Andrzej Posmyk[1], Jerzy Myalski[2]

[1] Silesian University of Technology, Faculty of Transport, ul. Krasińskiego 8, 40-019 Katowice, Poland
[2] Silesian University of Technology, Faculty of Materials Engineering and Metallurgy, ul. Krasińskiego 8, 40-019 Katowice, Poland
* Corresponding author: E-mail: andrzej.posmyk@polsl.pl

HYBRID COMPOSITES WITH CERAMIC REINFORCING PHASE MODIFIED BY SOLID LUBRICANTS DESTINED FOR VEHICLE SUBASSEMBLIES

The new trend in designing and manufacturing machines and devices e.g. for the food and pharmaceutical as well as automotive industry, is replacing lubricating oils with solid lubricants incorporated into the surface layer of engineering materials. Incorporating solid lubricants helps decrease both the friction resistance and wear of rubbing parts as well as reduce the amount of lubricating oils to ensure efficiency and effectiveness at much lower operational costs. Moreover, the use of a solid lubricant as an additional phase in a friction material does not damage the environment by oil penetration through leaks or accumulation of waste oil residues. At the Silesian University of Technology, a novel method of obtaining a new generation composite containing glassy carbon as a solid lubricant has been developed. The uniqueness of the elaborated technology is the fact that glassy carbon is produced directly in a ceramic from a previously introduced liquid precursor. Such a solution, compared to the so far applied methods where the prepared carbon particles are mixed with the alloy matrix, appear to offer some advantages. Firstly, the manufacturing costs are lower because there is no need for the expensive procedure of mixing the reinforcing phase with the liquid metal matrix. Secondly, glassy carbon distribution throughout the entire volume of the composite is uniform, free from sedimentation or agglomeration and particles clustering. The presence of uniformly distributed glassy carbon greatly affects the tribological properties of the composite. This is possible due to the low shear resistance and high hardness as well as excessive thermal stability of the glassy carbon. An additional advantage seems to be its low thermal expansion. The friction coefficient determined during rubbing against cast iron GJL-300 in the conditions of friction in air ranges between 0.08 to 0.14.

Keywords: hybrid composite, glassy carbon, precursor, pyrolysis, ceramic foam, solid lubricant

KOMPOZYTY HYBRYDOWE Z CERAMICZNĄ FAZĄ ZBROJĄCĄ MODYFIKOWANĄ SMARAMI STAŁYMI PRZEZNACZONE NA PODZESPOŁY POJAZDÓW

Nowym kierunkiem w projektowaniu i wytwarzaniu maszyn i urządzeń, np. dla przemysłu spożywczego, farmaceutycznego czy produkującego podzespoły pojazdów, jest zastępowanie olejów smarowych smarami stałymi wbudowanymi w warstwy powierzchniowe tworzyw konstrukcyjnych. Wbudowanie smarów stałych pozwala zmniejszyć opory tarcia i zużycie współpracujących części oraz zmniejszyć ilość olejów smarowych niezbędnych do zapewnienia niezawodnej współpracy przy utrzymaniu dotychczasowej sprawności, co obniża koszty eksploatacji. Ponadto zastosowanie smaru stałego stanowiącego dodatkową fazę w materiale ciernym zmniejsza obciążenie środowiska olejami przedostającymi się przez nieszczelności oraz pozostałościami po olejach przepracowanych. Na Politechnice Śląskiej opracowano metodę wytwarzania kompozytu nowej generacji zawierającego wbudowany węgiel szklisty pełniący rolę smaru stałego. Nowością w opracowanej technologii jest to, że węgiel szklisty jest wytwarzany bezpośrednio w ceramice z uprzednio wprowadzonego płynnego prekursora. Takie rozwiązanie, w porównaniu z dotychczasowymi metodami, polegającymi na mieszaniu preparowanych cząstek węgla ze stopem osnowy, ma kilka zalet. Pierwszą z nich są mniejsze koszty wytwarzania, ponieważ nie wymaga kosztownego mieszania fazy zbrojącej z ciekłym metalem osnowy. Drugą jest równomierny rozkład węgla szklistego w całej objętości kompozytu, bez sedymentacji lub aglomeracji i grupowania cząstek. Obecność równomiernie rozłożonego węgla szklistego wywiera istotny wpływ na właściwości tribologiczne kompozytu. Jest to możliwe dzięki małej wytrzymałości na ścinanie (30 MPa) i dużej twardości (6÷7 w skali Mohsa, 230÷340 HV) oraz bardzo dużej stabilności termicznej węgla szklistego. Dodatkowym atutem jest mała rozszerzalność cieplna (1,2 do 3,2 x 10^{-6} K^{-1}). Współczynnik tarcia we współpracy z żeliwem GJL-300 w warunkach tarcia technicznie suchego mieści się w przedziale 0,08 do 0,14.

