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CHARACTERISATION OF MICROMECHANICAL AND TRIBOLOGICAL PROPERTIES OF TITANIUM GRADE 2 AFTER CYCLIC OXIDATION

CHARAKTERYSTYKA WŁAŚCIWOŚCI MIKROMECHANICZNYCH I TRIBOLOGICZNYCH TYTANU GRADE 2 PO UTLENIANIU CYKLICZNYM

Key words: cyclic oxidation, oxide layers, microindentation, friction, wear.

Abstract: This paper presents the characterisation of micromechanical and tribological properties of titanium Grade 2 before and after cyclic oxidation. The oxidation process was carried out at temperatures of 600°C, 650°C and 700°C in 4 and 12 cycles. Microscopic studies showed that oxide particle size increased with increasing oxidation temperature and the number of cycles. Titanium Grade 2 showed up to 3 times higher hardness after cyclic oxidation. The highest hardness (8.4 GPa) was obtained after 12 cycles of titanium oxidation at 650°C. Tribological tests were conducted in pairs with different materials (Al_2O_3, ZrO_2, bearing steel 100Cr6). The presence of oxide layers obtained on the titanium surface resulted in a significant reduction in specific wear rate. Titanium Grade 2 showed the best resistance to sliding wear after cyclic oxidation at 600°C during sliding interaction with ZrO_2 and 100Cr6 balls (unmeasurable wear under assumed test conditions). In the other test variants, the reduction in wear ranged from 37 to 96%.

Słowa kluczowe: utlenianie cykliczne, warstwy tlenkowe, mikroindentacja, tarcie, zużycie.

Streszczenie: W pracy przedstawiono charakterystykę właściwości mikromechanicznych i tribologicznych tytanu Grade 2 przed i po utlenianiu cyklicznym. Proces utleniania realizowano w temperaturze 600°C, 650°C i 700°C w 4 i 12 cyklach. W badaniach mikroskopowych wykazano, że wielkość cząstek tlenków rosła wraz ze wzrostem temperatury utleniania oraz liczby cykli. Tytan Grade 2 po utlenianiu cyklicznym charakteryzował się nawet 3-krotnie wyższą twardością. Największą twardość (8.4 GPa) uzyskano po 12 cyklach utleniania tytanu w temperaturze 650°C. Testy tribologiczne realizowano w skojarzeniu z różnymi materiałami (Al_2O_3, ZrO_2, stal łożyskowa 100Cr6). Obecność warstw tlenkowych otrzymanych na powierzchni tytanu spowodowała znaczną redukcję zużycia objętościowego. Najlepszą odpornością na zużycie ścierne tytan Grade 2 charakteryzował się po utlenianiu cyklicznym w temperaturze 600°C podczas współpracy ciernej z kulkami ZrO_2 oraz 100Cr6 (zużycie niemierzalne w przyjętych warunkach badań). W pozostałych wariantach badań redukcja zużycia wynosiła od 37 do 96%.

INTRODUCTION

Titanium and its alloys are among the most important metals in industry and medicine. The combination of low density, very good corrosion resistance and unique mechanical properties has an effect in a wide application range of titanium-based materials in a number of industries **[L. 1]**. The main areas of engineering applications for titanium and its alloys are the aircraft, aerospace, power, chemical and automotive industries. Due to their excellent biocompatibility, titanium materials are also increasingly used in many areas of medicine. In biomedical applications, these materials are used, inter alia, for hip and knee replacements, spinal stabilisers or prostheses, and dental implants **[L. 2]**.

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Their high biocompatibility and corrosion resistance are the result of the spontaneous formation of a passive oxide film on the surface of titanium and its alloys. Due to its small thickness, however, the passive layer is not an effective protective barrier against tribological processes. Poor tribological properties of titanium materials generate a number of different problems and also result in limitations on the applicability of these materials in friction couples **[L. 2, 3]**. Friction and wear processes may also cause damage to the passive layer, resulting in a weakening of corrosion resistance. This phenomenon is not a problem in an atmospheric environment, as the passive layer is gradually restored, reducing the extent of corrosion. However, the situation is different in physiological environments, where the rate of re-passivation is too slow to prevent advanced corrosion, which leads to implant failure **[L. 2]**. In some cases, such as inflammation, rapid passivation of the metal surfaces of implants may occur **[L. 4]**. A significant problem is also the wear products penetrating into tissues, which can induce an immune response in the body. Wear products can accumulate in organs such as the liver, spleen or abdominal lymph nodes **[L. 2, 5]**. In addition to biomedical aspects, the poor friction-wear characteristics of titanium materials also contribute to many operational problems in technical engineering. Titanium and its alloys are prone to excessive adhesive wear and scoring due to, among other things, a high and unstable coefficient of friction **[L. 6]**. For the aforementioned reasons, achieving improvements in micromechanical and tribological characteristics is key to ensuring the required durability of titanium materials used in both medical and technical applications.

