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PROPERTIES OF A TRIBOLOGICAL SYSTEM WITH A DIAMOND-LIKE CARBON COATING LUBRICATED WITH ENVIRONMENTALLY FRIENDLY CUTTING FLUID

WŁAŚCIWOŚCI SYSTEMÓW TRIBOLOGICZNYCH Z POWŁOKAMI DIAMENTOPODOBNYMI SMAROWANYMI WYBRANYMI PROEKOLOGICZNYMI CIECZAMI

Key words: non-toxic cutting fluid, a-C:H:Si coating, 100Cr6 steel, friction, wear.

Abstract This article presents experimental results obtained for an a-C:H:Si coating deposited on a 100Cr6 steel disc in sliding contact with a 100Cr6 steel ball in the presence of zinc aspartate-based cutting fluid. The study involved scanning electron microscopic examinations, contact angle measurements, tribological tests, and surface texture analysis. The experimental data suggest that the tribological properties of the diamond-like carbon (DLC) coating are satisfactory and that the non-toxic cutting fluid is well-suited to replace conventional fuels, which are toxic.

Słowa kluczowe: nietoksyczne chłodziwo, powłoka a-C:H:Si, stal 100Cr6, tarcie, zużycie.

Streszczenie Przedstawiono wyniki badań tribologicznych powłoki a-C:H:Si naniesionej na stali 100Cr6. Badania te przeprowadzono na testerze T-01 M pracującym w skojarzeniu trącym kula–tarcza w ruchu ślizgowym. Testy zrealizowano w warunkach tarcia technicznie suchego i ze smarowaniem chłodziwem zawierającym asparginian cynku oraz konwencjonalnym chłodziwem na bazie oleju mineralnego. Ponadto wykonano badania identyfikacji pierwiastków wchodzących w skład powłoki a-C:H:Si, pomiar kąta zwilżania oraz analizę struktury geometrycznej powierzchni tarcz przed oraz po testach tribologicznych. Zastosowane w badaniach nietoksyczne chłodziwo wpłynęło na zmniejszenie zużycia liniowego, co bezpośrednio wpłynęło na mniejsze ślady wytarcia. Powłoka a-C:H:Si charakteryzowała się zadowalającymi właściwościami tribologicznymi.

INTRODUCTION

Diamond-like carbon (DLC) coatings are widely used because of their very good tribological properties, including a low coefficient of friction and high wear resistance, good mechanical properties, especially high hardness, and also an aesthetic function. To further improve the parameters of DLC coatings, elements such as Ti, Si, or W can be added. The tribological properties of DLC coatings are good both when they act as dry film lubricant coatings and when a 'regular' lubricant is present. When two surfaces slide against each other, it is certain that the softer material will wear out faster. The protective film that forms at the interface protects the DLC coating surface against wear and reduces the coefficient of friction, because the material has a graphite-like structure, which allows it to function as a lubricant. A DLC coating applied on one element of the pair of surfaces in contact does offer higher hardness than the other material, but there will still be some evidence of wear.

Most of today's mechanical systems operate under large loads, at high temperature (approx. 500°C), and in corrosive environments. This is particularly true for machining processes [**L. 1**], which are common in the manufacturing sector [**L. 2**]. In machining, an element is shaped by removing unwanted material with a cutting tool [**L. 2, 3**], which undergoes wear [**L. 2**]. The friction

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between the tool and the workpiece that occurs during machining generates heat, which has a negative effect both on the tool and the workpiece. Cutting fluids are thus required to reduce the temperature at the interface. Cutting fluids also have other functions: they reduce friction and tool wear, improve the workpiece surface quality, transport chips, and prevent the thermal expansion of the workpiece [**L. 4–7**].

