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SELF-LUBRICATING PROPERTIES OF THIN COATINGS BASED ON MOLYBDENUM DISULPHIDE

WŁAŚCIWOŚCI SAMOSMARNE CIENKICH POWŁOK NA BAZIE DWUSIARCZKU MOLIBDENU

Key words:

molybdenum disulphide, thin coatings, self-lubricating tribolayer, friction, wear resistance, elevated temperature

Słowa kluczowe:

dwusiarczek molibdenu, cienkie powłoki, samosmarna tribowarstwa, tarcie, odporność na zużycie, podwyższona temperatura

Abstract

The paper presents an analysis of the friction and wear processes of a composite coating based on molybdenum disulphide doped by tungsten and titanium, taking into account the impact of load and temperature in the contact zone. The tribological tests were performed at room temperature and at 300°C and 350°C in non-lubricated sliding contact with an Al_2O_3 ball. The characterization of the micromechanical properties and the adhesion of coatings to steel substrates were done by scratch testing. The analysis of the coatings wear and the sliding tribolayer formation was conducted by the observation of the friction track

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using light microscopy (LM) and scanning electron microscopy (SEM). The low hardness of the MoS_2(Ti,W) coating, equal to 6 GPa, with the predominantly amorphous structure, allows for quick formation of the tribological contact and the sliding tribolayer creation. Due to self-lubricating properties, the coating has a high wear resistance and a low friction coefficient (below 0.1), both at room and elevated temperatures. The study allowed the determination of the operating temperature limit of the coating-substrate system in sliding point contact, which helped to specify the application area of such material.

INTRODUCTION

The dynamic development of technology and many new branches of industry force the necessity of the creation modern materials whose structure can be optimized in terms of their potential applications. In machine design, the important elements are kinematic pairs, in which the top surface layers of contacting elements play a crucial role and provide adequate reliability, durability, and the proper exploitation process of devices. The kinematic pairs usually work at continuous or periodic lubrication conditions using oils or greases. Many lubricants like motor oils contain chemical substances as additives, for example, molybdenum dithiocarbamate (MoDTC) or zinc dithiophosphate (ZnDTP). They are composed of complex organic molecules containing sulphur and phosphorus **[L. 1]**. Their operation mechanism is based on the chemical reactions that require high temperature and lead to the formation of compounds reducing the friction and limiting the wear, but it also leads to the formation of volatile harmful compounds **[L. 2]**. Nanoparticles are a modern group of lubricant additives, among which are fullerenes, transition metal dichalcogenides (MoS_2, SeS_2, of WS_2, NbS_2), as well as inorganic fullerene-like particles of WS_2, MoS_2 **[L. 3]** or carbon onion nanocrystallites, with a spheroidal, nested structure **[L. 4]**.

Among the numerous ways to reduce the adverse effects arising from the friction, the innovative technologies of surface layer modifications and coating deposition are used. They provide a means of producing new composite materials with significantly improved tribological properties in comparison to the base materials. The low-friction coatings based on materials with layered structures, such as MoS_2, WS_2 **[L. 5, 10, 12, 15]** or an amorphous carbon structure, can be used in highly loaded friction pairs **[L. 6, 7]** or in places where the use of lubricants is limited due to the environmental, structural, or hygienic reasons.

The good tribological properties of such low-friction coatings are provided by the formation of a sliding tribolayer on the counterpart **[L. 8, 9]**. Particularly difficult cooperation conditions occur during friction at elevated temperatures, when the source of heat is derived from the frictional heating and also from the external environment. Coatings destined for the use in such conditions should meet the standard mechanical requirements and exhibit improved oxidation resistance that is additionally activated by friction in hot air or exhaust gases. The oxidation process in such conditions is inevitable, so the solution for that problem was sought in the design of coatings that would form during friction producing an additional surface layer with good tribological properties **[L. 10–13]**. In this area, among others, the coatings of molybdenum disulphide are used. The latest literature studies show that the introduction of Ti, Nb, W elements into MoS_2, during coatings deposition, causes an increase in the coating hardness and wear resistance, an improvement in thermal stability, and a reduction in sensitivity to water vapour during friction **[L. 14**, **15]**, in comparison to undoped MoS_2.

