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CHARACTERISTIC OF OXIDE LAYERS OBTAINED ON TITANIUM IN THE PROCESS OF THERMAL OXIDATION

Thermal oxidation in air may be one method to improve the properties of titanium and its alloys through its influence on the structure and properties of the material's surface layer. This paper presents a description of oxide layers obtained on the surface of Grade 2 titanium as a result of oxidation at temperatures of 600 and 700°C. On the basis of kinetic curves, it was found that the intensity of oxide layer growth increased with oxidation temperature. Studies of the surface morphology of oxide layers showed that the size of the formed oxide particles was greater following oxidation at 600°C. The obtained layers were subjected to X-ray phase analysis and microhardness measurements. Irrespective of oxidation temperature, the scale consisted of TiO_2 oxide in the crystallographic form of rutile and of Ti_3O oxide. The hardness of oxide layers amounted to around 1265 HV and was more than 4 times higher compared to the material in its initial state.

Keywords: titanium; oxidation; scale; structure; hardness

1. Introduction

Titanium, once considered a rare metal, is nowadays one of the most important metals in industry [1]. Titanium and its alloys are widely used in engineering and biomedical applications due to a favourable ratio of strength to specific gravity, a high level of corrosion resistance, and high biocompatibility [1–5]. The high level of biocompatibility of titanium and its alloys results mainly from their spontaneous formation of passive layers. A natural oxide layer plays a crucial role in biocompatibility and reduces the penetration of ions of alloying elements to the human body. However, because the passive layers, in their natural form, are very thin, they do not ensure an appropriate level of resistance to tribological wear, which limits the broader application of titanium in medicine [6, 7]. The poor tribological properties of titanium result primarily from a high and unstable coefficient of friction [8].

To improve its mechanical and tribological properties, corrosion resistance, and biocompatibility, it is possible to use titanium's high affinity for oxygen, which on one hand limits the application of titanium at higher temperatures but on the other enables the characteristics of the surface layer to be changed by means of thermal oxidation in air. This process enables the acquisition of a thicker oxide scale layer with a controlled structure and specified properties. These properties have a significant impact on tribological and corrosion resistance and play an important role in interactions with the surrounding environment. A titanium surface modified by means of thermal oxidation displays very good properties, mainly due to the presence of a relatively thick crystalline layer of TiO_2 (in the form of rutile), an oxide characterised by properties better than those of brookite and anatase [8]. It has been established that thermal oxidation produces a layered structure comprising an oxide layer on the surface and a hardened oxygen diffusion zone on the subsurface of titanium [7]. The oxide layer may be characterised by low wear rates [9], while the oxygen diffusion zone may be beneficial in enhancing the load-bearing capacity, lubrication ability, and abrasive wear resistance of titanium [10, 11]. According to the authors of paper [12], the use of the thermal oxidation technique enables substantial improvement of the poor tribological properties of titanium and its alloys, which in turn enables the reduction of abrasive wear by 4 to 6 times. In papers [8, 13] it was found that oxide layer thickness is one of the most important factors determining titanium's corrosion resistance. Comparative investigations on the corrosion and hydrogen uptake resistance of pickled, anodised, and thermally oxidised titanium have indicated that thermal oxidation generally offers better protective performance than anodising or pickling [14]. The additional protection offered by thermal oxides, compared to anodised film, is consistent with findings that thermal oxidation produces a thick, highly crystalline rutile oxide film, whereas anodising generates anatase and/or hydrated oxides of low crystallinity [14]. Thermal oxidation also ensures the acquisition of a uniformly rough titanium surface and results in increased surface energy. The roughness of oxidised surfaces increases as a result of oxidation at higher temperatures [3, 15].

Oxide layers produced during thermal oxidation at a temperature above 800°C and during a longer period are characterised by sufficient thickness, but are brittle and frequently subject to spalling (especially on pure titanium) [8, 16], whereas layers obtained at a lower temperature, after a short oxidation period, may be too thin for tribological applications.

In the present study, an attempt has been made to develop a uniform oxide layer on the surface of titanium by means of thermal oxidation at temperatures of 600 and 700°C. The study

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comprised the analysis of oxidation kinetics and determination of the phase composition, surface morphology, and hardness of the produced oxide layers.

2. Experimental procedures

Commercially pure Grade 2 titanium was the tested material in the form of bars 12 mm in diameter, manufactured by S-Tech Corporation. A control analysis of chemical composition was carried out at the Institute of Ferrous Metallurgy in Gliwice (Poland). The following research techniques were used: ICP-OES (Inductively Coupled Plasma - Optical Emission Spectroscopy), HFIR, and high-temperature extraction. The results of this analysis are presented in Table 1. The chemical composition was consistent with the certificate delivered by the material's manufacturer.

