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KOMPOZYTY
COMPOSITES

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CERAMIC-CARBON COMPOSITES DESIGNED FOR PISTON GROUP OF COMBUSTION ENGINES

The paper presents the production technology of ceramic-carbon composites designed for cylinder inserts of piston devices. Porous oxide ceramics with an assumpted porosity (20, 30 and 35%) obtained by the method of sintering grains of ceramic powder was used as a composite matrix. In the method, the sintering process is carried out in such a way that the ceramic powder particles form durable bonds (they sinter) in a properly prepared shaped sample but at the same time they do not form a dense polycrystalline material. The composite was obtained by introducing a glassy carbon precursor into the open pores of the ceramic and was then subjected to pyrolysis in the atmosphere of argon. As a result of the conducted technological tests, diverse contents of glassy carbon in the ceramic matrix were obtained. The influence of the open porosity of an oxide ceramic matrix upon the tribological properties of the fabricated composite sliding against a cast iron piston ring in the conditions of friction in air was examined. The material is destined for cylinder inserts in machines and piston devices e.g. combustion engines, air compressors and pneumatic servo-motors. The material was obtained in three consecutive stages i.e. ceramic samples with a given porosity were obtained by the gel casting method, saturation of the porous samples with a carbon precursor, and finally pyrolysis of carbon precursor introduced into the pores of oxide ceramics. The obtained ceramic-glassy carbon composite (CGC) features low thermal conductivity close to conductivity of oxide ceramics (λ = 20 W/mK), a high wear resistance and friction coefficient which allows sliding in the conditions of limited lubrication. The fabricated material was subjected to tribological tests on a pin-on-disc stand sliding against a cast iron pin in the conditions of friction in air. The friction coefficient of the examined contact largely depends upon the ceramic matrix porosity. The lowest value ($\mu \approx 0.3$, at $p = 0.8$ MPa, $v = 2.5$ m/s, $s = 5000$ m) was obtained in the contact with 30% matrix porosity. The results are the basis for further investigations on optimal chemical composition and manufacturing processes in order to reach the required utility properties. Composites manufactured upon an oxide ceramic matrix with a 30% porosity feature the best tribological properties. Such properties are achieved due to a sufficient amount of glassy carbon present in the oxide ceramics pores. Glassy carbon is marked by low shear resistance and high ceramic matrix hardness therefore low values of friction forces are possible to be reached.

Keywords: **porous ceramic, composite, glassy carbon, sliding, cylinder liner**

KOMPOZYTY CERAMICZNO-WĘGLOWE PRZEZNACZONE NA ELEMENTY GRUPY TŁOKOWEJ SILNIKÓW SPALINOWYCH

Opisano technologię wytwarzania kompozytów ceramiczno-węglowych przeznaczonych na tuleje cylindrowe maszyn tłokowych. Jako osnowę kompozytu zastosowano porowatą ceramikę tlenkową o założonej porowatości (20, 30 i 35%) wytworzoną metodą spiekających się ziaren proszku ceramicznego. W metodzie tej proces spiekania prowadzi się w taki sposób, aby ziarna proszku ceramicznego w odpowiednio przygotowanej kształtce utworzyły trwałe połączenia między sobą (spiekły się), nie tworząc jednocześnie gęstego polikrystalicznego spieku. Kompozyt wytworzono, wprowadzając w pory otwarte ceramiki prekursor węgla szklistego i poddając go pirolizie w atmosferze argonu. W wyniku przeprowadzonych badań technologicznych uzyskano różne zawartości węgla szklistego w ceramicznej osnowie. Przebadano wpływ porowatości otwartej ceramicznej osnowy tlenkowej na właściwości tribologiczne wytworzonego kompozytu we współpracy z żeliwnym pierścieniem tłokowych w warunkach tarcia technicznie suchego. Materiał ten jest przeznaczony na wkładki do tulei cylindrowych maszyn i urządzeń tłokowych, np. silników spalinowych, sprężarek powietrza, siłowników pneumatycznych. Materiał ten został wytworzony w trzech etapach, tj.: wytwarzanie metodą gel casting kształtek ceramicznych o zadanej porowatości, nasączanie porowatych kształtek prekursorem węgla, karbonizacja prekursora wprowadzonego w pory ceramiki tlenkowej. Wytworzony kompozyt ceramika-węgiel szklisty (CWS) charakteryzuje się małą przewodnością cieplną zbliżoną do przewodności ceramik tlenkowych (λ = 20 W/mK), odpornością na zużycie tribologiczne i współczynnikiem tarcia pozwalającym na współpracę w warunkach ograniczonego smarowania. Wytworzony materiał poddano badaniom tribologicznym na stanowisku „trzpień-tarcza” w warunkach tarcia technicznie suchego we współpracy z trzpieniem żeliwnym. Współczynnik tarcia badanych skojarzeń zależy od porowatości osnowy ceramicznej. Najniższą jego wartość ($\mu \approx 0{,}3$, przy $p = 0{,}8$ MPa, $v = 2{,}5$ m/s, $s = 5000$ m) uzyskano w skojarzeniu z osnową o porowatości 30%. Uzyskane wyniki są podstawą do prowadzenia badań optymalizacji składu chemicznego i procesów wytwarzania w celu uzyskania wymaganych właściwości użytkowych. Najlepsze właściwości tribologiczne wykazują kompozyty wytworzone na osnowie ceramiki tlenkowej o porowatości 30%. Przyczyną takich właściwości jest wystarczająca ilość węgla szklistego umieszczonego w porach ceramiki tlenkowej. Dzięki małej wytrzymałości na ścinanie węgla szklistego i dużej twardości osnowy ceramicznej jest możliwe uzyskanie mniejszych wartości sił tarcia.

