



Self-lubricated nanoporous TiO₂-TiN films fabricated on nanocrystalline layer of titanium with enhanced tribological properties

Yongda Ye^{a,b,c}, Song-Zhu Kure-Chu^{b,*}, Zhiyan Sun^{a,c}, Takashi Matsubara^b, Guoyi Tang^{a,*}, Takehiko Hihara^b, Masazumi Okido^d, Hitoshi Yashiro^e

^a Advanced Materials Institute, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, PR China

^b Department of Materials Function and Design, Nagoya Institute of Technology, Nagoya 466-8555, Japan

^c School of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

^d Institute of Materials and Systems for Sustainability Division of Materials Research, Nagoya University, 464-8603, Japan

^e Department of Chemistry and Bio-sciences, Iwate University, Morioka 020-8551, Japan

ARTICLE INFO

Keywords:

Nanoporous TiO₂-TiN films
Sparkling anodization
Titanium
Electropulsing assisted ultrasonic surface rolling process
Nanocrystalline layer
Tribological properties

ABSTRACT

Nanoporous TiO₂-TiN composite films with enhanced tribological properties were fabricated on commercial pure titanium by combining a mechanical surface modification process, i.e., electropulsing assisted ultrasonic surface rolling process (EP-USRP), and an electrochemical process, i.e. sparking anodization (SA) in an aqueous ammonia sulfate electrolyte. The EP-USRP endowed a gradient nanocrystalline layer with high surface hardness of ~295 HV (strengthened by ~41.1% to untreated sample) and deep hardening depth (> 600 μm). In addition, TiO₂-TiN composite films fabricated on EP-USRP treated surface exhibited smoother morphology and more uniform pores than that of anodization without EP-USRP. The SA produced a sponge-like nanoporous TiO₂-TiN composite film with anatase and rutile-TiO₂ phases. Moreover, the surface wettability was remarkably improved compared to EP-USRP. The combinatorial technique led to lower friction coefficient and effectively inhibited the adhesion during wear test compared with turning, EP-USRP and anodization without EP-USRP, which could be attributed to the synergetic effects of the self-lubrication nature of nanoporous TiO₂-TiN films by SA and the ultra-smooth and hardening nanocrystalline layer by EP-USRP. The promoted elastic deformation and the reduced adhesion wear rate by rutile-TiO₂ phase as well as the lubricating and wettable grinding powder should be the primary intrinsic reasons for the improvements.

1. Introduction

Titanium and its alloys have been widely used as excellent structural material in many fields due to their special performances, such as specific strength, low density, superior corrosion resistance and biocompatibility [1]. However, the poor wear resistance because of their low resistance to plastic shearing, low work hardening and low protection exerted by the surface oxide, has been the major obstacles for widespread applications of titanium alloys [2,3]. Furthermore, titanium and its alloys possess chemical activity and have high ductility, which generate a strong tendency to adhesion during friction, leading to severe adhesive wear damages to the surface [4]. Thus, improving the surface mechanical properties of titanium and its alloys through effective surface processing techniques are highly required.

Recently, a mechanical processing technique, so-called electropulsing-assisted ultrasonic surface rolling process (EP-USRP) [5–7], was

explored to achieve enhanced surface mechanical properties for various materials such as SUS, Mg alloys, Ti alloys, etc. EP-USRP is known as an effective surface processing technique to optimize surface mechanical properties on metals, which is based on severe plastic deformation (SPD) and electro-plasticity [8,9]. Previous studies [9,10] reported that EP-USRP produced smaller surface roughness, higher hardness and lower friction coefficient compared to conventional ultrasonic surface rolling process (USRP). However, for EP-USRP, it would bring in surface oxide by temperature rise due to the high energy input from electropulsing as well as the low thermal conductivity and high chemical activity of Ti. Moreover, both EP-USRP and USRP cannot effectively change the adhesive nature of materials during friction because of the unchanged chemical compositions. Thus, in order to fully utilize the advantages of EP-USRP, such as low surface roughness, high hardness and high value of compressive residual stress, fabricating a transition layer on the EP-USRP-treated strengthened layer is desired.

* Corresponding authors.

