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COMPOSITES THEORY AND PRACTICE

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STUDIES ON INFLUENCE OF GRAPHITE INCLUSION SIZE ON PROPERTIES OF SiC-GRAPHITE COMPOSITES

The study presents research on the influence of the size of solid lubricant inclusions-graphite on the properties of pressureless sintered SiC-graphite composites. The purpose of these composites is to achieve a self-lubricating effect between the working elements of a friction seal. For this purpose, studies were carried out, on the basis of which the composite with the inclusion size that provides the optimal mechanical andtribological properties was selected. The apparent density, hardness, bending strength, abrasive wear resistance, friction coefficient and linear wear in contact of the same kind of material pairs were determined. Mechanical and tribological tests were correlated with qualitative and quantitative microstructure analyses, on the basis of which it was found that SiC-graphite composites with inclusions not larger than 0.056 mm meet the requirements for the materials used to produce self-lubricanting elements of face seals. It was then observed that small inclusions of graphite are more uniformly distributed in the SiC matrix.

Keywords: pressureless sintering, silicon carbide, solid lubricant-graphite, face seal

BADANIA NAD WPŁYWEM WIELKOŚCI WTRĄCEŃ GRAFITU NA WŁAŚCIWOŚCI KOMPOZYTÓW SiC-GRAFIT

Przedstawiono badania poświęcone wpływowi wielkości wtrąceń smaru suchego - grafitu na właściwości spiekanych swobodnie kompozytów SiC-grafit. Zadaniem takich kompozytów jest uzyskanie efektu samosmarowania pomiędzy pracującymi, w styku ślizgowym elementami uszczelnienia czołowego. W tym celu wykonano badania, na podstawie których wybrano kompozyt z wielkością wtrąceń zapewniającą optymalne właściwości mechaniczno-tribologiczne. Wyznaczono gęstość pozorną, twardość, wytrzymałość na zginanie, odporność na zużycie ścierne, wartość współczynnika tarcia i zużycia liniowego w kontakcie jednoimiennym. Wykonane badania mechaniczno-tribologiczne skorelowano z jakościową i ilościową analizą mikrostruktury, na tej podstawie stwierdzono, że wymogi stawiane materiałom służącym do budowy elementów konstrukcyjnych samosmarujących się uszczelnień czołowych spełniają kompozyty SiC-grafit o wtrąceniach nie większych niż 0.056 mm. Zaobserwowano wówczas, że drobne wtrącenia grafitu są gęściej i równomierniej rozmieszczone w osnowie SiC.

Słowa kluczowe: spiekanie bezciśnieniowe, węglik krzemu, smar stały-grafit, uszczelnienie czołowe

INTRODUCTION

Friction and wear are phenomena that have a significant influence on the durability and reliability of mechanical parts of machines in industry, as well as in our daily life. In some cases, these phenomena are strongly desirable, while in others one seeks to eliminate them. Significant reduction in friction is desired in face seals - elements of pumps - especially in self-lubricating face seals [1]. Face seals are made of different materials, including ceramic ones. They should fulfil a number of requirements listed in Table 1 [2].

One of the most common ceramic materials used to produce face seals is silicon carbide. Silicon carbide is in common use because it fulfils a number of conditions imposed upon materials for face seal elements. Silicon carbide is hard (HV = 25÷30 GPa), has a high Young's modulus (400 GPa), low thermal expansion coefficient α ($3.5\cdot10^{-6}$ to $4.2\cdot10^{-6}$ K^{-1} in the range of 20÷400°C), very high chemical resistance and good mechanical parameters [3]. It is usually used as a dense, single-phase sinter, but also as a matrix in self-lubricating materials. The effect of self-lubrication can be achieved in two ways. The first way is by producing a controlled porous microstructure in the matrix [4]. The intentionally introduced lubricant gathers in pores due to surface tension action, and during sliding it is released and deposits on the friction pair elements and facilitates sliding (Hexoloy® SP material produced by Saint-Gobain Ceramics) [5]. The second way is to produce granular composites in which so-called solid lubricants are present as a dispersed phase. Solid lubricants are materials with a layered structure and low shear strength e.g. graphite, hBN and MoS_2. SC-DSG produced by Coorstek and Ekasic® G made by ESK Ceramics GmbH [6] are examples of commercial materials containing a dispersed phase of solid lubricant i.e. graphite in a silicon carbide matrix.

