al-SiC-CNT	0.53÷0.69	0.004
Al-SiC-GC	0.67÷0.70	–0.014

The next step of the performed works was evaluation of the tribological properties at high temperature (450°C), as an attempt to achieve the real working conditions of the friction couple. All the materials were tested in comparable conditions to the test at room temperature. The results of the conducted tests are shown in Table 3. For the Al-SiC and Al-SiC-CNT composites, the increase in working temperature led to an increase in the average friction coefficient value. An increase from 0.5 up to 0.63 for the Al-SiC composite and from 0.63 up to 0.79 for Al-SiC-CNT was noted. An opposite tendency was observed for the Al-SiC-GC composite. At high temperature, this material was characterized by a friction coefficient at the level of 0.53, while at room temperature - 0.68. Notwithstanding, the most significant changes are variations of the friction coefficient in the time periods. The material without carbon additions at high temperature revealed abrupt changes in the friction coefficient with a downward tendency. A similar tendency was not recorded at room temperature. The addition of CNT did not result in significant improvement of the properties. This material was characterized by periodic, abrupt changes in the friction coefficient value, in the range between 0.6÷1. The glassy carbon component had a significant influence on friction coefficient stabilization. After initial lapping (about 25 m), the specimen exhibited distinct stabilization at the level of 0.55, which is a desirable value for friction material used as brake pads. The subsequent analysed parameter was the wear value for the materials after tribological tests.

TABLE 3. **Results of friction tests at 450°C**
TABELA 3. **Wyniki testu ciernego w 450°C**

Composite	Parameter	
	Friction coefficient	Mass loss [g]
Al-SiC	0.43÷0.78	0.444
Al-SiC-CNT	0.60÷0.10	0.149
Al-SiC-GC	0.52÷0.55	0.073

The mass loss of the Al-SiC and Al-SiC-CNT materials at 25°C were on a similar, low level. In the case of the material with the glassy carbon addition, a disc mass increase was observed after the conducted test. This phenomenon can be explained by counterpart material transmission on the composite disc surface as a reason for interaction between two friction surfaces. During the analyses, the mass loss obtained at 450°C showed a clear tendency to wear reduction for the materials with a carbon addiction. The material with CNT showed a three times lower mass loss than the material without carbon, while the material with glassy carbon revealed a more than six times lower mass loss (Tables 2, 3). For thorough understanding of the behaviour of the materials in friction conditions, analysis of the surfaces obtained as a result of interaction between the materials were conducted using SEM. In the analysis, both the composite disc and wear products, were taken into account.

Wear track research at 25°C

The predominant wear mechanisms in the case of the Al–SiC composite could be described by microcutting and ridging mechanisms. Characteristic similar deformed parallel lines are typical effects for a surface worn by plastic deformation (Fig. 2a). The small size of the torn debris and their shape indicates microcutting processes and the detachment of small fragments of a plastically deformed matrix (Fig. 2b).

The application of a carbon addition led to changes in the predominant wear mechanisms. The surface of the composite with CNT after the wear test was similar to the surface obtained during friction of a composite with a homogeneous reinforcement - SiC. However, in this case the plastic deformed areas were not uniform or continuous as in the composite without carbon particles. In the wear track, larger detached plastically deformed fragments of matrix were found (Fig. 3a). This phenomenon could be connected with the presence of carbon nanotubes. Moreover, large flattened particles observed among the debris confirmed the thesis of the plastic deformation of the matrix fragments (Fig. 3b).