Słowa kluczowe: kompozyt hybrydowy, węgiel szklisty, prekursor, piroliza, ceramika, smar stały

INTRODUCTION

Nowadays, the construction of vehicles aims at reducing the weight of vehicles for fuel saving as well as the amount of harmful wastes emitted into the environment. A lower vehicle mass improves the vehicle dy-

namics due to lower inertia of the moving parts. Mass reduction can be achieved through structural designing and the use of engineering materials with a lower density and higher strength. Thus, composites which feature a higher specific strength defined as the quotient of strength and density are classified as engineering materials. The new trend in designing and manufacturing vehicle parts is based on replacing lubricating oils with solid lubricants embedded into the surface layers of engineering materials [1, 2]. This enables one to reduce the friction resistance and wear of the sliding parts as well as to decrease the amount of lubricating oils used to ensure faultless sliding [3, 4].

At the Silesian University of Technology, the method of obtaining a new generation composite containing embedded glassy carbon which functions as a solid lubricant has been developed [5, 6]. The uniqueness of the elaborated technology is the fact that glassy carbon is generated directly into the ceramics from a previously introduced precursor.

Such a solution, compared to the so far applied methods, where the prepared carbon particles are mixed with the matrix alloy [7, 8], appear to offer some advantages. Firstly, the manufacturing costs are lower because there is no need for the expensive procedure of mixing the reinforcing phase with the melted matrix. Secondly, the glassy carbon distribution throughout the entire volume of the composite is uniform, with sedimentation or agglomeration and particles clustering being no matter of concern. A similar effect might be achieved in composites with a porous ceramic matrix saturated with a glassy carbon precursor subjected to pyrolysis in the presence of argon [9].

The presence of uniformly distributed glassy carbon greatly affects the tribological properties of the composite. This is possible due to the low shear resistance and high hardness as well as excessive resistance of glassy carbon to high temperatures. An additional advantage seems to be low thermal expansion (1.2 to 1.8 x 10^{-6} K^{-1}). The friction coefficient determined during rubbing against cast iron GJL-300 in the conditions of friction in air ranges between 0.08 to 0.14.

The presented article describes the method of manufacturing a new generation composite and its selected properties. The composite is characterized by a matrix of light metal casting alloys (Mg, Al), and a hybrid reinforcing phase of ceramic foam modified with glassy carbon which acts as a solid lubricant.

PRODUCTION OF COMPOSITES

Porous pre-forms made of aluminum oxide or silicon carbide with high open porosity into which a liquid carbon precursor is introduced e.g. furfuryl polyalcohol

constitutes the basis for the composite. A soaked porous ceramic sample is subjected to catalytic acting (e.g. hydrochloric acid) at a temperature ranging from 20 to 90ºC for monomer polymerization from furfuryl alcohol. This is then followed by precursor pyrolysis in argon atmosphere at the temperature of about 1000ºC. The result is a thin film of glassy carbon covering the walls of the ceramic spheres and filling the joint places. The last stage consists in pressure infiltration of pre-forms with a liquid matrix alloy. Two casting aluminum alloys i.e. AC-AlMg5 and AC-AlCu3Mg1 used for manufacturing machine parts have been used. Magnesium, copper and silver alloys can be used as the matrix material. Composites with a silver alloy matrix can be employed as the material for contacts of current switches working under high pressure since ceramic foam considerably boosts the compressive strength of a composite, whereas glassy carbon reduces the friction forces and increases the resistance to high temperatures caused by an electric arc during contact disconnection. The porosity of ceramics can range from 85 to 95%, which means that the composite would contain 15 to 5% of a ceramic reinforcing phase. Much more extensive porosity decreases the compressive strength of a composite as well as its wear resistance. The stereological parameters of ceramic spheres determine both the resistance and tribological properties of a composite. The shape and size of the pores in the walls of the spheres determine the possibility of impregnating carbon precursor and infiltration of the matrix metal liquid. The shape and size as well as the presence of open pores in the walls of the spheres determine their possibility of being saturated with the carbon precursor and being infiltrated with the liquid matrix metal. Larger pores make it easier for the precursor and matrix metal to penetrate. They also shorten the time which the precursor needs to fill the spheres. The impact of the stereological parameters of porous foam upon the properties of a composite requires some additional studies.