EXPERIMENTAL

The self-lubricating properties in the process of friction were studied on a nanocomposite coating of molybdenum disulphide doped with titanium and tungsten (MoS_2(Ti,W)). The 3 µm thick coating was deposited by reactive magnetron sputtering on a model-based Vanadis 23 tool steel (AISI M3:2). The hardness of the heat-treated steel substrates was approx. 9 GPa. The hardness and elasticity modulus of the coating-substrate system were determined by the instrumental indentation method using Micro-Combi Tester (MCT) CSEM. Ten measurements with a Vickers indenter at 10 mN load were made in various places of the coating. The adhesion of the coatings to the substrates was determined by scratch testing according to the PN-EN 1071-3 standard also using a MCT. The tests were performed using a Rockwell C indenter with 0.2 mm tip radius at the following parameters: increasing load within 0.01 to 30 N range, 5 mm scratch length, and with a 5 mm/min relative speed of the indenter.

The ball-on-disc tests were carried out according to ISO 18535:2016 standard using a T-21 apparatus made by ITeE Radom. Tests were performed in dry sliding contact with a 6 mm diameter Al_2O_3 ball at room temperature RT as well as at elevated temperatures of 300ºC and 350ºC. The experiments were performed under 1, 2.5, and 5 N loads that corresponds to initial mean contact pressure in a stationary condition 0.38, 0.51, and 0.65 GPa, respectively. The following test parameters were applied: a sliding speed of 0.05 m/s, a friction radius of 4 mm, and the number of cycles equal to 20000 and 40000. Profiles of the grooves formed by friction were measured by a stylus profilometer. The coefficient of friction and a specific wear rate calculated as a ratio of the volume of removed material to the load and sliding distance were determined. The analysis of the coating's wear and the process of tribolayer formation were based on the wear tracks and the surfaces of the balls examined by light microscopy (LM) and scanning electron microscopy (SEM).

RESULTS

Micromechanical properties and adhesion of the coating to the substrate

The applied 10 mN load in indentation tests resulted in a 242 ±15 nm penetration depth of the intender, which is less than 10% of the coating thickness. Therefore, it could be concluded that the substrate did not affect the obtained results. The MoS_2(Ti,W) coating exhibits a small hardness of 6.1 ±1.9 GPa and a modulus of elasticity equal to 110 ± 20 GPa. Such parameters are related to the microstructure of the coating, which is composed of an amorphous matrix with embedded 3 – 8 nm size MoS_2 clusters and a very low amount of well distributed Ti (α) and W nanocrystallites phases **[L. 12]**.

The adhesion of the coating to the substrate in the scratch tests was determined by the critical load L_{C1}, which caused the first cohesive cracks, and L_{C2}, which cause adhesive cracks. The tested coating exhibits good adhesion to the substrate and, even at a maximum load of 30 N, total delamination was not observed. At 20 N load, the formation of cohesive cracks occurred. These cracks were curved in the direction of the indenter movement, and they did not propagate above the scratch track (**Fig. 1a**). The failure of the coating intensified with the increase in load, and above 25 N load, the adhesive destruction, spalling, and removing of the small coating areas from the substrate appeared (**Fig. 1b**).

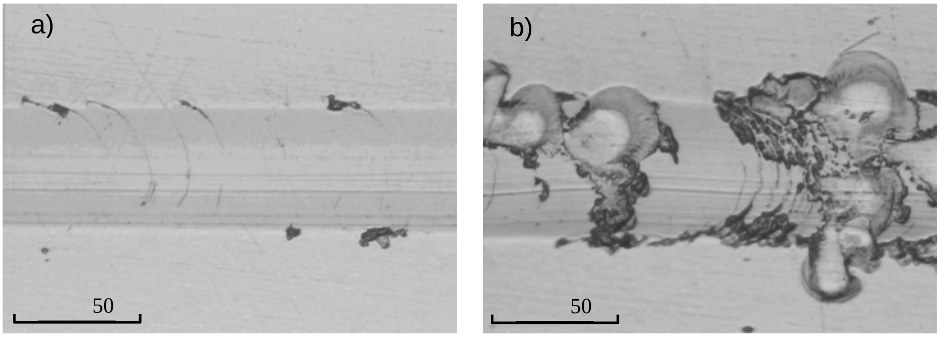

Fig. 1. Scratch track of the MoS_2(Ti,W) coating in the place where the specific cracks are formed: a) cohesive cracks, b) adhesive failure (LM, mag. 200x)