E-mail addresses: chusongz@nitech.ac.jp (S.-Z. Kure-Chu), tanggy@sz.tsinghua.edu.cn (G. Tang).

<https://doi.org/10.1016/j.surfcoat.2018.07.089>

Received 22 April 2018; Received in revised form 28 July 2018; Accepted 31 July 2018

Available online 01 August 2018

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On the other hand, sparking anodization in acidic or alkaline electrolytes, also called as plasma electrolytic oxidation (PEO) [11–13] or micro-arc oxidation (MAO) [14,15], have attracted increasing attention to improve various surface properties, including corrosion, friction and biocompatibility of titanium alloys [16–19]. The sparking phenomenon during anodizing process occurs because of the dielectric breakdown of the anodic oxide at high voltages above 100 V. This sparking micro-discharge usually produces a thick, highly crystalline and melt-quenched high temperature oxide coating, which improves effectively the surface mechanical properties of Ti alloys, including corrosion resistance and wear resistance due to its high hardness and insulativity [20–22]. However, most of the sparking anodization techniques can only get dense or meso-porous oxide layers with large volcano-shaped pores, which would lead to serious surface roughness and high friction coefficient [17,23]. Moreover, the improvement of wear resistance only from the hard oxide coatings on the “soft” Ti substrates is limited. It is highly desirable to explore a combined surface finishing technique on Ti to enhance both the surface chemical properties and the mechanical properties. Aliofkhaezai et al. [24–26] combined the surface mechanical attrition treatment (SMAT) and micro-arc oxidation (MAO) on aluminum alloy and magnesium alloy and found that the nanocrystallization by SMAT improved the growth and thickness of oxide layer as well as reduced fluctuations in friction coefficient curve, which should be attributed to the increase in matrix reactivity and the reduction of stick/slip phenomenon, respectively.

Recently, we have reported in a previous study to fabricate a nanoporous TiO_2 -TiN composite film on commercial pure titanium by anodized in an ammonia nitrate electrolyte at 110 V [27]. Moreover, EP-USRP is a more effective and controllable method than SMAT mentioned above, which could bring in ultra-smooth surface and high hardness with several hundred micrometers hardening depth. Our previous study [28] demonstrated that EP-USRP at an optimum parameter would produce an ultra-smooth surface with roughness of R_a 0.026 μm on commercial pure titanium, which cannot be achieved by SMAT. In the present study, to solve the shortcomings of EP-USRP and sparking anodization and to obtain outstanding surface properties of commercial pure titanium through using both the advantages of these two methods, we propose a novel combinatorial surface finishing process of Ti materials to combine an electrochemical surface finishing technology with a mechanical surface processing technique to enhance wear resistance, i.e., coupling the electro-pulsing-assisted ultrasonic rolling process (EP-USRP) with the sparking anodizing (SA) in an ammonia nitrate electrolyte. Thus, the effect of nanoporous TiO_2 -TiN composite film and nanocrystalline layer on tribological properties of commercial pure titanium is investigated in this article.

2. Experimental

The annealed commercial pure titanium materials with the chemical compositions of 0.14 Fe, 0.02C, 0.03 N, 0.12 O, 0.006 H and Ti (bal.) in wt% were used as starting materials. The Ti rods were turned into the bars with a dimension of $\Phi 14.8 \times 150$ mm before EP-USRP process to obtain uniform surface roughness. The EP-USRP was carried on the self-design platform based on a CNC lathe and the set-up had been described in detail elsewhere [10]. The optimum parameters of EP-USRP in the present study are according to our previous studies to prepare a suitable surface for subsequent anodization (like smaller surface roughness, deeper hardening depth and higher surface hardness) and the parameters are as follows: rolling line speed was 14.5 m/min, feeding rate was 13 mm/min, static force was 1030 N and processing length was 50 mm. The parameters of electropulsing are: frequency (550 Hz), root-mean-square current density (0.938 A/mm²), amplitude current density (4.98 A/mm²), duration (135 μs) and temperature (133 °C) [28].