TABLE 1

Chemical composition of titanium Grade 2

Component content (wt%)				
C	Fe	H	N	O
0.008	0.13	0.0019	0.010	0.18

Studies of the microstructure of the as-delivered material were carried out using an Olympus GX51 optical microscope at magnifications of 100, 200 and 500×. The surface of the specimen was mechanically wet ground and polished. Abrasive papers with the following grades were used: 600, 1200, 2000, 3000, and 5000. The polishing was done using diamond pastes with grain sizes of 3 and 1 μm. The obtained microsection was cleaned using acetone and etched in Kroll's reagent.

The process of thermal oxidation was carried out in an FCF 22 HM laboratory chamber furnace in air. Specimens for oxidation kinetic studies, in the form of discs approximately 2 mm thick, were ground using abrasive papers of grades up to 5000 and then polished, rinsed with water and degreased in acetone. Oxidation was carried out at temperatures of 600 and 700°C for 20 and 40 min. as well as for 1, 2, 6, 24, 48, and 72 h. After a specified period of annealing at a given temperature, specimens were removed from the furnace and cooled in air. The oxidation kinetics were described based on the increase in the weight of the specimens after a specified annealing time. The weight increase during oxidation was determined on a Radwag XA 110 microbalance with an accuracy of 0.01 mg.

The surface morphology of the produced oxide layers was examined on a JEOL JSM-6480 scanning electron microscope at magnifications of 1000, 2000, 5000 and 7000×. Observations were carried out on specimens oxidised for 72 h.

X-ray studies were carried out using a Philips X'Pert PW3040/60 X-ray diffractometer, with monochromatic X-ray radiation from a copper tube, with a wavelength of $K_{\alpha 1}$ = 1.5406 Å. For studies using a fixed incidence angle (FIA), a flat graphite monochromator was used, with a divergence slit D_S of 1/32° on the incident beam. The X-ray tube was supplied with an electric current at a voltage of U = 40 kV and intensity of I = 30 mA. The studies were carried out at fixed incidence angles of a = 0.25, 0.50, 1.00, 1.50, and 2.50°. The counter moved within an angular range from 10° to 90° 2θ,

with a measuring step of 0.05° 2θ, and the time of one step measurement was 40 s.

The microhardness of the surface layer at different loads was measured on a Vickers 401MVD microhardness tester with an applied load ranging from 25 to 200g (245–1.960 mN). Load-holding time was 15 s. Each presented hardness result is the arithmetic mean of 7 measurements.

3. Results and discussion

3.1. Microstructure of the as-delivered material

Microscopic metallographic examinations showed that the as-delivered Grade 2 titanium was characterised by a grain structure with grain size 9 according to the ASTM scale (Fig. 1).
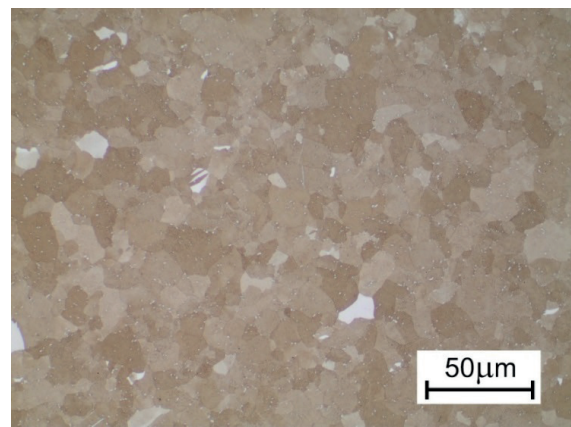

Fig. 1. Microstructure of the as-delivered Grade 2 titanium

3.2. Oxidation kinetics

Fig. 2 presents the obtained relationships of mass change, normalised relative to the specimen surface, versus temperature and oxidation time.
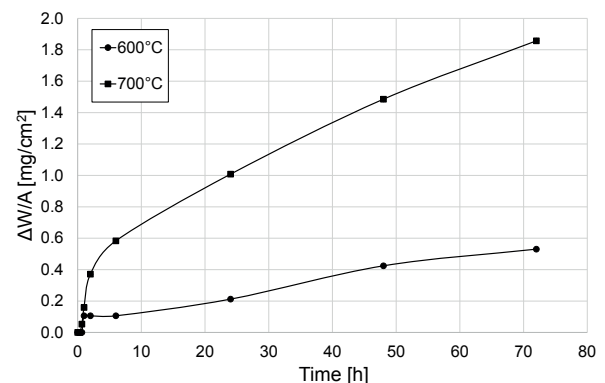

Fig. 2. Oxidation kinetics of Grade 2 titanium vs temperature and oxidation time

With increasing oxidation temperatures, the intensity of oxide layer build-up increased. For specimens oxidised at 600°C, the most intensive weight increase occurred during the first hour of oxidation; in the case of the temperature of 700°C, during the initial six h. After this time had passed, the course of

oxidation curves stabilised. After 72 h of oxidation at 700°C, the growth of specimen weight was nearly three times higher than after oxidation at 600°C.