Titanium and its alloys are susceptible to intense oxidation at temperatures in excess of 600°C, a result of both titanium's high affinity for oxygen and the significant solubility of oxygen in titanium **[L. 7]**. This phenomenon makes it possible to increase the thickness of the natural passive layer and thus improve the poor tribological characteristics of titanium-based materials. The high-temperature oxidation process can be carried out under isothermal or cyclic conditions. Cyclic oxidation, compared to isothermal, is characterised by a higher intensity, which allows for obtaining oxide layers with greater thickness and hardness **[L. 8]**. The primary objective of the research work conducted was to improve the micromechanical and tribological properties of titanium Grade 2 by cyclic oxidation for future applications in medicine and technology. The cyclic oxidation process was carried out at 600°C, 650°C and 700°C in 4 and 12 cycles. The micromechanical and tribological characteristics were determined for titanium Grade 2 before and after cyclic oxidation. The tribological properties of the titanium were determined for different material couples: ceramic (Al_2O_3, ZrO_2) and metallic (bearing steel 100Cr6).

MATERIALS AND METHODS

The material used in the tests was titanium Grade 2 in the form of 40 mm diameter rods. The chemical composition of the tested material is presented in **Table 1**.

Table 1. Chemical composition of titanium Grade 2
Tabela 1. Skład chemiczny tytanu Grade 2

	Chemical Composition (wt. %)					
	Ti	Fe	C	N	O	H
Requirement	Remainder	≤0.30	≤0.08	≤0.03	≤0.25	≤0.015
Result	Remainder	0.15	0.02	0.02	0.12	0.001

Samples for the tests in the form of discs, 40 mm in diameter and 5 mm thick, were ground using grinder/polishing machines. Grinding was performed using abrasive paper with a grit size of 300, 600, 800 and 1200, keeping a 90° rotation angle when changing the grit size. After grinding, the specimens were cleaned in acetone.

The parameters of cyclic oxidation were chosen based on the results of previous studies presented in paper **[L. 8]**. The oxidation process was carried out at temperatures of 600°C, 650°C and 700°C in 4 and 12 cycles of oxidation, each lasting 6 hours. After each oxidation cycle, the specimens were removed from the furnace and cooled in the air to ambient temperature. The applied oxidation parameters allowed for varying the morphology, thickness, hardness and tribological characteristics of the oxide layers formed on the titanium surface.

Microscopic observation of the titanium Grade 2 surface after cyclic oxidation was conducted using a JEOL JSM 6480 scanning electron microscope. Tests were performed at 2000x magnification on samples cycled at 600°C, 650°C and 700°C (for 4 and 12 oxidation cycles).

Micromechanical testing of titanium Grade 2 in its initial state and after oxide layers had been formed on its surface was performed using a Micro Combi Tester – MCT (Anton Paar, Switzerland). The tests were carried out per the standards of ISO 14577 **[L. 9]** and ASTM E2546 **[L. 10]**. The load-unload curves (P-h) were recorded in a continuous manner. A Berkovich indenter with the angle: α = 65.3° ± 0.3° was used. The test parameters were as follows: max load: 500 mN, loading rate: 16.7 mN/s, unloading rate: 16.7 mN/s, pause: 10 s. Hardness H_{IT} and indentation modulus E_{IT} were determined using the Oliver & Pharr method **[L. 11]**.

Tribological tests were carried out using a TRN Tribometer (Anton Paar, Switzerland) operating in the ball-on-disc system in rotary motion. The specific wear rate and coefficient of friction were determined for the tribological couples studied. The tribological tests were repeated four times each, at a temperature of 21±1°C and humidity of 40±5%. The specimens were 40 mm diameter discs made of titanium Grade 2, while balls made of aluminium oxide (Al_2O_3), zirconium oxide (ZrO_2) and bearing steel (100Cr6) served as counter-specimens. The parameters of the tests were selected based on preliminary studies. The tests were conducted under the following conditions:

- load – F = 5 N,
- linear velocity – v = 0.1 m/s,
- friction distance – s = 1000 m.

After tribological tests, the specific wear rate was determined for a titanium Grade 2 disc subjected and not subjected to cyclic oxidation. Wear trace profiles were recorded on a Mitutoyo SJ-500 contact profilometer. The specific wear rate was calculated based on the dependencies **[L. 12]**:

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

where:
V_v – specific wear rate [mm/N·m],
V – volume of the material removed during friction [mm],
F – load [N],
s – friction distance [m].

RESULTS AND DISCUSSION

Microstructure of titanium Grade 2 surface after cyclic oxidation

Microscopic images showing the microstructure of titanium Grade 2 surface after cyclic oxidation are shown in **Figs. 1–3**.