The viscosity of the carbon precursor should be adjusted to the size of the pores in the ceramic spheres and to the required thickness of the glassy carbon film covering their walls. A lower viscosity facilitates penetration of the precursor. However, when it is too low it might lead to the situation where the precursor not only covers the walls but fills them, blocking the introduction of the matrix metal.

Figure 1 shows the diagram of ceramic, porous spheres immersed in the liquid precursor. It also presents the places (4) impossible for the precursor to reach if introduced under atmospheric pressure. For better filling the spaces (4) between the joined spheres, pressure infiltration is required, though the hydrostatic pressure should not be so high as to cause damage of the porous structure.
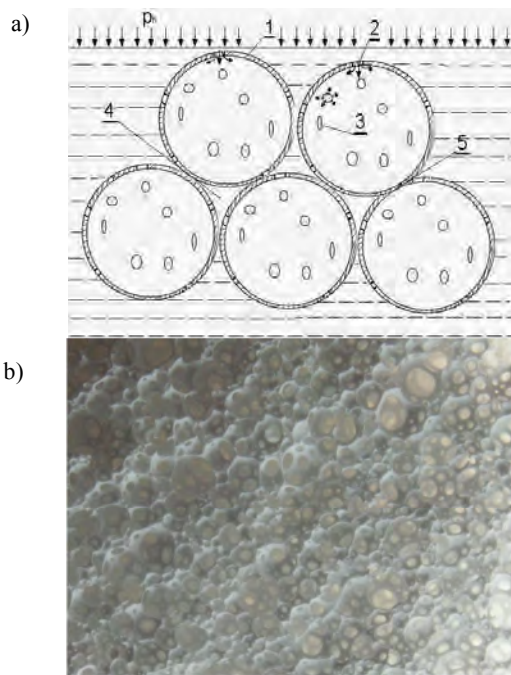
Fig. 1. Model of filling ceramic structure with liquid carbon precursor (a) and macrographs of ceramic structure (b) (x10), 1 - sphere wall, 2 - pore in cross section, 3 - view of pore, 4 - closed spaces between spheres which might not be penetrated by precursor, 5 - joined sphere walls, p_h - hydrostatic pressure of liquid precursor facilitating its penetration into porous spheres

Rys. 1. Model wypełnienia struktury ceramicznej płynnym prekursorem węglowym (a) i makrofotografia (b) (pow. x10), 1 - ścianka sfery, 2 - por w płaszczyźnie przekroju, 3 - por w widoku, 4 - zamknięte przestrzenie pomiędzy sferami, do których może nie dostać się prekursor, 5 - zlepione ścianki sfer, p_h - parcie hydrostatyczne płynnego prekursora ułatwiające wnikanie do porowatych sfer

STRUCTURE AND TRIBOLOGICAL PROPERTIES OF COMPOSITE

Scanning Microscopic investigations of the structure of the composites in individual stages of their production have been performed. Figure 2 presents the structure of the ceramic foam before saturation with the carbon precursor. Figure 2a includes a larger area in order to show the homogeneity of the ceramic foam. Figure 2b shows the pores in the ceramic spheroids walls.

Figure 3a presents the foam structure after saturation with the carbon precursor and their pyrolysis. Figure 3b (magnified part of Fig. 3a) shows the joints of the spheres filled with glassy carbon as well as the pores in the walls of the spheres covered with glassy carbon film. Pieces of glassy carbon film are located in the spheres [6].

