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CHARACTERIZATION OF TRIBOLOGICAL PROPERTIES OF OXIDE LAYERS OBTAINED ON TITANIUM IN DIFFERENT FRICTION COUPLES

CHARAKTERYSTYKA WŁAŚCIWOŚCI TRIBOLOGICZNYCH WARSTW TLENKOWYCH OTRZYMANYCH NA TYTANIE W RÓŻNYCH SKOJARZENIACH CIERNYCH

Key words: titanium, thermal oxidation, oxide layers, tribological properties.

Abstract The paper presents the characterization of tribological properties of titanium Grade 2 before and after isothermal oxidation in different friction couples. Examinations of the surface morphology after oxidation at a temperature of 600°C showed the presence of scratches on the surface, which indicated a low thickness of the oxide layers obtained. On the surface oxidized at 700°C, the morphology was characterized by the presence of small clusters of oxides which formed into shapes resembling flakes. In that case, no scratches were found, which testified to a higher thickness of the oxide layer. Tribological tests were conducted for different friction couples (Al_2O_3, ZrO_2, and 100Cr6 balls). It was found that isothermal oxidation is an effective method to improve the resistance of titanium Grade 2 to sliding wear. Oxide layers obtained at temperatures of 600°C and 700°C allowed achieving a considerable reduction of volumetric wear. The best resistance to sliding wear was achieved during a tribological interaction of oxidized titanium Grade 2 with bearing steel 100Cr6. Examination of the morphology of the wear trace surface showed the presence of "corrugation wear" on the non-oxidized surface, regardless of the counter-specimen used. It was found that the presence of oxide layers on the surface of titanium Grade 2 effectively eliminated this adverse phenomenon.

Słowa kluczowe: tytan, utlenianie termiczne, warstwy tlenkowe, właściwości tribologiczne.

Streszczenie W pracy przedstawiono charakterystykę właściwości tribologicznych tytanu Grade 2 przed i po utlenianiu izotermicznym w różnych skojarzeniach ciernych. Badania morfologii powierzchni po utlenianiu w temperaturze 600°C wykazały obecność rys na powierzchni, co świadczyło o niewielkiej grubości otrzymanych w arstw tlenkowych. Na powierzchni utlenionej w temperaturze 700°C morfologia charakteryzowała się występowaniem drobnych skupisk tlenków uformowanych w kształty przypominające „płatki". W tym przypadku nie stwierdzono obecności rys, co świadczyło o większej grubości warstwy tlenkowej. Badania tribologiczne realizowano w różnych skojarzeniach ciernych (kulki Al_2O_3, ZrO_2 oraz 100Cr6). Stwierdzono, że utlenianie izotermiczne jest skuteczną metodą w zakresie poprawy odporności na zużycie ścierne tytanu Grade 2. Warstwy tlenkowe otrzymane w temperaturze 600 oraz 700°C pozwoliły uzyskać znaczą redukcję zużycia objętościowego. Najlepszą odporność na zużycie ścierne uzyskano podczas współpracy tribologicznej utlenionego tytanu Grade 2 ze stalą łożyskową 100Cr6. Badania morfologii powierzchni śladów zużycia wykazały na powierzchni nieutlenionej obecność tzw. zużycia falistego niezależnie od zastosowanej przeciwpróbki. Stwierdzono, że obecność warstw tlenkowych na powierzchni tytanu Grade 2 skutecznie eliminuje to niekorzystne zjawisko.

INTRODUCTION

Among metallic materials, titanium and its alloys are considered the basic materials in implantology due to their favourable mechanical properties and high biocompatibility [**L. 1, 2**]. They are highly competitive with medical austenitic steels or cobalt-based alloys [**L. 3**]. Apart from biomedical applications, titanium and

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its alloys are also very popular in aerospace technology. For nearly 60 years, they have been used for the construction of aircraft structural elements. In recent years, an upward trend has been observed in the amount of titanium used in the commercial aviation industry [**L. 4, 5**].

