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THE TRIBOLOGICAL CHARACTERISTICS OF ZIRCONIUM DIBORIDE PARTICLE REINFORCED COMPOSITES PROCESSED BY SPS

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The tribological properties of composites based on 316L steel reinforced with zirconium diboride (5 and 10 wt.%) were described. The composites were fabricated by the spark plasma sintering (SPS) method. Wear resistance tests were carried out using the ball-on-disc method at room temperature under dry friction conditions. Countersamples made of SiC, Si_3N_4, ZrO_2 and AISI52100 steel were used in the tests. The determined parameters included the coefficient of friction μ, mass loss Δm and specific wear rate $W_{s(disc)}$. After the tribological tests, the surfaces of the samples were examined under a confocal microscope. The obtained research results showed that the tribological properties depend on the test conditions (the type of countersample) and on the content of the ZrB_2 reinforcing phase.

Keywords: **composites, zirconium diboride (ZrB_2), ball-on-disc method, wear rate, coefficient of friction**

CHARAKTERYSTYKA TRIBOLOGICZNA KOMPOZYTÓW WZMOCNIONYCH CZĄSTKAMI DIBORKU CYRKONU SPIEKANYCH METODĄ SPS

Przedstawiono właściwości tribologiczne kompozytów na osnowie stali 316L wzmocnionych diborkiem cyrkonu (5 i 10% wag.). Kompozyty zostały wytworzone z zastosowaniem metody Spark Plasma Sintering (SPS). Badania odporności na zużycie przeprowadzono, wykorzystując metodę ball-on-disc w temperaturze pokojowej w warunkach tarcia suchego. Testy przeprowadzono, stosując następujące przeciwpróbki: SiC, Si_3N_4, ZrO_2 i stal AISI52100. Wyznaczono współczynnik tarcia μ, ubytek masy Δm i wskaźnik zużycia $W_{s(disc)}$. Powierzchnie próbek po testach tribologicznych obserwowano za pomocą mikroskopu konfokalnego. Uzyskane wyniki badań wykazały, że właściwości tribologiczne zależą od warunków badań (rodzaju przeciwpróbki) i ilość fazy wzmacnianej ZrB_2.

Słowa kluczowe: **kompozyty, diborek cyrkonu (ZrB_2), metoda ball-on-disc, szybkość zużycia, współczynnik tarcia**

INTRODUCTION

Abrasive wear is the dominant type of wear under conditions of dry friction, and this process is related to the bulk properties of the material. Abrasive wear is a mechanical process of material wear [1, 2]. The resistance to abrasive wear depends on the test conditions (friction force, rotational speed, distance, temperature) and on the type of tribological pair [3, 4]. The wear behaviour of composite materials is affected by the morphology, type, amount, arrangement and properties of the reinforcing phase [5, 6]. According to literature [7-10], studies were carried out to explain the effect of various ceramic particles (TiB_2, TiC, Al_2O_3, Y_2O_3, SiC, MoS_2) on the tribological properties of composites based on stainless steel. The introduction of a ceramic phase into the steel matrix improves the abrasion resistance of such materials [11-14]. Tjong and Lau [8] investigated the effect of changing load (15, 35 and 55 N) and sliding speed (1 and 3 m s^{-1}) on the wear behaviour of 304 steel+20 wt.% TiB_2 composites. It was shown that the wear rate of the 304 steel without the reinforcing phase grows rapidly with increasing load and sliding speed. On the other hand, the opposite trend was observed in the 304 steel+20 wt.% TiB_2, composites, where the volumetric wear decreased with the increase in the applied load and sliding speed. Srivastava and Das [15] demonstrated that composites reinforced with TiC and (Ti, W)C offer better wear resistance than austenitic steel without reinforcement. The research demonstrated the superior resistance to abrasive wear of the composites containing (Ti, W)C as compared to the composites reinforced with TiC. It was also been shown that the abrasive wear resistance and coefficient of friction of austenitic steel and composites reinforced with particles of TiC and (Ti, W)C decrease with increasing load.