Metalworking fluids generally have mineral oil as the base oil and many different additives such as sulphur, chloride, and phosphorus [**L. 8–10**]. They also contain biocides to eliminate bacteria. Some cutting fluids are carcinogenic, because of the presence of a large number of additives. As such, they pose a serious threat to the environment: soil, air, and water. Spent cutting fluids are considered hazardous waste by many environmental organizations and legal institutions. According to Health, Safety and Environment (HSE) regulations [**L. 11**], operators frequently exposed to cutting fluids are likely to suffer from skin diseases, such as allergy, oil acne, and hyperpigmentation. HSE data concerning occupational diseases reveal that as many as 23% of the patients with eczema have occasionally been exposed to cutting fluids [**L. 7**]. Fatal cases have also been reported. A good solution is to use non-toxic cutting fluids based on vegetable oils, whose advantages include nontoxicity, recyclability, environmental friendliness, and biodegradability. Such fluids are also characterized by good lubricity, low volatility, low emission of hydrocarbons, and good thermal properties [**L. 12**]. Presently, much of the research on the subject focuses on the performance of cutting fluids based on vegetable oils, e.g., soya oil, castor oil, palm oil, etc. [**L. 12–14**].

MATERIALS

a-C:H:Si coating

The experiments were conducted for an a-C:H:Si coating produced by plasma-assisted physical vapour deposition (PAPVD). The coating was deposited on 100Cr6 bearing steel characterized by high hardness, high abrasion resistance, high fatigue strength, and appropriate ductility. The steel is quenched in oil after austenitization at 820–840°C and then tempered at 150–180°C for 2 h. 100Cr6 steel can be used for cold working, and its hardness after heat treatment (thermal hardening) should be above 62 HRC. The chemical composition of the material is shown in **Table 1**.

Table 1. Composition of 100Cr6 steel
Tabela 1. Skład chemiczny stali 100Cr6

Element	**C**	**Mn**	**Si**	**P**	**S**	**Cr**	**Al**	**Ni**	**Mo**	**W**	**V**	**Co**	**Cu**	**O**
Content, %	0.93–1.05	0.25–0.45	0.15–0.35	< 0.025	< 0.030	1.35–1.60	< 0.1	–	–	–	–	–	<0.30	<0.0015

Cutting fluids

The tests were carried out using a non-toxic metalworking fluid containing alkanolamine borate, which is a biodegradable oligomer – zinc aspartate, and DEMI water. Its biostability is due to the presence of zinc polyaspartate, which is responsible for good lubrication of the moving parts in a machine tool, having a positive effect on its maintenance. The zinc ion present in the cutting fluid is not toxic to the human organism. The physical and chemical properties of the non-toxic cutting fluid are shown in **Table 2**.

Table 2. Properties of the zinc aspartate-based cutting fluid
Tabela 2. Właściwości cieczy chłodząco-smarującej zawierającej asparginian cynku

Colour	**Odour**	**Density, g/cm³**	**Solubility in water**
from orange to red	mild, non-irritant	1.200–1.250	soluble

Table 3. Main parameters of the cutting fluid containing mineral oil
Tabela 3. Podstawowe parametry cieczy chłodząco-smarującej zawierającej olej mineralny

Colour	**Odour**	**Mineral oil content**	**Density, g/cm³**	**Solubility in water**
yellowish-brown	mineral oil-like	56%	0.92–0.96	soluble

The non-toxic cutting fluid was compared with a conventional metalworking fluid based on mineral oil, which is used for the machining of steel, cast steel, non-ferrous metals, aluminium alloys, brass, and copper. Its basic parameters are given in **Table 3**.

METHODS

The investigations aimed at assessing the tribological properties of the a-C:H:Si coating.

Scanning electron microscopy (SEM/EDS)

A JSM-7100F scanning electron microscope equipped with an EDS microanalyser was employed to measure the thickness of the a-C:H:Si coating and identify the elements present in it.

Contact angle measurement

The contact angle was determined using an Attension Theta tensiometer from Biolin Scientific. The measurement involved placing a drop of the fluid tested (approx. 4 µl) on the surface of a metal specimen. The drop behaviour was registered for about 10 seconds by means of a superfast USB3 video camera with a frame rate of up to 3009 fps. The results subjected to analysis were those obtained about 0.2 seconds after the drop was placed on the surface, which were averaged and then represented graphically in Excel.

The measurements were performed for both cutting fluids (vol. 1%, 2.5% and 5%), distilled water, alcohol, and glycerine placed on 100Cr6 steel specimens coated with a-C:H:Si.

Surface texture analysis

A Talysurf CCI Lite optical profiler was employed to analyse the surface texture of the specimens before and after the tribological tests.