The high interest in titanium and its alloys compared to other construction materials is mainly due to their high specific strength (Rm/ρ), good corrosion resistance, fatigue resistance, and a low, compared to other metallic materials, value of Young's modulus, coupled with low density (ca. 4.5 g/cm^3) [**L. 6**]. However, apart from the undeniable advantages, titanium and its alloys are characterized by very weak tribological properties that significantly reduce the possibility of using them in friction couples. Poor tribological properties of these materials result from their insufficient hardness as well as a high and unstable friction coefficient [**L. 7**]. This contributes to shortening the service life of components made of titanium and titanium alloys in a number of technical or biomedical applications. The natural passive layer present on the surface of titanium and its alloys, which provides these materials with very good corrosion resistance, does not improve their tribological properties due to the low thickness (up to 10 nm). One of the methods that enable increasing the thickness of the natural passive layer is isothermal oxidation in the air atmosphere. This type of treatment is an alternative technique for modifying the surface of titanium and its alloys, which allows, among other things, increasing their resistance to sliding wear and high-temperature corrosion. This technique utilizes the phenomenon of oxygen diffusion at higher temperatures, thereby allowing one to harden the upper layer by creating a relatively thick film of TiO_2, mainly in the crystallographic form of rutile [**L. 8–11**]. The formation of an oxide layer that performs its function properly under specific operating conditions requires an appropriate selection of the parameters of their production process and appropriate preparation of the substrate surface.

This study encompasses issues related to the determination of the effect of isothermal oxidation temperature on the morphology and resistance to sliding wear of oxide layers formed on titanium Grade 2, depending on the material of the counter specimen used (Al_2O_3, ZrO_2, and 100Cr6 steel balls).

EXPERIMENTAL PROCEDURES

Titanium Grade 2 in the form of a 40 mm diameter rod was used in the tests. Specimens were cut from the rod in the form of discs, 40 mm in diameter and 5 mm thick, which were ground by hand on grinder/polishing machines. Polishing was done with abrasive paper with gradation of 300, 600, 800, and 1200, with a 90° angle of rotation when changing the abrasive paper gradation. After grinding, the specimens were cleaned in acetone and then oxidized in a laboratory chamber furnace in the air atmosphere. The oxidation process was conducted at temperatures of 600 and 700°C for 72 hours. After oxidation, the specimens were quenched in the air to ambient temperature.

Observations of the morphology of the oxide scale surface and of the traces of wear obtained after friction tests were conducted with a scanning electron microscope, JEOL JSM 6480. During observation, magnifications from 500 to 5000× were applied. The surface of oxide layers and traces of wear were observed together with the wear products that remained on the surface. The paper presents the results of observations obtained at a magnification of 5000× (morphology of oxide layer surfaces) and 1000× (traces of wear).

Tribological tests were performed under constant measurement conditions on a tribological tester, TRN Tribometer (Anton Paar, Switzerland), at a temperature of 21±1°C and humidity of 40±5%. The specimens were 40 mm diameter discs made of titanium Grade 2, and 6 mm diameter balls made of aluminium oxide (Al_2O_3), zirconium oxide (ZrO_2), and bearing steel (100Cr6) served as counter-specimens. The following parameters were applied in the tests:

- Load – 5 N,
- Speed – 0.1 m/s,
- Friction distance – 1000 m.

After tribological tests, the volumetric wear was determined for discs made of titanium Grade 2, both subjected and not subjected to isothermal oxidation. Volumetric wear calculated from the formula:

$$V_v = \frac{V}{F \cdot s} \tag{1}$$

where

V_v – wear ratio [mm^3/N·m],
V – volume of the material removed during friction [mm^3],
F – load [N],
s – friction distance [m].

RESULTS AND DISCUSSION

The morphology of oxidized and non-oxidized surfaces

Figure 1 presents images of the surface of titanium Grade 2 before and after oxidation at temperatures of 600 and 700°C for 72 hours.