Based on the analysis of microscopic images of titanium Grade 2 surfaces after cyclic oxidation, it was shown that the variation of process parameters (temperature, number of cycles) significantly affects the morphological characteristics of oxide layers. It was found that the obtained oxide layers

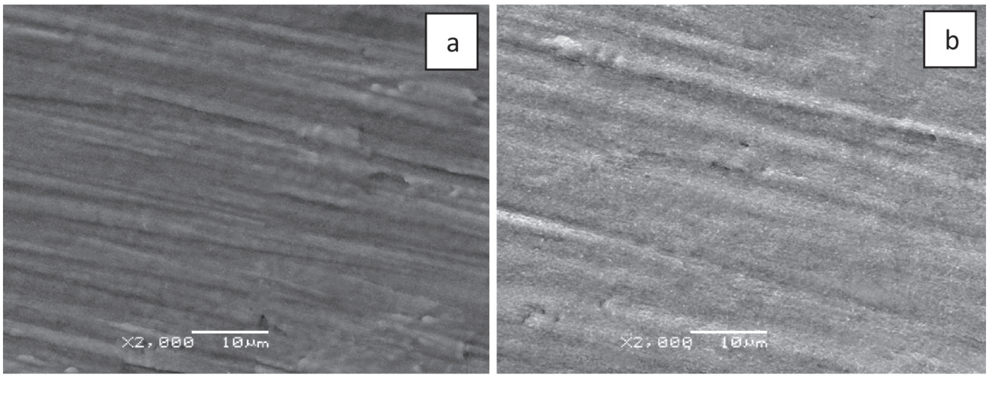


Fig. 1. Microstructure of titanium Grade 2 surface after cyclic oxidation at 600°C (Fig. a – 4 cycles, Fig. b – 12 cycles)
Rys. 1. Mikrostruktura powierzchni tytanu Grade 2 po utlenianiu cyklicznym w temperaturze 600°C (rys. a – 4 cykle, rys. b – 12 cykli)

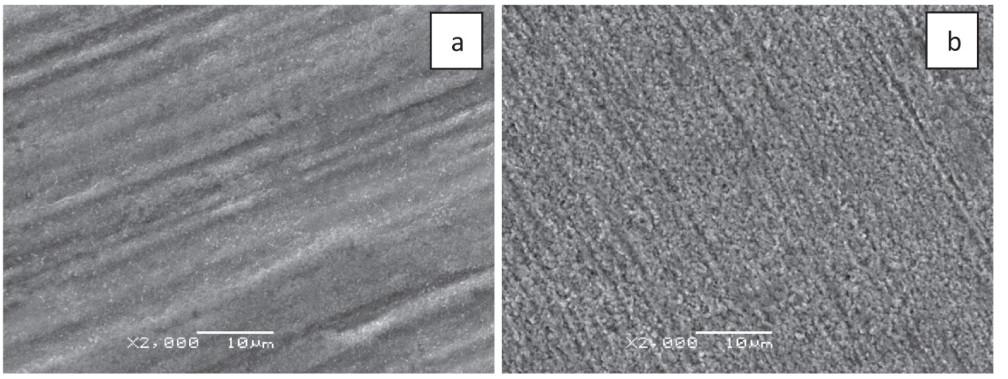


Fig. 2. Microstructure of titanium Grade 2 surface after cyclic oxidation at 650°C (Fig. a – 4 cycles, Fig. b – 12 cycles)
Rys. 2. Mikrostruktura powierzchni tytanu Grade 2 po utlenianiu cyklicznym w temperaturze 650°C (rys. a – 4 cykle, rys. b – 12 cykli)