TABLE 1. **Ceramic material properties useful in mechanical seals [2]**

TABELA 1. **Właściwości materiałów ceramicznych użyteczne w uszczelnieniach mechanicznych [2]**

Desired properties	Benefit
hardness	increased wear resistance
high Young's modulus	high stability of dimensions
compression strength	the ability to work under high loads
thermal shock resistance	the ability to work in temperature gradients
low coefficient of thermal expansion	maintaining stability of dimensions
corrosion resistance	the ability to work in highly corrosive conditions
low chemical reactivity	

The aim of the study was to determine the influence of the size of solid lubricant inclusions (graphite) on the mechanical and tribological properties of SiC-graphite composites. The density, Young's and Kirchhoff's moduli, Vickers hardness, flexural strength and fracture toughness were measured to determine the influence of the size of dry lubricant inclusions on the composite properties. Abrasion measurements in the presence of loose abrasives and wear tests during operation in sliding contact were also carried out. Then, some attempts were made to correlate the measured properties with qualitative and quantitative analyses of the microstructure.

PREPARATION AND MEASUREMENT METHODOLOGY

The first stage of preparation was to produce granulates of solid lubricants (graphite). For this purpose, graphite powder (Merck graphite fine powder extra pure 1.04206.9050) and residual wood dust were mixed in a volume ratio of 1:1. Nowolak MR phenol formaldehyde resin (Organika - Sarzyna) was applied as the binder. The resin was homogenized with the wood dust and graphite mixture in a 1.5:1 mass ratio in a SiC ball mill, with isopropyl alcohol for 12 hours. On the basis of works [7, 8], the graphite granulate composition was selected. Then the granulates were produced by sieving the mixture through a perlon sieve after alcohol evaporation under an IR irradiator. The granulates were sieved through sieves of different mesh sizes, listed in Table 2. Various granulate fractions were obtained in this way, the description of which is also presented in Table 2.

TABLE 2. **Applied graphite granulate fractions and SiC--graphite composite designations**

TABELA 2. **Zastosowane frakcje granulatu grafitowego i oznaczenia kompozytów SiC-grafit**

	D1	D2	D3	D4	D5
Size of sieve mesh	0.2 mm	0.1 mm	0.056 mm	0.04 mm	0.04 mm
Grain fraction	d > 0.2 mm	0.2÷0.1 mm	0.1÷0.056 mm	0.056÷0.04 mm	*d* < 0.04 mm

The last preparation step was dry homogenizing of the graphite granulates with Sika Tech FCP 15 RTP (*Saint-Gobain*) silicon carbide sinterable granulate in the volumetric ratio 1:9 in each case. Cylindrical samples of various diameters and heights were formed by the uniaxial pressing technique of silicon carbide - graphite granulate mixtures. The samples were designed for physical, mechanical, elastic and tribological characteristics as well as for microscopic observation. All the samples were pressureless sintered according to the diagram shown in Figure 1. The apparent density of the composites was measured using the Archimedes method. The phase composition was determined by means of the XRD method. Microstructure observations were conducted using a Nikon Epiphot 300 light microscope and an FEI Nova Nano SEM 200 scanning electron microscope.

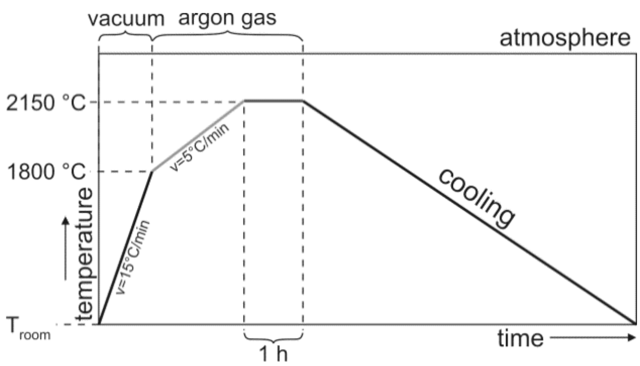

Fig. 1. Composite pressureless sintering process scheme

Rys. 1. Schemat procesu spiekania kompozytów

Measurements of the Vickers hardness and double--axis bending strength were performed on the composites. The elastic properties such as Young's modulus, Kirchhoff's modulus and Poisson's ratio were evaluated using the ultrasonic method. For hardness measurements, a load of 1 kg was applied, which corresponds to the force of approximately 9.81 N. Tribological properties were tested by measuring abrasive wear resistance in the presence of loose abrasives (dry sand test) and material wear in sliding contact, determining at the same time the coefficient of friction. The coefficient of friction and wear measurements in sliding contact were conducted using the pin-on-disc method. All the above mentioned tests were correlated with microstructure observations under light and scanning microscopes.