The analysis of microscopic photographs taken on the non-oxidized surface showed the presence of scratches which were the result of grinding the specimens on abrasive paper. The observed surface was of good quality and thus provided a good substrate for the deposition of oxide layers (**Fig. 1a**). Microscopic

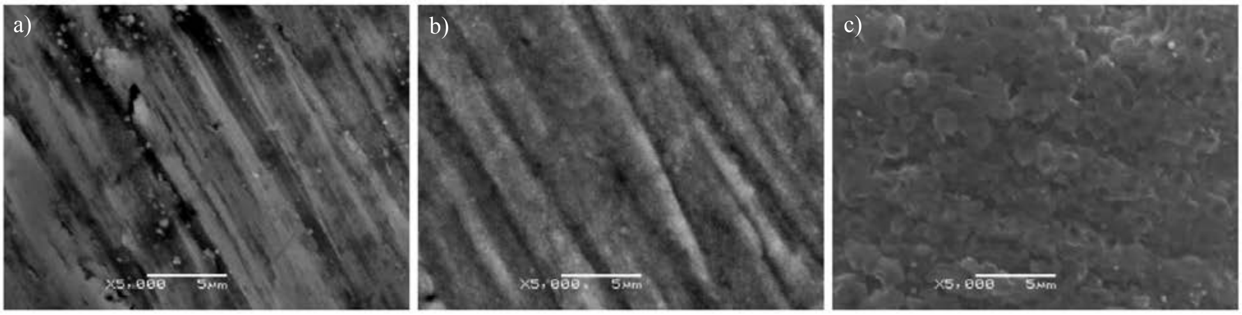

Fig. 1. Surface morphology of titanium Grade 2 before (Fig. a) and after isothermal oxidation at 600°C (Fig. b) and 700°C (Fig. c)

Rys. 1. Morfologia powierzchni tytanu Grade 2 przed (**Rys. a**) oraz po utlenianiu izotermicznym w temperaturze 600°C (rys. b) i 700°C (rys. c)

observations on the surface coated with oxide layers obtained at temperatures of 600 and 700°C showed that their morphology was closely related to the isothermal oxidation temperature. At a lower oxidation temperature, characteristic mapping of the surface topography before oxidation was observed (scratches are still visible on the surface – **Fig. 1b**). This indicates that the oxide layer obtained was not very thick. In addition, it was found that, after oxidation at a temperature of 600°C, the oxide layer was composed of very fine oxide particles. As the oxidation temperature increased, it was observed that the oxide layer obtained was composed of larger oxide particles, which concentrated into shapes resembling flakes. At a higher oxidation temperature, the scratches disappeared, which indicated that the thickness of the oxide layer increased (**Fig. 1c**). According to Kumar et al, large oxide grains form by way of nucleation and merging of finer oxide grains, which, in consequence, leads to the formation of large grains [**L. 11**]. The growth mode involves the formation of a thin oxide scale followed by its agglomeration and growth to completely cover the surface [**L. 12**].

Friction coefficient

Figure 2 presents a collation of friction coefficient values after tribological tests of non-oxidized and oxidized samples at temperatures of 600 and 700°C, depending on the material of the counter-specimen used.

On the basis of the analysis of the obtained results, it was found that the lowest values of the friction coefficient (equal to approx. 0.5) occurred in the initial period of the tribological interaction of the non-oxidized surface, especially with ZrO_2 and 100Cr6 balls. Once the tribological test conditions had stabilized, the friction coefficient was slightly increasing (up to the value of ca. 0.65–0.7). The tribological interaction of titanium Grade 2 with the oxide layers produced led to a significant increase of the friction coefficient, regardless of the counter-specimen material used. In some cases, the friction coefficient increased by as much as 50% (**Fig. 2**). The highest values of the friction coefficient were obtained during a friction interaction with ZrO_2 balls. One of the main reasons for the increase in the friction coefficient was the increase in surface roughness after oxidation. The effect of the increase in the friction coefficient was different compared to some literature data [**L. 13–15**], which indicated that the presence of oxide layers obtained by isothermal oxidation reduced its value. The authors of paper [**L. 14**] showed that oxide layers allow reducing the value of friction coefficient, however, at an insignificant load (1N). At the same time, tests carried out at load of 2 and 5 N showed an increase in the friction coefficient significantly above the value obtained for the non-oxidized surface, which is consistent with the results obtained in this study.