Tribological tests

The tribological tests were performed using a T-01M system for a ball-on-disc configuration with an uncoated 100Cr6 steel ball and an a-C:H:Si coated 100Cr6 steel disc. The tests were carried out in accordance with the ASTM G 99 standard at the following parameters: load P = 50 N, sliding speed v = 0.1 m/s, sliding distance s = 1000 m, relative humidity 40 ± 5%, and ambient temperature T_0 = 23±1°C. Dry friction and lubricated friction conditions were analysed. Cutting fluids containing zinc aspartate and a cutting fluid based on mineral oil, Bechem Avantin 361, were used.

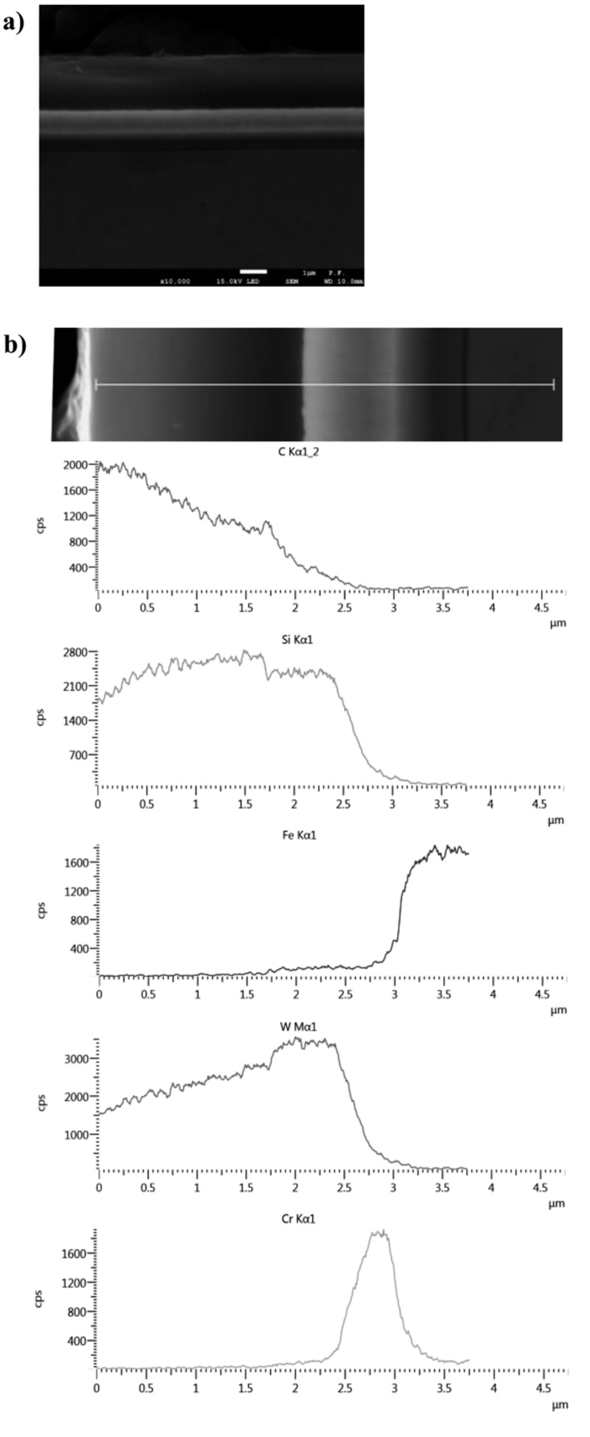

Fig. 1. SEM data for the a-C:H:Si coating: a) cross-sectional view, b) EDS results

Rys. 1. Wyniki badań uzyskane za pomocą mikroskopii skaningowej SEM oraz mikroanalizy rentgenowskiej EDS: a) przekrój poprzeczny powłoki a-C:H:Si, b) analiza EDS

RESULTS AND DISCUSSION

SEM/EDS data for the a-C:H:Si coating

Figure 1 illustrates results of the SEM analysis obtained for the a-C:H:Si coating. **Figure 1a** shows a cross-sectional view of the 3.1 µm thick coating deposited on 100Cr6 steel.