The main purpose of this study is to investigate the tribological properties of steel+5% ZrB_2 and steel+10% ZrB_2 composites. The effect of the different countersample type and ZrB_2 on the coefficient of friction, mass loss and specific wear rate was studied.

MATERIALS AND METHODS

In the present work, powders of 316L austenitic stainless steel (particle size of 25 μm, Hoganas), zirconium diboride (ZrB_2, particle size of 2.5-3.5 μm, H.C. Starck) were used as the raw material for the research. ZrB_2 particles were added to the steel powders in amounts of 5 and 10 weight percent. The composites were sintered using spark plasma sintering (SPS) in vacuum under the pressure of 35 MPa, at the temperature of 1373 K and for the time of 300 seconds. The density of the sintered composites was determined by the Archimedes' method [16]. Young's modulus was measured using an ultrasonic flaw detector ZBM ULTRA. The microstructure of the sintered materials was evaluated by means of a scanning electron microscope (SEM) Hitachi SU-70 (Tokyo, Japan) with wavelength dispersive spectroscopy (WDS). Next, the hardness was determined using the microhardness tester NEXUS 4000 (Innovatest).

Vickers hardness measurements were carried out with a 2.942 N load and a loading time of 10 s. The tests were conducted in accordance with the requirements of the Polish Standard [17].

The abrasion resistance tests of the sintered steel+ZrB_2 composites were performed by the ball-on-disc method using an ELBIT universal tribotester in accordance with the standard [18]. All the tests were carried out under the following conditions: dry friction, temperature of 22 °C, load of 5 N, speed of 0.1 m/s and time of 10,000 seconds. Countersamples (balls with a diameter of 3.175 mm) made of various materials, i.e. SiC, Si_3N_4, ZrO_2 and AISI52100 steel, were used in the tests. During the test, each sample was paired with a new ball surface [19]. Before the tests, the balls and the samples were washed with ethyl alcohol in an ultrasonic washer. They were weighed on a RADWAG AS 220/C/2 balance before and after each abrasion test.

Mass loss (Δm) was calculated from the following equation:

$$\Delta m = \frac{m_0 - m_k}{m_0} 100\% \quad (1)$$

where: m_0 – initial mass [g], m_k – final mass [g].

The specific wear rate was calculated by means of the equation:

$$W_{V(disc)} = \frac{V_{disc}}{F_n \cdot L} \quad (2)$$

where: F_n – applied load [N], V_{disc} – wear volume of the disc specimen [mm^3], L – sliding distance [m].

The wear volume of the disc specimen was calculated from following equation:

$$V_{disc} = \frac{\Pi}{2} \cdot R \cdot (S_1 + S_2 + S_3 + S_4) \quad (3)$$

where: R – radius of wear track [mm], S_1 to S_4 – cross-sectional areas at four places on the wear track circle [mm^2] [19].

When the tests were completed, the abrasion marks were subjected to microscopic analysis employing an OLYMPUS LEXT OLS5100 confocal microscope with OLS5100 Analysis Application software dedicated to surface analysis.

RESULTS AND DISCUSSION

SEM micrographs of the steel+ZrB_2 composites are shown in Figures 1-3. The WDS examinations of the chemical composition confirmed the presence of ZrB_2 particles (bright phase) evenly distributed along the grain boundaries in the steel matrix. The matrix was also observed to contain very fine (below 1 μm) precipitates of chromium.

The physical and mechanical properties are presented in Table 1. For the steel+ZrB_2 composites sintered by the SPS method, a high degree of compaction was obtained using the sintering time of 300 seconds. The apparent density of the sinters was in the range of 94-95% of the theoretical density. The results showed that the apparent density gradually decreased with increasing content of ZrB_2 in the steel matrix. This effect was due to the lower density of zirconium diboride (6.08 g/cm^3) compared to the density of 316L steel (8.00 g/cm^3) [20, 21].