Rys. 1. Obrazy toru zarysowania powłoki MoS_2(Ti,W) w miejscu występowania: a) pęknięć kohezyjnych, b) zniszczeń adhezyjnych (LM, pow. 200x)

Tribological properties

The MoS_2(Ti,W) coating shows a very low resistance to motion during friction with the Al_2O_3 ball within the applied loads range, both at room temperature (RT) and 300°C. **Figure 2** presents the average value of friction coefficient determined from subsequent tests performed at RT under 1, 2.5, and 5 N load.

The friction process proceeded in several stages. In the initial stage, when the contact was forming, the resistance to motion was the highest (additionally, for the loads 1 and 2.5 N, it increased). Then, the resistance to motion reduced as a result of the self-lubricating tribolayer formation. The image of the ball surface with formed tribolayer is shown in **Fig. 6**.

After the formation of tribolayer, the cooperation was stable, and the friction coefficient has established in the 0.06-0.08 range. The alteration of the friction coefficient due to the load increase was evident only for the highest load. At 5 N load, the different nature of the changes in the friction coefficient was observed; at the early stage, its value rapidly decreased reaching its lowest level of 0.05. This behaviour could be due to the rapid formation of the sliding tribolayer as a result of the higher energy supplied to the system. The presence of tribolayer provides an easier sliding of cooperating parts, in spite of the greatest deformation in the contact zone caused by a load of 5 N. However, during the friction at elevated temperatures, the coefficient of friction at the initial stage was small (0.05) and increased with the time up to a value of 0.07 (**Fig. 2**). Exposure of MoS_2(Ti,W) coating to high temperatures results in the oxidation of the surface layers and the formation of variable oxides, such as MoO_3 **[L. 13**, **14]**, MoO_2 **[L. 12]** and TiO_2 **[L. 14]**.

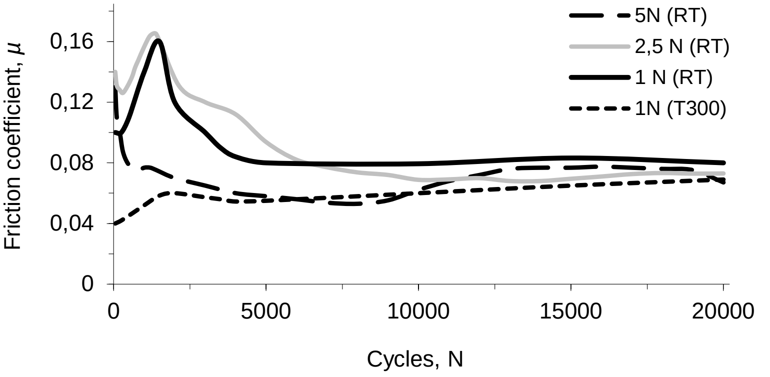

Fig. 2. Friction coefficient of the MoS_2(Ti,W) coatings in contact with Al_2O_3 ball at RT (F_n= 1; 2.5 i 5 [N]) and 300°C (F_n= 1 N)

Rys. 2. Współczynnik tarcia powłoki MoS_2(Ti,W) w styku z kulą Al_2O_3 podczas tarcia w RT (F_n= 1; 2,5 i 5 [N]) i 300°C (F_n= 1 N)

It is worth noticing that the influence of such oxide structures present in the friction on the wear and friction coefficient of molybdenum disulphide coating is inconclusive and needs further investigation. On the one hand, MoO_3 has a lamellar structure and a low shear strength in the direction of the surface plane, indicating an improvement in the tribological properties **[L. 17]**;

however, the nanocrystallites of MoO_3 present in the contact zone can cause a concentration of the contact stresses and the increase the wear in micro-regions **[L. 13, 14]**.