Słowa kluczowe: **ceramika porowata, kompozyt, węgiel szklisty, tarcie ślizgowe, tuleje cylindrowe**

INTRODUCTION

Engineering materials and operational materials such as fuels and lubricants, are being increasingly used nowadays for the construction of combustion engines. Their chief function is to achieve a reduction of mass loss and prolong durability as well as improve the efficiency of engines. Mass reduction of the engine can be achieved by applying materials with high relative strength (*Rw*), defined as the ratio of tensile strength (*Rm*) to density (ρ). The effect of longer durability is achieved by the application of wear resistant engineering materials while efficiency improvement is secured by engineering materials of a low friction coefficient sliding against tribological partners. Operational materials which reduce friction should positively affect the durability as well.

Ceramic composites are materials which can help carry out all the three above mentioned goals. The idea of using composites with a ceramic matrix for whole sub-assembles of engines was rejected because of the high brittleness of composites and the fact that fractures would occur during engine operation. Engine elements only partly covered with ceramics performed well in practice and improved the efficiency of combustion engines [1].

Tests on materials which are to replace classic oil lubrication and introduce lubrication with solid lubricants built into surface layers of the sliding engine parts are being carried out in the laboratories of combustion engines manufacturers. The Institute of Automotive Vehicle Service of the Silesian University of Technology, the Interfaculty Structural Testing Laboratory of the University of Silesia, the Laboratory of Inorganic Technology and Ceramic of the Warsaw University of Technology conducted mutual cooperation and developed a composite material with a ceramic oxide matrix and glassy carbon nanotubes. The material is designed for cylinder inserts of machines and piston devices e.g. combustion engines, air compressors or pneumatic servo-motors. The composite was manufactured in the three following stages:

- manufacture of ceramic samples with a given porosity by gel casting method,
- saturation of porous samples with carbon precursor,
- carbonization of precursor introduced into pores of oxide ceramics.

The obtained ceramics-glassy carbon composite (CGC) features low thermal conductivity close to oxide ceramics conductivity (λ = 20 W/mK), tribological wear resistance, and a friction coefficient which enables sliding under limited lubrication conditions. Low thermal conductivity is of great importance when combustion engines as well as adiabatic engines are constructed.

The material obtained was subjected to tribological tests on a pin-on-disc test apparatus in the conditions of friction in air, sliding against a cast iron pin. The results constitute the base for further tests on optimization of the chemical composition and manufacturing process which would ensure the required utility properties.

PREPARING COMPOSITE MATRIX

The initial material for the ceramic-glassy carbon composite was the ceramic matrix of an assumpted open porosity (20, 30 and 35%), formed by the method of sintering grains of ceramic powder. The sintering process is ran in such a way that the ceramic powder particles form durable bonds with one another in a properly prepared sample and at the same time do not form a dense polycrystalline material. The porosity and the pores sizes of the obtained matrix samples are monitored by appropriate selection of the ceramic powder particle size, conditions of the forming process and sintering temperature. Moreover, the addition of a high temperature binder is essential. In order to estimate the mean pore size, the following simplified dependence [2] was applied:

$$D_p = 0{,}315\, D_z$$

where:
D_p - diameter of ceramic pores,
D_z - diameter of grains used for samples fabrication.