The results of the EDS analysis provided in **Figure 1b** confirm that the main elements of the coatings are carbon and silicon. It can be seen, however, that the interlayer formed at the interface consists of tungsten and chromium, which ensure good adhesion of the coating to the substrate.

Contact angle measurement

The contact angle measurements were performed for cutting fluids (vol. 1%, 2.5% and 5%), distilled water, alcohol, and glycerine. An Attension Theta tensiometer was used. **Figures 2–4** show the average values from five measurements taken for the a-C:H:Si coated 100Cr6 steel discs with 5 percent error bars.

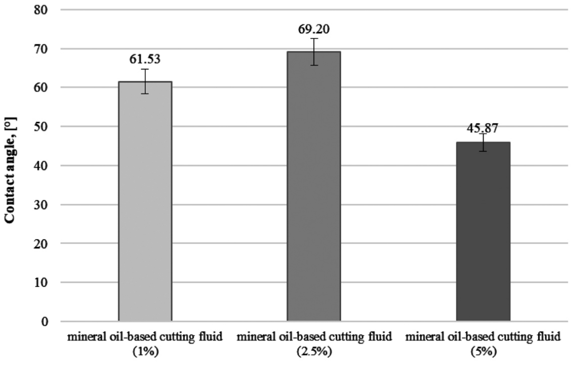

Fig. 2. Contact angle of the mineral oil-based cutting fluid on a 100Cr6 steel disc coated with a-C:H:Si

Rys. 2. Kąt zwilżania chłodziwa na bazie oleju mineralnego powierzchni tarczy ze stali 100Cr6 z naniesioną powłoką a-C:H:Si

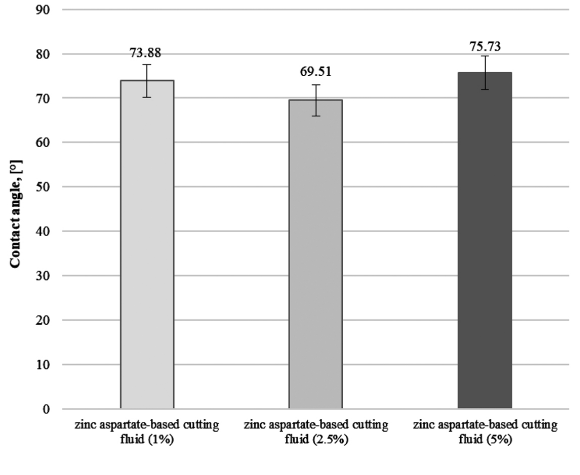

Fig. 3. Contact angle of the cutting fluid containing zinc aspartate on an a-C:H:Si coated 100Cr6 steel disc

Rys. 3. Kąt zwilżania chłodziwa z asparginianem cynku powierzchni tarczy ze stali 100Cr6 z naniesioną powłoką a-C:H:Si

The smallest contact angle, and consequently the best wetting, was reported for alcohol. The worst wetting was observed for glycerine (98.61). The result, which is greater than 90°, suggests that glycerine does not wet the a-C:H:Si coating.

From the comparative analysis of the contact angles obtained for the two cutting fluids, it is clear that smaller contact angles were recorded for the cutting fluid based on mineral oil than for the cutting fluid containing zinc aspartate. This indicates that the mineral oil-based cutting fluid offers better wetting.

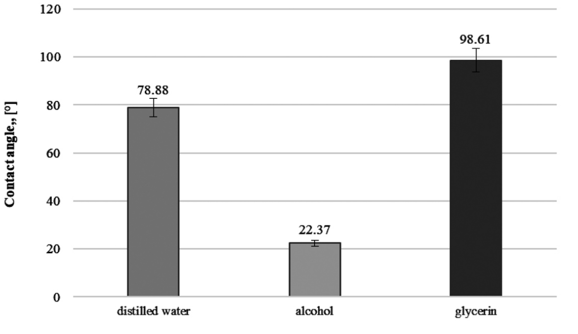

Fig. 4. Contact angle of distilled water, alcohol and glycerin on a 100Cr6 steel disc coated with a-C:H:Si

Rys. 4. Kąt zwilżania wodą destylowaną, alkoholem oraz gliceryną powierzchni tarczy ze stali 100Cr6 z naniesioną powłoką a-C:H:Si

The smallest contact angles of the mineral oil-based cutting fluid and the cutting fluid containing zinc aspartate were observed when their concentrations were 5% and 2.5%, respectively.