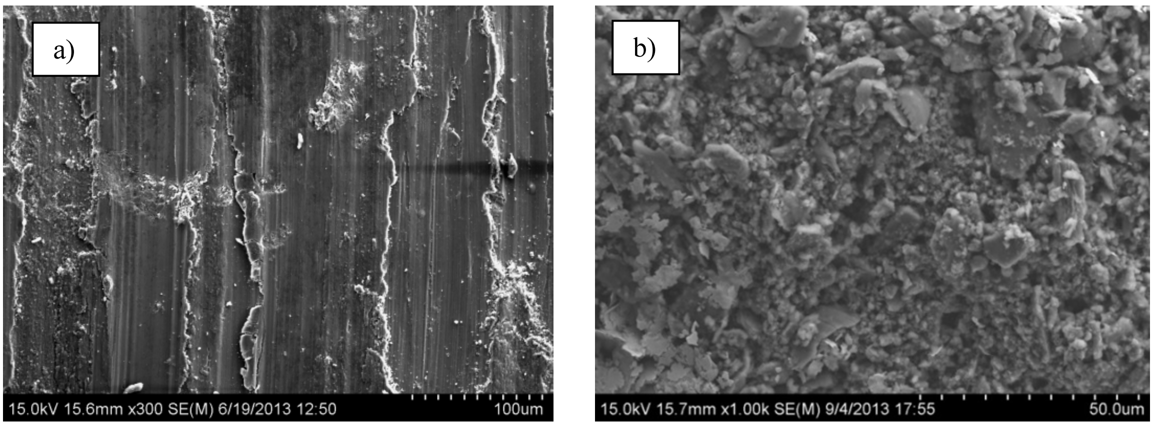

Fig. 2. Wear track surface (a) and debris (b) of composites without carbon obtained at 25°C
Rys. 2. Powierzchnia śladu wytarcia (a) oraz produktów zużycia (b) kompozytu bez węgla otrzymanego w 25°C

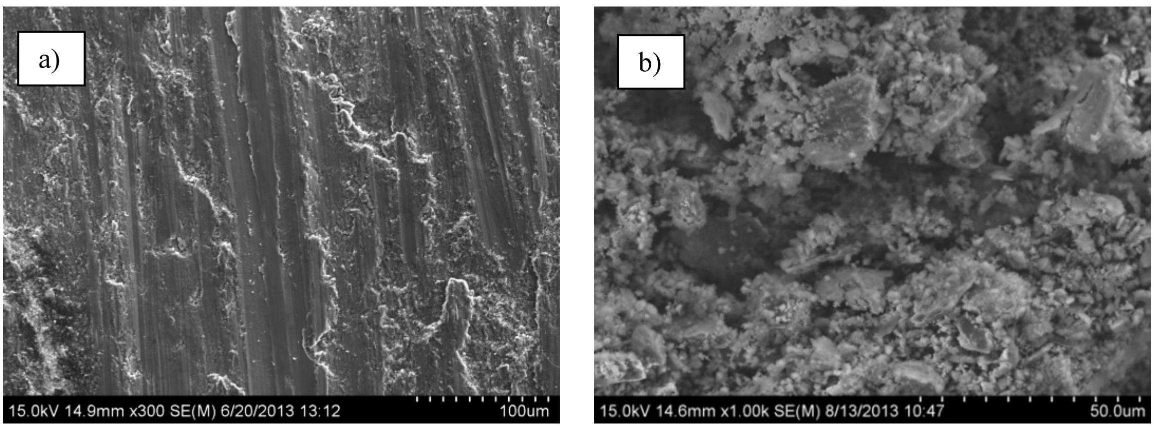

Fig. 3. Wear track surface (a) and debris (b) of composites with CNT particles obtained at 25°C
Rys. 3. Powierzchnia śladu wytarcia (a) oraz produktów zużycia (b) kompozytu z CNT otrzymanego w 25°C

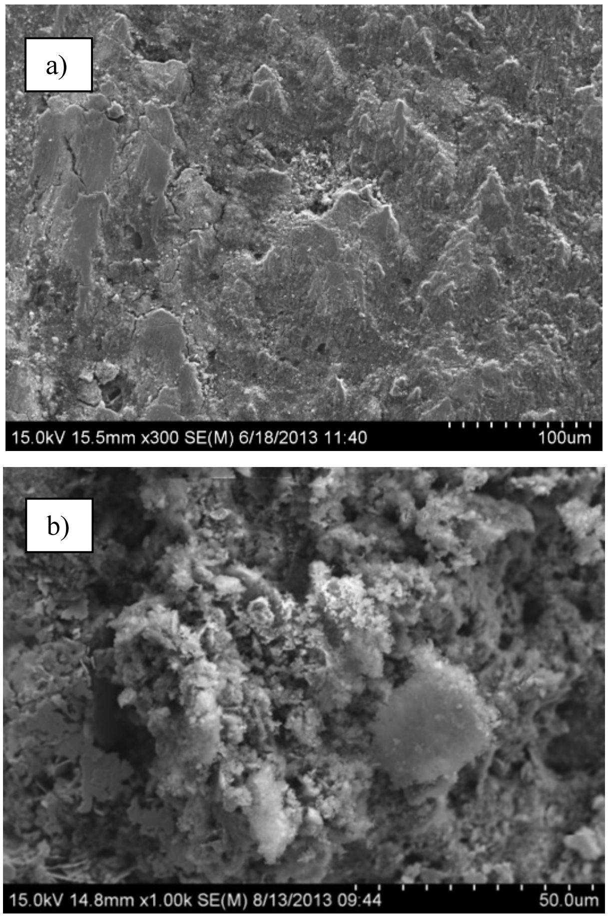

Fig. 4. Wear track surface (a) and debris (b) of composites with GC particles obtained at 25°C