Alcoa aluminum oxide powder A 16 SG was used to obtain the ceramic matrix. Its mean diameter of 0.5 μm, specific surface measured by the BET (ASAP 2020, Micromeritics) method which equals 8.25 m^2/g, and true density measured by the picnometric method (AccuPyc1330, Micromeritics) which is 3895 kg/m^3 are the parameters of the powder. As the technological binder and the agent facilitating pressing, a 5 wt.% water solution of polyvinyl alcohol with a molecular weight of 88.000 and hydrolysis ratio of 88% was used. Before the aluminum oxide powder was used, it had been subjected to a purifying procedure which eliminated potential impurities. Then the aluminum oxide powder was rinsed in distilled water, dried and roasted at 500°C.

To prepare raw shaped samples (Fig. 1a), the Al_2O_3 powder was mixed with a 10% additive of a 5 wt.% water solution of polyvinyl alcohol. After thorough homogenizing the prepared mass was subjected to uniaxial pressing in a steel mould with an inner diameter of 20 mm and a pressure of 50 MPa. Raw samples prepared in such a way were dried for 24 h at 70°C. Next they were sintered at three different temperatures 1200, 1250 and 1300°C. The samples were then heated at the rate of 5°C/min and the sintering time was 2 h in each case. Table 1 presents the dependencies between the open porosity (P_o) of the obtained sample and the sintering temperature applied. The open porosity was measured by the hydrostatic method.

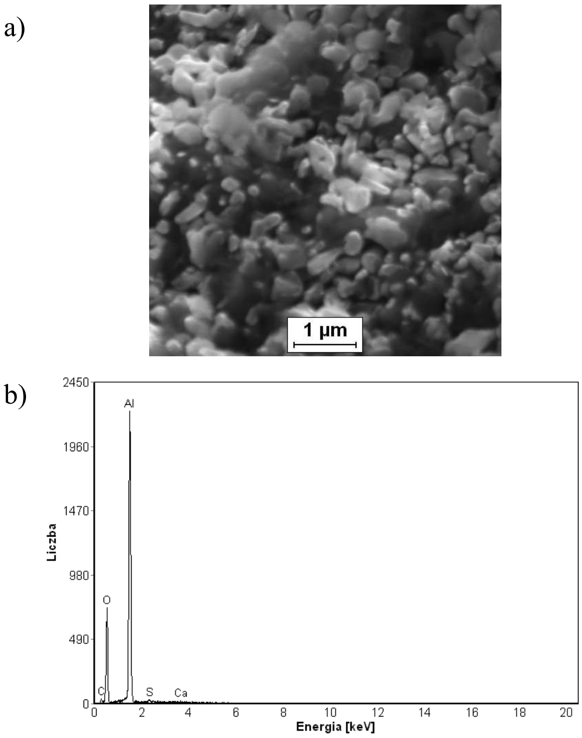

Fig. 1. Fracture of CGC composite with Al_2O_3 grains covered with glassy carbon (a), elements content (b)

Rys. 1. Przełom kompozytu CWS z widocznymi ziarnami Al_2O_3 pokrytymi prawdopodobnie węglem szklistym (a), zawartość pierwiastków (b)

TABLE 1. **Dependence between open porosity (P_o) and sintering temperature**

TABELA 1. **Zależność porowatości otwartej od temperatury spiekania**

Sintering temperature, °C	1200	1250	1300
Open porosity P_o, %	36	30	21

PREPARING CGC COMPOSITE

The samples of the CGC composites were obtained by introducing a carbon precursor into the previously fabricated oxide matrix followed by its pyrolysis performed in monitored conditions. PTSA acid (1M ethanol solution) was used as a precursor. Impregnated samples were treated with furfuryl alcohol at 20÷90°C for 5 h. Then the samples were placed in a furnace with a protective argon atmosphere and subjected to pyrolysis at a temperature of about 1000°C for 3 h. As a result, an oxide ceramics was obtained with pores partly filled with glassy carbon. Identification of the glassy carbon was carried out during separate investigations described in paper [3]. The glassy carbon covered the surface of the Al_2O_3 grains (Fig. 1). The conducted investigations showed a small content of carbon on the alumina grains (small C peak in Fig. 1b). The surface of the discs is also covered with a layer of glassy carbon and its thickness depends, among others, upon the surface topography of the ceramic samples and viscosity of the precursor. A higher surface roughness increases the absorbance of the precursor.