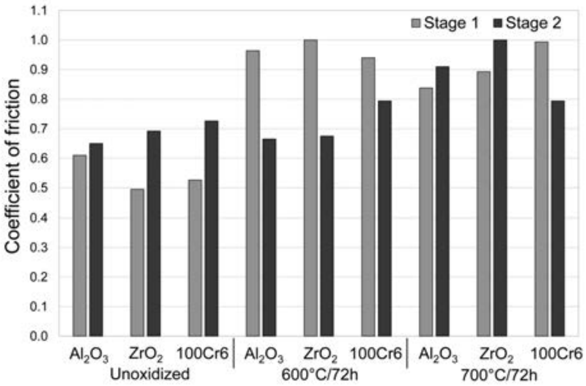

Fig. 2. Collation of friction coefficient values after the tribological interaction of Al_2O_3, ZrO_2, and 100Cr6 balls with non-oxidized and oxidized titanium Grade 2 (Stage 1 – friction coefficient at the initial stage of tribological interaction; Stage 2 – friction coefficient at an advanced stage of the tribological test)

Rys. 2. Zestawienie wartości współczynnika tarcia po współpracy tribologicznej kulek Al_2O_3, ZrO_2, 100Cr6 z nieutlenionym oraz utlenionym tytanem Grade 2 (stage 1 – współczynnik tarcia w początkowym etapie współpracy tribologicznej, stage 2 – współczynnik tarcia w zaawansowanym etapie testu tribologicznego)

In some cases, it was observed that the oxide layer got worn through, which resulted in an abrupt decrease in the friction coefficient value and widening of its amplitude. This phenomenon was particularly visible in the case of oxide layers obtained at a temperature of 600°C, where the thickness of the oxide layer was lower – **Fig. 3**. The widening of the amplitude of the friction coefficient after wearing through of the oxide layer was a result of the tribological interaction of the Al_2O_3 ball directly with the titanium Grade 2 substrate. Such a phenomenon is typical of titanium and is associated with the occurrence of a friction coefficient with a very unstable course.

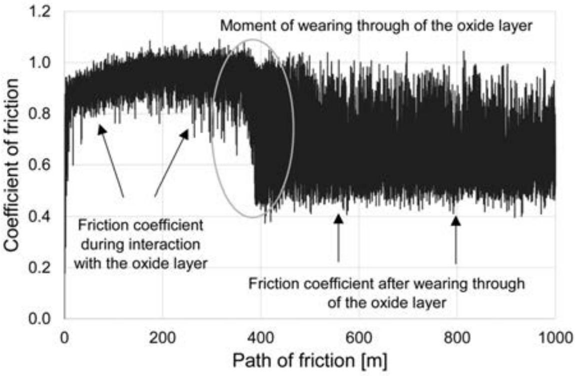

Fig. 3. Example of the course of changes in the friction coefficient during the tribological interaction of titanium Grade 2 oxidized at 600°C with an Al_2O_3 ball

Rys. 3. Przykładowy przebieg zmian współczynnika tarcia podczas współpracy tribologicznej tytanu Grade 2 utlenionego w temperaturze 600°C z kulką Al_2O_3

Volumetric wear

Figure 4 presents the results of volumetric wear for a disc made of titanium Grade 2, non-oxidized and subjected to isothermal oxidation, after an interaction with Al_2O_3, ZrO_2, and 100Cr6 balls.

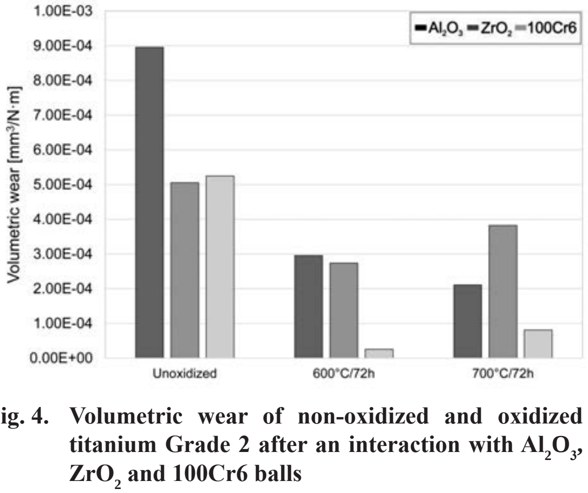

Fig. 4. Volumetric wear of non-oxidized and oxidized titanium Grade 2 after an interaction with Al_2O_3, ZrO_2 and 100Cr6 balls

Rys. 4. Zużycie objętościowe nieutlenionego oraz utlenionego tytanu Grade 2 po współpracy z kulkami: Al_2O_3, ZrO_2 oraz 100Cr6

Based on the analysis of the obtained results, it was found that the type of the counter-specimen used (a ball) had a significant impact on volumetric wear of the titanium Grade 2 disc. The highest wear was observed on the non-oxidized surface during a tribological interaction with Al_2O_3 balls. The tribological interaction with balls made of ZrO_2 and 100Cr6 resulted in a volumetric wear value lower by ca. 42%.