Surface texture before the tribological tests

Figure 5 shows the surface topography and the surface roughness profile obtained for the disc coated with a-C:H:Si before the tribological tests.

The isometric view and the primary profile of the a-C:H:Si coated 100Cr6 steel in **Figure 5** show that the surface is smooth with peaks of approx. 0.03 μm and valleys of about 0.05 μm.

Tribological tests

Figure 6 shows the coefficients of friction registered under dry friction conditions and under lubricated friction conditions for both cutting fluids.

The lowest average coefficient of friction was reported under lubricated friction conditions when the reference cutting fluid, i.e., the one based on mineral oil, was used ($\mu \cong 0.11$). The highest average coefficient of friction was observed under dry friction conditions ($\mu \cong 0.53$).

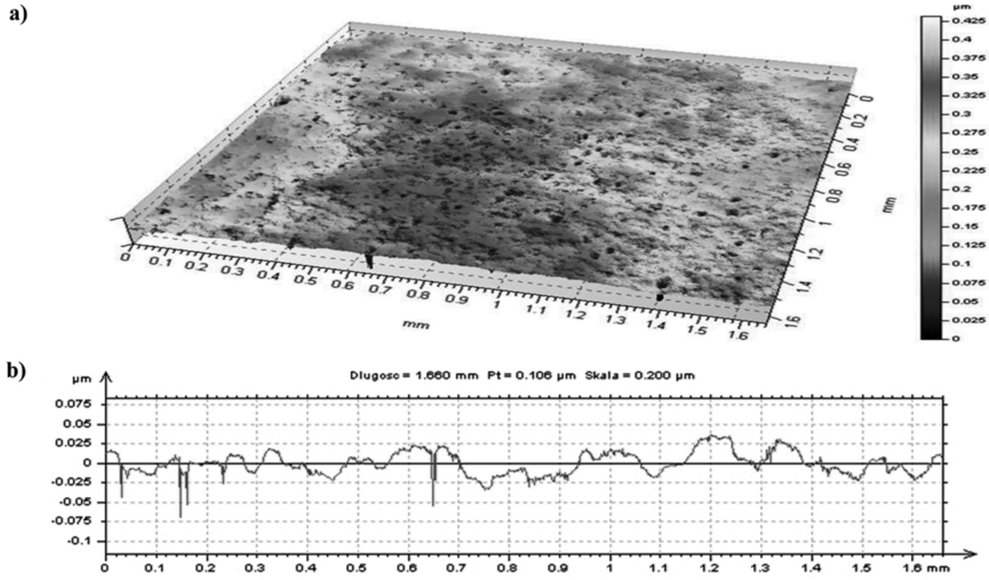

Fig. 5. Surface texture of the 100Cr6 steel disc coated with a-C:H:Si: a) isometric view, b) primary profile

Rys. 5. Struktura geometryczna powierzchni tarczy ze stali 100Cr6 z powłoką a-C:H:Si: a) obraz izometryczny, b) profil pierwotny

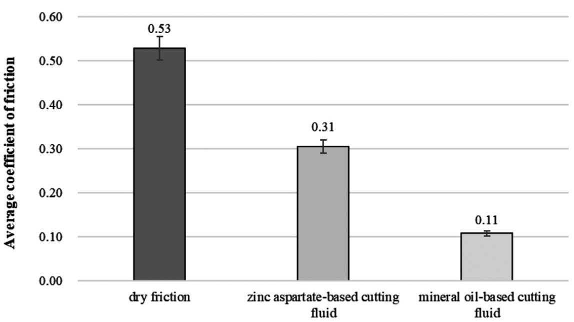

Fig. 6. Average values of the coefficient of friction obtained for the a-C:H:Si coating under dry and lubricated friction conditions

Rys. 6. Średnie współczynniki tarcia w zależności od substancji smarowej dla powłoki a-C:H:Si