Rys. 4. Powierzchnia śladu wytarcia (a) oraz produktów zużycia (b) kompozytu z GC otrzymanego w 25°C

Figure 4A is evidence of the changing predominant wear mechanism after carbon application (GC). The wear track is characterized by high roughness. Only an insignificant part of the track was covered by the plastically deformed matrix. A large detachment from the external layer with a delamination feature were dominant mechanisms observed in this case. This phenomenon could be explained by the presence of a higher content of carbon addition characterized by weak bonding to the matrix. The products formed as a result of friction wear were bonded to the surface by the adhesive mechanism. This effect was confirmed by increased disc mass after the tribological test (Table 2). The wear products of the glassy carbon reinforced composite were characterized by the presence of iron particles of a relatively large size obtained as a result of grinding during contact with SiC particles (Fig. 4b). Iron particles were not found among the debris in the case of the Al-SiC and Al-SiC-CNT composites (Fig. 2b, 3b).

Wear track research at 450°C

Observation of the composite surface obtained as a result of friction tests at 450°C revealed various features of wear when compared to the track created at room temperature. The wear tracks of the composite without carbon and with carbon nanotubes were characterized by similar predominant wear mechanisms. In those cases, effects of the delamination layer created by plastic deformation and oxidation phenomenon were found (Fig. 5a). Lines parallel to surface cracks were observed on the oxidized layer (Fig. 6a). This oxidized part of material was very hard, thin and poorly bonded to the composite materials. The load and the sliding motion of the ball led to cracking of the oxidized layer on a short distance. Such a carbon containing composite with increased tribological properties can be applied, especially for materials working in high temperature conditions. Moreover, a small amount of carbon nanotubes provides a reduction in thermal degradation processes.

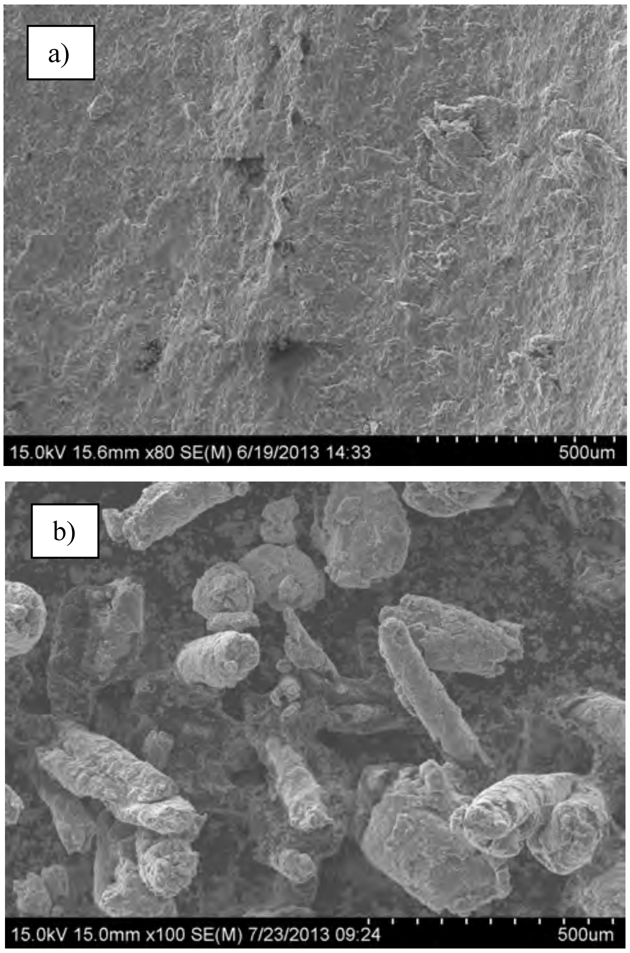

Fig. 5. Wear track surface (a) and debris (b) of composites without carbon obtained at 450°C

Rys. 5. Powierzchnia śladu wytarcia (a) oraz produktów zużycia (b) kompozytu bez węgla otrzymanego w 450°C

The physico-chemical processes were limited because thermal energy (obtained as a result of friction) was accumulated by the CNT particles. Ipso facto, the areas of thermal destruction and indirect oxidation processes were reduced. The shape of the wear products shown in Figures 5b and 6b confirmed the presented thesis. The delamination products were crushed. In the case of the material with CNT additions, large flatted particles were observed (Fig. 6b).