3.3. Surface morphology of the scale

Fig. 3 shows the scanning electron micrographs of the top surface of thermally oxidised Ti at 600 and 700°C for 72 h.
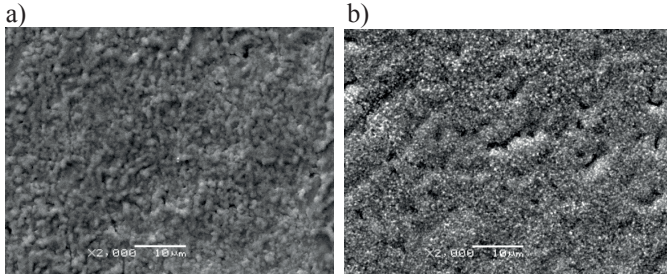

Fig. 3. Morphology of the titanium surface after oxidation at temperatures of 600 (a) and 700°C (b) for 72 h (SEM)

Studies of titanium thermally oxidised at temperatures of 600 and 700°C showed the presence of a uniform oxide layer on the whole surface. No symptoms of scale spalling were found. After oxidation at 700°C, the grains of the formed oxides were clearly larger, consisting of numerous very fine particles of nanometric size. Similar morphology of an oxide layer surface was observed in paper [17] in the case of a Ti-6Al-7Nb alloy oxidised at temperatures of 600 and 700°C. However, scanning electron micrographs (Fig. 7a, b, [17]) and the shape of kinetic curves (Fig. 4, [17]) show that oxidation of the titanium alloy proceeded more slowly.

3.4. Phase composition of oxide layers

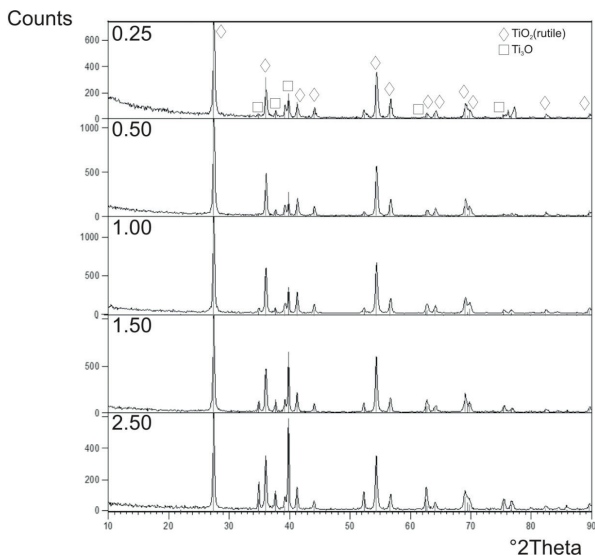The X-ray diffraction spectra of furnace-treated samples at 600 and 700°C are shown in Figs. 4 and 5.

Fig. 4. Set of diffraction patterns obtained using the GIXD method at beam incidence angles α = 0.25, 0.50, 1.00, 1.50, and 2.50° for the specimen oxidised at 600°C
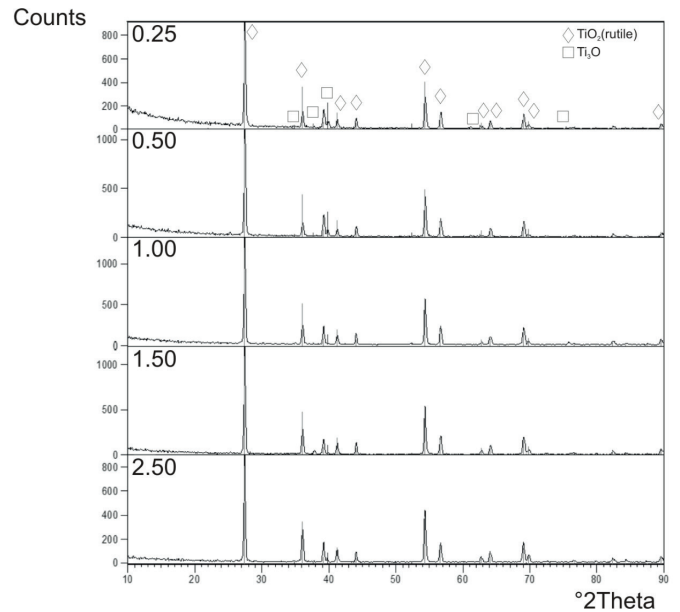