This hybrid composite has been designed to be used for the cylinder liners of piston machines e.g. air compressors working in the conditions of friction in air or combustion engines operating in the conditions of limited lubrication. Preliminary, comparative tribological research has been carried out on two composite materials with AC-AlCu3Mg1 alloy matrix, which:

- includes only aluminum oxide spheres as a reinforcement,
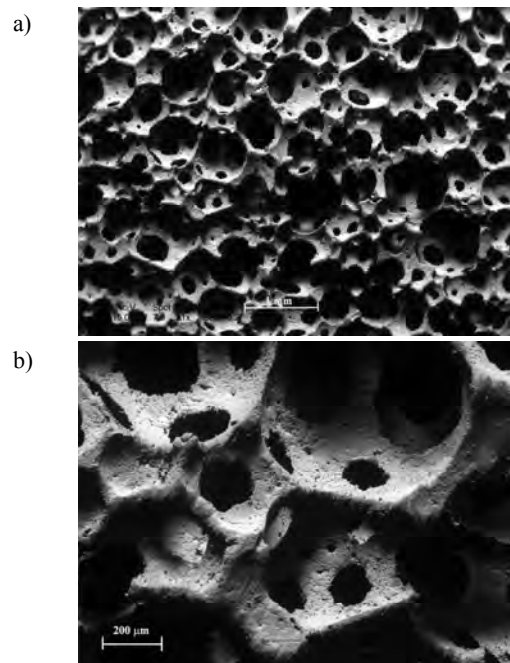- includes aluminium oxide spheres as a reinforcement and additionally glassy carbon as a solid lubricant.

Fig. 2. Ceramic foam before infiltration and pyrolysis (b - magnified part of Fig. 2a)

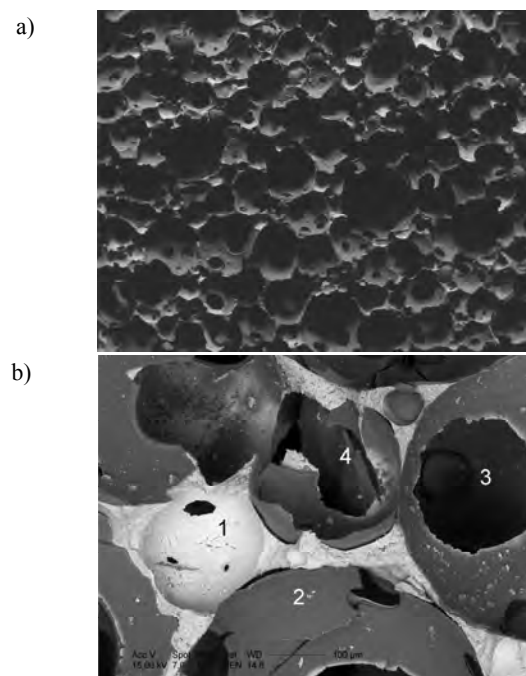Rys. 2. Pianka ceramiczna przed nasączaniem i pirolizą (b - powiększona część rys. 2a)

Fig. 3. Ceramic foam after saturation with precursor and pyrolysis: 1 - ceramic sphere covered with glassy carbon, 2 - glassy carbon plate, 3 - pore partially closed with carbon, 4 - glassy carbon bundles in sphere

Rys. 3. Pianka ceramiczna po nasączeniu prekursorem i pirolizie 1 - sfera ceramiczna pokryta węglem szklistym, 2 - płytka węgla szklistego, 3 - por zamknięty częściowo przez węgiel, 4 - wiązki węgla w sferze

The cold start of piston machines perform when the cold oil viscosity is too high and splash lubrication is ineffective. Segments cut out of the piston skirt (composite cube with sides of 10 mm) and cylinder liner (cast iron GJL-300 cuboid 140x16x8 mm) constitute the friction contact on the testing stand. The short investigation duration results from the time which a cold machine needs to reach a thermodynamic equilibrium.

Table 1 lists the friction coefficient values measured during the sliding of both composites.

TABLE 1. **Dependence between friction coefficient and sliding time of tested materials (p = 2 MPa, v = 2.5 m/s, friction in air)**

TABELA 1. **Zależność współczynnika tarcia od czasu współpracy badanych materiałów (p = 2 MPa, v = 2.5 m/s, tarcie technicznie suche)**

	Friction coefficient μ						
Sliding time [min]	0	5	10	15	20	25	30
Composite without GC	0.25	0.30	0.30	0.30	0.32	0.32	0.32
Composite with GC	0.06	0.28	0.18	0.14	0.08	0.12	0.12