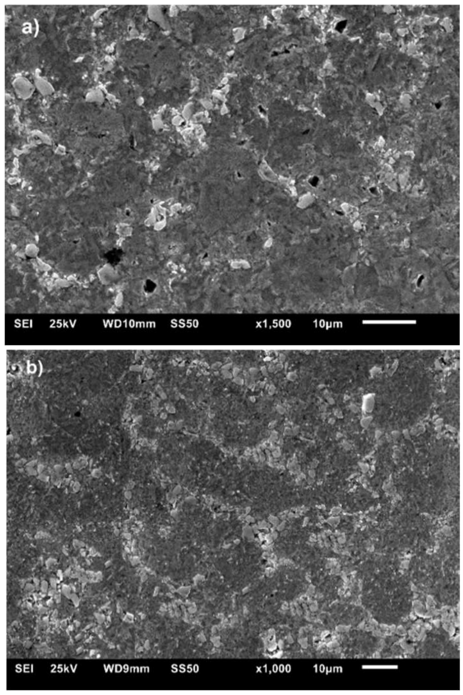

Fig. 1. SEM micrographs showing distribution of ZrB_2 reinforcement in: a) steel+5% ZrB_2, b) steel+10% ZrB_2 composites

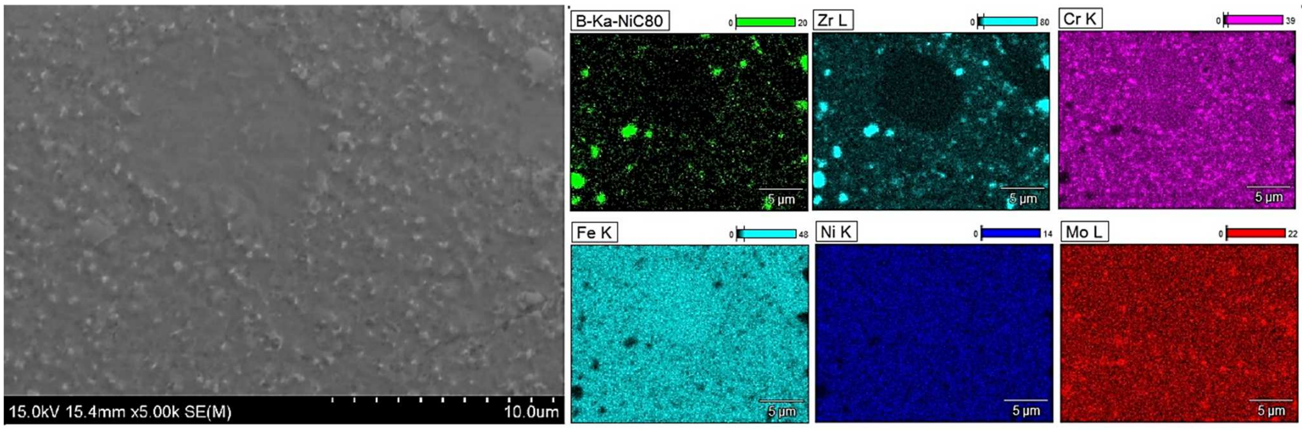

Fig. 2. Microstructure (SEM) and WDS composition analysis of steel+5% ZrB_2 composite

