Thin Solid Films 626 (2017) 25–37

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Growth kinetics and some mechanical properties of two-phase boride layers produced on commercially pure titanium during plasma paste boriding

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ARTICLE INFO

Article history:
Received 21 November 2016
Received in revised form 27 January 2017
Accepted 11 February 2017
Available online 12 February 2017

Keywords:
Plasma paste boriding
Commercially pure titanium
Growth kinetics of borides
Boron activation energy
Hardness
Wear resistance

ABSTRACT

In this study, the plasma paste boriding (PPB) was applied in order to produce the boride layers on commercially pure titanium (Cp-Ti). PPB process was carried out in 50% H_2–50% Ar atmosphere under a reduced pressure at various parameters (temperature and duration). The boride layers consisted of two zones: a continuous TiB_2 zone close to the surface and a zone with TiB whiskers below the first one. The growth of both zones obeyed the parabolic growth law. The model of growth kinetics of such layers was analyzed. The parabolic growth constants were calculated and the boron diffusion coefficients were determined. Activation energy values of 123.33 and 178.71 kJ mol^{-1} were obtained for TiB_2 and TiB phases, respectively. The calculated value for TiB_2 phase was lower compared to the other boriding processes. Microhardness profile was determined for the layer of the highest depth. The maximal microhardness was characteristic of TiB_2 zone (2452 HV). Nanomechanical properties (nanohardness and Young's modulus) were studied using the nanoindenter. TiB_2 zone was characterized by the nanohardness of 2867.6 HV and indentation modulus $E_{IT} = 383$ GPa. Wear resistance of plasma paste borided layers was up to 9 times higher when comparing to the untreated Cp-Ti.

1. Introduction

Titanium and its alloys are characterized by excellent corrosion resistance. Therefore, they are extensively used as an attractive material for chemical and petrochemical processing equipment [1]. These materials are also often applied in the marine or aerospace applications due to their unique properties, especially, sensational strength-to-weight ratio (even at high temperature), high stiffness and toughness, resistance to oxidation or erosion. Moreover, the low elastic modulus, the excellent biocompatibility and bioadhesion of Ti-based alloys are the reason for their use in biomedical applications, e.g. dental implants, bone plates, screws, hip joint implants, stents, heart valves [2]. Unfortunately, titanium and its alloys are usually characterized by poor wear resistance [3]. Their application under conditions of appreciable mechanical wear requires a suitable surface treatment. Different methods of such a treatment, including nitriding [4] or boriding [5–17], are applied in order to improve the wear resistance of these materials.

Boriding is a well-known thermochemical technique, in which boron atoms diffuse into a workpiece in order to form the hard metal borides. Various methods of this process, such as pack boriding [5–9], boriding in a fluidized bed reactor [10], boriding in borax salt bath [11], electrochemical boriding [12] or plasma assisted boriding [15–17], are used in order to form titanium borides close to the surface of titanium and its alloys. The microstructure, thickness and phase composition of the produced layers depend on boriding method and parameters used (e.g. temperature, time, current density, pressure). Diffusion process usually results in the formation of two zones: continuous TiB_2 layer close to the surface, and TiB whiskers below the first one.

Pack boronizing of titanium and its alloys was in common use. Commercially pure titanium (Cp-Ti) was borided in a powder mixture, consisting of 50 wt.% of amorphous boron, 15 wt.% of an activator ($NaCO_3$) and 35 wt.% of filler (charcoal activated) [5]. The boriding process was carried out in the range of temperatures 850–1050 °C (1123 − 1323 K) for 1, 3 and 5 h. The total thicknesses of the generated layers were measured considering both the continuous TiB_2 zone and the zone with TiB whiskers. The higher temperature and the longer duration of the process, the thicker boride layer was obtained. The average total thickness of the layers was found to be 19.21, 26.36 and 18.18 μm for the specimens borided for 5 h at 850, 910, and 1050 °C (1123, 1183 and 1323 K), respectively. However, the presence of long single TiB whiskers influenced strongly the increase in total thickness. The thicknesses of the continuous TiB_2 zone were significantly lower, with the

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http://dx.doi.org/10.1016/j.tsf.2017.02.033
0040-6090/

values of 1.7, 1.77 and 2.78 μm for 850, 910, and 1050 °C (1123, 1183 and 1323 K), respectively. The formation of TiB_2 was the reason for high hardness. The hardness diminished with the appearance of the TiB whiskers (in the distance above 5 μm from the top surface). The maximal hardness (2968 HV) was obtained in the case of the specimen, borided at 1050 °C (1323K). Whereas the layer, produced at 850 °C (1123K), was characterized by the reduced hardness (2422 HV). This clearly indicated that the thickness of the continuous TiB_2 zone influenced strongly the hardness of the layer. The pure titanium was also borided using a powder mixture, consisting of amorphous boron as a boron source and KBF_4 as an activator [6]. The boriding process was carried out at very high temperature 1300 °C (1573 K) for 3 h. The total thickness of the layer (TiB_2 + TiB) was equal to 28 μm, whereas the obtained thickness of TiB_2 zone was only 8 μm. Growth kinetics of boride layers, produced by powder-pack boriding of Cp-Ti, was studied at temperatures in the range of 850–1050 °C (1123–1323 K) for different durations of the process (from 3 h up to 24 h) [7]. However, the thickness measurements of the whole layer (TiB_2 + TiB whiskers) took into account the depth of the farthest location of the tips of TiB whiskers. Therefore, the total layer thickness was equal even to 57 μm for boriding at 1050 °C (1323 K) for 24 h. This value didn't correspond to an average thickness of the entire layer, which had to be thinner. The maximal thickness of TIB_2 zone obtained was 17 μm. However, the formation of such thick outer zone also required the highest temperature (1050 °C) and the longest duration (24 h). The same process, carried out for Ti6Al4V alloy [8], resulted in a significantly thinner TiB_2 zone (5 μm), and the entire layer (TIB_2 + TiB) was only 17 μm. The boride layer was characterized by high hardness (20–25 GPa) and the improved tribological properties. As a consequence of the pack-boriding of this alloy in Ekabor II powder at 1100 °C (1373 K) for 2.5 h [9], a 10 μm thick two-phase boride layer (TiB_2 + TiB) was produced. Below this layer, a 50 μm thick zone, containing the randomly oriented whiskers mixed with the microstructure of the base metal, was observed. The borided alloy was characterized by a high hardness (1500–2700 HV) as well as excellent wear resistance along with a diminished coefficient of friction. Less commonly used methods of boriding of Ti-based alloys were as follows: fluidized bed technology [10] or boriding in borax salt bath [11].