Additionally, quantitative analysis of the microstructure was carried out using Aphelion software. The mean equivalent diameter of insertion d_2 [μm] and the oriented Feret's diameters such as the longer (MBR_WIDTH) and the shorter (MBR_HIGH) [μm] were determined. The main aim of this analysis was to determine the size of graphite inclusions created in the composites. In addition, the CV (AIZ) parameter was calculated, which is a measure of the homogeneity of inclusion distribution, and which in this case, can be defined as follows:

$$CV_{(A_{IZ})} = \frac{SD_{(A_{IZ})}}{E_{(A_{IZ})}}$$

where: $SD_{(AIZ)}$ - standard deviation of the surface of the influence field A_{IZ} [μm^2], $E_{(AIZ)}$ - average value of the surface of the influence field A_{IZ} [μm^2].

When the CV parameter value is lower, then the graphite granules in the SiC matrix are uniformly distributed.

RESULTS AND DISCUSSION

Table 3 presents the results of the study, i.e. density measurements and phase composition. The microstructures of the composites of silicon carbide –10 vol.% graphite granules of various sizes are illustrated in Figure 2.

All the produced composites have a high density of 96÷98%, regardless of the size of introduced graphite granules. The granules, as shown by the microstructure images, are not pulled out during the polishing process. It can also be observed that the distribution of smaller graphite granules (D4 and D5 composites) is denser and more homogeneous in the SiC matrix as compared to larger granules (D1, D2 and D3 composites). In their case, clusters of inclusions in the silicon carbide matrix are noticeable. These observations confirm the calculations of the CV parameters, which show smaller values for the D4 and D5 composites, i.e. the composites with the smallest graphite inclusions (Table 3).

TABLE 3. **Phase compositions, density and calculated microstructure parameters of SiC-graphite composites**
TABELA 3. **Skład fazowy, gęstości oraz obliczone parametry mikrostruktury kompozytów SiC-grafit**

SiC-graphite composites	XRD analysis	Theoretical density [g/cm^3]*	Apparent density [g/cm^3]	Relative density [%]	Average equivalent diameter of inclusions d_2 [μm]	$CV_{(AIZ)}$
D1	SiC, graphite	3.06	2.949±0.011	96.37±0.38	58.52±51.48	0.891
D2			2.952±0.004	96.47±0.16	59.07±54.77	0.920
D3			2.957±0.005	96.63±0.18	27.78±20.79	0.871
D4			2.964±0.004	96.86±0.14	23.53±13.03	0.669
D5			2.974±0.005	97.18±0.18	13.87±8.05	0.717

*) calculated by rule of mixtures

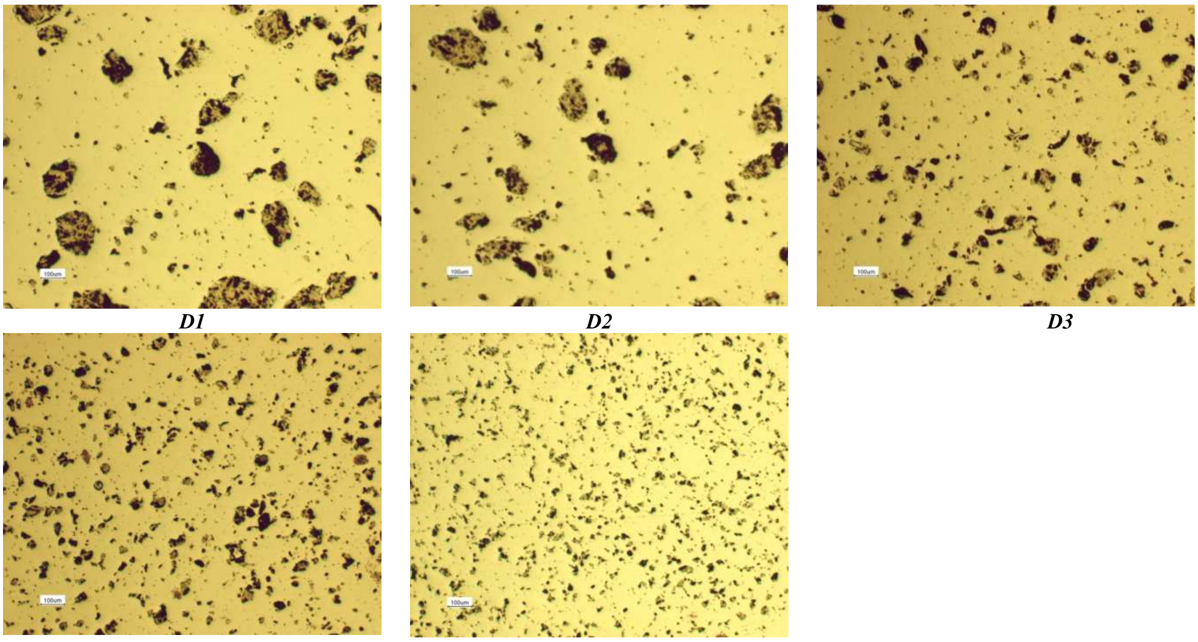
D1 D2 D3 D4 D5

Fig. 2. Composite microstructures (light microscope)
Rys. 2. Mikrostruktury kompozytów SiC-grafit (mikroskop optyczny)