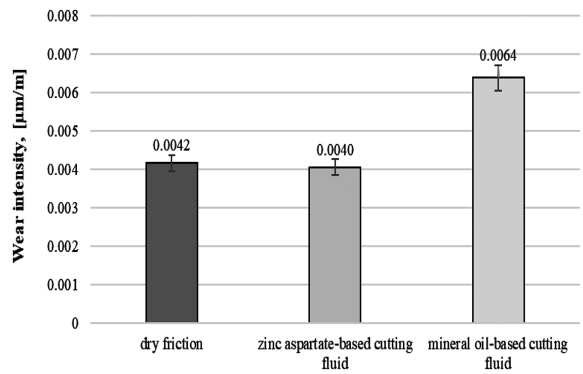

Fig. 7. Wear intensity for the a-C:H:Si coating depending on the friction conditions

Rys. 7. Intensywność zużywania liniowego w zależności od substancji smarowej dla powłoki a-C:H:Si

Figure 7 shows the intensity of linear wear under dry friction conditions and under lubricated friction conditions for both cutting fluids.

The lowest intensity of linear wear was reported after tests when the cutting fluid containing zinc aspartate was used. The highest value was observed after friction tests carried out for the cutting fluid based on mineral oil.

Surface texture after the tribological tests

Figures 8–10 show the surface topographies and roughness profiles obtained for the a-C:H:Si coated discs after the tribological tests under different friction conditions.

After the tribological tests, the shallowest wear track of about 0.4 µm was observed after friction in the presence of the cutting fluid containing zinc aspartate. The highest wear, which was similar to that reported for the configuration operating under dry friction conditions, was observed after the tribological tests when the cutting fluid containing mineral oil was used.

Table 4 shows the surface texture parameters measured before and after the tribological tests.

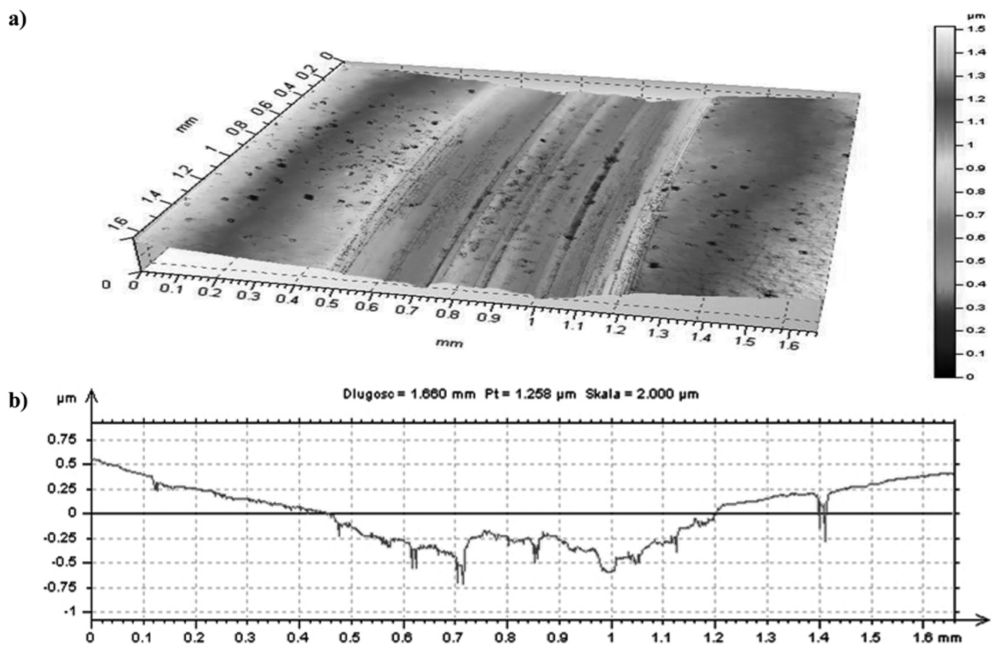

Fig. 8. Surface texture of a 100Cr6 steel disc coated with a-C:H:Si after dry friction: a) isometric view, b) primary profile