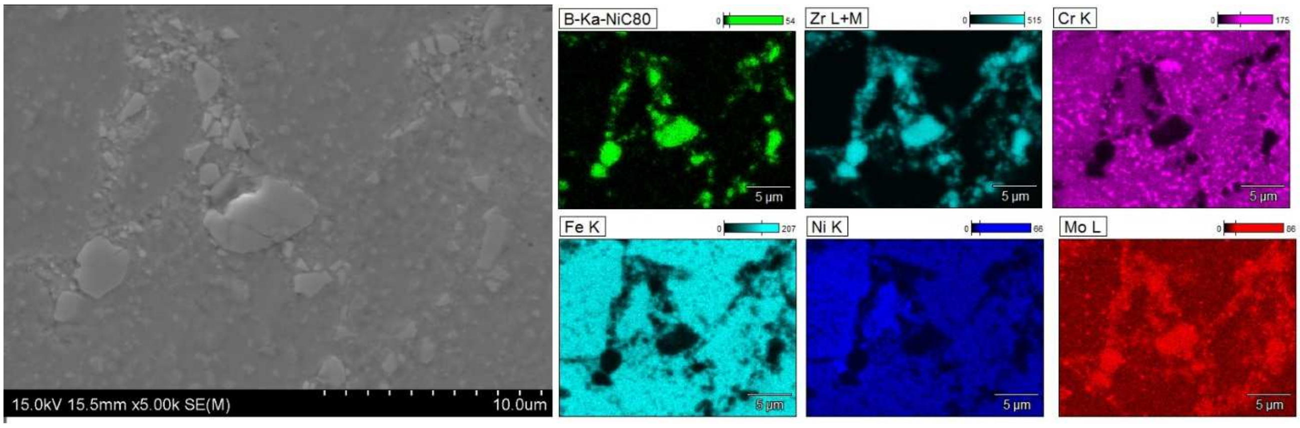

Fig. 3. Microstructure (SEM) and WDS composition analysis of steel+10% ZrB_2 composite

TABLE 1. **Properties of steel+ZrB_2 composites sintered by SPS method**

Sintered composites	Relative density [g/cm^3]	Apparent density [%]	Porosity [%]	Young's modulus [GPa]	Hardness [$HV_{0.3}$]
steel	7,82	98	0.58	197	212
steel+5% ZrB_2	7.35	94	0.71	210	297
steel+10% ZrB_2	7.22	95	0.82	218	381

The composite sinters were characterized by a low open porosity in the range of 0.71-0.82%. The ultrasonic method was used to determine Young's modulus. The value of Young's modulus depends on the microstructure of the sintered composite. The presence of a large number of defects and inhomogeneities in the material affects the attenuation of ultrasonic waves during measurements and low values of Young's modulus are obtained [22, 23]. Data analysis (Table 1) showed that with an increasing content of the reinforcing phase, Young's modulus also increased and amounted to 205 GPa and 216 GPa for the composites reinforced with 5% and 10% ZrB_2, respectively. According to literature [24], Young's modulus of 316L steel sintered under the same conditions is 196 GPa. The research (Table 1) showed that the hardness of the composites also gradually improved with the increasing addition of ZrB_2 particles. For the composites containing 10% ZrB_2 it was 381 $HV_{0.3}$ against only 225 $HV_{0.3}$ [25] obtained for the sintered 316L steel.

Using the ball-on-disc method, the tribological properties of the steel+ZrB_2 composites were investigated. Figure 4 shows changes in the coefficient of friction depending on the test time. From the obtained results (Table 2) it follows that the tribological properties of the sintered composites depend on the content of the reinforcing phase and on the type of countersample used. By examining the effect of the reinforcing phase, it can be concluded that the increase in the content of ZrB_2 in the steel matrix causes an increase in the value of the coefficient of friction and a simultaneous decrease in the mass loss and wear index (Table 2, Fig. 5). This trend prevailed in all the tests performed with different countersamples. Additionally, the analysis of the results shows that the coefficient of friction depends on the type of countersample used.

The highest values of the coefficient of friction, i.e. 0.57 and 0.62, were obtained for the steel+5% ZrB_2 and steel+10% ZrB_2 composites, respectively, using AISI52100 steel countersamples during the tests. The use of ceramic countersamples significantly reduced the coefficient of friction of the composites. The lowest coefficient was obtained during tests with the ZrO_2 countersample.

Introducing ZrB_2 particles in the amounts of 5 and 10 wt.% into the steel matrix gradually reduced the value of the wear rate (Table 2, Fig. 5b). With a higher content of the reinforcing phase, a lower value of the wear rate was obtained. This effect was clearly visible in the composites tested with ceramic countersamples, i.e. Si_3N_4, SiC, ZrO_2. It is very important that the wear rate assumed different values depending on the type of counter-sample used. The lowest value of the wear rate ($42·10^{-6}$ mm^3/Nm) was obtained for the steel+ 10% ZrB_2 composites tested with the ZrO_2 countersample.