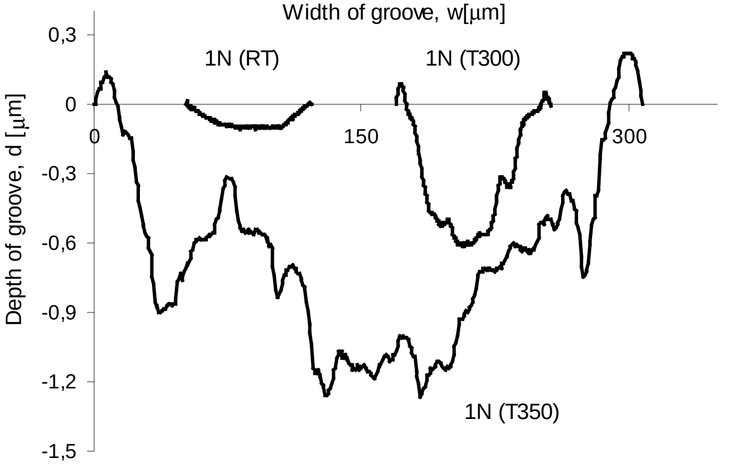

Fig. 3. Wear track profiles of the MoS_2(Ti,W) coatings after the tests at 1N and RT, 300°C and 350°C

Rys. 3. Profile toru tarcia powłoki MoS_2(Ti,W) po testach przy obciążeniu 1N i temperaturze RT, 300 i 350°C

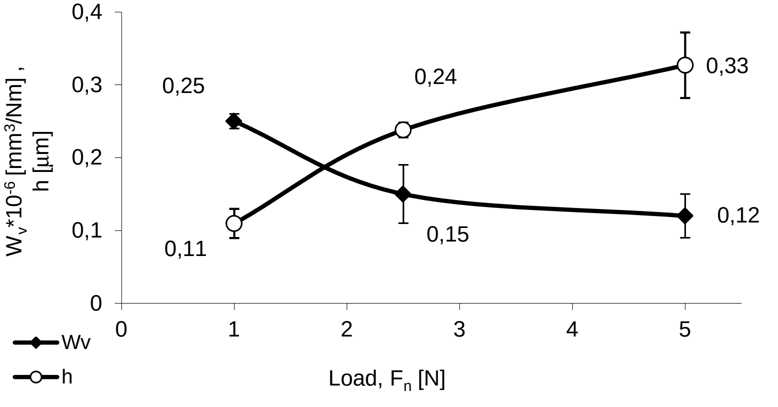

Fig. 4. Specific wear rate (W_v) of the MoS_2(Ti,W) coatings obtained at RT and 20000 cycles as well as groove depth (h)

Rys. 4. Wskaźnik zużycia objętościowego (W_v) powłok MoS_2(Ti,W) określony po tarciu w RT w zakresie do 20000 cykli oraz głębokość bruzdy (h)

This behaviour was found during friction at an elevated temperature up to 300°C, where the wear of the coating was 4-fold higher than during the friction at RT, despite the favourable conditions for the creation of a sliding tribolayer (the lowest friction coefficient equal to 0.07). In addition, doubling exposure to high temperatures (in the test at 40000 cycles) caused an increase in the resistance to motion and a particular reduction in the wear resistance.

The resulting hard oxides, mainly MoO_2 intensify the abrasion process of coating, and hence the wear index equals to 2.3 ±0.13*10^{-6} mm^3/Nm determined from the tests with 40000 cycles was twice as large Wv=1.15 ±0.11* 10^{-6} mm^3/Nm as determined after 20000 cycles. Under these conditions, the depth of the groove was the largest and reached 0.53 microns after 20000 cycles and 1.09 microns after 40000 cycles. Definitely more severe conditions of cooperation occurred during friction at 350°C, where non uniform and several times larger wear (**Fig. 3**) and local chipping of the coating from the substrate were found.

a) b) c)

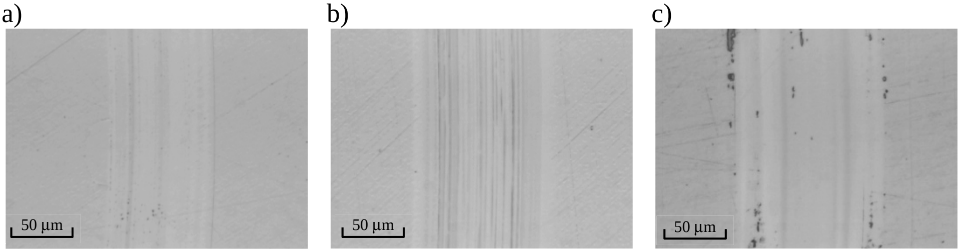

Fig. 5. Wear tracks of the MoS_2(Ti,W) coating after friction under 20000 cycles: a) at 1 N, RT; b) at 5 N, RT; c) at 1 N, 300°C (LM, mag. 200x)