Rys. 8. Struktura geometryczna powierzchni tarczy ze stali 100Cr6 z powłoką a-C:H:Si: a) obraz izometryczny, b) profil pierwotny po tarciu technicznie suchym

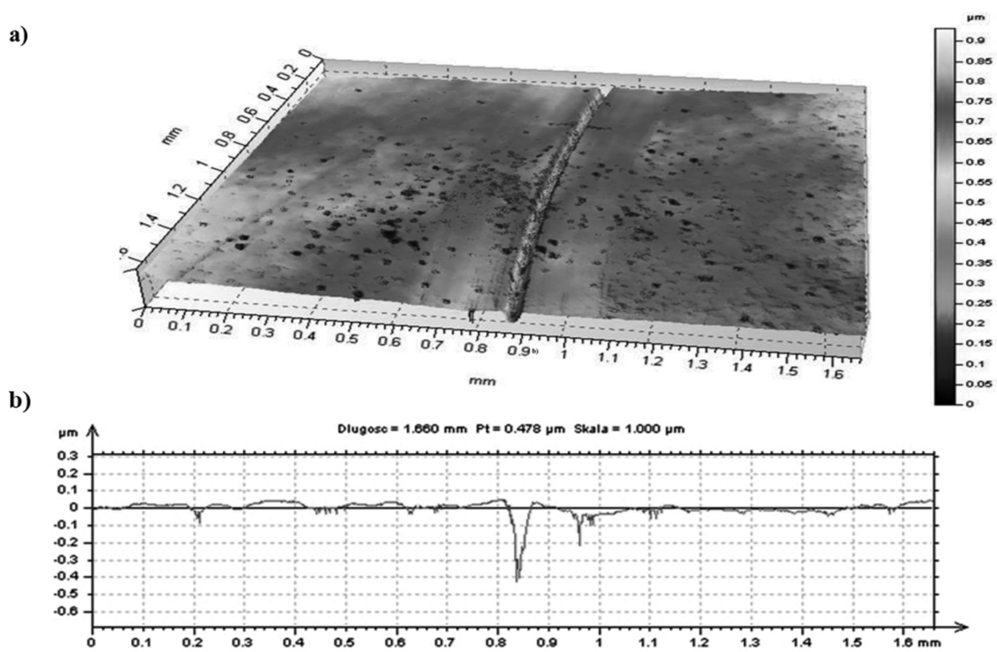

Fig. 9. Surface texture of a 100Cr6 steel disc coated with a-C:H:Si after tests with the cutting fluid containing zinc aspartate: a) isometric view, b) primary profile

Rys. 9. Struktura geometryczna powierzchni tarczy ze stali 100Cr6 z powłoką a-C:H:Si: a) obraz izometryczny, b) profil pierwotny po tarciu ze smarowaniem chłodziwem z asparginianem cynku

