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COMPOSITES THEORY AND PRACTICE

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THE INFLUENCE OF RESIDUAL STRESSES IN SELECTED NON-OXIDE CERAMICS COMPOSITES ON THEIR WEAR RESISTANCE IN DIFFERENT ENVIRONMENTS

The application of structural non-oxide ceramics is at present a common trend in machines and the construction of mechanical devices. Dense ceramic sinters made of silicon carbide or silicon nitride very often replace metallic parts. The advantages of ceramics are especially evident when they work as parts of machinery exposed to the action of loose and hard particles. The paper compares the abrasive wear susceptibility of both the mentioned phases and two particulate composites made on SiC and Si_3N_4 matrices. Two types of tests were performed. The Dry Sand Test, which indicates the wear susceptibility of the material to wear during the abrasive action of hard particles without any lubricant, was the first one. The Miller Test was the second. This test examined the wear of materials during the action of hard particles in a wet environment (pulp). In both tests the same abrasive, silicon carbide powder, was used.

Keywords: ceramic matrix composites, abrasive wear, silicon carbide, silicon nitride, particulate composites, dry sand test, Miller test

WPŁYW NAPRĘŻEŃ RESZTKOWYCH W WYBRANYCH NIETLENKOWYCH KOMPOZYTACH CERAMICZNYCH NA ICH ODPORNOŚĆ NA ZUŻYCIE ŚCIERNE W RÓŻNYCH ŚRODOWISKACH

Zastosowanie ceramiki nietlenkowej jest obecnie powszechnym trendem w konstruowaniu części maszyn i urządzeń. Gęste spieki z węglika krzemu i azotku krzemu bardzo często zastępują części metaliczne. Zalety materiałów ceramicznych są wyraźnie widoczne wówczas, gdy części maszyn są narażone na działanie luźnych, twardych cząstek. Prezentowany artykuł porównuje podatność na zużycie ścierne obu wymienionych faz, a także kompozytów na ich osnowach. Wykonano dwa rodzaje testów zużycia. Pierwszy to tzw. Dry Sand Test, który mierzy podatność na zużycie ścierne luźnym ścierniwem, w warunkach suchych, bez smarowania. Drugim testem był tzw. test Millera, który pozwala uzyskać informacje na temat zużywania się materiałów podczas działania luźnych, twardych cząstek w środowisku mokrej pulpy, tj. gęstej zawiesiny. W obu testach użyto tych samych ziaren ściernych, gruboziarnistego węglika krzemu.

Słowa kluczowe: kompozyty z osnową ceramiczną, zużycie ścierne, węglik krzemu, azotek krzemu, kompozyty ziarniste, test suchego ścierniwa, test Millera

INTRODUCTION

The exploitation of many mechanical devices consists in the movement of different parts which are very often exposed to the action of loose hard particles. This may cause many problems due to deterioration of the surface quality and tightness of part connections. The intensive wear rate in relatively small areas could destroy even large and complicated devices. Ceramic materials are very promising from this point of view as they can offer very good mechanical properties, especially hardness and stiffness, which are very important for the wear resistance of materials. Additionally, polycrystalline ceramics give the opportunity of manufacturing particulate composites. The proper phase composition of ceramic matrix composites can produce compressed stresses in the matrix, caused by the mismatch of thermal expansion coefficients of the constituent phases [1, 2]. Such stresses could act additionally as a toughening mechanism [3, 4] and also improve the abrasive wear resistance. Generation of the mentioned stress state is considered to be an important factor of strength and fracture toughness improvement. The presented work investigates the role of residual stresses in composites for abrasive wear susceptibility.

MATERIALS AND METHODS

Materials

The materials investigated in this work were fabricated by means of utilizing commercially available ceramic powders: SiC powder - Starck UF-15; Si_3N_4 powder - Starck Grade M11 AB168322; TiB_2 powder - Starck Grade F-A AB134577. Additionally, some ceramic powders were used as sintering additives for silicon nitride: Y_2O_3 - Starck Grade C-A AB134554 and Al_2O_3 - TM-DAR Taimei Chemical. Silicon carbide was sintered with an addition of amorphous boron, Fluka cat. no. 15580, and a carbon precursor which was introduced as phenolic resin Novolak MR, produced by Nowa Sarzyna (Poland).

