Piotr DUDA[*], Karolina JURKIEWICZ[**], Sławomir KAPTACZ[*], Piotr SALWA[*]

TRIBOLOGICAL CHARACTERISTICS OF CARBON MATERIALS SUBJECTED TO ANNEALING INTENDED FOR USE IN HEART VALVES

CHARAKTERYSTYKI TRIBOLOGICZNE MATERIAŁÓW WĘGLOWYCH PODDANYCH WYGRZEWANIU PRZEZNACZONYCH NA PŁATKI ZASTAWEK SERCA

Key words:

glassy carbon, tribological characteristics, hardness, geometric surface texture

Słowa kluczowe:

węgiel szklisty, charakterystyki tribologiczne, twardość, struktura geometryczna powierzchni

Abstract

Carbon materials such as glassy carbon or C/C composites do not always meet the requirements set down for them in technical and biomechanical applications. The most important problem of the manufacturing process that the authors have managed to overcome was the elimination of internal cracks, which cause

[*] Institute of Computer Science, Faculty of Computer Science and Materials Science, University of Silesia, ul. Będzińska 39, 41-200 Sosnowiec, Poland, e-mail: piotr.duda@us.edu.pl.

[**] A. Chełkowski Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland; Silesian Center for Education and Interdisciplinary Research, ul. 75 Pułku Piechoty 1A, 41-500 Chorzów, Poland.

splitting, in the finished samples. The resulting uniform research material, due to the extremely sensitive implantation site, must meet the following numerous requirements: have high mechanical and chemical strength, exhibit biotolerance, and have high resistance to tribological wear. The paper presents the results of tribological, stereometric, and micromechanical tests of carbon materials that were annealed in a graphite furnace at temperatures of 1500°C, 2000°C, and 2500°C. In order to analyse tribological characteristics, a methodology for performing tests on the ball-on-disk apparatus (T-01 testing machine) was developed that reflect load conditions prevailing in the real node. The tribological tests of glassy carbon confirmed predictions that the temperature of manufacturing has a big impact on its tribological properties, and a higher temperature of annealing does not always improve the material properties.

INTRODUCTION

Directed flow and prevention of the backflow of blood from the atria to the ventricles are the important roles that valves play in the human heart **[L. 1]**. Cardiovascular diseases such as atherosclerosis and infarction may also cause pathologies within the work or the construction of heart valves. Damage to the valve leads to the narrowing of outlets or reverse leakage, or regurgitation. However, drug therapy is not always possible or sufficient. When pharmacological treatment is not possible, attempts are made to correct the impaired valve surgically or eventually replace it **[L. 2]**.

Mechanical valves, as compared to valves of biological origin, are characterized by high durability. Their design and the materials from which they are made enable one to estimate their longevity at 30-50 years. For this reason, they are intended for young and middle-aged patients, since they reduce the risk of reoperation in the case of their dysfunction **[L. 3]**. High thrombogenicity, manifested by the formation of blood clots on the implant, is one of the biggest disadvantages of mechanical valves. The tribological cooperation signs of wear are conducive to this phenomenon.

The most commonly used mechanical valves have a monoleaflet or bileaflet construction **[L. 4** and **5]**. Common materials from which the valve leaflets are made are carbon materials, especially pyrolytic carbon and glassy carbon. The task of the Interdepartmental Laboratory of Structural Research at the University of Silesia was to obtain such material for the purposes of cardiac applications. In the initial stage of developing the manufacturing technology, they had to face the problem of high internal stresses, which resulted in the sample cracking. At the present stage, the manufacturing technology is being modified in order to improve the tribological and mechanical properties. The positive effects of annealing that the authors expect to see are a reduction in the friction coefficient and wear intensity as well as a reduction in hardness and the modulus of elasticity as compared to the sample that has not been subjected to the process.