After the tribological investigation, the surfaces of the samples and countersamples was investigated using a scanning electron microscope. The results are presented in Figures 4 and 5.
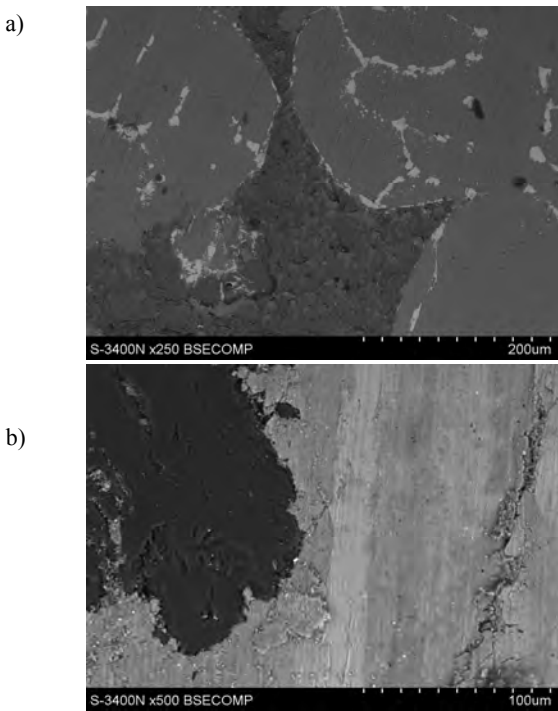
a)

b)

Fig. 4. View of composite surface after sliding against cast iron GJL-300 (friction in air, p = 2 MPa, v = 2.5 m/s, τ = 30 min)

Rys. 4. Widok powierzchni kompozytu po współpracy ślizgowej z żeliwem GJL-300 (tarcie technicznie suche, p = 2 MPa, v = 2,5 m/s, τ = 30 min)

Figure 4 presents the view of the composite surface after sliding against cast iron. Oxide spheres filled with the matrix alloy (Fig. 4a) and the surface of one sphere

covered with the glassy carbon film (black area) recovered during friction, Figure 4b, can be observed.

The views of the cast iron surface after sliding against the investigated composite are presented in Figure 5. The SEM micrograph in Figure 5a shows a general view including many recovered oxide spheres covered with glassy carbon. Part of the glassy carbon is plated on the matrix material near the oxide spheres.
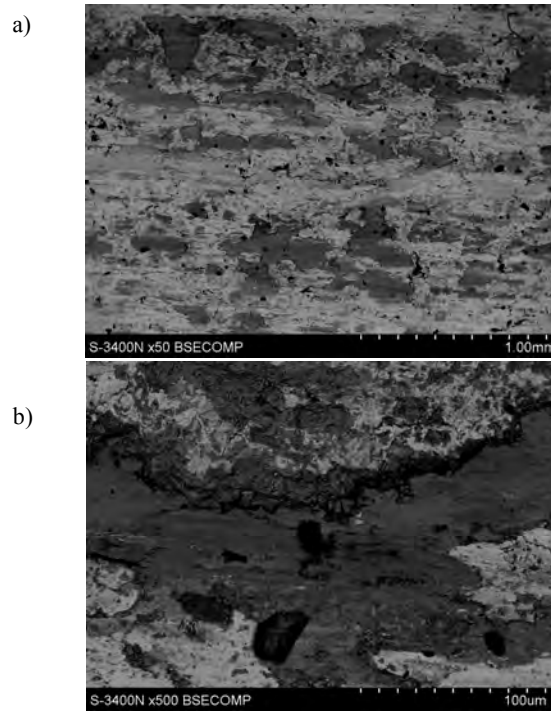
a)

b)

Fig. 5. View of cast iron surface after sliding against hybrid composite (glassy carbon - black areas)

Rys. 5. Widok z powierzchni żeliwa po współpracy ślizgowej z kompozytem hybrydowym (węgiel szklisty - ciemne obszary)
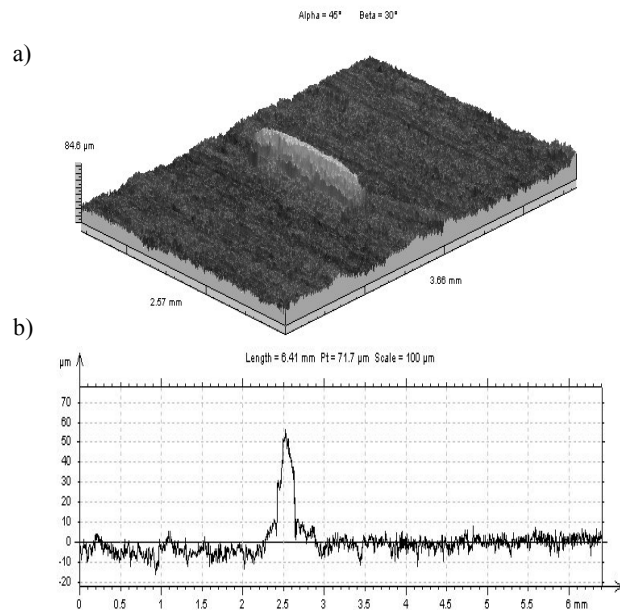
a)

b)

