



Mechanical and tribological properties of oxide layers obtained on titanium in the thermal oxidation process



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ABSTRACT

The paper presents the results of tests concerning a modification to the surface of titanium Grade 2 in the thermal oxidation process. It describes the oxidation kinetics of the tested material in the temperature range of 600–800 °C, with a duration from 20 min to 72 h. The greatest increase in mass was found in specimens oxidised at a temperature of 800 °C. The morphology of the obtained oxide layers was determined. The particles of oxides formed were noticeably larger after oxidation at a temperature of 600 °C. Raising temperature resulted in the formation of fine compact particles in the oxide layer. A phase analysis of oxidation products showed that TiO₂ in the crystallographic form of rutile and Ti₃O are the prevalent types of oxide at a temperature of 600 and 700 °C. On the other hand, only rutile formed at a temperature of 800 °C. Tribological tests showed that the presence of an oxide layer on the surface of titanium significantly improved resistance to abrasive wear. It was found that volumetric wear had decreased by 48% for a specimen oxidised at a temperature of 600 °C and by more than 60% for a specimen subjected to isothermal soaking at a temperature of 700 °C.

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1. Introduction

Titanium and its alloys are very popular in medicine and in a large number of technology fields. Due to a combination of low density and high corrosion resistance with good plasticity and mechanical properties these materials are widely used in engineering [1]. Titanium and its alloys are characterised by the best biocompatibility among metallic materials, which makes them particularly appealing in medicinal applications [2,3]. The high biocompatibility of titanium is caused mainly by the formation of spontaneous passive layers [4,5].

Titanium is a highly reactive metal which, when exposed to the environment, reacts with oxygen in a matter of microseconds, creating a several-nanometre-thick oxide layer which reduces further oxidation and diffusion of oxides at lower temperatures [6]. However, passive layers in their natural form do not ensure appropriate resistance to tribological wear, which limits wider application of titanium and its alloys in medicine [7,8]. From the medical point of view low resistance to abrasive wear is a highly disadvantageous phenomenon which leads, among others, to the loosening of joint endoprostheses. Degradation processes caused by tribological wear cause approximately 80% of revision surgeries. It was

also determined that abrasive wear products might accumulate in internal organs, such as the liver, spleen and abdominal cavity [9]. Low resistance to abrasive wear and the high friction coefficient of titanium and its alloys require the use of an appropriate modification technology in order to improve the properties of the surface layer [5]. Another frequent problem is biocorrosion of titanium and its alloys caused by the impact of the bacterial environment in the human body. [10].

Various surface enrichment methods, which make it possible to create coatings with a wide range of properties, are used to improve mechanical and tribological properties, as well as the corrosion resistance and biocompatibility of titanium and its alloys. The increasing of the thickness of passive layers through the application of thermal oxidation is a relatively simple and economical method of modifying the surface of titanium and its alloys [9]. This method utilises the low resistance of titanium to oxidation and oxygen diffusion at higher temperatures, which makes it possible to harden the surface layer by creating a relatively thick TiO₂ layer over the oxygen diffusion area [5,11,12]. At a sufficiently high temperature oxygen diffuses through the oxygen layer at a contact point between metal and oxygen, and reacts with the formed TiO₂. Temperature growth increases the oxidation rate, allowing the formation of a thicker oxide layer. An oxide layer formed in this manner, which tightly adheres to the substrate, is conducive to an increase in resistance to corrosion and tribological wear. A titanium surface modified in this manner exhibits advantageous properties,

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which result from the formation of a highly crystalline oxide layer in the form of rutile [7].

Individual technologies of thermal oxidation in the air differ mainly in the range of the applied temperature, the methodology of preparation of the material surface, oxidation time and the design of furnaces used. Appropriate preparation of the surface of titanium before oxidation is of the utmost importance. Surface quality affects the growth rate and adhesion of the oxide layer on titanium [3,5,7,9].

The properties of scale (chemical and phase composition, thickness, morphology and structure) have a significant impact of tribological and corrosion durability and play an important role in interactions with the immediate environment. According to the authors of one paper [13], the use of thermal oxidation allows a significant improvement of the low tribological properties of titanium and its alloys. This method enables a 4- to 6-fold reduction in abrasive wear. The results of previous tests clearly show that in certain conditions thermal oxidation may be a more effective tribological wear protection method than ion nitriding [13]. The formation of oxide layers on titanium and its alloys, with a predetermined structure, phase composition and high resistance to corrosion and abrasive wear, may contribute to a significant improvement of the functional properties of these materials [9,14,15].

This paper covers issues related to the thermal oxidation of titanium. The tests presented in the paper focus on the determination of the impact of oxidation time and temperature on the morphology, hardness and resistance to abrasive wear of oxide layers formed as a result of single-stage thermal oxidation on the surface of titanium.