RESEARCH MATERIAL

The research material was the shields of glassy carbon obtained with the technologies that have been known and used for several decades **[L. 6–8]**. The test samples were prepared by pyrolysis of a polymer of furfuryl alcohol. The polymerization of furfuryl alcohol (purchased from SAFC, purity ≥ 98%) was initiated by adding 5% (v/v) of 0.1 molar solution of p-toluenesulfonic acid (purchased from Acros Organics, 99% purity) in ethanol. In order to obtain a homogeneous distribution of the catalyst in the precursor, a magnetic stirrer was used. After 30 hours of stirring, the resulting resin was poured into moulds having a diameter of about 30mm and a thickness of about 5 mm. The moulds were then placed in a furnace to cure the cross-linked resin. The drying temperature was raised at a rate of 40°C/24 h to 100°C and 80°C/24 h to a final temperature of 200°C. After removing the moulds, the disks of polymerized resin were pre-polished with sandpaper. The polymer samples thus prepared were annealed in a quartz tube furnace equipped with a temperature controller, under an inert atmosphere of argon. The heating rate was 10°C/h to achieve 200°C, 3°C/h to 700°C, and 5°C/h to achieve a final temperature of 980°C. The final pyrolysis temperature was maintained for 2 hours, and then the samples were cooled to room temperature under a flow of argon. During the thermal decomposition process, there was a large weight loss due to the release of gaseous decomposition products. The average linear shrinkage of the sample thickness was about 20%.

The obtained disks of glassy carbon were divided into four parts. The first part was not subjected to further heat treatment. The other parts were annealed in a graphite furnace at temperatures of 1500°C, 2000°C, and 2500°C, respectively, under a flow of argon. The samples placed in the furnace were covered with carbon black to prevent thermal shocks and cracking of the prepared disks. The heating rate in the high-temperature processing was 4°C/min from room temperature to the desired temperature of pyrolysis with a stage of heating at that temperature for 2 hours. Then the samples were cooled under a flow of argon to room temperature and purified from the remaining carbon black. Next, the samples were labelled with maximum annealing temperatures (980, 1500, 2000, and 2500).

The samples for tribological, stereometric, and hardness tests were prepared using the above technology. The external appearance of the samples after cold mounting is shown in **Fig. 1**. The mounting was performed in order to enable the measurement of hardness, fit the shield size to the handle in the tribotester, and allow for semi-automatic polishing. Various diameters of disks caused by considerable shrinkage at the various stages of the technological process of manufacturing carbon materials could significantly impede multiple measurements. The samples, after tribological tests, were measured using a surface profilometer and microhardness tester, and then for any subsequent

repetitions they were polished to remove the surface layer along with the traces of cooperation.

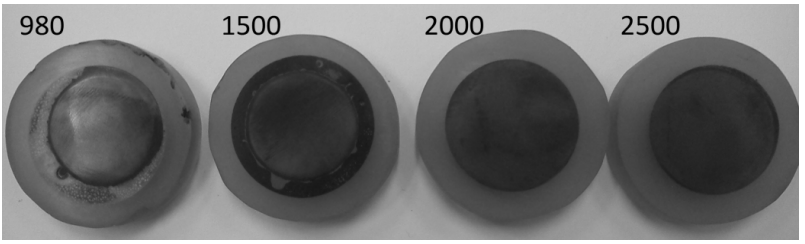

Fig. 1. The image of exemplary samples before tribological tests
Rys. 1. Zdjęcia przykładowych próbek przed testem tribologicznym

RESEARCH METHODOLOGY

The study of surface geometrical structure (SGS) and the disk wear after tribological tests were determined based on measurements made on Talysurf 3D profilographometer from Taylor Hobson **[L. 9]**. The analysis of results was performed using TalyMap software. For each sample, data were collected from three areas.

Micromechanical properties were determined by means of the Micron-Gamma microhardness tester (micron-Systema Kiev Ukraine) **[L. 10]**. A Berkovich Indenter was used to perform the measurements. The tests were conducted at a speed of loading and unloading of 1N/min to a maximum load of 1N. The presented results are the mean values from a minimum of seven measurements for each sample.

The studies of tribological characteristics were conducted on a T-01 ball-on-disk apparatus (from ITeE – PIB) **[L. 11]**. Cooperation of elements of the examined combination took place in conditions of dry friction with the following contact parameters: the speed of rotation of the disk – 72rev/min, load – 5N, radius of the friction path – 6mm, and sliding distance – 4 000m. This value was close to the actual diameter of the cooperation that occurs in artificial heart valves **[L. 12, 13]**. Humidity in the air in the laboratory was maintained in accordance with the recommendations of the VAMAS technical note **[L. 14]** at the level of 50±10% and at a temperature of 23°C±1°C.