Four different types of materials were prepared; silicon carbide, silicon carbide/titanium diboride composite, silicon nitride and silicon nitride/silicon carbide composite. In the paper they have been described respectively as: **SC**, **SC/TB**, **SN** and **SN/SC**.

The silicon carbide powder was prepared for sintering by an addition of 0.5% amorphous boron and 3% carbon precursor, which was introduced as phenolic resin into SiC powder [5, 6] and homogenized by 24 hour mixing in a ball mill, using 10 mm SiC balls. Sintering of the **SC** samples was conducted in a hot-press (Thermal Technology) with a graphite heating element, in argon atmosphere, under the pressure of 25 MPa, at 2150°C with a 1 hour dwell time at the maximum temperature. The sintered bodies were 10 mm thick and 75 mm in diameter. These dimensions were also achieved for the rest of the non-oxide samples - **SC/TB**, **SN** and **SN/SC**.

The silicon carbide/titanium diboride composite (**SC/TB**) powder was prepared by mixing the TiB_2 powder with SiC and sintering additives in the same conditions as the SiC powder. The volumetric ratio of silicon carbide to titanium diboride was 90:10. The sintering conditions of the **SC/TB** material were the same as the **SC** one.

The silicon nitride powder **SN** was prepared for sintering by an addition of sintering aids - 3% Y_2O_3 and 4.6% Al_2O_3 [7]. Homogenization of the powders was conducted in the ball mill using the same parameters and conditions as for the preparation of the SiC powder. The composite silicon nitride silicon carbide powder **SN/SC** was prepared in the same way. The volumetric ratio of silicon nitride to silicon carbide was 90:10.

Sintering of the **SN** and **SN/SC** samples was conducted in the Thermal Technology hot-press with a graphite heating element, in argon atmosphere, under the pressure of 25 MPa, at 1650°C with 1 hour dwell time at the maximum temperature.

Property measurements

The apparent densities of the samples were determined by hydrostatic weighing after sintering. The relative densities were calculated for each sample as the ratio of apparent density to the theoretical one. The theoretical densities were calculated using the producer's values for individual phases and the authors' knowledge about the phase content of the materials. The samples for wear tests were cut using Struers equipment (Accutom 5).

The residual stress state in the sintered bodies caused by the mismatch of thermal expansion coefficients of the constituent phases was calculated using Taya's model [8]. The values of thermal expansion coefficient (α) of the phases utilized in the investigations were as follow: $\alpha_{Si3N4} = 3.3 \cdot 10^{-6}$°C; $\alpha_{SiC} = 4.3 \cdot 10^{-6}$°C and $\alpha_{TiB2} = 8.5 \cdot 10^{-6}$°C. The basic mechanical properties of the sintered bodies were determined using commonly used methods. The data for σ strength analysis were collected from four-point bending tests made on 45 x 4 x 3 mm bars, 5 samples for each material type (Zwick-Roel Z2.5). Hardness was measured using an indenter with Knoop's geometry and the applied load was 9.81 N in each case. The mean HK value was calculated from 10 independent measurements. Fracture toughness K_{Ic} was determined by the Vickers indentation method, based on the Niihara calculation model and Palmqvist crack model, using Nanotech MV-700 equipment. The load for the K_{Ic} calculations was 98.1 N. The mean value of K_{Ic} was calculated from 5 independent indentations. Microstructural observations of worn surfaces were performed with NovaNano 200 SEM equipment produced by FEI.

The abrasive wear susceptibility under the Dry Sand Test [9] conditions was determined using the abrasive medium silicon carbide powder (SiC 80) with the grain size range of 160÷200 micrometers. The number of rotations of the rubber wheel during each test was 2000. Two different samples were tested for each material type. The temperature during the test was 20°C.

The abrasive wear susceptibility in a water suspension of hard particles (slurry) was determined partially utilizing the Miller Test [10] by means of the Nova Werke AG apparatus to determine the abrasive properties of slurry in relation to a particular material (Miller Number). In the presented paper the authors established the slurry parameters and made tests with the same slurry for different materials. The slurry content was 200 g of distilled water and 200 g of SiC 80 (with the grain size ranging 160÷200 micrometers). The temperature of the water during the test was 18°C, the test duration was 6 hours for each material and two different samples were tested for each material type. Actually, the authors determined the Slurry Abrasion Response of Materials (*SAR Number*). The wear kinetics was calculated as a *VLR Number* (volume loose rate) from the wear diagrams prepared after every 2 hours of testing according to the procedures described in the standard in [10].