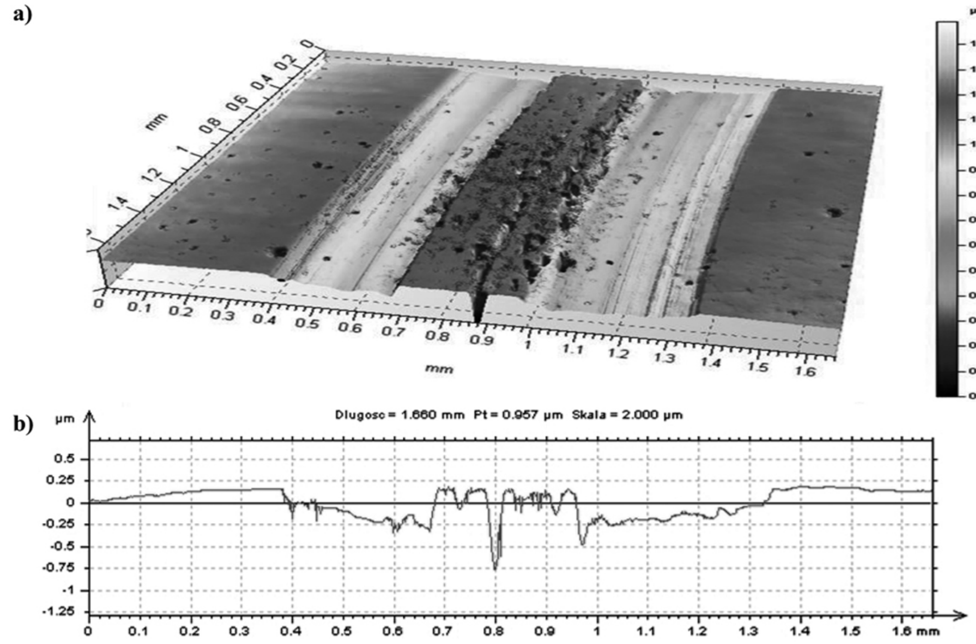

Fig. 10. Surface texture of a 100Cr6 steel disc coated with a-C:H:Si after tests with the cutting fluid containing mineral oil: a) isometric view, b) primary profile

Rys. 10. Struktura geometryczna powierzchni tarczy ze stali 100Cr6 z powłoką a-C:H:Si: a) obraz izometryczny, b) profil pierwotny po tarciu ze smarowaniem chłodziwem z olejem mineralnym

Table 4. Surface texture parameters for 100Cr6 steel discs coated with a-C:H:Si

Tabela 4. Parametry struktury geometrycznej powierzchni tarcz ze stali 100Cr6 z naniesioną powłoką a-C:H:Si

Test conditions	Disc	Surface roughness parameters						
		Sa [µm]	Sq [µm]	Sp [µm]	Sv [µm]	Sz [µm]	Ssk [–]	Sku [–]
No friction	a-C:H:Si	0.03	0.04	0.16	0.28	0.43	–1.65	11.39
Dry friction	a-C:H:Si	0.11	0.16	0.54	2.86	3.40	–3.57	41.02
Lubricated friction (zinc aspartate-based cutting fluid)	a-C:H:Si	0.11	0.16	0.42	2.21	2.63	–2.93	21.50
Lubricated friction (mineral oil-based cutting fluid)	a-C:H:Si	0.15	0.23	0.92	2.96	3.88	–3.14	26.82

The lowest values of the amplitude parameters, Sa, Sq, Sp, Sv, Sz, Ssk, and Sku, were obtained for the a-C:H:Si coating before the tribological tests. The disc had a smooth plateau-like surface with peaks characterized by gentle slopes and rounded tops. After the tribological tests, the lowest values of the surface texture parameters were observed after friction with the zinc aspartate-based cutting fluid. The highest values of the amplitude parameters Sa, Sq, Sp, Sv, and Sz were reported under lubricated friction conditions when the cutting fluid based on mineral oil was used. However, the highest values of the parameters Ssk and Sku were observed under dry friction conditions, this indicates that the surface had a plateau texture with many irregularities, i.e., deep valleys and high peaks.

CONCLUSIONS

The research described in this article keeps up with the current trends to look for stronger engineering materials and eco-friendly lubricants. Because of the new legal and health and safety requirements concerning metalworking fluids, research in this field is focused on cutting fluids that are non-toxic and therefore safe to operators and the environment.

The results of this study show that the structure of the coating formed by PAPVD was the same as that predetermined at the design stage. The elemental analysis of the a-C:H:Si-type diamond-like carbon coating confirmed the presence of carbon and silicon and chromium and tungsten, which constituted the interlayer responsible for better adhesion of the coating to the steel substrate.

The tribological tests showed that the lowest coefficient of friction was reached under lubricated friction conditions when mineral oil-based fluid was used. However, the lowest intensity of wear was recorded in the presence of the zinc aspartate-based cutting fluid.

From the isometric views, primary profiles and roughness parameters obtained for the discs after the tribological tests, it is evident that the use of the non-toxic fluid containing zinc aspartate resulted in the shallowest wear track and the lowest values of the amplitude parameters. The deepest wear track and the lowest values of the roughness parameters, Sa, Sq, Sp, Sv, and Sz, were obtained under lubricated friction conditions in the presence of the mineral oil-based cutting fluid.

The performance of the non-toxic fluid when in contact with the a-C:H:Si coating was better than that of the cutting fluid containing mineral oil. This non-toxic fluid is safe for operators and the environment, and it also conforms to the requirements set by the European Union and Poland.

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