Because the device is not really designed to study small-diameter balls equal to 1 mm, it was equipped with a special handle designed by the authors. Before the measurements, the main loading arm of the device was levelled and balanced. The companions to the test materials in tribological tests were metal balls made of AISI 52100 steel (EN 100Cr6, PN ŁH15, DIN 1.3505) having a diameter of 1mm. All tribological tests were performed at least three times for each variant.

RESULTS AND ANALYSIS

First, the results of the stereometric analysis of the carbon disk surface before and after a tribological test are presented. The values of stereometric parameters of disks were averaged and are presented in the graphs **(Figs. 2a** and **b**, and **Fig. 3)**. The results show similar values of the amplitude of surface geometrical structure (SGS) prior to tribological tests – (arithmetical mean height of the surface (Sa), root mean square height of the surface (Sq), maximum height of peaks (Sp), maximum depth of valleys (Sv), total height (St), ten-point height of surface irregularities (Sz), skewness of height distribution (Ssk), kurtosis of height distribution (Sku)).

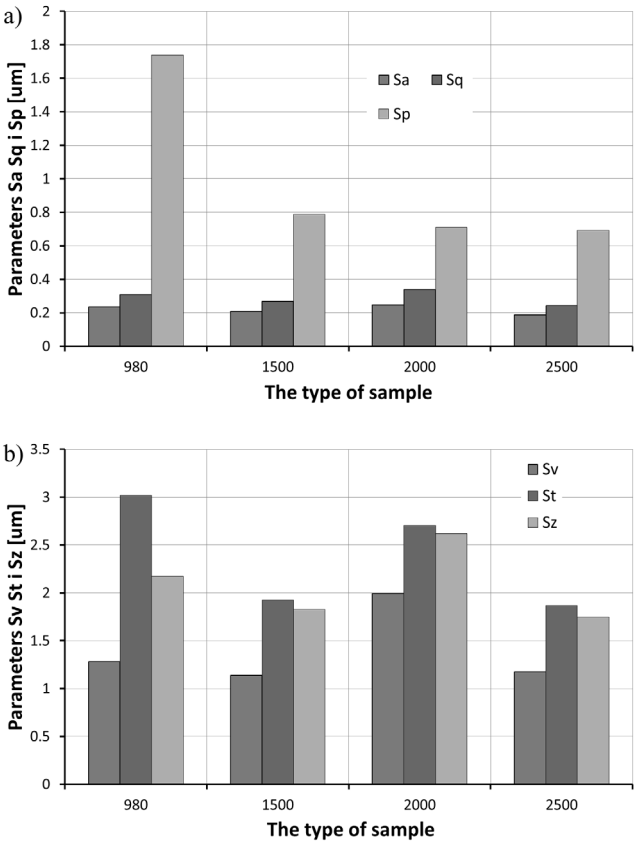

Fig. 2. The parameters of surface geometrical structure
Rys. 2. Parametry struktury geometrycznej powierzchni

The possibility of obtaining multiple repetitions of tribological tests was achieved by polishing the samples after each tribological test. Polishing was continued until all the traces of wear were removed. The most representative of

the amplitude parameters, namely the arithmetic mean and the root mean square deviation of the height of surface irregularities from the reference plane, do not reveal significant differences between the samples prepared for testing. This demonstrates the proper preparation of the surface for testing. When analysing strongly correlated parameters Sp, Sv, St, and Sz, it can be observed that there are fewer individual peaks on the surface than pits, and the latter ones have a greater impact on the height of irregularities **[L. 15]**.

The analysis of the coefficient of skewness and the concentration of the distribution of ordinates (Ssk and Sku) confirms the observed findings. The negative values of the parameter Ssk and the medium and large values of the parameter Sku indicate a smooth surface with flat peaks, which can pass into a flat surface with dominant small pits. In the case of the sample 980, the positive value of Ssk as well as the small value of Sz and the medium value of Sku indicate a flat surface with only a few peaks. Very similar SGP parameters were obtained in studies aimed at developing the most optimal technology of manufacturing carbon disks **[L. 16]**.