After isothermal oxidation, a significant reduction in the volumetric wear rate was observed, which was strictly dependent on the parameters of the oxidation process and the counter-specimen used. A similar effect was obtained in studies [**L. 2, 9, 13**] after isothermal oxidation of the Ti-6Al-4V alloy. In the case of the tribological interaction of with Al_2O_3 balls, it was shown that oxide layers had a positive effect on reducing volumetric wear, and resistance to sliding wear increased along with the oxidation temperature. Where the oxide layers interacted with ZrO_2 balls, the greatest reduction in volumetric wear was observed during the interaction with an oxide layer obtained at a temperature of 600°C. Increased oxidation temperature caused deterioration of tribological properties. The best resistance to sliding wear was achieved during a tribological interaction of oxide layers with 100Cr6 steel balls (**Fig. 4**). In this friction couple, volumetric wear was reduced by ca. 95% in comparison with the non-oxidized variant. The highest reduction in volumetric wear of the 100Cr6 balls could be attributed to the fact that steel has lower hardness than that of the oxide layers obtained by isothermal oxidation. This resulted in an increase in the intensity of wear of steel balls compared to ceramic balls.

Microscopic analysis of wear traces

Microphotographs showing traces of wear for titanium in the non-oxidized and oxidized condition are shown in **Figures 5–9**. Tribological tests of non-oxidized specimens showed the occurrence of the "corrugation wear," regardless of the counter-specimen used. Corrugation wear was characterized with the presence of alternate regions in a dark and light colour. One of those regions was an elevation and the other a depression. In region A, numerous wear products caused by friction are visible (**Figs. 5a, 6a, 7a**). In region B (**Figs. 5b, 6b, 7b**), a small amount of wear products was observed along with visible scratches left after a friction interaction.

Surfaces of wear traces after interactions with oxide layers are presented in **Figures 8** and **9**. No corrugation wear was found in the case of oxidized specimens. **Figure 8** presents microphotographs of wear traces for specimens oxidized at 600°C. After the oxidation process, milder and less visible scratches were found for the traces formed after interaction with ceramic balls. In addition, the presence of wear products in the form of fine particles was found on the working surface. A completely different morphology was observed for the wear trace obtained after interaction with a ball

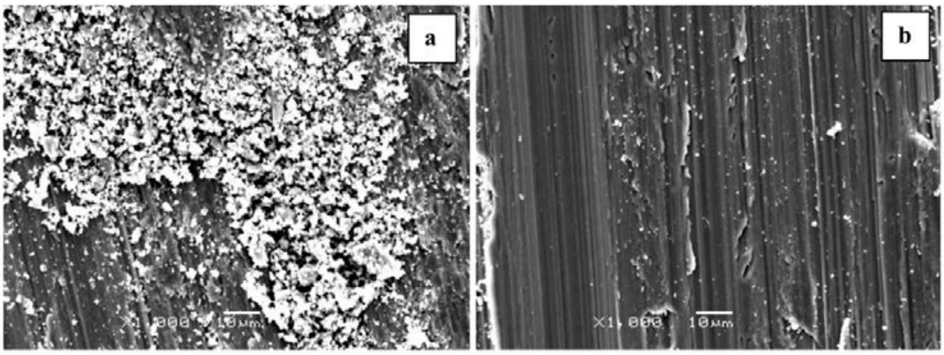

Fig. 5. Surface of the wear trace on a non-oxidized specimen of titanium Grade 2 after interaction with an Al_2O_3 ball
Rys. 5. Powierzchnia śladu zużycia próbki nieutlenionej z tytanu Grade 2 po współpracy z kulką Al_2O_3