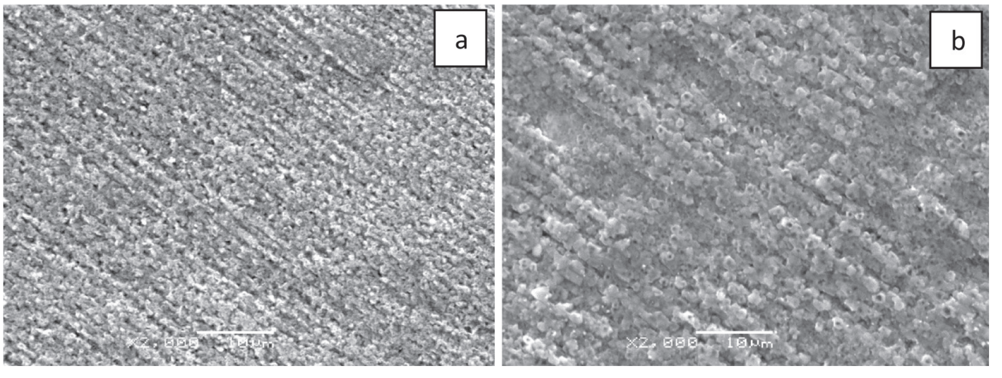


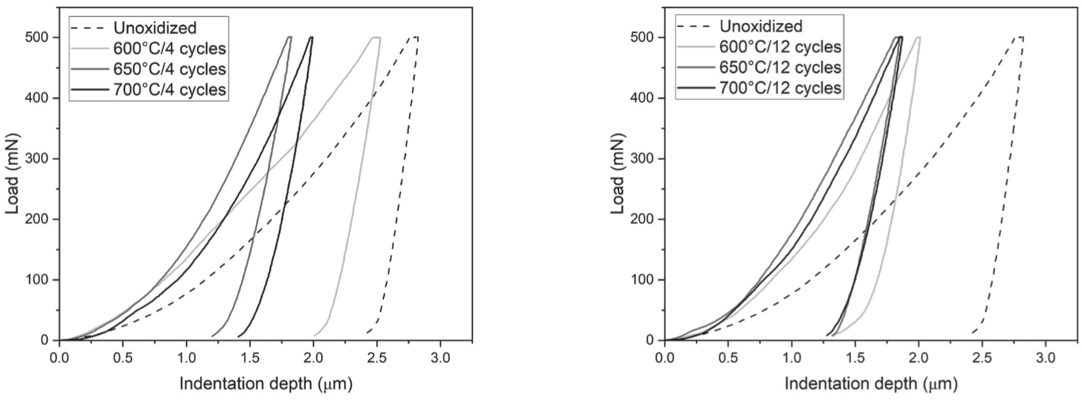
Fig. 3. Microstructure of titanium Grade 2 surface after cyclic oxidation at 700°C (Fig. a – 4 cycles, Fig. b – 12 cycles)
Rys. 3. Mikrostruktura powierzchni tytanu Grade 2 po utlenianiu cyklicznym w temperaturze 700°C (rys. a – 4 cykle, rys. b – 12 cykli)

were continuous and covered the entire surface of the specimens.

After oxidation of the titanium at 600°C, oxide layers were obtained, which consisted of fine oxide particles covering surface irregularities left after grinding the specimens for tribological tests. The microscopic images clearly show the direction of grinding, which indicates the small thickness of the oxides produced (**Fig. 1a**). Due to the greater thickness of the oxide layers obtained after 12 cycles of oxidation at 600ºC, it was found that the scratches on the surface were somewhat softer (**Fig. 1b**). After four oxidation cycles at a temperature of 650°C, a similar surface morphology was obtained (**Fig. 2a**). It was found that increasing the number of cycles (up to 12) contributed to the intensification of the oxidation process, which was directly reflected in a marked increase in the oxide particle size (**Fig. 2b**). After cyclic oxidation at 700°C (four cycles), the oxide layers produced were composed of oxide particles of even larger size (**Fig. 3a**). Layers with the largest oxide particle size were obtained after 12 oxidation cycles at 700°C (**Fig. 3b**). A similar surface microstructure was obtained on titanium Grade 2 after isothermal oxidation **[L. 13]**. The reason for the increase in oxidation intensity, the growth rate of oxide layers and the size of oxide particles were mainly due to the increase in cyclic oxidation temperature. The formation of large oxide grains was associated with the nucleation and agglomeration of finer oxide particles **[L. 14]**. The oxidation process conducted at a higher temperature further facilitated the agglomeration of oxide grains. The growth of each oxide grain promoted attachment to neighbouring grains, leading to uniform surface coverage as the thickness of the oxide layer increased **[L. 14, 15]**.

Examination of micromechanical properties

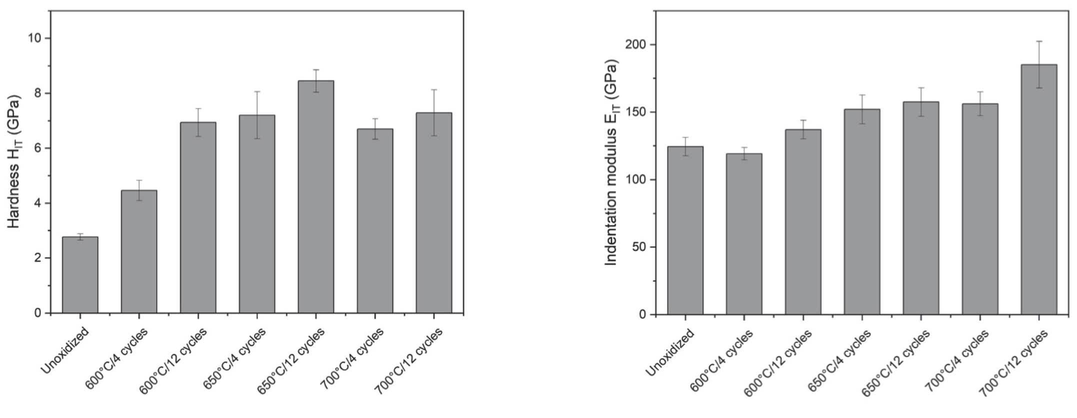
Figures 4 and **5** present the results of micromechanical tests of titanium Grade 2 in the non-oxidised state and after cyclic oxidation at 600°C, 650°C and 700°C, obtained at a maximum load of 500 mN, and a load/unload rate of 16.7 mN/s.



a b

Fig. 4. Examples of load-unload curves (P-h) recorded during micromechanical tests of titanium Grade 2 in the non-oxidised state and after cyclic oxidation (Fig. a – 4 cycles, Fig. b – 12 cycles)

Rys. 4. Przykładowe krzywe obciążenie-odciążenie (P-h) zarejestrowane podczas testów mikromechanicznych tytanu Grade 2 w stanie nieutlenionym oraz po utlenianiu cyklicznym (rys. a – 4 cykle, rys. b – 12 cykli)



a b

Fig. 5. Hardness HIT (a) and indentation modulus EIT (b) of titanium Grade 2 depending on the oxidation temperature and the number of cycles