TABLE 2. **Tribological properties of composites sintered by SPS method**

Sintered composites	Coefficient of friction μ [-]	Relative mass loss Δm [%]	Specific wear rate·10^{-6} W_v [mm^2/Nm]
AISI52100 steel			
steel	0.67	0.125	319
steel+5% ZrB_2	0.57	0.092	221
steel+10% ZrB_2	0.62	0.071	205
ball of Si_3N_4			
steel	0.61	0.158	456
steel+5% ZrB_2	0.40	0.068	119
steel+10% ZrB_2	0.46	0.031	64
ball of SiC			
steel	0.59	0.189	516
steel+5% ZrB_2	0.35	0.063	132
steel+10% ZrB_2	0.48	0.021	81
ball of ZrO_2			
steel	0.57	0.205	610
steel+5% ZrB_2	0.30	0.029	112
steel+10% ZrB_2	0.47	0.015	42

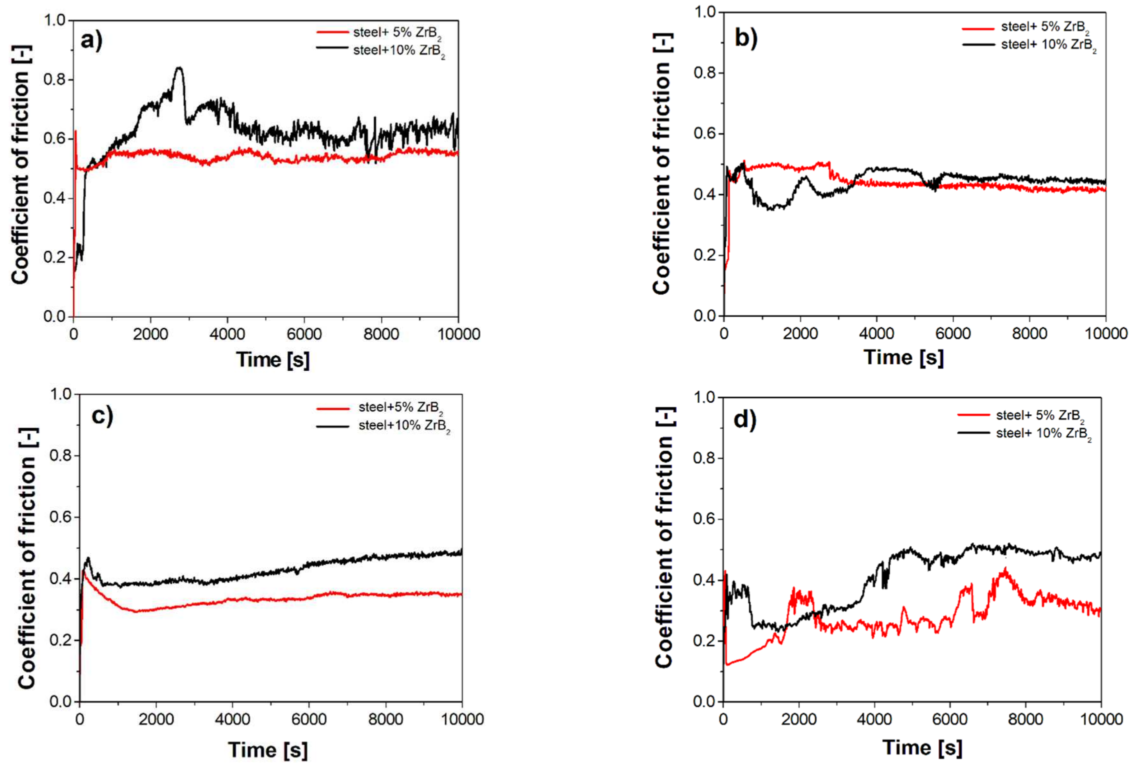

Fig. 4. Coefficient of friction of steel+5% ZrB_2 and steel+10% ZrB_2 composites as function of testing time, measured using different countersamples of: a) AISI52100 steel, b) Si_3N_4, c) SiC and d) ZrO_2