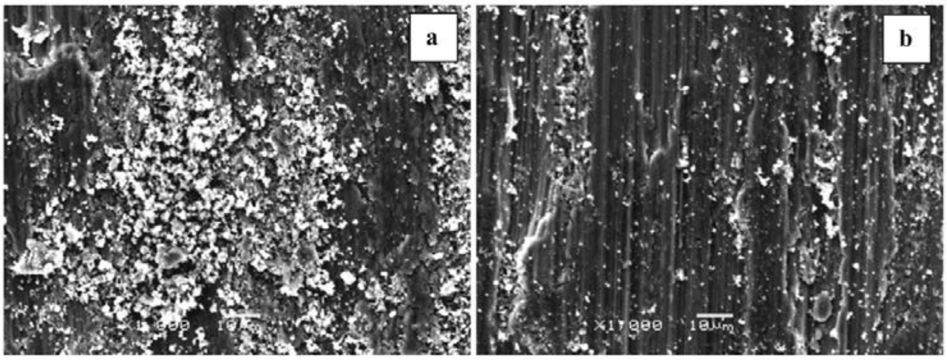

Fig. 6. Surface of the wear trace on a non-oxidized specimen of titanium Grade 2 after interaction with a ZrO_2 ball
Rys. 6. Powierzchnia śladu zużycia próbki nieutlenionej z tytanu Grade 2 po współpracy z kulką ZrO_2

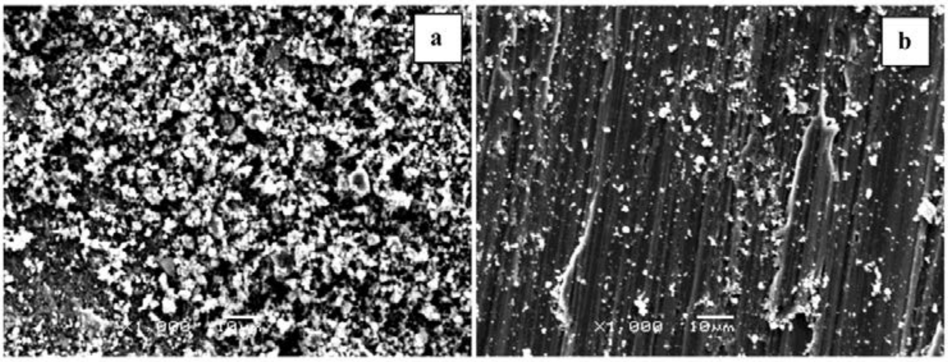

Fig. 7. Surface of the wear trace on a non-oxidized specimen of titanium Grade 2 after interaction with a 100Cr6 steel ball
Rys. 7. Powierzchnia śladu zużycia próbki nieutlenionej z tytanu Grade 2 po współpracy z kulką ze stali 100Cr6

made of the 100Cr6 bearing steel. It was similar to the morphology of the oxide layers deposited on titanium, which may indicate that, during tribological tests, an additional phenomenon of surface oxidation occurred as a result of friction and local temperature increase. The oxidation effect on the wear trace was observed for each test variant regardless of the oxidation temperature (**Figs. 8, 9**).

Surface morphology of the wear traces obtained on specimens oxidized at 700°C differed significantly from those formed at a lower oxidation temperature (**Fig. 9**). After interaction with ceramic balls, there was a much smaller amount of wear products on the surface compared to the wear traces on the specimens oxidized at 600°C. At the same time, it was found that the wear products had the form of particles with a higher dispersion. Very delicate and shallow scratches were observed also on the surface. Only in the case of the surface interacting with a 100Cr6 steel ball, was the oxidation of the working surface observed.