Rys. 5. Twardość H_{IT} (a) oraz moduł sprężystości E_{IT} (b) tytanu Grade 2 w zależności od temperatury utleniania oraz liczby cykli

Figure 4 shows examples of load-unload (P-h) curves recorded during micromechanical testing of titanium Grade 2 in the non-oxidised state and after cyclic oxidation. It was found that all load-unload curves obtained for different oxidation conditions overlapped well, indicating the reproducibility of the mechanical tests. It was shown that the indenter's penetration depth decreased after cyclic oxidation, which was associated with an increase in the hardness of the titanium surface (**Fig. 4**).

The tests also showed that the average hardness H_{IT} of titanium Grade 2 not subjected to oxidation was about 2.8 GPa. After cyclic oxidation, pure titanium was characterised by up to 3 times higher hardness. It was found that hardness (H_{IT}) increased with increasing oxidation temperature and the number of cycles. The highest hardness (8.4 GPa) was obtained after 12 oxidation cycles at 650°C. However, after oxidation at 700°C, a slight tendency to decrease in hardness was observed (**Fig. 5a**). The reason for the decrease in hardness of the oxide layers produced at 700°C may have been the greater effect of heat shocks after each oxidation cycle, which resulted in a deterioration of adhesion **[L. 8]**. This phenomenon could also occur due to a mismatch in thermal expansion coefficients between the substrate and the oxide layer **[L. 16]**. Another factor affecting the reduction in hardness was the higher surface roughness after oxidation at 700°C (roughness increased with increasing oxidation temperature). As shown in paper **[L. 17]**, the presence of topographic irregularities can significantly impact the results of hardness measurements. Consequently, this means that surfaces with higher roughness may have slightly lower hardness compared to smooth surfaces.

Figure 5b shows a graph of indentation modulus E_{IT} versus oxidation parameters. Titanium Grade 2 in the as-received condition had an indentation modulus value (E_{IT}) of approx. 124 GPa. The study showed that the value of the E_{IT} parameter increased with increasing oxidation temperature and the number of cycles (an increase of about 10–49%), which was closely related to the increase in hardness after oxidation. The highest value of indentation modulus E_{IT} (approx. 185 GPa) was obtained after 12 cycles of titanium oxidation at 700°C.

Examination of tribological properties

Figures 6-8 show the results of tribological tests performed on titanium Grade 2 before and after cyclic oxidation.

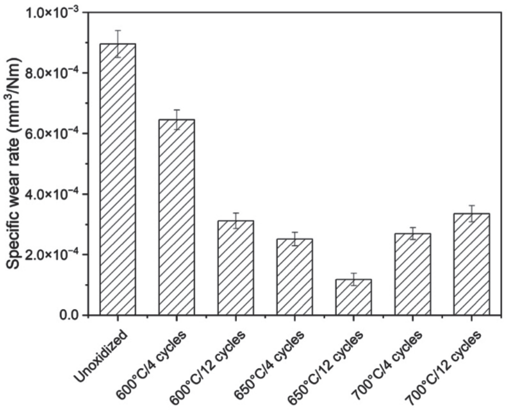


Fig. 6. Specific wear rate of titanium Grade 2 disc before and after cyclic oxidation during sliding interaction with Al_2O_3 balls

Rys. 6. Wskaźnik zużycia objętościowego tarczy z tytanu Grade 2 przed i po utlenianiu cyklicznym podczas współpracy ciernej z kulkami Al_2O_3

Based on the analysis of tribological test results, it was found that titanium Grade 2 in the non-oxidised state wore most intensively with Al_2O_3 balls. The specific wear rate during tests with ZrO_2 and 100Cr6 balls was nearly twice as low. The lower resistance to sliding wear of titanium in couples with Al_2O_3 balls was related to their higher hardness (about 1700 HV) compared to the other

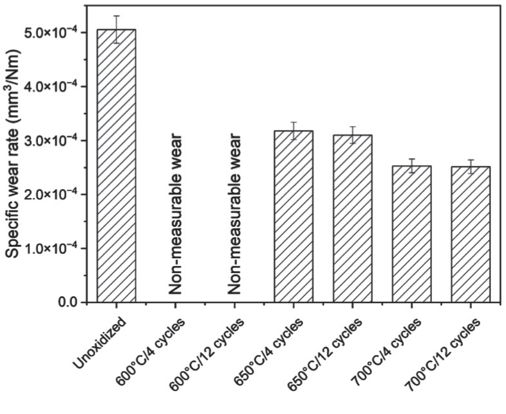


Fig. 7. Specific wear rate of titanium Grade 2 disc before and after cyclic oxidation during sliding interaction with ZrO_2 balls

Rys. 7. Wskaźnik zużycia objętościowego tarczy z tytanu Grade 2 przed i po utlenianiu cyklicznym podczas współpracy ciernej z kulkami ZrO_2