The measurements of the hardness of the carbon materials showed **(Fig. 4)** that the samples annealed at higher temperatures have slightly lower hardness than the base material that had not been subjected to further annealing (980). The Young's modulus obtained for the samples of glassy carbon in the test series is also significantly lower than that obtained in previous studies **[L. 16]** and fluctuates around 25-30 GPa. The lower values of modulus and hardness as well as a small number of broken carbon disks can suggest a reduction in internal stresses, which occur in the studied materials. As is the case of hardness, there is also a slightly lower modulus for the samples annealed at a temperature higher than 1000°C. The differences in Young's modulus and hardness due to the scatter of results are insignificant.

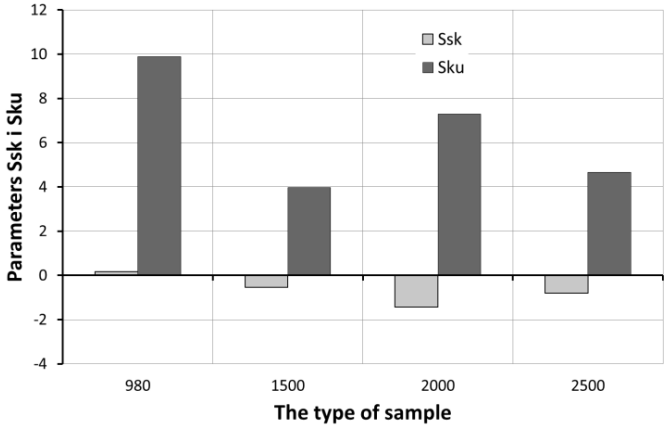

Fig. 3. The parameters Ssk and Sku
Rys. 3. Parametry Ssk i Sku

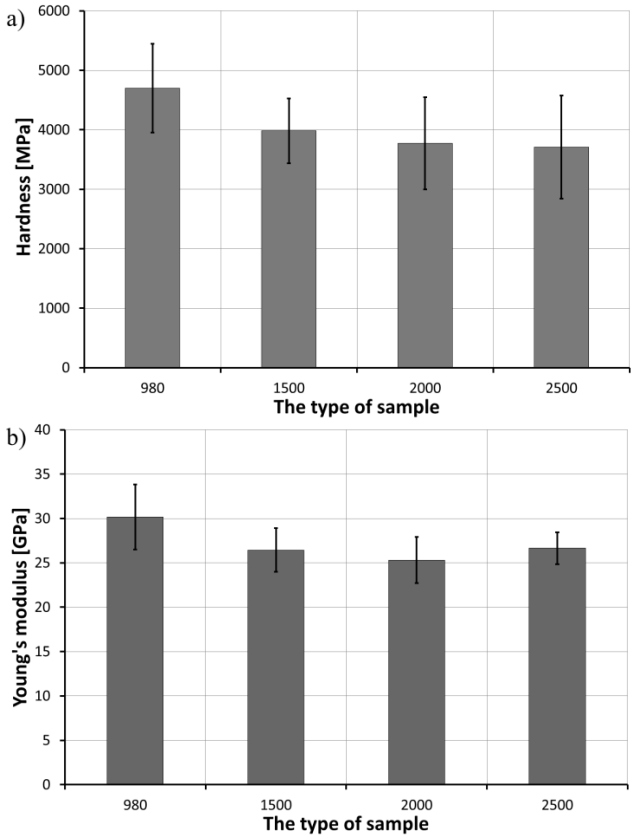

Fig. 4. Hardness (a), and Young's modulus (b) of carbon materials
Rys. 4. Twardość materiałów węglowych a) i moduł Younga b)

After developing the manufacturing technology optimal in terms of mechanical properties and biocompatibility, it was planned to perform tests on CSM Nano-Tribometer. The allowable test conditions are as follows: the maximum pressure of 1N, the diameter of the balls of 1 mm, the maximum friction diameter of 20mm, and the possibility of continuous recording of the friction force only **[L. 17]**. For this reason, in the analysis of tribological characteristics, the focus was mainly on the determination of the friction coefficient.