The tests verified the effect of the open porosity of the composite ceramic matrix upon its impregnation susceptibility with the carbon precursor as well as upon the tribological properties of the obtained composites. A higher porosity should allow a higher amount of the precursor to be introduced thus more glassy carbon to be obtained in the matrix. As a result, better lubrication of contacts with the use of the composite was achieved. The introduction of a glassy carbon into the ceramic matrix was aimed at lowering the friction coefficient in contact which arises from the Ernst and Merchant dependence [4] i.e.

$$\mu = \frac{\tau}{H} + tg\alpha$$

where: τ - shear strength of pure layers, free of sorbet, adhesive junction in contact zone calculated from Clausius-Clapeyron equation, a author's own research proves its shear strength is of a the weaker material i.e. glassy carbon and amounts from 30 to 60 MPa; H - hardness of the harder material in contact of described composites is aluminum oxide grains hardness and amounts up to 1500 HV; α - inclination angle of contact surface versus direction of movement in the friction zone is mean angle of surface peaks inclination of ceramic material, in ceramic surfaces tgα reaches level 0.1÷0.2.

TRIBOLOGICAL PROPERTIES OF CGC COMPOSITES

The shaped composite samples obtained were subjected to tribological tests on a pin-on-disc stand in the conditions of friction in air at a unit pressure of $p = 0.8$ MPa and relative velocity $v = 2.5$ m/s along a sliding distance of $s = 5000$ m. Such conditions are similar to the conditions of a piston oil scraper ring operation at the cold start of an engine when splash lubrication does not yet function effectively. Friction forces have been registered during the tests and the calculated coefficients of friction are shown in Figure 2. The samples after tribological tests are presented in Figure 3. The samples with wear debris are presented in Figures 3a and 3b. The sliding surfaces of cast iron pins are shown in Figure 4.

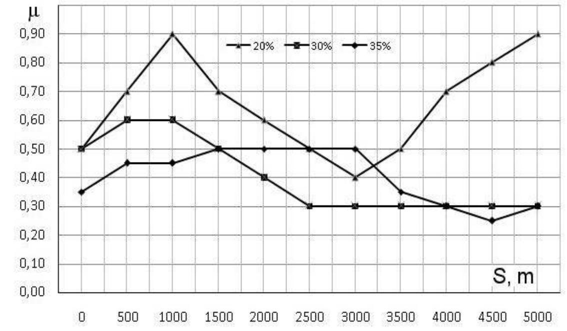

Fig. 2. Friction coefficients in contact GJL-350/CGC for different ceramic matrix porosity

Rys. 2. Współczynniki tarcia skojarzenia GJL-350/CWS dla różnej porowatości ceramicznej osnowy

When the composites slide against the cast iron pin significant jumps in the friction coefficient of the composite with the 20% matrix porosity are observed. Such a behavior is due to the very low matrix porosity by the given viscosity of the carbon precursor which did not penetrate deep inside the shaped samples. Weak precursor penetration into the matrix is reflected by the bright fracture of the shaped sample and small carbon content in the composite (small peak, Fig. 1b).

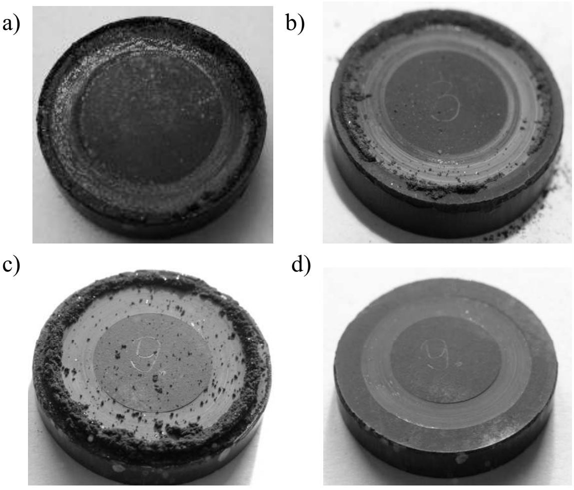

Fig. 3. Samples from CGC-composite after tribological tests: a) porosity 20%, b) 30%, c) and d) 35%

Rys. 3. Próbki z kompozytu CWS po badaniach tribologicznych: a) porowatość 20%, b) 30%, c) i d) 35%

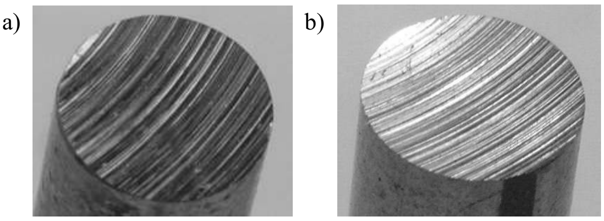

Fig. 4. Friction surface of cast-iron pin after sliding against composite CGC: a) matrix porosity 20%, b) matrix porosity 30%

Rys. 4. Powierzchnia tarcia trzpienia żeliwnego po współpracy ślizgowej z kompozytem CWS: a) porowatość osnowy 20%, b) porowatość osnowy 30%

Therefore a thin layer appeared on the surface and was removed by the sliding pin (large amount of wear debris on the disc surface after tests). This is accompanied by an increase of the friction coefficient up to 0.9 (Fig. 2).