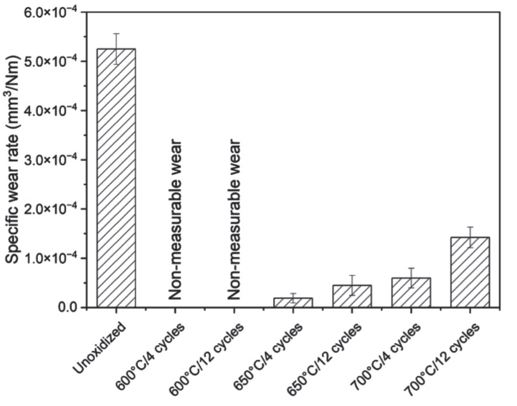


Fig. 8. Specific wear rate of titanium Grade 2 disc before and after cyclic oxidation during sliding interaction with 100Cr6 bearing steel balls

Rys. 8. Wskaźnik zużycia objętościowego tarczy z tytanu Grade 2 przed i po utlenianiu cyklicznym podczas współpracy ciernej z kulkami ze stali łożyskowej 100Cr6

balls (approx. 1350 HV – ZrO_2, approx. 830 HV – 100Cr6) **[L. 18, 19]**. After the cyclic oxidation process, there was a varying reduction in the specific wear rate of the titanium Grade 2 discs depending on the oxidation parameters and the materials used as counter-specimens. Tribological tests performed for couples with Al_2O_3 balls showed a systematic decrease in the specific wear rate of titanium with increasing oxidation temperature and the number of cycles. The greatest reduction in wear was observed after 12 cycles of titanium oxidation at 650°C (**Fig. 6**). The obtained result coincided with the results of hardness measurements (**Fig. 5a**). The oxide layers obtained at 700°C exhibited slightly weaker tribological properties, which could be related to a decrease in hardness and deterioration of adhesion **[L. 8]**. After friction contact of oxidised titanium with ZrO_2 balls, completely different tribological characteristics were demonstrated. After tests with ZrO_2 balls (under the accepted test conditions), no wear was found on the titanium Grade 2 disc after cyclic oxidation at 600°C. The test results obtained in this case were due to the lower coefficient of friction (**Fig. 10**), the lower hardness of zirconium oxide and its specific tribological properties **[L. 20]**. The cyclic oxidation process carried out at 650°C and 700°C caused a reduction in the specific wear rate of titanium in pairs with ZrO_2 balls by only 37–50%. After tribological tests of couples with 100Cr6 bearing steel balls, similarly to the ZrO_2 balls, no wear was observed on titanium oxidised at 600°C. The oxides obtained on titanium at 650°C and 700°C also provided very good tribological properties when tested with the 100Cr6 steel (wear reduction ranged from 73% to 96%). However, it was found that resistance to sliding wear deteriorated with increasing oxidation temperature and the number of cycles. The reason for the (slight) deterioration of the tribological properties of titanium may have been the increase in the size of oxide particles, resulting in a surface with greater roughness and this, consequently, led to an intensification of the sliding wear process **[L. 21]**.

Coefficient of friction

Figures 9–11 show graphs with the averaged (stabilised) coefficient of friction values as a function of cyclic oxidation parameters of titanium Grade 2, counter-specimen material and friction distance. The maximum friction coefficient values in the initial phase of tribological tests (in non-stabilised conditions from 0 to 200 m) are also presented.

Based on the analysis of the results obtained, it was found that the values of the coefficient of friction were closely dependent on the parameters of cyclic oxidation and the material couple used. It was shown that the coefficient of friction was most stable in the tests with titanium Grade 2 in the non-oxidised state with both ceramic and metallic balls. The averaged values of the coefficient of friction in stabilised conditions were 0.65 (Al_2O_3), 0.8 (ZrO_2) and 0.82 (100Cr6), respectively. Tribological

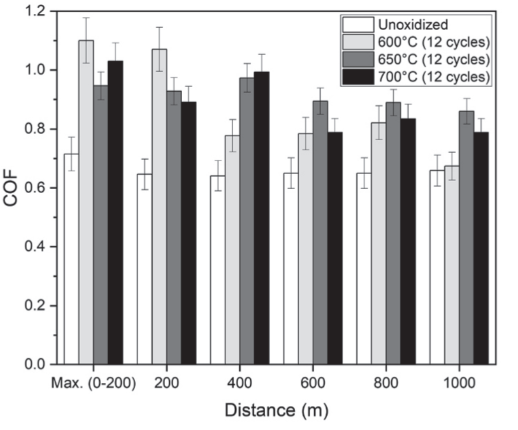


Fig. 9. Coefficient of friction during tribological tests of titanium Grade 2 with Al_2O_3 balls

Rys. 9. Współczynnik tarcia podczas testów tribologicznych tytanu Grade 2 z kulkami Al_2O_3