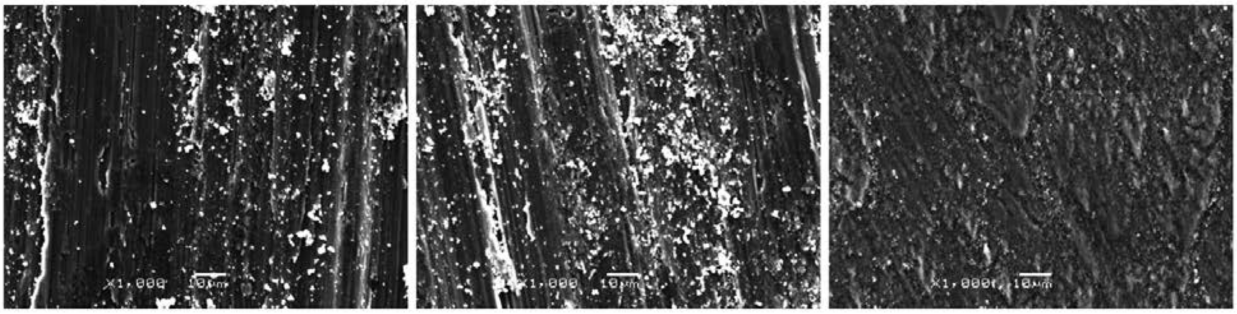

Fig. 8. Microphotographs showing the traces of wear on titanium Grade 2 oxidized at 600°C after using counter-specimens, from left: Al_2O_3, ZrO_2, 100Cr6

Rys. 8. Mikrofotografie przedstawiające ślady zużycia na tytanie Grade 2 poddanemu utlenianiu w temperaturze 600°C po zastosowaniu przeciwpróbek, od lewej: Al_2O_3, ZrO_2, 100Cr6

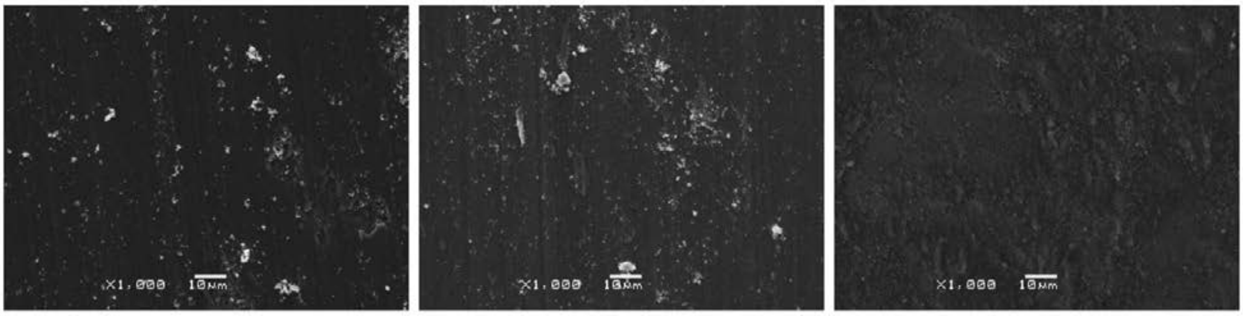

Fig. 9. Microphotographs showing the traces of wear on titanium Grade 2 oxidized at 700°C after using counter-specimens, from left: Al_2O_3, ZrO_2, 100Cr6

Rys. 9. Mikrofotografie przedstawiające ślady zużycia na tytanie Grade 2 poddanemu utlenianiu w temperaturze 700°C po zastosowaniu przeciwpróbek, od lewej: Al_2O_3, ZrO_2, 100Cr6

CONCLUSIONS

Based on the performed research and analysis of its results, the influence of isothermal oxidation parameters on tribological properties of oxide layers formed on the surface of titanium Grade 2 was determined, depending on the applied counter-specimen material. The following conclusions have been formulated:

1. Isothermal oxidation in the air atmosphere allowed the formation of oxide scale on the surface of titanium Grade 2. The scale became more compact as the oxidation temperature increased and covered the entire surface.
2. After oxidation at a temperature of 600°C, scratches which had formed as a result of polishing were found on the surface, which testifies to a low thickness of the oxide layers. On the surface of specimens oxidized at 700°C, the morphology was characterized by the presence of small clusters of oxides which formed into shapes resembling flakes. In that case, no scratches were found, which indicates a higher thickness of the oxide layer formed.
3. Non-oxidized titanium Grade 2 was characterized by a friction coefficient value of ca. 0.6–0.7. After isothermal oxidation, a ca. 10–38% increase in the friction coefficient value was observed, especially at the initial stage of tribological interaction.
4. Isothermal oxidation is an effective method to improve tribological properties of titanium Grade 2. The presence of an oxide layer significantly enhanced resistance to abrasive wear. Oxide layers produced at temperatures of 600–700°C caused a considerable reduction of volumetric wear. The highest resistance to sliding wear was found in the case of tribological interaction with 100Cr6 steel balls.
5. Microscopic examination of the morphology of the wear trace surface showed the presence of “corrugation wear” on the non-oxidized specimens. The isothermal oxidation process effectively eliminated this adverse phenomenon. After oxidation, gentle scratches with fine wear products were found on the friction surface, which had formed after interaction with ceramic balls. In the case of interaction with 100Cr6 steel balls, additional oxidation of the friction surface was observed.

