Surface & Coatings Technology 307 (2016) 610–621

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Friction reduction by nanothin titanium layers on anodized alumina

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ARTICLE INFO

Article history:
Received 31 May 2016
Revised 15 September 2016
Accepted in revised form 30 September 2016
Available online 1 October 2016

Keywords:
Anodising
Aluminum oxide
Magnetron sputtering
Pin on disc
Titanium coatings

ABSTRACT

Anodization of aluminum improves hardness, paintability or corrosion resistance but incidental friction may lead to major surface damages of anodized parts. Industrial alloys 1050A and 6082 were anodized to produce 60 μm coatings, then Ti layers of 16 nm, 75 nm and 2.3 μm thickness were deposited by magnetron sputtering. Reciprocal ball-on-plate tribotests under relatively high load of 10 N was used and high friction was observed on alloys before anodization with or without Ti layers. On anodized coatings friction was much lower but abrasion remained rapid. Deposition of 16 and 75 nm Ti layers prevented abrasion for significant durations, especially on anodized 6082, whose substrate was harder. Counterintuitively, deposition of 2.3 μm Ti layers was much less effective. On specimens with 75 nm Ti layers Energy-Dispersive X-ray Spectroscopy showed major delocalization of Ti aggregates in the friction zone with Ti concentration gradients of 10 times within 30 μm. Such material transfer might relate to improved tribological characteristics. Surprisingly good performance of 16 and 75 nm specimens suggests that incidental friction can be successfully inhibited by depositing nanothin Ti layers. Further studies of Ti deposition may lead to significant improvements in industrial anodization technology.

1. Introduction

Aluminum alloys are often anodized (electrochemically oxidized) to increase surface hardness, provide better paintability, improve corrosion resistance and other technical features [1–3]. Usually, highly porous nanostructured coatings of alumina (Al_2O_3) with vertical nanopores of uniform size and distribution are produced after anodizing [4,5]. Industrially, anodization is often carried out in sulfuric acid-based electrolytes, where positively charged Al is attacked by anions (HSO_4^-, $RCOO^-$, etc.). This electrochemically oxidizes the metal mostly into Al_2O_3, forming anodized coatings of various thickness, sometimes 100 μm or more. Despite better hardness, wear rate of anodized coatings is still high [5] presenting a major problem in many field applications. Although expensive technologically, metal or polymer based solid lubricants are often applied to reduce friction and wear of anodized surface. Incorporation of MoS_2 [6], nickel composite (e.g. Co-Ni-P) [7] and other substances might give a needed success in improving wear resistance. Nevertheless, industrially the most widespread method is still based on polytetrafluoroethylene, which usually reduces Coefficient of Friction (COF) to less than 0.2 [8] by functioning as a barrier lubricant.

In previous studies [9,10] titanium oxides and nitrides showed some effectiveness as protective, anti-frictional layers for various substrates, including anodized coatings. Particularly, coatings of TiN, TiSiN, TiSiCN demonstrated excellent wear resistance and low friction with COF 0.15–0.25 [9]. When Ti is exposed to air, a passive oxide film is spontaneously formed on its surface. Usually, such amorphous film is 5–10 nm thick and contains three layers: TiO next to metallic Ti, Ti_2O_3 in the middle and anatase TiO_2 [11] on the outer part. Titanium dioxide (TiO_2) is very stable, insoluble, non-toxic and chemically inert, resistant to most acids, alkalis and organic compounds. Because of chemical stability, corrosion-resistance, biocompatibility, non-toxicity and other desirable properties, deposition of Ti/TiO_2 layers is used in many applications, including biomedical materials due to effective protective and osseointegrative (direct bone to implant anchorage) properties [12,13]. For various technological purposes Ti layers have also been deposited on anodized alumina by magnetron sputtering [14], chemical vapor deposition [15], spraying [16], plasma electrolytic oxidation [17] and other methods. Deposition of Ti layers gains recognition in many high-tech processes, while anodization remains a major tool in the manufacture of advanced materials. Manipulation with nanopore sizes, their density, roughness, application of fillers or deposited layers and other parameters gives an opportunity to control wettability, permeability, adhesion, resistance, biocompatibility, nanostructurization and other properties of anodized surfaces. Many industrial items are exposed to friction during field applications, however, tribological properties of Ti layers on anodized alumina have not yet been studied in detail.