The Ti bars after EP-USRP were anodized in a 2 M $(\text{NH}_4)_2\text{SO}_4$ solution at 278 K to achieve a nanoporous TiO_2 -TiN composite film [23]. It was found in our previous study that a nanoporous TiO_2 -TiN

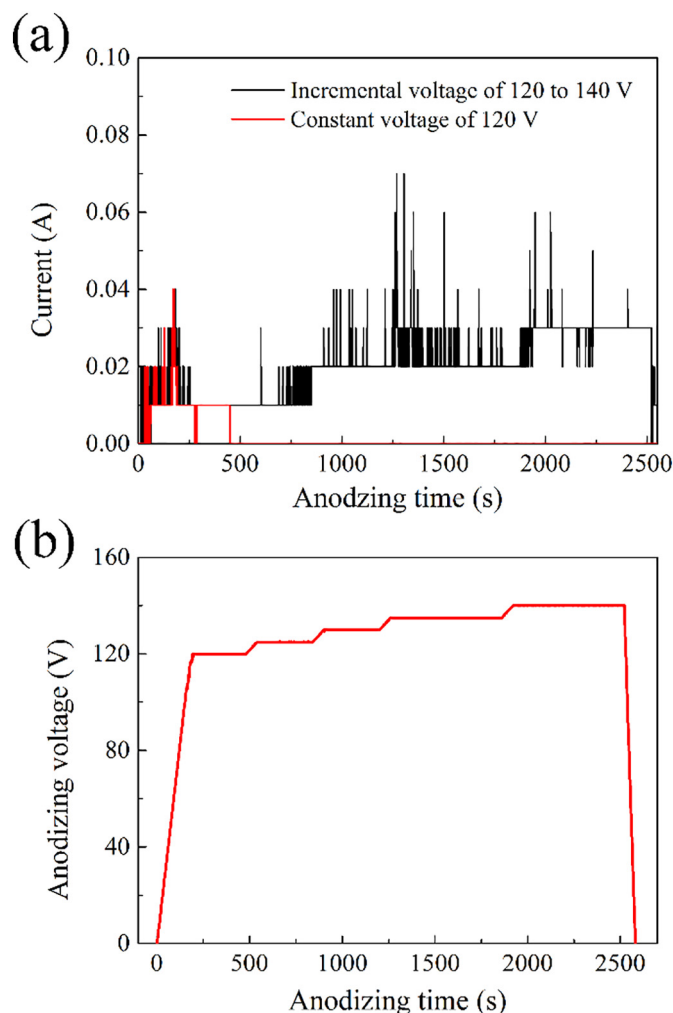


Fig. 1. (a) Current and (b) voltage vs. time cures of anodization.

composite film can be formed at 110 V by anodization in a 2 M $(\text{NH}_4)_2\text{SO}_4$ solution, accompanied by a sparking phenomenon. However, the film is very thin due to the highly insulative nature. In case of a constant-voltage is applied, the anodic current dropped quickly and the formation of TiO_2 -TiN film stopped, because the film thickness (or resistance) is proportional to the applied voltage. Prolonged anodizing process only increased the pore density but not film thickness. The phenomenon can be observed from Fig. 1(a), the processing current drops to 0 while a constant voltage of 120 V is introduced at about 490 s. Whereas in case of higher voltage above 130 V, a ‘burned’ phenomenon (or break-down of anodic film) occurred < 1 min and uniform film formed. Thus, to overcome the high insulation of TiO_2 -TiN composite film under constant-voltage during the whole treated time and to get thicker nanoporous films with highly crystalline structure, a new step-wise constant-voltage sparking anodization was adopted on the Ti bars, with the incremental parameters of 120 V (5 min) → 125 V (5 min) → 130 V (5 min) → 135 V (10 min) → 140 V (10 min). As presented in Fig. 1(b), applying incremental voltages lead to a continuous anodic current during the whole anodizing time. In addition, it was also found that using higher voltage than 140 V or longer anodizing time that 10 min led to ‘burned’ phenomenon.

The friction coefficient and wear resistance were measured by using a high frequency linear oscillating tribometer (Optimal Instruments, SRV-4) at a temperature of 25 °C against Si_3N_4 ceramic ball with a diameter of 10 mm under dry condition. The operating parameters of wear tests were as follows: load (10 N), frequency (10 Hz), stroke (200 μm), and time (600 s). For reproducibility of above results, all the

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