The analysed initial friction coefficient was not significantly different **(Fig. 5)**. The mean values of the friction coefficient oscillated around 0.12. Only for the variant 2500, a slightly lower value was observed at a fairly high standard deviation. In contrast, if the friction coefficient is stabilized, there is a significantly lower value for the variants 1500 and 2500 with respect to the samples that were not annealed (980). Here, a correlation was observed between

hardness, Young's modulus, and the value of the stabilized friction coefficient. A reduction in the hardness of the samples results in a lower value of the friction coefficient. For the annealed samples, there is a lower value of the stabilized friction coefficient compared to the initial one.

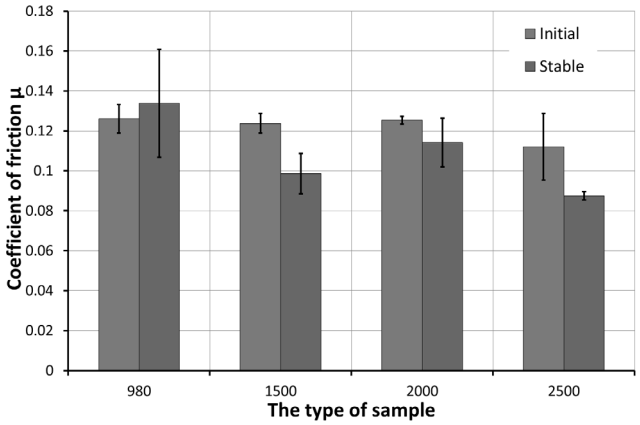

Fig. 5. Initial and stabilized friction coefficient
Rys. 5. Początkowy i ustabilizowany współczynnik tarcia

The graph of the friction coefficient as a function of the sliding distance **(Fig. 6)** confirms an advantageous reduction in the friction coefficient, when compared to the initial values. The most advantageous characteristics are observed for the variant 2500, whose mean friction coefficient decreased during the study and was characterized by the lowest standard deviation.

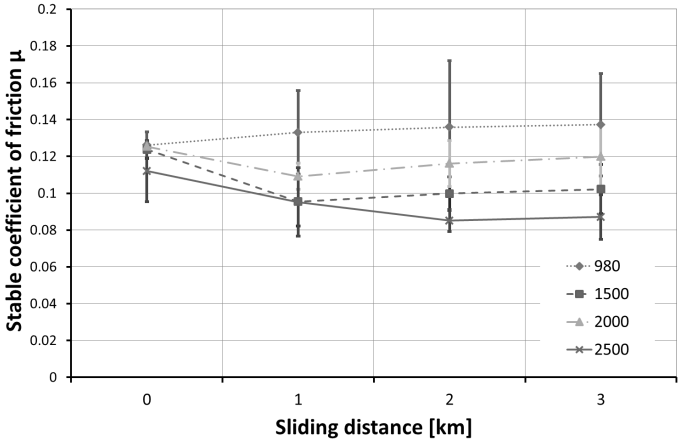

Fig. 6. Changes in the friction coefficient as a function of the sliding distance
Rys. 6. Zmiany współczynnika tarcia w funkcji drogi

The determination of the intensity of the wear of 52100 steel balls was not possible due to the weight loss being too low to register on the test equipment. Since the ball was mounted freely in the handle, it was not possible to specify the wear using microscopic methods either. The linear displacement registered on the ball-on-disk apparatus due to the small depth of wear was burdened with a large measurement error, which was also impeded by the axial run-out of the carbon disks and thermal expansion of the node elements. Profilographometric measurements were used to try to assess the wear. **Fig. 7** shows sample 2D and 3D isometric images of a selected measurement of the sliding interaction for the sample 2500.

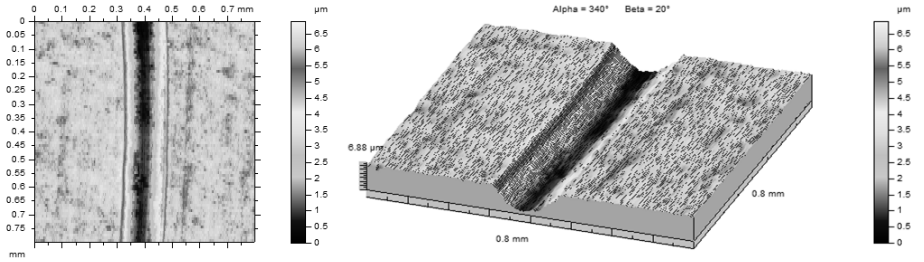

Fig. 7. 2D and 3D isometric image after a sliding interaction
Rys. 7. Obraz warstwicowy i izometryczny 3D po teście tribologicznym