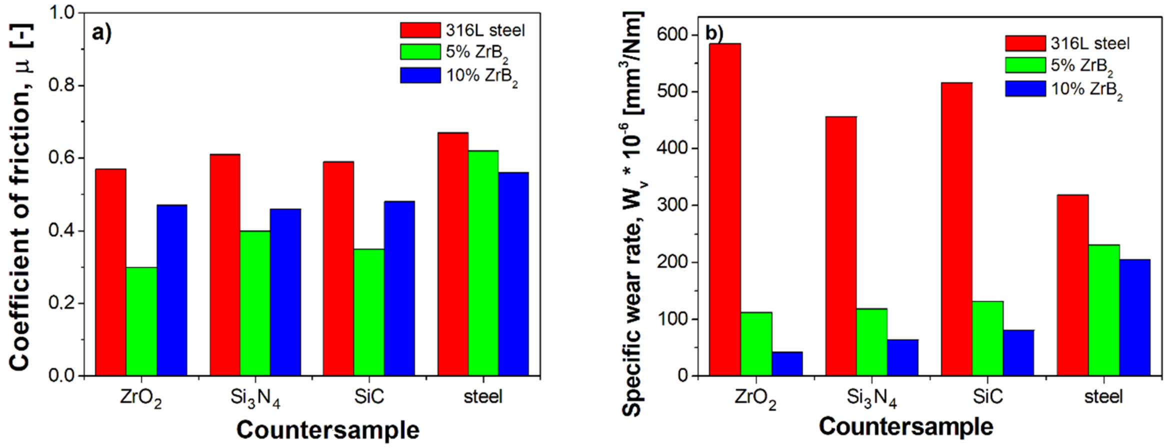

Fig. 5 Coefficient of friction (a) and specific wear rate measured using different countersamples (b)

After the tribological tests, microscopic analysis and geometrical measurements of the abrasion area were carried out for each sample using a confocal microscope.

Figures 6 and 7 include micrographs of the microstructures showing the surface condition and wear tracks left by the abrasion tests. Figure 8 compares examples of the wear profiles at four different spots in the steel+10% ZrB_2 composite sample after tests using a ZrO_2 counter-sample. The analysis of the wear tracks revealed that in all the tested composites, abrasion was the leading mechanism responsible for the wear. Scratches, damage and pits were observed in the area of the worn surfaces (abrasive type of wear). Moreover, local accumulation of wearing edges was observed in the researched materials (Fig. 8), which also indicates the abrasive nature of the wear.

Figure 9 presents the SEM micrographs of an exemplary surface of the steel+ZrB_2 composites after tests using a ZrO_2 countersample. Abrasive wear is present in the all composites as the scratches in the wear track indicate. Plastic deformation with characteristic grooves was observed.

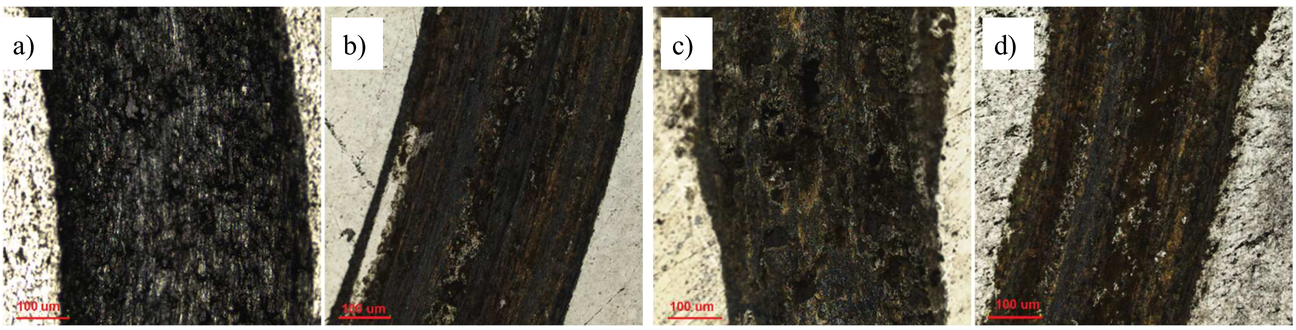

Fig. 6. Micrographs of worn surface of steel+5% ZrB_2 composites after wear test using different countersamples of: a) AISI52100 steel, b) SiC, c) Si_3N_4 and d) ZrO_2