All the methods, mentioned above, had the same disadvantage. They required the high temperature and long time duration in order to produce on Ti-based alloys the boride layers of applicable thickness. Therefore, the methods of boriding were intensively developed. Some of them, like electrochemical boriding [12], caused the significant decrease in a duration of the process. The relatively thick TiB_2 zone (8.5 μm) was obtained after boriding in a molten electrolyte at 950 °C (1223K) for 2 h. Below the compact TiB_2 layer, the relatively long TiB whiskers occurred. They obtained a length of 11 μm after a one-hour process. The hardness of the monolithic TiB_2 top layer was equal to about 39 GPa. Laser alloying with boron [13,14] caused the formation of a composite surface layer, consisting of the hard borides (TiB + TiB_2) located in the more soft matrix. This matrix was composed of eutectic mixture of $Ti_{\alpha'}$-phase with TiB whiskers. Laser-borided layer was characterized by a significantly increased thickness (up to 455 μm), high hardness (1250–1650 HV) and improved tribological properties [13].

The important difficulty during boriding of Ti-based alloys resulted from the unfavorable impact of the reactive nature of titanium and its susceptibility to oxidation. The relatively thin oxide film, quickly created even at ambient temperature, hindered the boron diffusion during the typical boriding. In general, this difficulty could be overcome by a suitable preparation of the surface, such as etching and phosphatizing as well as by glow-discharge or plasma treatment. Therefore, the plasma boriding process [15], eliminating the need of using expensive surface pre-treatment operations, provided an important advantage compared to other methods of boriding. Additionally, this process could be carried out at diminished temperature. However, some limitations were characteristic of the typical plasma boriding. The main disadvantage consisted in the use of gases (as a boron source) which were expensive, explosive or toxic (B_2H_6 or BCl_3). Moreover, the corrosion in the vacuum chamber and the porosity of boride layer were other serious difficulties characteristic of plasma boriding [16]. These limitations could be eliminated using plasma paste boriding (PPB) [17]. Some literature data also indicated that the plasma paste process resulted in lower activation energy for the formation of boride layer [18]. Such a process enabled the use of lower temperature and seemed to be more effective.

In this study, the growth kinetics of the boride layers, produced on commercially pure titanium using plasma paste boriding, was investigated. Therefore, the various processing parameters were applied. The thicknesses of both the outer TiB_2 zone and the entire boride layer (TiB_2 + TiB) were measured. The kinetic model of the growth of titanium borides was formulated in detail in the previous study [18]. The main novelty of this work was the increased temperature of PPB process as well as the special procedure of the thickness measurements in case of the total layer (TiB_2 + TiB). The temperature ranged from 750 to 850 °C (1023 − 1123 K), and process duration from 3 to 6 h. Boron diffusion coefficients in the TiB_2 and TiB zones as well as boron activation energies were calculated. The microstructure, chemical and phase composition, microhardness, wear resistance and nanomechanical properties were also investigated.

2. Experimental procedure

2.1. Material

Commercially pure titanium, Cp-Ti (Grade 2), was investigated. Its chemical composition was presented in Table 1. The specimens with the dimensions of Φ25 × 4 mm were used in the study.

2.2. Plasma paste boriding

Before the plasma paste boriding (PPB), the specimens were specially prepared. They were ground using 800 mesh SiC abrasive paper in order to obtain a suitable adhesive joint of the paste with a base material. Then, the specimens were coated with a borax paste ($Na_2B_4O_7$) of a thickness of about 1 mm. The drying of the coated specimens lasted 24 h at room temperature.

PPB process was carried out using devices presented in Fig. 1. The prepared samples (3) were placed in the vacuum chamber (1) this way that they had a contact with the cathode (4). Prior to gas input, the chamber was evacuated of air with a rotary vacuum pump (13) obtaining a base pressure of 2.5 Pa. The valve (10) was used in order to control the pressure in the range of 100–10,000 Pa during the process. The temperature was measured using a chrome-alumel thermocouple (6) that was placed at the bottom of the treated samples. Before the boriding process, a cleaning process was applied to minimize contamination and remove the dense oxide layer formed naturally on the surface of titanium by exposure to the air. The cleaning consisted in the bombardment of Ar^+ ions with the use of a high voltage (over 900 V) for 10 min at low gas pressure. The samples were plasma paste boronized at 750, 800 and 850 °C (1023, 1073 and 1123 K) for 3 and 6 h in a gas mixture of 50% H_2–50% Ar under a constant pressure of 500 Pa. The glow discharge was operated with a potential difference of 300–550 V using DC power supply (14) (3 kW) to obtain the prescribed boriding temperature. The boriding temperatures were controlled by changing the power input. The selection of process

Table 1
Chemical composition of Cp-Ti (wt%).

C	N	Fe	H	O	Residuals		Ti
					Each	Total	
0.02	0.02	0.05	0.001	0.15	<0.10	<0.40	REST