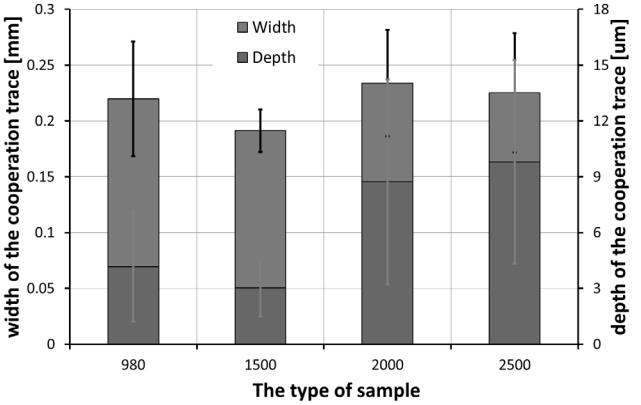

Fig. 8. Width and depth of the cooperation trace
Rys. 8. Szerokość i głębokość śladu współpracy

The intensity of the wear of the materials was compared by means of two parameters: the width of the cooperation trace and its depth **(Fig. 8)**. When analysing the width of the cooperation trace, no significant differences between the different types of samples were observed. A slightly lower value compared

to the other types of samples was recorded only for the variant 1500. The differences were noted in the analysis of the depth of the cooperation trace. Deeper cooperation traces were observed in the samples 2000 and 2500, whose values showed a fairly large scatter. The most preferred values were obtained for the variant 1500, which were also the most repeatable.

CONCLUSIONS

When producing glassy carbon using many technologies, in the first sample, there was a problem of cracking due to internal (own) stresses related to the manufacturing process. After solving this problem, one of the next challenges turned out to be the selection of production parameters that would provide the most favourable mechanical properties. Because these materials are assumed to be used in the kinematic components of implants, their tribological properties are essential. The research on carbon materials showed that the introduction of a high temperature annealing process into the manufacturing technology of glassy carbon can help to improve its tribological characteristics.

The study and analysis presented in this paper indicate that the technology of producing glassy carbon by means of annealing to temperatures of 1500, 2000, and 2500°C can result in improved micromechanical and tribological properties. The lower hardness and Young's modulus suggest a reduction in internal stresses **[L. 18–20]**, which may cause cracking and fragmentation of the samples. This effect is particularly undesirable in the finished product. The annealing process significantly decreased the values of the stabilized friction coefficient for the variants 1500 and 2500 and slightly decreased and stabilized the wear intensity for the sample 1500.

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Streszczenie

Materiały węglowe typu węgiel szklisty lub kompozyt C/C nie zawsze spełniają wymagania im stawiane w zastosowaniach technicznych i biomechanicznych. Najistotniejszym problemem procesu wytwarzania, który udało się autorom pokonać było wyeliminowanie pęknięć wewnętrznych w gotowych próbkach powodujących ich podzielenie. Uzyskany jednolity materiał badawczy ze względu na niezwykle newralgiczne miejsce wszczepienia musi spełniać liczne wymagania: wykazywać wysoką wytrzymałość mechaniczną i chemiczną, biotolerancję oraz wysoką odporność na zużycie tribologiczne. W pracy przedstawiono wyniki badań tribologicznych, stereometrycznych i mikromechanicznych materiałów węglowych, które zostały

wygrzane w piecu grafitowym, w temperaturach odpowiednio: 1500°C, 2000°C i 2500°C. W celu przeprowadzenia analiz charakterystyk tribologicznych opracowano metodykę badań na stanowisku kula–tarcza (tester T-01), która powinna odzwierciedlić warunki obciążeniowe panujące w rzeczywistym węźle. Przeprowadzone badania tribologiczne węgla szklistego potwierdziły przypuszczenia, iż temperatura wytwarzania tego materiału ma duży wpływ na jego własności tribologiczne, a wyższa temperatura wygrzewania nie zawsze oznacza poprawę właściwości materiału.