Abbreviations: 1050A, high purity industrial aluminum alloy; 6082, industrial aluminum alloy suitable for anodization; COF, Coefficient of Friction; EDS, Energy-Dispersive X-ray Spectroscopy; SEM, Scanning Electron Microscopy; Ti, titanium.

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http://dx.doi.org/10.1016/j.surfcoat.2016.09.083
0257-8972/

Some other types of substrates have already been investigated to some extent for tribological behavior of Ti or TiO_2 layers on fasteners [18], implants [19], turbine engines [20], aerospace or marine applications [21]. Still, the data volume remains limited, making it difficult or impossible to predict the effect of deposited Ti on frictional characteristics. In one particular study magnetron sputtering was used to deposit Ti/TiO_2 layers of ~200 nm thickness on Ti6Al4V substrate [19]. This reduced COF to 0.5 and assured stable friction for 10,000 cycles under 0.49 N load, 3 cm/s rotation speed with 4 mm rotation radius against 6 mm diameter SiC balls. From these and related studies it might appear that deposited Ti layers reduced friction only marginally compared to alloys without coating. In contrast, better achievements could be observed in Ti based multilayer coatings [9,22], where COF went down to 0.15. Such friction reduction was quite remarkable for dry coatings, unfortunately, no further study to investigate the causes of the tribological improvement was made available. Also, authors employed relatively light loads of 0.1 kgf and less, which would not always be relevant in field uses, where incidental friction might take place during manufacture, packaging, transportation, installation etc. So it remains unknown whether Ti-containing multilayers can provide friction reduction under more severe tribological regimes.

In this study the effectiveness of Ti layers was investigated under much higher load of 10 N. In addition, very few reports discuss the dependence of tribological properties on the thickness of Ti layers, so this aspect received particular attention in this investigation. Resistance to friction and wear under higher interfacial pressures is important for many applications, where anodized alumina is used, such as fasteners, positioners, biomedical devices [23], sliding surfaces, aerospace, robotic equipment, etc. Instead of pure aluminum, industrially relevant alloys 1050A and 6082 were utilized, while tribotests employed conventional ball-on-plate methodology, typically used in friction studies of anodized alumina and many other coatings.

2. Experimental

Two main processes were used for surface preparation: 1) anodization and 2) magnetron sputtering, see Fig. 1. The obtained specimens were evaluated by using optical and scanning electron microscopy. Then their friction and wear was compared using ball-on-plate tribotests. Most of the equipment, procedures and materials, which were used in this study, had already been previously presented in several proceedings articles [24–27]. Briefly, their descriptions are provided below.

2.1. Materials

Two Al alloys, 1050A of 99.62% purity (0.34% Fe; 0.1% Si; 0.01% Mn) and 6082 of 96.72% purity (1.1% Si; 1.02% Mg; 0.61% Mn; 0.54% Fe) with a sheet thickness of 1 mm and 2 mm respectively, from Aleris Rolled Products Germany GmbH were used as substrates. Reagent grade salts and electrolytes were employed for the anodization and laboratory grade solvents were used for cleaning and degreasing. Commercially available high purity Ti (99.995%) from Alfa Aesar GmbH (Germany) was used as magnetron sputtering target, Fig. 1, for deposition of Ti layers.