RESULTS AND DISCUSSION

Table 1 summarizes the density and porosity data of all the investigated materials. The theoretical values of

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the densities for each material were calculated taking into account the real content of the main phases and also the amount of sintering additives (carbon and boron for SiC based materials and alumina and yttria for Si_3N_4 based materials). All of them were relatively well densified, the porosity was limited to the closed one only. It is worth noticing that the composites were better densified than the sintered specimens made of pure matrix materials.

TABLE 1. **Densities and porosity of sintered samples**
TABELA 1. **Gęstości i porowatości spieczonych próbek**

Sample	Density			Tot. por. [%] ±less than 0.005
	Theor. [g/cm^3]	Apparent [g/cm^3] ±0.01	Relative [%] ±< 0.005	
SC	3.210	3.105	96.73	3.27
SCTB	3.304	3.270	97.90	2.10
SN	3.296	3.195	96.82	3.18
SNSC	3.291	3.201	97.27	2.73

The state of residual stresses values in the composites are collected in Table 2. In both composites the dispersed phase caused compressive stresses in the matrix due to their higher coefficient of thermal expansion when compared to the matrix. Such a stress state could be an important factor for mechanical properties (strength and fracture toughness) improvement. The mean values of stresses in the investigated composites were distinctly (more than 500%) different. The silicon carbide matrix was compressed with a mean value exceeding 250 MPa. In comparison, silicon nitride one was compressed "slightly" with a mean stress of less than 50 MPa.

TABLE 2. **Calculated values of residual stresses in composites**
TABELA 2. **Obliczone wartości naprężeń resztkowych w kompozytach**

Composite material	Mean value of compressive stress in matrix [MPa]	Mean value of tensile stress in inclusions [MPa]
SCTB	–258	2322
SNSC	–46	402

The data from Table 3 illustrate that such a state of stresses distinctly influenced the strength and fracture toughness of the composites. Improvement of the **SCTB** parameters compared to **SC** was noticeable in opposition to the **SN** and **SNSC** pair.

Table 4 directly shows the data of volumetric wear during the Dry Sand Test. The comparison of the silicon carbide and silicon nitride materials clearly indicates that the silicon nitride wear rate was two times lower than the silicon carbide one. The results of the wear test for the composites were diversified. The composite on the silicon nitride base (**SNSC**) showed an almost 30% better wear resistance than the **SN** matrix. The composite on the silicon carbide base (**SCTB**) showed practically the same wear rate as the **SC** matrix (the difference falls into the standard deviation of measurement results).

TABLE 3. **Mechanical properties of sintered samples**
TABELA 3. **Właściwości mechaniczne spieczonych próbek**

Sample	Vickers hardness HK [GPa]	Fracture toughness K_{Ic} [MPam$^{0.5}$]	Bending strength σ [MPa]
SC	19.5 ±1.2	4.6 ±0.7	351 ±45
SCTB	18.7 ±0.5	5.3 ±0.6	402 ±50
SN	13.1 ±0.2	5.1 ±0.5	613 ±40
SNSC	14.1±0.7	5.2±0.4	589 ±35

± denotes standard deviation

TABLE 4. **Results of Dry Sand Test**
TABELA 4. **Wyniki Dry Sand Test**

Sample	Volumetric wear determined according to Dry Sand Test [mm^3]
SC	9.79 ±1.73
SC/TB	9.33 ±0.22
SN	4.76 ±0.35
SN/SC	3.41 ±0.11

± denotes standard deviation

In Table 4 the volumetric wear of all the investigated materials is collected. The results of wear during the Miller Test are collected in Tables 5 and 6. Measurements were made after every 2 hours of testing, the results of which indicate that all the materials wore out in a monotonic manner. The values of the *SAR* and *VLR* numbers collected in Table 5, as calculated on the basis of volumetric wear data according to [10], confirm the differences in the wear process of the investigated materials.