Significant differences in the graphite inclusion size (Fig. 2) were confirmed by quantitative analysis of the microstructure. It can be noted, however, that during mixing with the SiC granules, the graphite granules are partially broken as indicated by the average equivalent diameter measurements of d_2 grains, presented in Table 2. Figure 3 shows the contribution of individual granules in the function of the shorter oriented Feret diameter (MBR_WIDTH). On the basis of these measurements we can distinguish groups of composites with similar sizes of graphite granule inclusions. The smallest concentration of about 50% of the finest sized granules (50 μm) is observed in the D1 and D2 composites. Approximately 70% contribution of the finest granules is found in composite D3. In the D4 and D5 composites the contribution of the finest granules is higher than 90%. The phase composition analyses (XRD method) confirmed (Table 3, Fig. 4) that carbon formed by pyrolysis of the Nowolak MR phenol formaldehyde resin, as well as carbon formed from the wood dust, possess the desired graphite-like structure (Table 2 and Fig. 4).

The results of the EDS analysis (Fig. 5) is also indirect proof of the presence of carbon (graphite) in the inclusions visible in Figure 2. In the deliberately introduced inclusions, the carbon peaks (Fig. 5; points 1 and 4) are significantly larger than in the SiC matrix (Fig. 5; points 2 and 3).

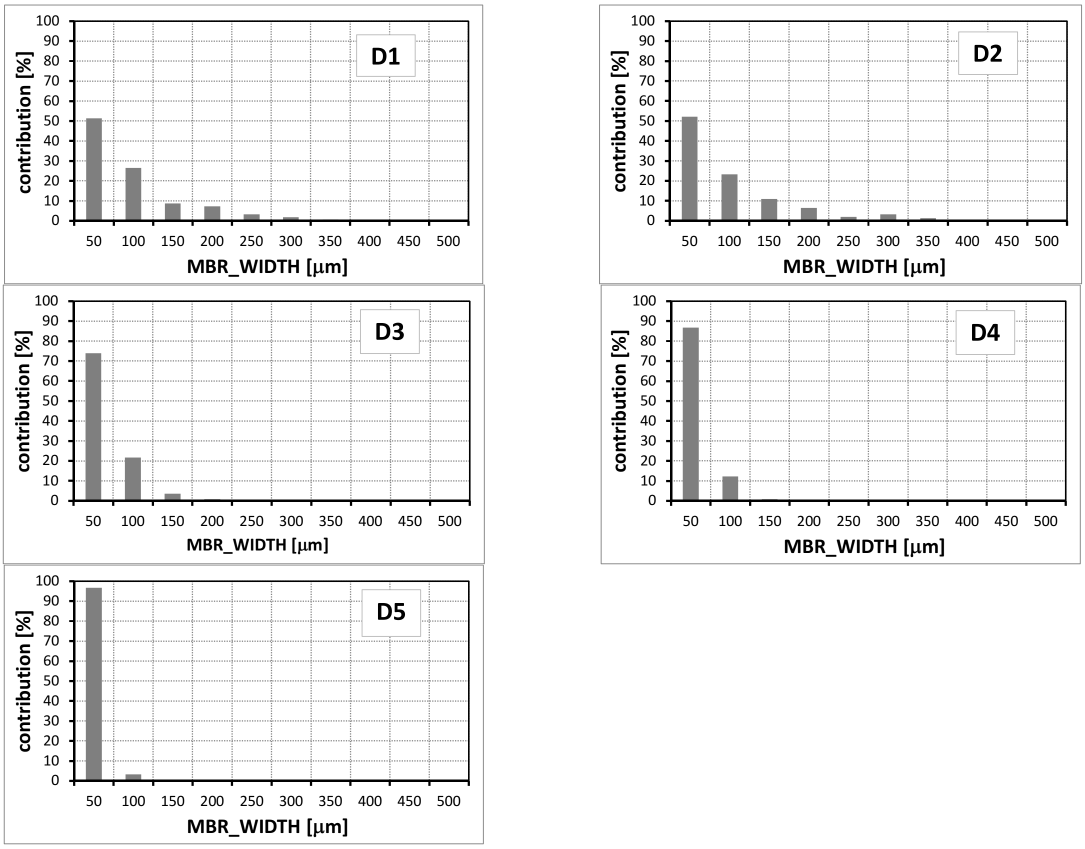

Fig. 3. Proportion of graphite inclusion size as function of shorter Feret diameter (MBR_WIDTH) in SiC-graphite composites