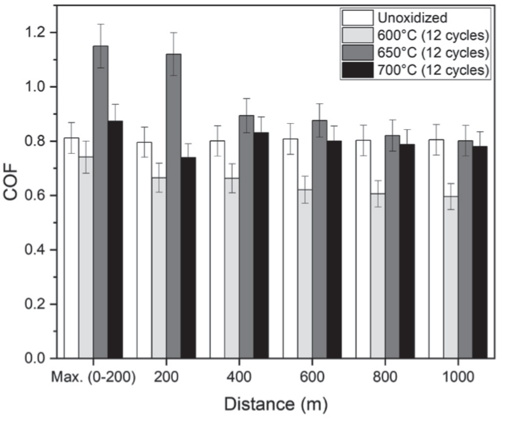


Fig. 10. Coefficient of friction during tribological tests of titanium Grade 2 with ZrO_2 balls

Rys. 10. Współczynnik tarcia podczas testów tribologicznych tytanu Grade 2 z kulkami ZrO_2

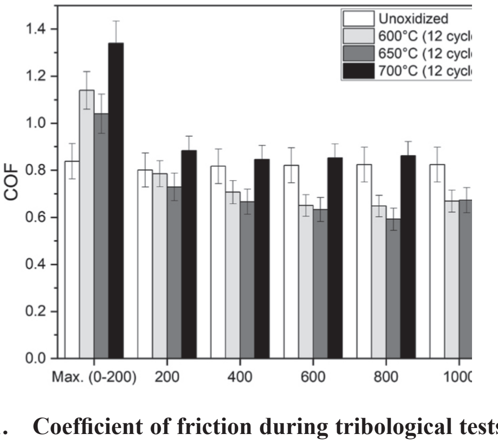


Fig. 11. Coefficient of friction during tribological tests of titanium Grade 2 with 100Cr6 bearing steel balls

Rys. 11. Współczynnik tarcia podczas testów tribologicznych tytanu Grade 2 z kulkami ze stali łożyskowej 100Cr6 tests of titanium Grade 2 after cyclic oxidation showed an increase in the coefficient of friction value (by about 40%) during sliding interaction with Al_2O_3 balls (**Fig. 9**). However, the increase in the coefficient of friction after oxidation of titanium Grade 2 did not translate into an increase in wear. On the other hand, after tests with ZrO_2 balls, a decrease in the coefficient of friction value (by about 20%) was observed for the oxide layers produced on titanium at a temperature of 600°C (no wear was observed for this oxidation variant). Similar results were obtained in the tests **[L. 22]** performed on thermally oxidised Ti-6Al-4V alloy when interacting with ZrO_2 balls both during dry friction and under serum lubrication. An increase in the coefficient of friction values during tests with ZrO_2 balls was observed only for the cyclically oxidised titanium at 650°C (especially in the initial phase of sliding contact). This could be due to the fact that for this temperature variant, the highest hardness of the oxide layers was obtained (**Fig. 5a**). After the oxidation of titanium at 700°C, the coefficient of friction during tests with ZrO_2 balls was similar in values to the non-oxidised sample. On the other hand, a beneficial effect of a reduction in the coefficient of friction after oxidation of titanium Grade 2 at 600°C and 650°C was obtained during tribological interaction with 100Cr6 bearing steel balls. It was observed that the coefficient of friction decreased as the friction distance increased. A slight increase in the coefficient of friction was observed only in the couples with oxide layers obtained on titanium at 700°C, which may have been caused by higher surface roughness **[L. 21]**.

CONCLUSIONS

Based on the performed tests and analysis of the obtained results, the effect of cyclic oxidation parameters on the micromechanical and tribological properties of titanium Grade 2 was determined. The following conclusions have been formulated:

1. The oxide layers obtained by cyclic oxidation were of good quality. It was found that the size of oxide particles formed on the titanium surface increased as the oxidation temperature and the number of cycles increased.
2. Hardness H_{IT} of titanium Grade 2 in the non-oxidised state was about 2.8 GPa. Up to a 3-fold increase in hardness was found after cyclic oxidation. The highest hardness of titanium (8.4 GPa) was obtained after 12 oxidation cycles at 650°C. Only after oxidation at 700°C a slight tendency to decrease in hardness was observed (deterioration of adhesion and increased surface roughness).
3. Titanium Grade 2 in the as-received condition had an indentation modulus value (E_{IT}) of approx. 124 GPa. After cyclic oxidation, an approx. 10–49% increase (to about 185 GPa) in the value of the E_{IT} parameter was found.
4. The cyclic oxidation process resulted in a significant improvement in the tribological characteristics of titanium Grade 2. Resistance to sliding wear was strictly dependent on the parameters of the oxidation process and the material couple. The best tribological characteristics were obtained after oxidation of titanium Grade 2 at 600°C during sliding contact with ZrO_2 and 100Cr6 balls (unmeasurable wear under the test conditions set). In the other test variants, the reduction in wear after oxidation ranged from 37 to 96%.
5. The coefficient of friction depended on the cyclic oxidation parameters and the material couple used. Cyclic oxidation of titanium Grade 2 showed an increase in the coefficient of friction value by about 40% during tests with Al_2O_3 balls. However, the higher friction coefficient values after oxidation of titanium Grade 2 did not translate into increased wear. A beneficial effect of a reduction in the coefficient of friction was obtained during sliding contact of oxidised titanium with ZrO_2 (after oxidation at 600°C) and 100Cr6 balls (after oxidation at 600°C and 650°C).