REFERENCES

1. Fellah M., Assala O., Labaïz M., Dekhil L., Iost A.: Friction and Wear Behavior of Ti-6Al-7Nb Biomaterial Alloy. Journal of Biomaterials and Nanobiotechnology 4 (2013), pp. 374–384.
2. Guleryuz H., Cimenoglu H.: Effect of thermal oxidation on corrosion and corrosion–wear behaviour of a Ti-6Al-4V alloy. Biomaterials 25 (2004), pp. 3325–3333.
3. Wang S., Liao Z., Liu Y., Liu W.: Different tribological behaviors of titanium alloys modified by thermal oxidation and spraying diamond like carbon. Surface & Coatings Technology 252 (2014), pp. 64–73.
4. Dudek Ł., Hryniewicz T., Rokosz K.: Zastosowanie tytanu i wybranych stopów tytanu w lotnictwie. Autobusy 8 (2016), pp. 62–66.
5. Niesłony P., Małecka J., Hepner M., Bogdan-Chudy M.: Badania tarcia i mechanizmów zużycia stopu tytanu Ti6Al4V w skojarzeniu z węglikiem spiekanym z powłoką PVD-TiAlN na tribometrze pin-on-disc. Tribologia 2 (2015), pp. 87–101.
6. Jeziorski L., Nabiałek M., Szota M., Frączek T., Jędryka J., Olejnik M.: Właściwości stopów Ti-6Al-4V wytwarzanych konwencjonalnie oraz metodą szybkiego chłodzenia. Inżynieria Materiałowa Vol. 33, nr 3 (2012), pp. 126–128.
7. Dong H., Bell T.: Enhanced wear resistance of titanium surfaces by a new thermal oxidation treatment. Wear 238 (2000), pp. 131–137.
8. Cimenoglu H., Meydanoglu O., Baydogan M., Bermek H., Huner P., Sabri Kayali E.: Characterization of Thermally Oxidized Ti6Al7Nb Alloy for Biological Applications. Met. Mater. Int., Vol. 17 (5) (2011), pp. 765–770.
9. Wang S., Liao Z., Liu Y., Liu W.: Influence of thermal oxidation duration on the microstructure and fretting wear behavior of Ti6Al4V alloy. Materials Chemistry and Physics 159 (2015), pp. 139–151.
10. Diamanti M.V., Codeluppi S., Cordioli A., Pedeferri M.P.: Effect of thermal oxidation on titanium oxides characteristics. NSTI-Nanotech 1 (2008), pp. 1012–1015.
11. Kumar S., Sankara Narayanana T.S.N., Sundara Raman S.G., Seshadri S.K.: Thermal oxidation of Ti6Al4V alloy: Microstructural and electrochemical characterization. Materials Chemistry and Physics 119 (2010), pp. 337–346.
12. Kumar S., Sankara Narayanana T.S.N., Sundara Raman S.G., Seshadri S.K.: Thermal oxidation of CP Ti – An electrochemical and structural characterization. Materials Characterization 61 (2010), pp. 589–597.
13. Wang S., Liao Z., Liu Y., Liu W.: Influence of thermal oxidation temperature on the microstructural and tribological behavior of Ti6Al4V alloy. Surface & Coatings Technology 240 (2014), pp. 470–477.
14. Bailey R., Sun Y.: Unlubricated sliding friction and wear characteristics of thermally oxidized commercially pure titanium. Wear 308 (2013), pp. 61–70.
15. Guleryuz H., Cimenoglu H.: Surface modification of a Ti-6Al-4V alloy by thermal oxidation. Surface & Coatings Technology 192 (2005), pp. 164–170.