The structure of sliding contact does not allow the removal of wear debris beyond the friction zone therefore when more of it accumulated, some parts returned between the pin and the disc causing a decrease of the friction coefficient (between 1000 and 3000 m sliding distance). Lower friction is also achieved because the sliding surfaces are worn-in.

A matrix porosity above 30% is just right for the samples to be saturated with the carbon precursor which penetrated into their entire volume (the fracture in the entire volume is of a carbon colour). The obtained glassy carbon upon the samples surface slightly increases the friction coefficient at its initial sliding with its layer being slowly removed. Finally, when the contact is ran-in, the value of the friction coefficient drops and stabilizes at about 0.3 (Fig. 2). Figure 5 shows scanning micrographs of the composite sample surfaces before and after sliding against cast iron. Figure 5b presents some residue of the thin glassy carbon layer which was removed by wearing. After the layer is removed, the pin slides against the ceramics but is separated by carbon residue which still remains on the surface and in the oxide pores.

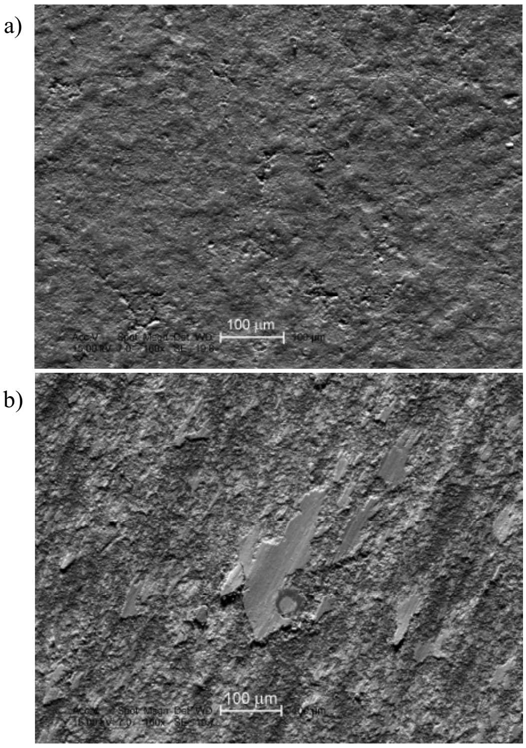

Fig. 5. Surface of CGC composite with 30% porosity: a) before sliding, b) after sliding against GJL-350 cast iron pin

Rys. 5. Powierzchnia kompozytu CWS o porowatości 30%: a) przed współpracą ślizgową, b) po współpracy z trzpieniem z żeliwa GJL-350

The abrasive wear of the cast iron pin (Fig. 4) through the microroughness of the oxide ceramic surface predominates during the process of sliding of the tested composites. Slight differences in wear traces might be noted upon the friction surface of the pin. Scratches which occur after sliding against the composite with 20% porosity are slightly deeper than those which occur in the case of the 30% porosity composite. To lower the intensity of pin wear, a smaller granularity of aluminum oxide used for matrix fabrication (average diameter less than 0.5 μm) or the addition of materials reducing friction can be used.

SUMMARY

The conducted technological and tribological tests on ceramic-carbon composites designed for cylinder inserts of piston machines proved that it is possible to obtain such composites with the use of a porous matrix and liquid carbon precursor which is then subjected to pyrolyse in an inert gas atmosphere. The attempts made so far to obtain a ceramic composite with carbon nanotubes failed in the case of materials with homogeneous properties because of numerous complications connected with components mixing. The method presented by the authors allows one to obtain a composite with an equal distribution of small contents of glassy carbon (near 2 mm under the sample surface) and satisfying tribological properties. The ceramic matrix should feature 30% porosity for the most favourable friction coefficient value. Regarding porosity of 35%, the wear track on the composite disc is much deeper (Fig. 3d) than on the discs with porosity of 20% and 30% and composite brittleness is observed in the form of chips coming off the sample edges.

The examinations performed should be treated as preliminary. The stage which follows should reveal the effect of aluminum oxide granularity and methods of matrix saturation with a carbon precursor upon the friction coefficient and the wear of cast iron pin/composite disc contact.

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