Rys. 3. Udział poszczególnych wielkości wtrąceń grafitu w funkcji krótszej zorientowanej średnicy Fereta (MBR_WIDTH) w kompozytach SiC-grafit

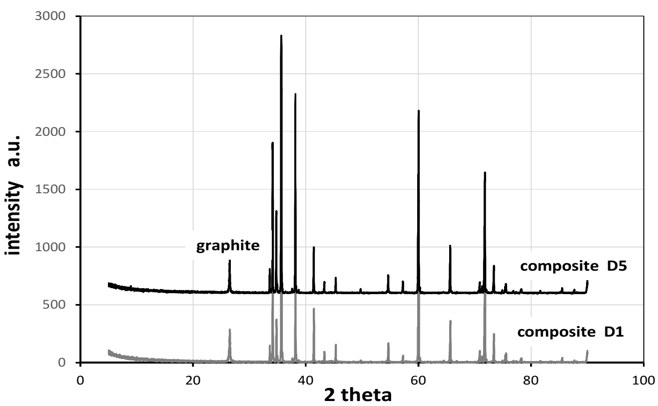

Fig. 4. XRD pattern of composites D1 and D5 (other peaks indicate presence of silicon carbide)

Rys. 4. Przykładowe dyfraktogramy kompozytów D1 i D5 (pozostałe refleksy pochodzą od węglika krzemu)

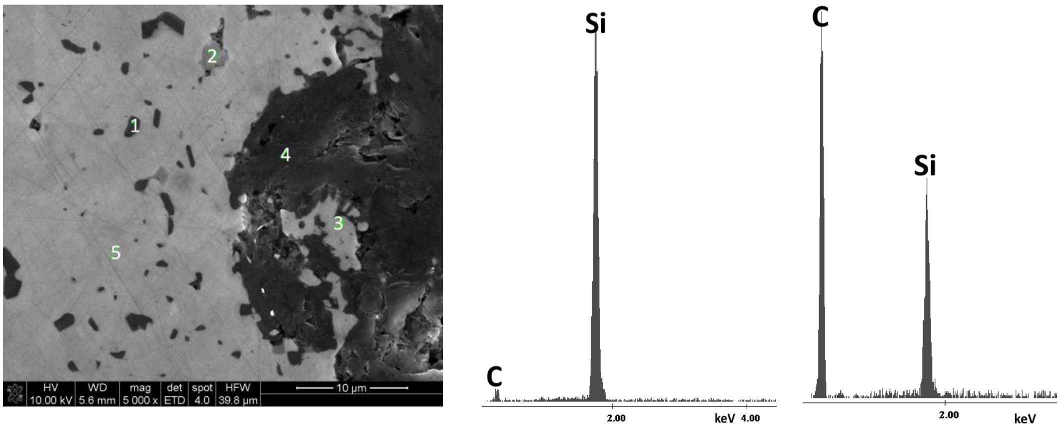

Fig. 5. EDS analysis of SiC - graphite composite

Rys. 5. Wyniki analiz składu chemicznego EDS przykładowego kompozytu SiC - grafit

Hardness is the function of the volumetric proportions of the phases forming the composites, i.e. graphite and SiC. In the case of the studied composites, the hardness of the matrix - SiC - was measured. The density of the composites increases with a decrease in the size of graphite granules, which correlates with the hardness measurements of the composite matrix. Vickers hardness is higher with finer graphite granules (Fig. 6).

A similar dependence can be observed in the case of bending strength (Fig. 7), the highest values of which, similar to the SiC matrix strength, reached by the D4 and D5 composites, is approx. 260 MPa for the D4 composites and approx. 320 MPa for the D5 composites. For other composites, the bending strength does not exceed 250 MPa. Probably the higher density of the composites with fine graphite inclusions and their homogeneous distribution in the SiC matrix effectively reduces the number of defects concentrating stresses, which favourably influences the strength of the composites.

Figure 8 shows the values of Young's and Kirchhoff's moduli, measured by the ultrasonic method. Regardless of the introduced graphite granule size, the measured values of both modules are similar. The Young's modulus amounts to approximately 350 GPa and Kirchhoff's modulus around 150 GPa.