REFERENCES

1. Zhou Y., Zhang Q.Y., Liu J.Q., Cui X.H., Mo J.G., Wang S.Q.: Wear characteristics of a thermally oxidized and vacuum diffusion heat treated coating on Ti–6Al–4V alloy. Wear 344–345, 2015, pp. 9–21.
2. Unune D.R., Brown G.R., Reilly G.C.: Thermal based surface modification techniques for enhancing the corrosion and wear resistance of metallic implants: A review. Vacuum 203, 2022, p. 111298.
3. Niu Y., Pang X., Yue S., Wang S., Song C., Shangguan B., Zhang Y.: Improving tribological properties of Ti–Zr alloys under starved lubrication by combining thermal oxidation and laser surface texturing. Wear 496–497, 2022, p. 204279.
4. Brończyk A., Kowalewski P., Samoraj M.: Tribocorrosion behaviour of Ti6Al4V and AISI 316L in simulated normal and inflammatory conditions. Wear 434–435, 2019, p. 202966.
5. Cimenoglu H., Meydanoglu O., Baydogan M., Bermek H., Huner P., Kayali S.: Characterization of Thermally Oxidized Ti6Al7Nb Alloy for Biological Applications. Met. Mater. Int. 17(5), 2011, pp. 765–770.
6. Yadav S., Kumar A., Paramesh T., Sunita K.: A Review on Enhancement of Wear Resistance Properties of Titanium Alloy using Nano-Composite Coating. IOP Conf. Series: Materials Science and Engineering 455, 2018, p. 012120.
7. Chou K., Li N., Marquis E.A.: Enhanced work hardening from oxygen-stabilized ω precipitates in an aged metastable β Ti-Nb alloy. Acta Materialia 220, 2021, p. 117302.
8. Aniołek K., Barylski A., Kupka M., Dercz G.: Cyclic Oxidation of Titanium Grade 2. Materials 13(23), 2020, p. 5431.
9. ISO 14577-1:2015. Metallic materials – Instrumented indentation test for hardness and materials parameters – Part 1: Test method.
10. ASTM E2546. Standard Practice for Instrumented Indentation Testing.
11. Oliver W.C., Pharr G.M.: An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. J. Mater. Research 7, 1992, pp. 1564–1583.
12. Aniołek K., Barylski A., Kupka M., Tylka J.: The influence of thermal oxidation parameters on structural, friction, and wear characteristics of oxide layers produced on the surface of Ti–6Al–7Nb alloy. Journal of Tribology 141, 2019, pp. 031605-1-031605-9.
13. Aniołek K., Barylski A., Kupka M., Kaptacz S., Czajerek P.: Characterization of tribological properties of oxide layers obtained on titanium in different friction couples. Tribologia 2, 2018, pp. 5–11.
14. Kumar S., Sankara Narayanan 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.
15. Somsanith N., Sankara Narayanan T.S.N., Kim Y.-K., Park I.-S., Bae T.-S., Lee M.-H.: Surface medication of Ti–15Mo alloy by thermal oxidation: Evaluation of surface characteristics and corrosion resistance in Ringer's solution. Applied Surface Science 356, 2015, pp. 1117–1126.
16. Ebach-Stahl A., Eilers C., Laska N., Braun R.: Cyclic oxidation behaviour of the titanium alloys Ti-6242 and Ti-17 with Ti–Al–Cr–Y coatings at 600 and 700 °C in air. Surface & Coatings Technology 223, 2013, pp. 24–31.
17. Münchow E.A., Correa M.B., Ogliari F.A., Piva E., Zanchi C.H.: Correlation between surface roughness and microhardness of experimental composites with varying filler concentration. The Journal of Contemporary Dental Practice 13(3), 2012, pp. 299–304.
18. Aniołek K., Barylski A., Kowalewski P., Kaptacz S.: Investigation of dry sliding friction, wear and mechanical behavior of the Ti-6Al-7Nb alloy after thermal oxidation. Materials 15, 2022, p. 3168.
19. Ouyang J.H., Yang Z.L., Liu Z.G., Liang X.S.: Friction and wear properties of reactive hot-pressed TiB_2–TiN composites in sliding against Al_2O_3 ball at elevated temperatures. Wear 271, 2011, pp. 1966–1973.
20. Jitwirachot K., Rungsiyakull P., Holloway J.A., Jia-mahasap W.: Wear Behavior of Different Generations of Zirconia: Present Literature. Hindawi International Journal of Dentistry 2022, 2022, p. 9341616.

21. Correaa D.R.N., Grandini C.R., Rocha L.A., Proença J.P., Sottovia L., Cruz N.C., Rangel E.C., Hanawa T.: Effect of temperature on thermal oxidation behavior of biomedical Ti-Zr- Mo alloys. Journal of Alloys and Compounds 905, 2022, p. 164202.
22. 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.