Rys. 5. Obrazy toru tarcia powłoki MoS_2(Ti,W) po 20000 cykli; a) przy 1 N, RT; b) przy 5 N, RT; c) przy 1 N, 300°C (LM, pow. 200x)

a) b) c)

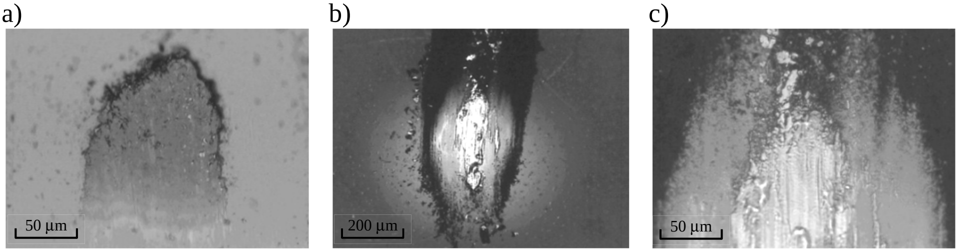

Fig. 6. Tribolayer formed on Al_2O_3 ball after friction with MoS_2(Ti,W) coating under 20000 cycles; a) at 1 N, RT; b), c) at 1 N, 300°C (LM, mag. 50x, 200x)

Rys. 6. Tribowarstwa na powierzchni kuli Al_2O_3 po tarciu z powłoką MoS_2(Ti,W) po 20000 cykli; a) przy 1 N, RT; b), c) przy 1 N, 300°C (LM, pow. 50x, 200x)