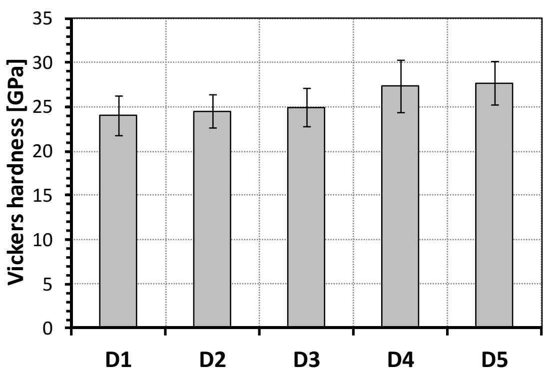

Fig. 6. Vickers hardness of SiC - graphite composites

Rys. 6. Twardość Vickersa kompozytów SiC - grafit

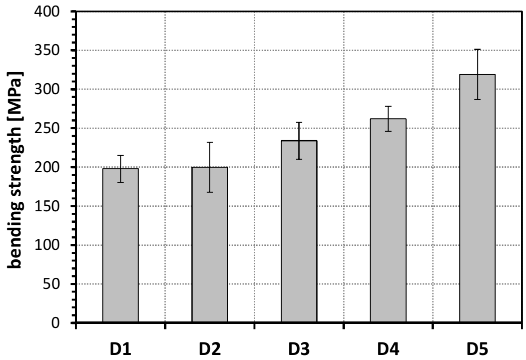

Fig. 7. Bending strength of SiC - graphite composites

Rys. 7. Wytrzymałość na zginanie kompozytów SiC - grafit

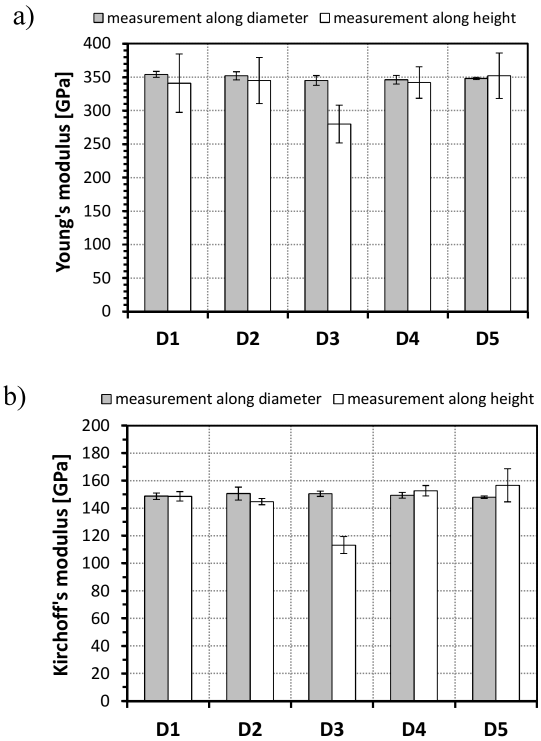

Fig. 8. Results of Young's (a) and Kirchhoff's moduli (b) measured along diameter and height of samples

Rys. 8. Wyniki pomiarów modułów Younga (a) i Kirchhoffa (b) wzdłuż średnicy i wysokości badanych próbek kompozytów

The measured values are characteristic of materials with a dominant covalent component of the chemical bond, which includes a matrix of silicon carbide based composites. Moreover, from measurements of the elastic constants along the diameter and height of the specimens, it can be concluded that all the created composites are isotropic, i.e. that the distribution of graphite granules in the volume of the samples is homogeneous. The measured values of both moduli along the diameter and height of the samples are similar (Fig. 8).

Figure 9 illustrates the abrasive wear measurements in the form of volumetric loss of the composites, which was generated during abrasion tests by means of the dry sand test. Also in this case, composites with the smallest graphite inclusions exhibit the highest abrasive wear resistance (the smallest volumetric loss). Therefore, it can be suggested that the graphite-dry lubricant is effectively released from the inclusions and thus significantly reduces the abrasion wear of composites. Moreover, more homogeneous distribution of fine graphite granules ensures that the lubricant is uniformly lifted out of the inclusions and spreads uniformly over the interacting surfaces.

The tests in the pin-disc configuration carried out in contact with the same kind of materials (Figs. 9-12), show unequivocally that the pair produced of composites (D4 and D5) - into which the smallest graphite granules were introduced - demonstrates the most stable character of interaction. This is attested by the smallest volumetric loss of samples (Fig. 9), the lowest average value of friction coefficient μ (Fig. 10) and the lowest linear wear as a function of the friction distance (Fig. 11). In addition, the graphs depicting changes in the values of the friction coefficient as a function of the friction distance show results without sudden jumps in the friction coefficient value (Fig. 12b), as opposed to the composites containing the largest graphite inclusions, i.e. composites D1 and D2 (Fig. 12a). In the case of the composites with the largest graphite inclusions, the co-active nature of the contact parts is unstable, which is indicated by frequent, sudden changes in the friction coefficient. The observations of the composite surface after tribological tests of the same kind of material pairs (Fig. 13) do not reveal any significant differences. Small matrix fragments from the surface of the SiC matrix are crushed, while the solid graphite lubricant is extracted from the inclusion. It can only be assumed that during the co-action of the contact pairs, which are made of composites containing larger graphite granules, when the crushed fragments of the hard SiC matrix penetrate between the abrasive elements, the graphite lubricant does not work effectively and does not compensate friction significantly. The homogeneous distribution of smaller inclusions of the solid lubricant - graphite in the SiC matrix provides better lubrication effects and thus more stable performance of the contact pairs.