TABLE 5. **Results of volumetric wear during Miller Test**
TABELA 5. **Wyniki zużycia objetościowego w teście Millera**

Sample	Vol. wear 2 h [mm^3]	Vol. wear 4 h [mm^3]	Vol. wear 6 h [mm^3]
SC	17.84 ±3.76	34.55 ±5.18	51.73 ±1.83
SCTB	16.61 ±0.82	32.57 ±1.83	51.87 ±1.73
SN	12.13 ±0.55	21.14 ±2.35	34.98 ±5.84
SNSC	10.20 ±0.10	18.60 ±2.14	24.70 ±3.70

± denotes standard deviation

TABLE 6. **Results of *SAR* and *VLR* number calculations**
TABELA 6. **Wyniki obliczeń liczb *SAR* i *VLR***

Sample	*SAR number*	*VLR number*
SC	155 ±10	8.55 ±0.58
SCTB	149 ±7	8.19 ±0.38
SN	98 ±14	5.42 ±0.75
SNSC	75 ±14	4.14 ±0.76

± denotes standard deviation

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The level of degradation was significantly different for both the investigated groups of materials. The **SN** and **SNSC** materials were distinctly less susceptible to degradation.

The **SN** matrix was about 32% more resistant to the applied wear process than **SC**. The behaviour of the **SNSC** composite showed the mentioned property 30% better than the **SN** material.

In the SiC based materials wear behaviour improvement did not take place. **SC** and **SCTB** have practically the same wear parameters. The comparison of both the applied test results shows a similarity. In both tests the ranking of the wear resistance is the same. The most resistant was the **SN** material followed by the **SNSC** composite. The worst results were obtained by the **SC** and **SCTB** ones. The presence of water did not change the relations between the wear rates. Observations of the SEM images of the worn surfaces of all the investigated samples (Figs. 1-8) confirm that the test environment has no influence on the abrasive wear mechanisms of the investigated materials.

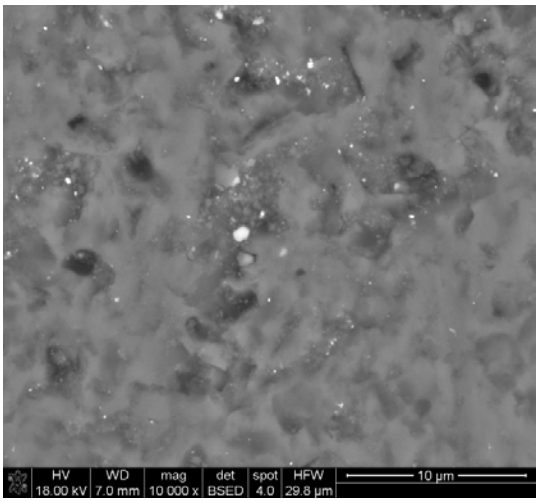

Fig. 1. SEM image of worn SC sample surface after Dry Sand Test

Rys. 1. Mikrofotografia SEM powierzchni próbki SC zużytej w teście suchego ścierniwa

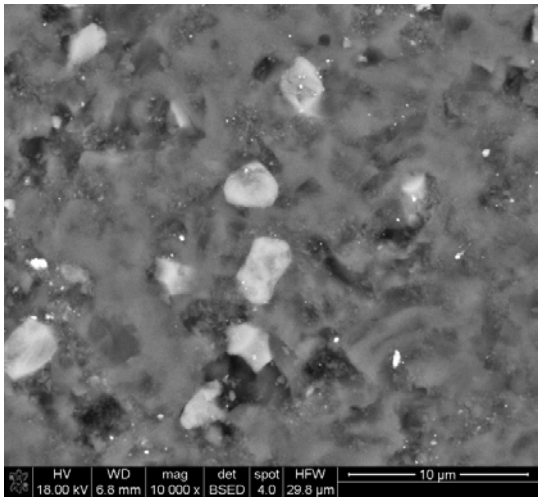

Fig. 2. SEM image of worn SCTB sample surface after Dry Sand Test

Rys. 2. Mikrofotografia SEM powierzchni próbki SCTB zużytej w teście suchego ścierniwa