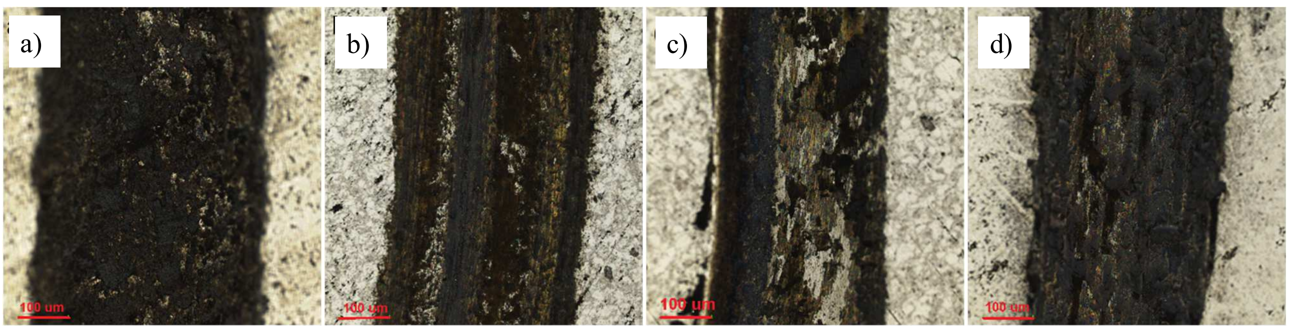

Fig. 7. Micrographs of worn surface of steel+10% ZrB_2 composites after wear test using different countersamples of: a) AISI52100 steel, b) SiC, c) Si_3N_4 and d) ZrO_2