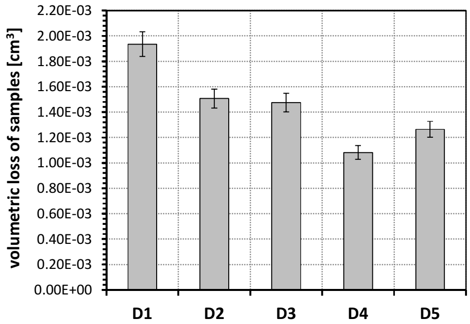

Fig. 9. Volumetric loss of composites occurring during dry sand test

Rys. 9. Ubytek objętościowy kompozytów powstały podczas prób ścieralności wykonanych metodą dry sand test

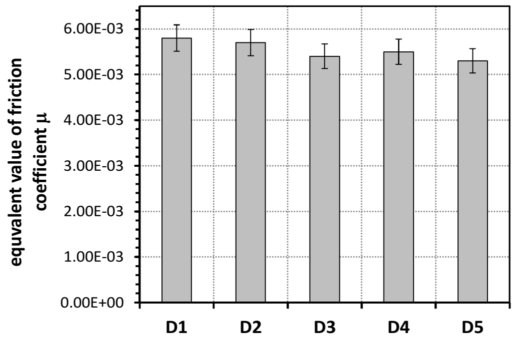

Fig. 10. Coefficient of friction determined by pin-on-disc method

Rys. 10. Współczynnik tarcia określony metodą pin-on-disc dla par jednoimiennych

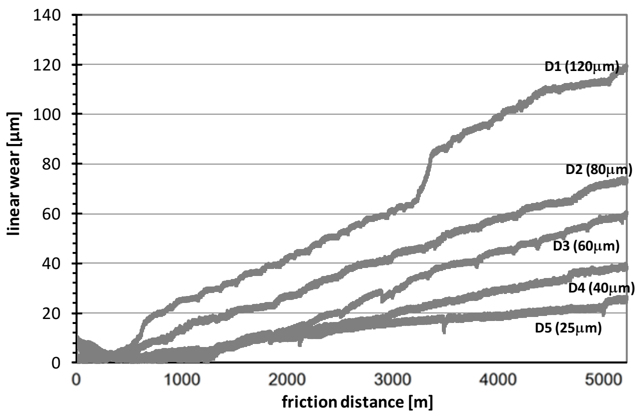

Fig. 11. Linear wear as function of friction path determined by pin-on-disc method

Rys. 11. Zużycie liniowe w funkcji drogi tarcia wyznaczone metodą pin-on-disc

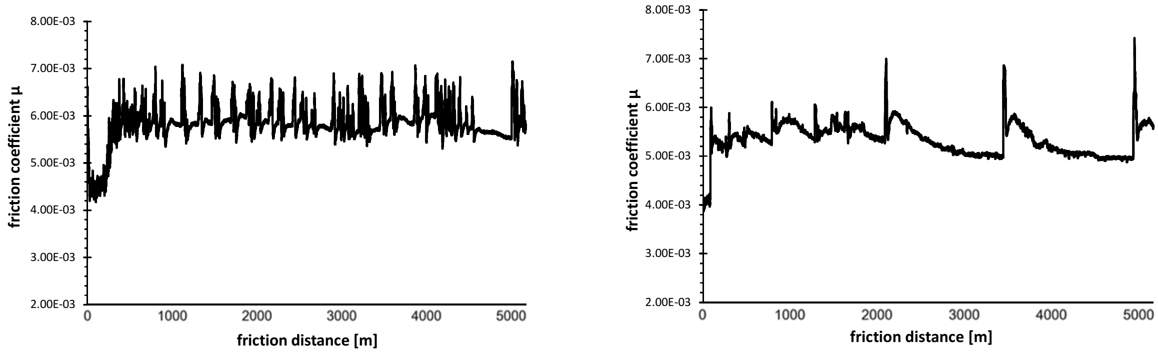

Fig. 12. Coefficient of friction as function of friction distance for composites D1 (a) and D5 (b)