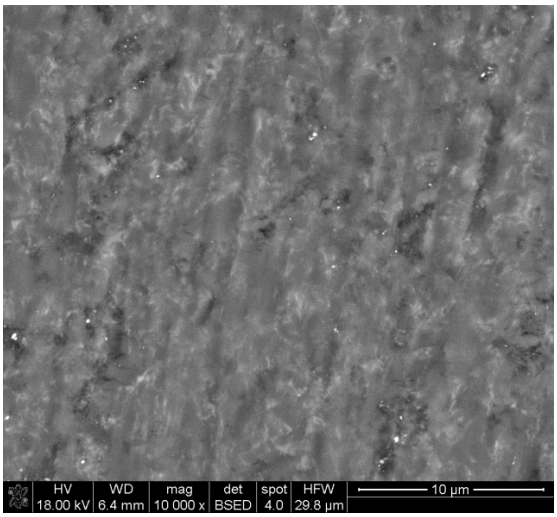

Fig. 3. SEM image of worn SN sample surface after Dry Sand Test

Rys. 3. Mikrofotografia SEM powierzchni próbki SN zużytej w teście suchego ścierniwa

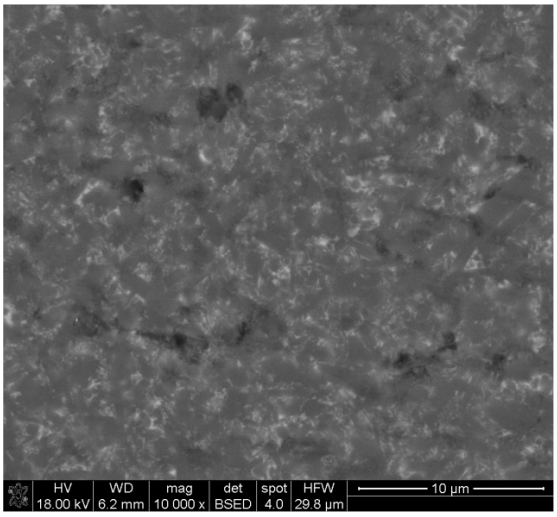

Fig. 4. SEM image of worn SNSC sample surface after Dry Sand Test

Rys. 4. Mikrofotografie SEM powierzchni próbki SNSC zużytej w teście suchego ścierniwa

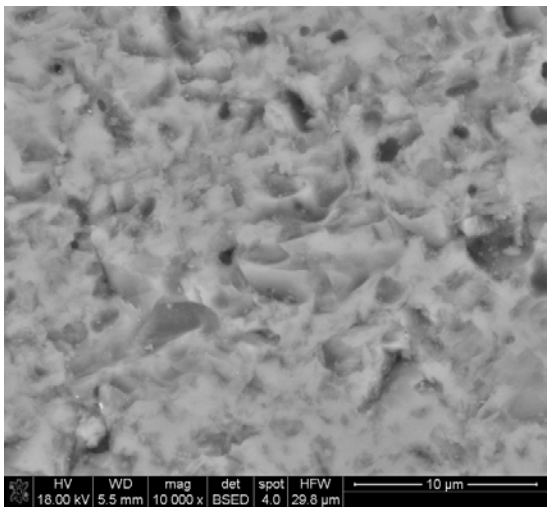

Fig. 5. SEM image of worn SC sample surface after Miller Test

Rys. 5. Mikrofotografia SEM powierzchni próbki SC zużytej w teście Millera

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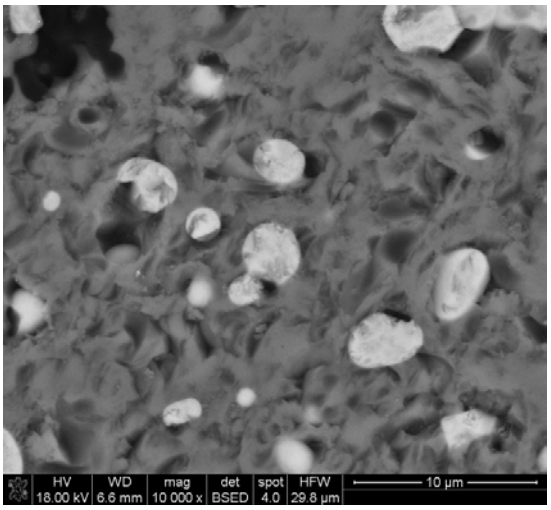