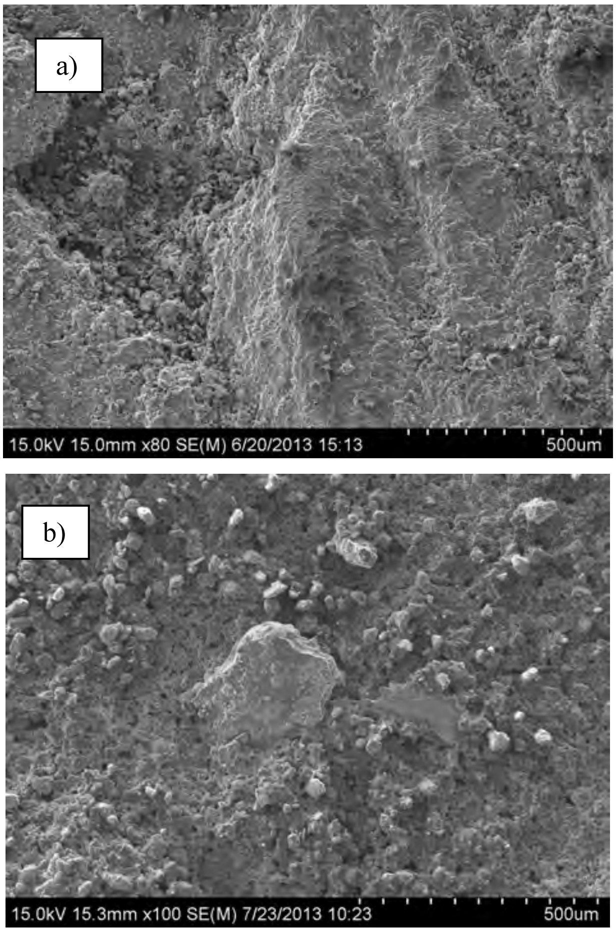

Fig. 6. Wear track surface (a) and debris (b) of composites with CNT particles obtained at 450°C

Rys. 6. Powierzchnia śladu wytarcia (a) oraz produktów zużycia (b) kompozytu z CNT otrzymanego w 450°C

Changes in debris shape were observed as a result of high temperature and acting forces on the specimen without carbon. The obtained aluminum debris was rolled and showed shapes similar to fibres (Fig. 5b). The presence of glassy carbon particles provided a significant reduction in oxidation and thermal degradation processes. This phenomena could be connected with the higher content of carbon (5 wt.%) in comparison to the Al-SiC-CNT composite (1 wt.%). In this case, an oxidized layer as a result of tribo-chemical processes was also found. However, the thickness of this layer was lower and the delaminated areas were substantially smaller than in the materials with the carbon nanotubes additions (Figs. 7a, 7b). The advantageous influence of the carbon addition on the wear processes is confirmed by mass loss analyses after the tribological tests. The presence and quantity of carbon additions extremely effectively decreased the level of wear, especially at a high temperature (Tab. 3).

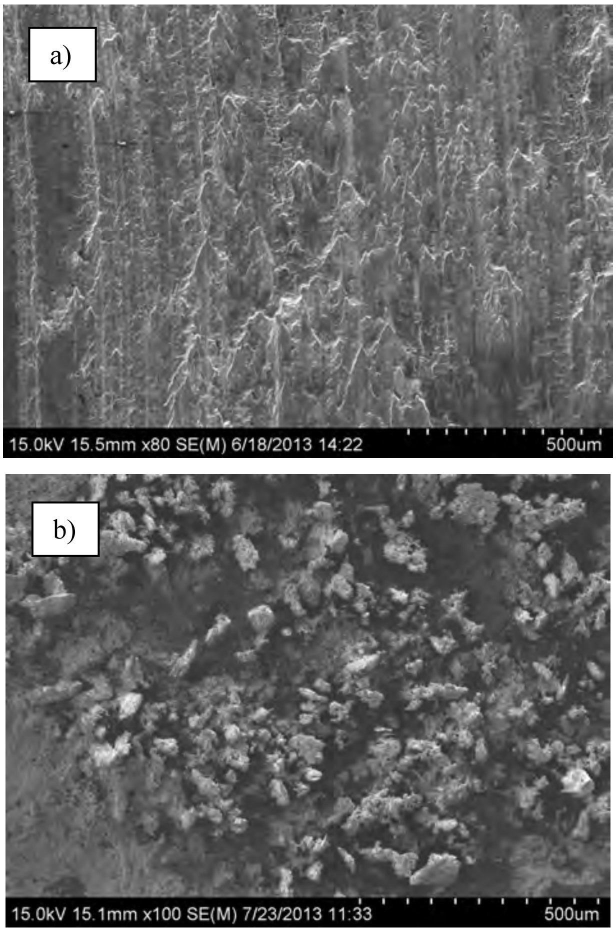

Fig. 7. Wear track surface (a) and debris (b) of composites with GC particles obtained at 450°C