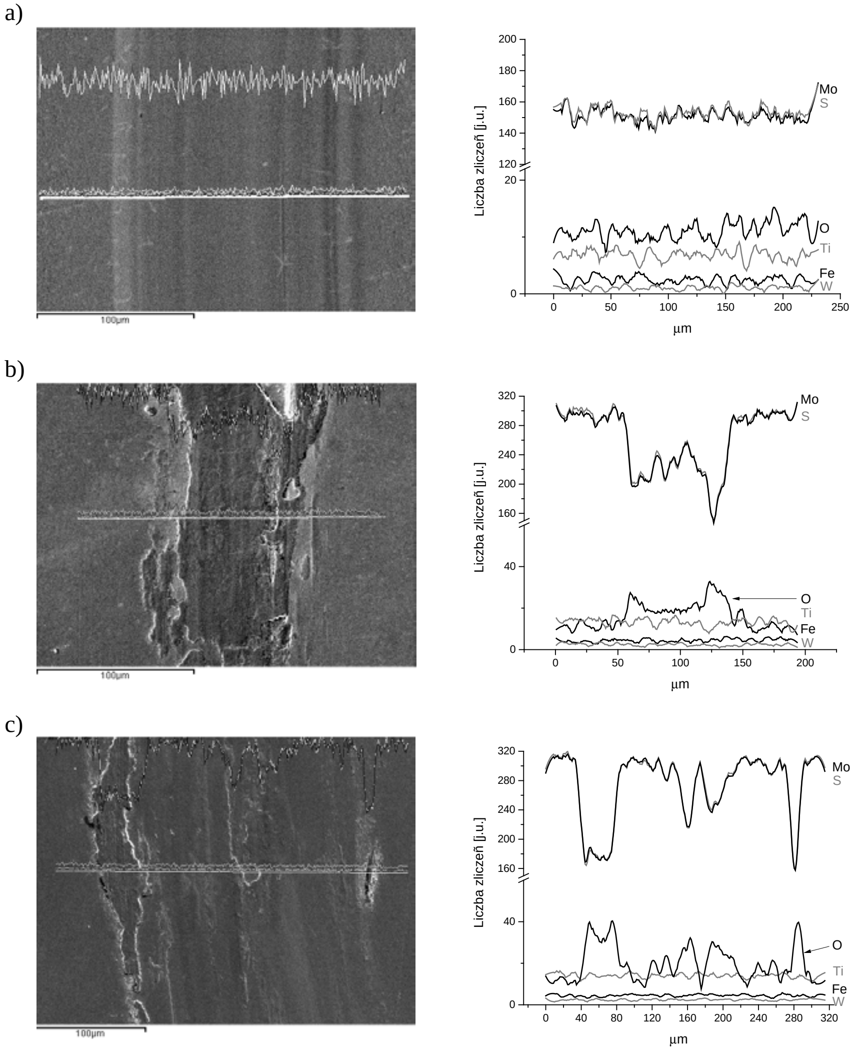

Fig. 7. SEM-EDS analysis from the line crossing the wear track created at: (a) 5N, 20000 cycles, RT; (b) 1N, 20000 cycles, 300°C; and, (c) 1N, 40000 cycles, 300°C

Rys. 7. Analiza SEM-EDS z linii poprowadzonej przez tor tarcia powstały przy: a) 5N, 20000 cykli, RT; b) 1N, 20000 cykli, 300°C; c) 1N, 40000 cykli, 300°C

The durability of the tribolayer significantly affects the friction coefficient and wear resistance, because it protects the surface of the coating from direct contact with the counterpart material. This is of particular importance during friction at elevated temperatures, when the adhesion of tribolayer to the counterpart is hindered due to thermal effects in the surroundings of the friction pair.

CONCLUSION

Molybdenum disulphide coatings are an interesting group of self-lubricating materials for use at elevated temperatures. In order to further enhance the coatings mechanical properties and thermal resistance, Ti and W atoms are introduced into the MoS_2 structure.

The test results indicate that the friction coefficient of the MoS_2(Ti,W) composite coating decreased with an increase in the contact load and the temperature in the location of the friction pair. This behaviour was related to the influence of both load and temperature on the dynamics of process of the layer formation, which determines the sliding properties. The tribolayer was composed mainly of the wear products of a coating and was the source of the substrates for the oxidation reaction. This layer and MoS_2(Ti,W) coating created a self-lubricating system with a friction coefficient in the 0.06-0.08 range. The wear resistance of MoS_2(Ti,W) coatings was four times lower at 300°C than at RT.

Wear intensity was strongly dependent on the lifetime of the tribolayer formed on a counterpart, especially under the influence of elevated temperatures. After a tribolayer is continuous and well separates the surfaces of the cooperating elements, the favourable conditions for a sliding and the low wear rate exist. The temperature increase in the contact zone is unfavourable for the adhesion of the tribolayer to the counterpart and leads to its destruction, which was particularly observed during the friction at 350°C. As a result of investigation, 300°C was established as a limiting operating temperature for MoS_2(Ti,W) coating on Vanadis 23 steel in sliding point contact.

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Streszczenie

W pracy przedstawiono analizę procesu tarcia i zużycia kompozytowej powłoki na bazie dwusiarczku molibdenu dotowanego wolframem i tytanem z uwzględnieniem wpływu obciążenia i temperatury w strefie styku. Badania tribologiczne przeprowadzono w temperaturze pokojowej oraz 300°C i 350°C w niesmarowanym styku ślizgowym z kulą Al_2O_3. Dokonano charakterystyki właściwości mikromechanicznych oraz zbadano adhezję powłok do stalowego podłoża metodą zarysowania. W analizie zużycia powłoki i procesu tworzenia ślizgowej tribowarstwy posłużono się wynikami obserwacji powierzchni tarcia przy użyciu mikroskopii świetlnej (LM) oraz elektronowej mikroskopii skaningowej (SEM). Nieduża twardość powłoki

MoS_2(Ti,W) wynosząca 6 GPa, której struktura jest głównie amorficzna, pozwala na szybkie dopasowanie styku tribologicznego i utworzenie ślizgowej tribowarstwy. Dzięki samosmarnym właściwościom powłoka charakteryzuje się dobrą odpornością na zużycie i bardzo niskim współczynnikiem tarcia (poniżej 0,1), zarówno w temperaturze pokojowej, jak i w temperaturze podwyższonej. Badania umożliwiły wyznaczenie granicznej temperatury pracy układu powłoka/podłoże w ślizgowym styku skoncentrowanym, co jest pomocne w określeniu obszaru aplikacyjnego materiału.