Fig. 5. Set of diffraction patterns obtained using the GIXD method at beam incidence angles α = 0.25, 0.50, 1.00, 1.50, and 2.50° for the specimen oxidised at 700°C

In the case of the specimen oxidised at 600°C (Fig. 4) the presence of two phases was found in the oxide layer: TiO_2 in the form of rutile and Ti_3O. With an increase in angle α, the intensity of reflections originating from the titanium-richer phase (Ti_3O) increased, which may prove that the amount of this phase in the oxide layer was greater in the vicinity of the titanium substrate. In the scale formed at 700°C, the same oxide phases existed (Fig. 5); however, no changes were observed in the intensity of Ti_3O phase reflections with increasing beam incidence angles.

3.5. Microhardness measurements

A detailed study of the hardness of the unoxidised titanium and oxide surfaces was undertaken, using a Vickers microindentation hardness tester over a wide range of applied loads. Fig. 6 shows the effect of oxidation temperature on hardness distribution with load.
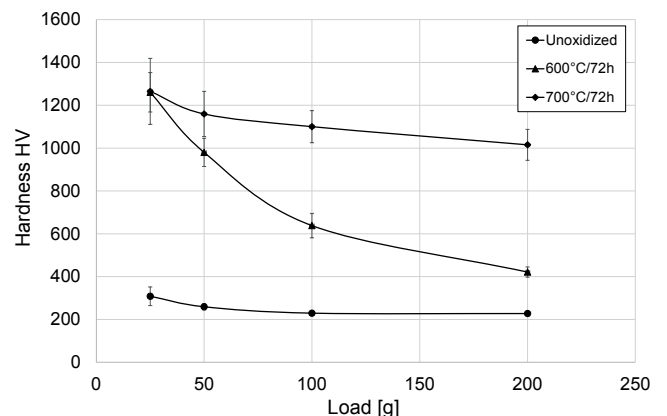

Fig. 6. Variation of hardness profile with load for pure unoxidised and oxidised titanium at various temperatures but the same time periods

In the untreated sample, the hardness value remains almost constant at about 275 HV. After thermal oxidation, the titanium surface was characterised by much greater hardness. It was found that, at a load of 25 g, hardness was approximately 1265 HV irrespective of the oxidation temperature. That meant more than a fourfold increase in hardness compared with the unoxidised material. A similar increase in hardness was observed in paper [18], in the case of a Ti-6Al-4V alloy oxidised at a temperature of 600°C for 60 h, in which hardness increased from 290 HV to 1100 HV. The high hardness value for the oxidised surface is due mainly to the formation of an oxide phase layer. The hardness of rutile is approximately 1733 HV [19]. The hardness of the oxidised surface was found to decrease with load. This can be attributed to the response of the indenter at high penetration depths to softer regions. A higher hardness value (at an indenter load exceeding 25 g) was obtained at the higher oxidation temperature (700°C), most likely due to formation of a thicker and more uniform oxide layer.

4. Conclusions

Titanium and its alloys are among the most promising engineering and biomedical materials. However, due to its insufficient thickness, the protective passive layer formed spontaneously on these materials does not ensure appropriate tribological wear resistance. The formation of an oxide layer of sufficient thickness by means of thermal oxidation may be a relatively simple and economic method for surface modification of titanium and its alloys. In the present study, thermal oxidation of pure titanium was carried out at temperatures of 600 and 700°C for a period of 0.3–72 h at each temperature. Based on analysis of kinetic curves, it was found that more intensive growth of the oxide phase occurred at 700°C. Studies of the surface of titanium oxidised at 600 and 700°C showed the existence of a uniform, crack-free layer consisting of oxide particles of various sizes. The layer of scale formed at the temperature of 600°C featured a more developed surface. After oxidation at 700°C, oxide grains were clearly larger and consisted of numerous very fine particles of nanometric size. Based on the X-ray phase analysis, it was found that titanium oxides in the form of rutile TiO_2 and Ti_3O formed during oxidation of titanium at both temperatures.

Scale hardness was more than 4 times higher compared to pure titanium. Thermal oxidation can be used to improve the surface hardness and wear resistance of titanium and titanium alloy components.

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