Rys. 7. Powierzchnia śladu wytarcia (a) oraz produktów zużycia (b) kompozytu z GC otrzymanego w 450°C

DISCUSSION

The conducted research clearly showed the merit of carbon compounds application as a new material solution for metal-ceramic composites. The application of multi-walled carbon nanotubes led to a change in the composite tribological properties. Changes in the predominant wear mechanism and a reduction in thermal destruction processes were observed for this material. Those effects had a strong influence on mass loss values and led to elongation of the material lifetime. However, a significant influence of CNT on friction coefficient stability was not found. Despite the application of carbon nanotubes, abrupt changes in friction coefficient values were not avoided. Inhomogeneous carbon location in the volume of the composite can be the reason for this phenomena. Detailed analyses of each of the technological stages is necessary to eliminate those undesirable effects.

In the case of applying the other forms of carbon (GC), the obtained results explicitly showed an increase in the friction properties. Glassy carbon limited oxidation and delamination mechanisms. Moreover, the mechanism of adhesive bonding led to surface protection against wearing and to increasing the composite mass after the test in the extreme case (room temperature test). The composite with the glassy carbon addition showed high stability of the tribological properties at both analysed temperatures as well. Moreover, this composite revealed similar average friction coefficient values during both tests at the 0.6 level, which makes it the proper material solution for friction couple material in the automotive industry.

SUMMARY

The application of carbon in the form of GC of CNTs led to an increase in the tribological properties of an aluminum based composite reinforced with silicon carbide. The most significant effects, observed for the materials with a carbon addition are:

1. Increased friction coefficient stability during work (elimination of abrupt changes in friction coefficient in short time periods).
2. Similar average value of friction coefficient in a wide range of temperature (especially for the composite with GC).
3. Decrease in undesirable effects of wear by reducing thermal degradation.
4. Limitation of mass loss extends material life.

Acknowledgement

The results were obtained in the framework of the Matera project "SiNACERDI" (MATERA/HPE-2217) funded by NCBiR in Poland and FNR in Luxembourg.

REFERENCES

[1] Eriksson M., Bergman F., Jacobson S., On the nature of tribological contact in automotive brakes, Wear 2002, 252, 26-36.
[2] Hekner B., Myalski J., Pawlik T., Michalik D., Kelepir O. E., Aluminum-ceramic composite materials reinforced with nanoparticles prepared via powder metallurgy method, Composites Theory and Practice 2013, 13(3), 203-207.
[3] Sopicka Lizer M., High-Energy Ball Milling. Mechanochemical Processing of Nanopowders, Woodhead Publishing Limited 2010.
[4] Posmyk A., Myalski J., Hybrid composites with ceramic reinforcing phase modified by solid lubricants destined for vehicle subassemblies, Composites Theory and Practice 2013, 13(2), 135-140.
[5] Gubernat A., Stobierski L., Zimowski S., Hydzik P., Self-lubricating SiC matrix composites, Composites Theory and Practice 2012, 12(4), 219-227.
[6] Dolata-Grosz A., Dyzia M., Śleziona J., Rozmieszczenie cząstek zbrojących w kompozycie AK12/SiC+C kształtowane podczas krzepnięcia odlewu, Kompozyty 2008, 8(3), 296-301.
[7] Olszówka-Myalska A., Myalski J., Botor-Probierz A., Effect of glassy carbon particles on wear resistance of AZ91E matrix composite, Solid State Phenomena 2011, 176, 127.
[8] Dolata-Grosz A., Wieczorek J., Śleziona J., Myalski J., Tribological properties of heterophase composite obtained by centrifugal casting, Kompozyty 2007, 7(1), 46-50.
[9] Myalski J., Kształtowanie właściwości tribologicznych kompozytów zawierających węgiel szklisty, Wyd. Politechniki Śląskiej, Gliwice 2011.
[10] Myalski J., Wieczorek J., Płachta A., Physical and mechanical properties of composites with aluminum alloy matrix designed for metal forming, Solid State Phenomena 2013, 212, 59.