Fig. 6. Roughness profile of cast iron surface after sliding against hybrid composite: a) 3D, b) 2D

Rys. 6. Profil chropowatości powierzchni żeliwa po współpracy z kompozytem hybrydowym: a) 3D, b) 2D

The micrograph in Figure 5b shows a place with a bigger area of glassy carbon. On the carbon surface are small displacements visible. On the borders small, cracked carbon wear debris has been deposited. The cast iron surfaces after sliding against the hybrid composite have been investigated using an optical profilometer. The selected place with an incrusted Al_2O_3 splinter is presented in Figure 6.

DISCUSSION OF RESULTS

The carried out investigations have shown that it is possible to introduce a liquid glassy carbon precursor through the pores into the Al_2O_3 spheres (Fig. 1) used as a reinforcing phase. The liquid precursor wets the surface of aluminium oxide well, which causes sedimentation of a thin layer of carbon. The pyrolysis of the precursor causes the blocking of some pores of a smaller diameter (Fig. 3b).

Figures 3a and 3b show that the liquid carbon precursor introduced into the porous spheres and its pyrolysis are effective. Thin films of glassy carbon developed upon the walls of the Al_2O_3 spheres and in the places of their joints. Some spheres were filled with carbon strips and pores while other spheres were closed with a carbon film. Their resistance to pressure is lower than the pressure resulting from the hydrostatic pressure of the liquid matrix alloy of the composite. Therefore after infiltration, spheres which were not filled with the alloy were observed. As a result of the infiltration, a composite with a homogenous structure and with an almost uniform distribution of reinforcing material i.e. ceramic spheres and solid lubricant (glassy carbon) has been obtained.

The performed tribological research proved that the introduced glassy carbon improves the tribological properties of the composite. For comparison, tests on a composite which contained only ceramic spheres were done where a friction coefficient of about 0.30 was obtained during the entire test time. The contact surface was lubricated only with graphite included in the cast iron. GJL-300 cast iron has a hard pearlitic matrix and soft lamellar graphite precipitates. The precipitates were after a short time removed from the cast iron matrix. Small splinters of aluminium oxide (a brighter, about 2 mm long and 0.25 mm wide protrusion in Figure 6a and high peak in Figure 6b) has been incrusted in the cast iron surface and caused abrasive wear of the composite surface.

During friction of the composite with the spheres and solid lubricant, the friction coefficient value was initially 0.06 and 0.2, 25 minutes after the sliding was initiated. The initial friction coefficient values were caused by the glassy carbon film on the oxide walls. After a short time some of the oxide spheres were broken (damaged during machining) and their splinters caused an increase in the friction forces ($\mu = 0.28$). When the splinters disintegrated, the friction was mitigated and stabilized at the 0.12 level.

The view of the composite surface (Fig. 4) and cast iron (Fig. 5) after sliding is evidence of soft friction and dominant abrasive wear which is proved by slight scratches along the friction direction. Figure 4 shows the revealed carbon film covering the aluminum oxide sphere with some traces of wear, being the result of friction. The wear products are deposited upon the cast iron surface forming a discontinuous sliding film, which is presented in Figure 5a in the form of numerous dark spots. The magnification of one of them is presented in Figure 5b. The presence of sliding film from the glassy carbon reduces the intensity of the wear and friction coefficient in cast iron contact.

SUMMARY

The carried out investigations have shown that it is possible to introduce a liquid glassy carbon precursor through the pores into the aluminium oxide spheres and have confirmed the possibility of producing a hybrid composite including ceramic foam modified with glassy carbon as a solid lubricant. The glassy carbon in the form of a thin coating on the ceramic spheres is regularly distributed throughout the whole composite, which results in better tribological properties ($\mu = 0.12$) compared to the composite including only ceramic spheres ($\mu = 0.32$). The presented material requires further investigation to determine the optimal production parameters for tribological purposes.

Acknowledgements

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