Fig. 6. SEM image of worn SCTB sample surface after Miller Test

Rys. 6. Mikrofotografia SEM powierzchni próbki SCTB zużytej w teście Millera

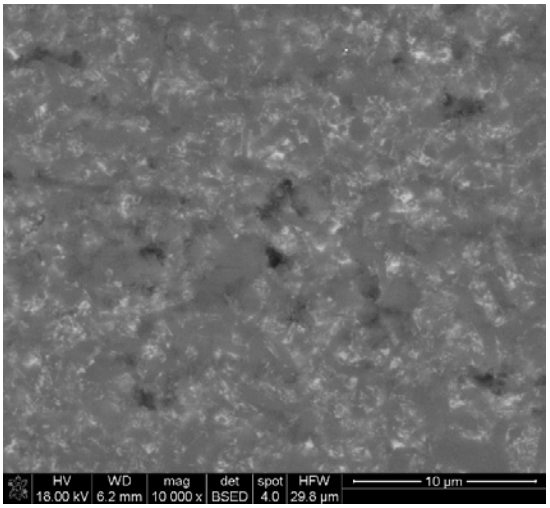

Fig. 7. SEM image of worn SN sample surface after Miller Test Test

Rys. 7. Mikrofotografia SEM powierzchni próbki SN zużytej w teście Millera

The highest values of compressive stresses in the silicon carbide matrix were calculated for the **SCTB** material. The results suggest that the stress state does not have a decisive influence on reducing the wear rate in composites.

This statement is confirmed by the observation that the lowest level of wear susceptibility was detected for the composite with the lowest level of residual stresses. Similar results were reported for composites with an alumina matrix [11]. The wear resistance in the Miller Test did not correlate with the mechanical properties. The materials with the highest hardness (**SC**, **SCTB**) performed the worst during the wear test. Fracture toughness improvement (**SC** → **SCTB**) did not positively influence the wear resistance. The changes in bending strength did not correlate with the wear behavior either. Analysis of the microstructures in Figures 1-8 showed that the SiC based materials had a distinctly different wear surface when compared to the Si_3N_4 based materials. The **SC** and **SCTB** materials surfaces were much rougher than the **SN** and **SNSC** ones. It suggests that for the wear resistance of the **SC** and **SCTB** materials, the decisive factor was SiC matrix resistance. The high level of residual stresses was practically not important for the wear rate of the composite. The main reason for **SC** and **SCTB** material degradation during the Miller Test was local damages in small areas where single SiC grains were crushed into small debris. It most probably caused higher friction and intensified damage forces on the surface.

For both the investigated silicon nitride based materials, the measured wear resistance was much lower than that observed for the silicon carbide based ones. The most important observation was that in this case, the composite material was distinctly better than the pure matrix.

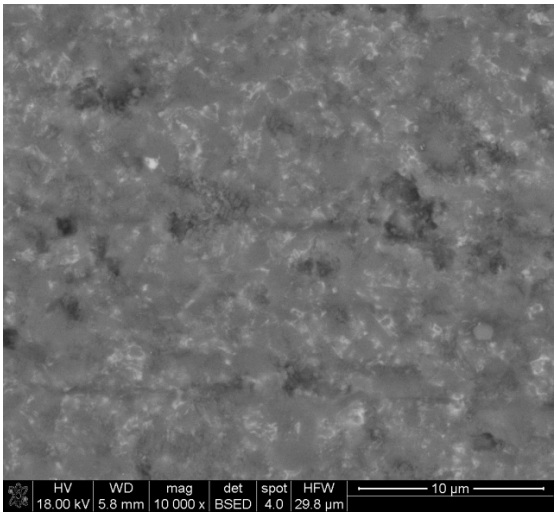

Fig. 8. SEM image of worn SNSC sample surface after Miller Test

Rys. 8. Mikrofotografia SEM powierzchni próbki SNSC zużytej w teście Millera

CONCLUSION

Although manufacturing particulate composites could be an effective way to improve the mechanical properties in structural ceramic sinters, the performed experiments proved that such a mechanism is not always successful for improving useful properties, which depends on many different, simultaneously acting factors. For the two investigated pairs of materials (silicon carbide **SC**; silicon carbide/titanium diboride composite **SCTB** and silicon nitride **SN**; silicon nitride/silicon carbide composite **SNSC**), the presence of compressive stress in the matrix acted in different ways.

Probably, in order to improve the wear resistance of the investigated materials, the properties of the grain boundaries between the constituent phases play a decisive role. In the case of the **SCTB** composite, the interphase SiC-TiB_2 boundaries were subjected to a much more complicated stress state than the Si_3N_4-SiC boundaries in the **SNSC** material.

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