2. Experimental procedures

Commercially pure Grade 2 titanium, in the form of bars 12 and 39 mm in diameter, was used in the tests. A check analysis of the chemical composition showed that the delivered materials were compliant with the certificate enclosed by the manufacturer of the material. Grade 2 titanium was selected for tests due wide application possibilities and a universal availability. This is also the most popular grade of pure titanium. Apart from Grade 2 titanium also three other grades are distinguished—titanium Grade 1, 3 and 4. These grades differ in the concentration of carbon, iron, nitrogen, hydrogen and oxygen and feature diversified mechanical properties (Table 1).

The studies on the oxidation kinetics, surface morphology, phase composition and hardness of obtained oxide layers were carried out on specimens cut from a bar smaller in diameter—12 mm. Instead, tribological tests because of the instrument technical requirement were performed on specimens larger in diameter (39 mm). Details have been described in the Experimental section below.

Specimens in the form of 2-mm-high disks with a diameter of 12 mm were used in oxidation kinetics tests. Specimens were polished on abrasive papers with gradation up to 5000, and then burnished and degreased. The oxidation process was conducted in a chamber furnace, in air atmosphere, at temperatures of 500, 600, 700 and 800 °C, over 20 and 40 min, as well as 1, 2, 6, 24, 48, and 72 h. After a specified soaking time at a given temperature the specimens were removed from the furnace and cooled in the air. Oxidation kinetics were described using the gravimetric method, which consists in the measurement of the increase in the mass of specimens after a specified soaking time at a given temperature. The tested specimens were weighed before and after oxidation with an accuracy of 0.01 mg on an XA 110 laboratory microbalance manufactured by Radwag. An exponential law described by

the following formula was used to characterise the course of the oxidation of titanium [11,16]:

$$\left(\frac{\Delta W}{A}\right)^n = k_n t \quad (1)$$

where ΔW —increase in specimen mass, A —specimen surface area, t —oxidation time, k_n —exponential constant of oxidation rate.

Values of the constant K_p were obtained from the inclination of a straight line adjusted by means of linear regression to the dependence $(\Delta W/A)^2$ in relation to time t . The oxidation process activation energy was determined based on the Arrhenius equation correlating the value of the constant K_p with temperature T [11,16]:

$$K_p = K_0 \exp(-Q/RT) \quad (2)$$

where Q —oxidation process activation energy, K_0 —pre-exponential factor, R —gas constant (8.3144 J/mol/K), T —absolute temperature.

The morphology of the surface of the oxide scale formed on titanium Grade 2 was observed on a JEOL JSM 6480 scanning electron microscope at the following magnifications: 1000, 2000, 5000 and 7000 $\times$. The observations were conducted on specimens oxidised for 72 h at temperatures of 600 and 700 °C.

X-ray examinations were performed using a Philips PW3040/60 X'Pert X-ray diffractometer. Monochromatic X-ray radiation emitted by a copper lamp with a length of $K_{\alpha 1} = 1.5406 \text{ \AA}$ was used. The constant incidence angle method made use of a flat graphite monochromator, and the slit on the incident beam D_5 (Divergent Slit) was $1/32^\circ$. An X-ray lamp was supplied with current with voltage $U = 40 \text{ kV}$ and strength $I = 30 \text{ mA}$. The test was performed at the following constant incidence angles $\alpha = 0.25^\circ$; 0.50° ; 1.00° ; 1.50° and 2.50° . The counter moved in an angular range from 10° to 90° 2θ with a measuring step of 0.05° 2θ . The measuring time per step was 40 s.

Tests of the microhardness of a surface layer covered with an oxide layer and without that layer were performed on a Vickers 401MVD microhardness tester. The tests were conducted in the indenter load range from 25 to 500 g (245–4900 mN). Indenter loads were selected in such a way that the penetration depth remained within the range of oxide layer thickness, and at the same time covered the measurements of the layer along with the substrate. Seven indentations were made on each specimen and then the obtained measurement results were averaged. The load was held for 15 s.

Tests of abrasive wear resistance of oxide layers were performed on a ball-on-disc tribological station (T-01) manufactured by the Institute for Sustainable Technologies—National Research Institute in Radom. The specimens were discs with a diameter of 39 mm, while counter-specimens were Al_2O_3 balls with a diameter of 10 mm. The tests were performed on a non-oxidised and an oxidised surface at temperatures of 600 and 700 °C over 72 h. The parameters of the tribological tests were selected in accordance with the recommendations of VAMAS, as follows:

- Pressure at the test contact point—10 N.
- Sliding speed—0.10 m/s.
- Friction distance—1000 m.
- Friction working diameter—24 mm.
- Air temperature— $21 \pm 1^\circ \text{C}$.
- Air humidity— $50 \pm 1^\circ \text{C}$.

3. Results and discussion

3.1. Titanium oxidation kinetics

The performed thermal oxidation kinetics tests made it possible to determine the impact of temperature and time on the rate

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