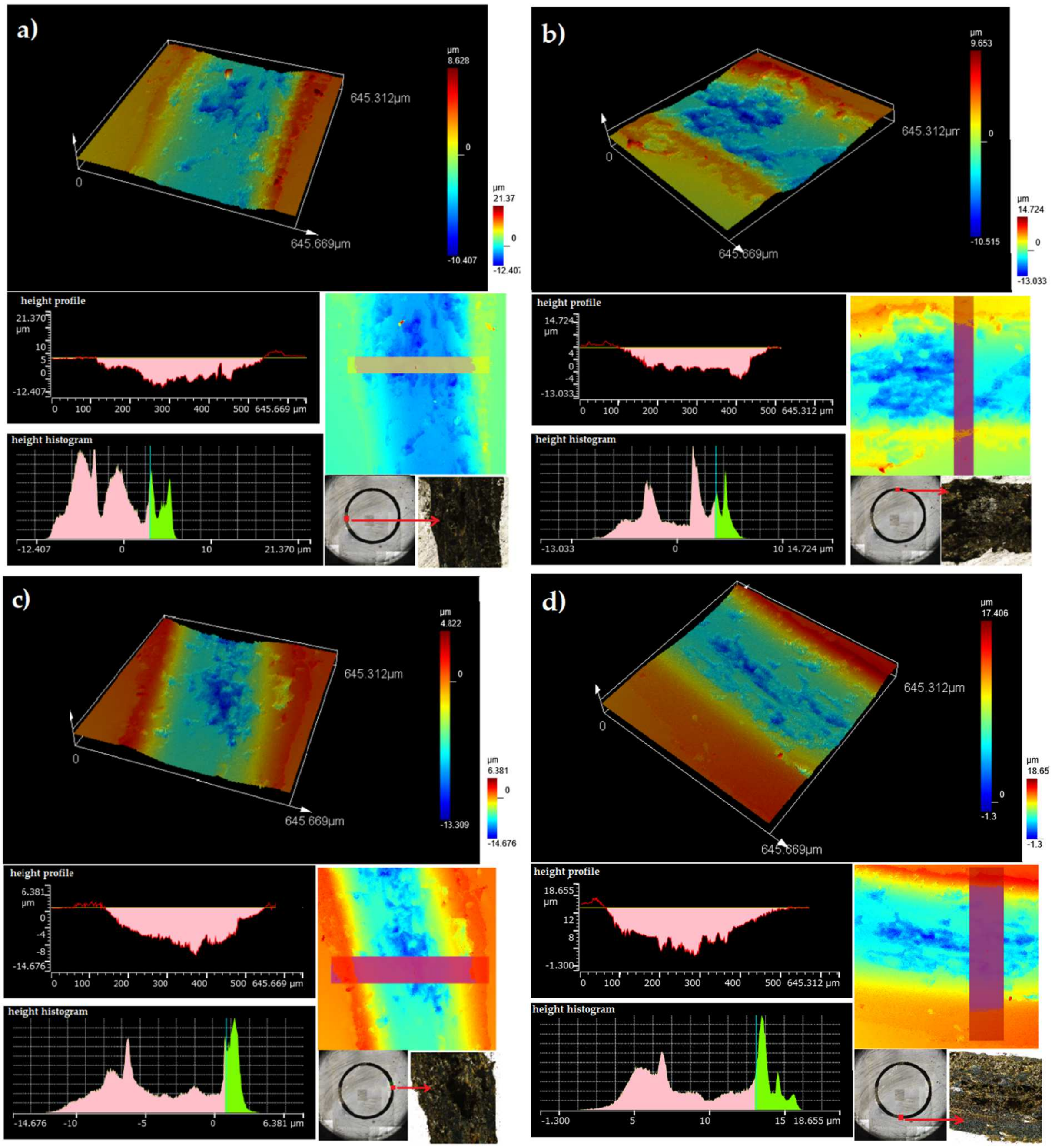

Fig. 8. Comparison of results of analysis of wear tracks and wear profiles of steel+10% ZrB_2 composite sample examined under Olympus LEXT OLS5100 confocal microscope (ZrO_2 countersample)

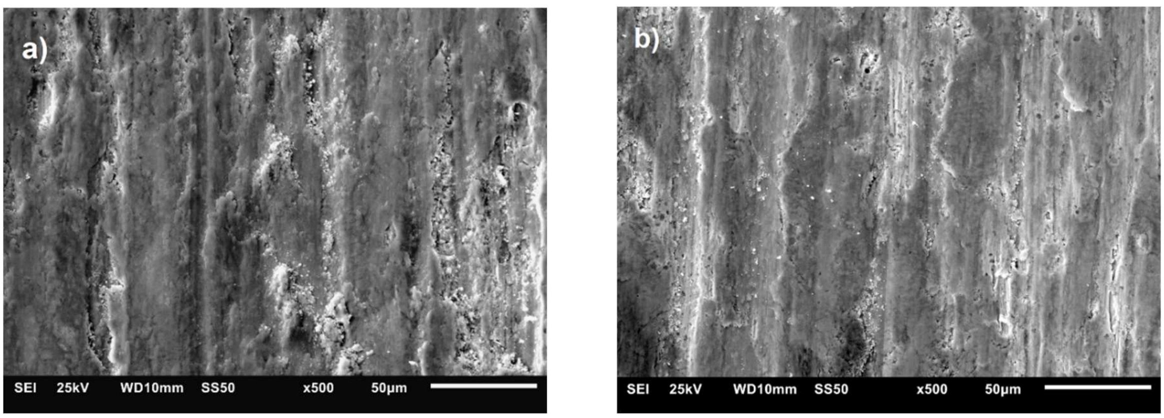

Fig. 9. SEM micrograph of worn surface of steel+10% ZrB_2 (a) and steel+20% ZrB_2 (b) composite after tests using ZrO_2 countersample

CONCLUSIONS

The increase in the mass fraction of ZrB_2 increases the density, Young's modulus and hardness of the 316L steel-based composites sintered by the SPS method.

The results of the wear test have shown that increasing the content of the ZrB_2 reinforcing phase improves the wear resistance of the composites. The wear rate depends on the type of countersample used. Among all the tested friction pairs, the lowest value of wear rate was obtained for the steel+10% ZrB_2 composite tested with the countersample made of ZrO_2.

The coefficient of friction rises with the increasing content of ZrB_2 when the tests are conducted with the ceramic countersamples made of Si_3N_4, SiC, and ZrO_2. The lowest value of the coefficient of friction was obtained for the steel+5% ZrB_2 composite tested with the countersample made of ZrO_2.

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