2.2. Anodization

The anodization was performed in H_2SO_4/oxalic acid electrolyte in compliance with Type III procedures. This type of electrolyte is widely used to produce relatively thick, hard Al_2O_3 coatings [2,4], so the referenced solutions and procedures were used as a basis for this study. Before anodization the disc-shaped specimens of 1.5 cm OD were etched in an alkaline solution of 30 g/L NaOH + 25 g/L Na_3PO_4 + 75 g/L Na_2CO_3 for 30 s at 60 °C. After rinsing in deionized water they were cleaned for 1–2 min in 10% HNO_3 and rinsed in water again. Then the discs were placed into the continuously mixed electrolyte of 175 g/L H_2SO_4 + 30 g/L $(COOH)_2 \cdot 2H_2O$ + 55.5 g/L $Al_2(SO_4)_3 \cdot 18H_2O$ at 15 °C and 200 A/m^2 anodic current density for 70 min. Coatings were periodically checked with CM-8825FN device (Guangzhou Landtek Instruments Co., China) to obtain 60 ± 10 μm thickness. After anodizing, the discs were immersed into 170 W ultrasonic bath VTUSC3 (Velleman, Belgium) and sonicated at full power for 10 to 20 min in deionized water without heat for rinsing. Then the discs were dried at 100 °C for 30 to 60 min and stored in dry environment for 1 to 7 days for further experiments.

2.3. Magnetron sputtering

Deposition of Ti layers of 16 nm, 75 nm and 2.3 μm thickness was performed on Al specimens with or without anodization by DC/RF magnetron sputtering device Univex 350 (Leybold Vacuum Systems, Germany). Before sputtering the discs of untreated alloys (without anodization) were etched in an alkaline solution for 30 s at 60 °C and cleaned for 1–2 min in 10% HNO_3 to remove all impurities of the surface. The specimens were placed into the rotary holder of the magnetron apparatus, the lid was closed and the chamber was vacuumized for at least 16 h before actual sputtering. The base pressure of the system was 250 μPa and the working pressure of Ar gas was kept constant at 250 mPa maintaining substrate temperature at 12 °C. Thermal regime was balanced using two controls: 1) cooling by circulating cold water through the magnetrons and the specimen holder; 2) heating with integrated quartz halogen lamps, interfaced via programmable "SHQ15A TC/PID" controller (AJA International, USA). The distance of 20–25 cm between the target and specimens was too large to significantly affect the temperature of substrate, when coating 16 nm and 75 nm Ti layers. Sputtering time, current and voltage were adapted to obtain a necessary thickness of Ti layers: 16 nm ($t_1 = 15$ min, $I_1 = 100$ mA, $U_1 = 421$ V),

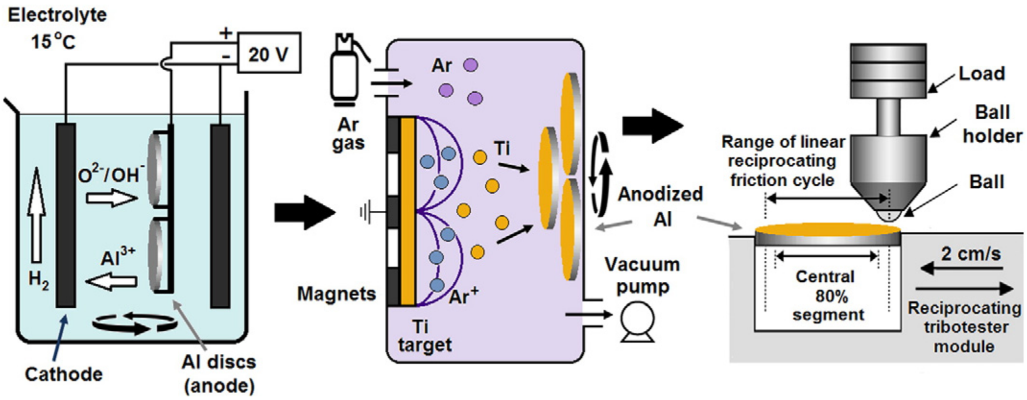

Fig. 1. The principal scheme of specimen preparation and investigation in three main stages (from left): anodization → magnetron sputtering → tribotesting / microscopy.