Rys. 12. Zależność współczynnika tarcia w funkcji drogi tarcia dla kompozytów D1 (a) i D5 (b)

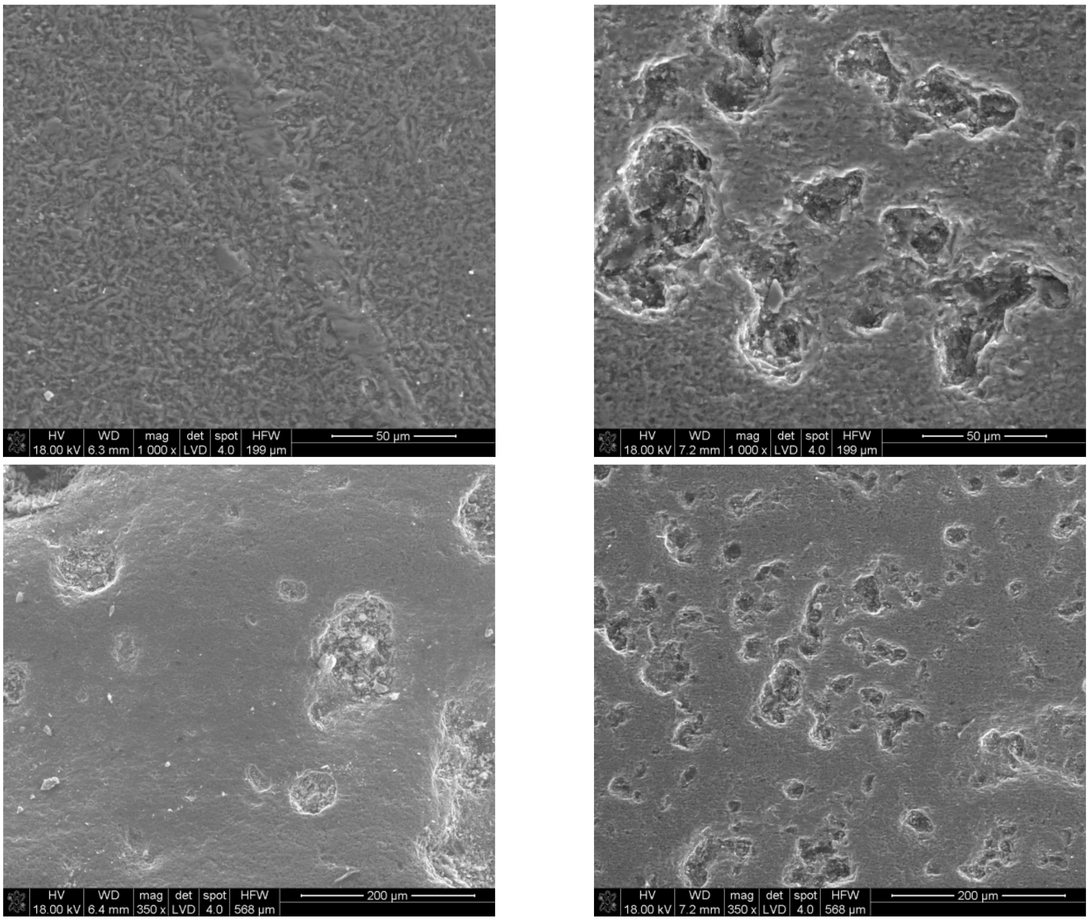

Fig. 13. SEM micrographs of composite surfaces after friction tests: a) composite D1 and b) composite D5

Rys. 13. Zdjęcia SEM powierzchni kompozytów po testach tarcia w parach jednoimiennych: a) kompozyt D1 i b) kompozyt D5

CONCLUSIONS

The following conclusions can be drawn on the basis of the research undertaken in the paper:

1. It is possible to produce dense SiC-graphite composites via pressureless sintering with self-lubricating properties, regardless of the size of inclusions of solid lubricant - graphite. Different sizes of granules made from mixtures of graphite, wood dust and phenol formaldehyde resin were introduced into the sinterable SiC granulate at 10 vol.%.
2. During sintering of the composites, both phenol formaldehyde resin and wood dust are graphitized.
3. According to both the qualitative and quantitative analyses of the microstructure, it was found that the distribution of graphite inclusions with a size lower than 0.056 mm is more homogeneous as compared to inclusions with a size larger than 0.1 mm.

4. Composites with smaller inclusions, i.e. D4 and D5 exhibit better mechanical and tribological properties in comparison to the composites with larger inclusions, i.e. D1 and D2, which are influenced by the higher density of the D4 and D5 composites and more uniform distribution of graphite granules in the SiC matrix.

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