Journal of the Korean Vacuum Society
Vol.12, No.S1, 2003, pp.21~27

Duplex Surface Modification with Micro-arc Discharge Oxidation and Magnetron Sputtering for Aluminum Alloys

Honghui Tong†, Fanya Jin, and Heng He*

Southwestern Institute of Physics, Chengdu, Sichuan, 610041, China
**Sichuan Chengfa Aero-Science & Technology Co., Ltd, Chengdu, Sichuan, 610067, China*

Abstract

Micro-arc discharge oxidation (MDO) is a cost-effective plasma electrolytic process which can be used to improve the wear and corrosion resistance of Al-alloy parts by forming a alumina coating on the component surface. However, the MDO coated Al-alloy components often exhibit relatively high friction coefficients and low wear resistance fitted with many counterface materials, additionally, the pitting corrosion for the MDO coated Al-alloy components, especially for a thinner alumina coating, often occurs in atmosphere circumstance due to the porous alumina coats. Therefore, a duplex treatment, combining a MDO coated alumina thin layer with a TiN coating, prepared by magnetron sputtering (MS), has been investigated. The Vicker's microhardness, pin-on-disc, electrochemical measurement, salt spray, XRD and SEM tests were used to characterize and analyze the treated samples. The work demonstrates that the MDO/MS coated samples have a combination of a very low friction coefficient and good wear resistance as well as corrosion since the micro-holes on alumina coating are partly or fully covered by TiN material.

Keywords : Micro-arc discharge oxidation, magnetron sputtering

1. Introduction

The lightweight aluminum alloys are widely used in many industrial fields such as automotive engine parts as well as aerospace industry and textile machinery, due to its good mechanical machining and modeling, low density, high strength and fatigue resistance. However, the high friction coefficient and wear resistance for most of counter-materials and relatively poor corrosion resistance are inadequate for some applications. So it is very important in finding an economic way to improve its surface properties in order to extensive applications in industry. The protection of aluminum alloys from wear and corrosion by applying topcoats of ceramic materials is currently of great interest. Anodizing has been primary process to form protective oxide layers on aluminum components. However, this method needs a rather complicated pre-treatment processing and has relatively high expenses [1-5]. A number of other techniques have been investigated to produce a thicker ceramic materials on aluminum component surface, including arc-discharge plasma and gas- flame spray, vacuum deposition methods and high temperature glass enameling [6-8]. But these techniques require a high substrate temperature to provide adequate coating adhesion at high contact load. Besides, these processes can not compete in coating uniformity or production costs with anodizing.

For recent years, a new process called for micro-arc discharge oxidation (MDO) has been extensively developed in the worlds to provide ceramic overcoats for aluminum, titanium and magnesium materials, and protected them

---

† E-mail : thonghui@hotmail.com

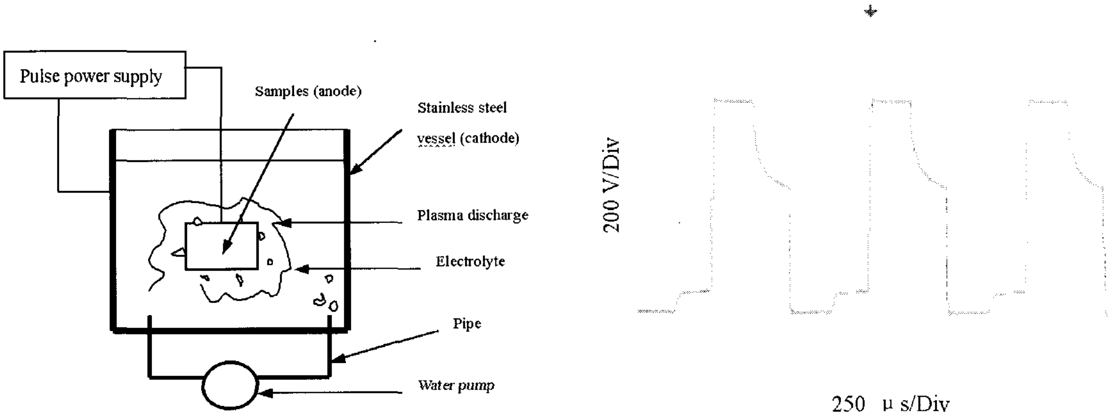
from severe wear and corrosion [9-11]. The process combines electrochemical oxidation with a high voltage spark treatment in an electrolyte bath, results in a uniform dense complex compound overcoats including the substrate materials, surface oxides and electrolyte modifier. Moreover, this layer is growing directly from the substrate materials, thus, the process produces ceramic coatings with a high adhesion and hardness, relatively good corrosion resistance, while keeping the cost of the production close to that of the anodizing process.

Previous studies of micro-arc discharge oxidized aluminum alloys have shown that as-deposited (and polished) alumina coatings have a relatively high friction coefficient (0.6-0.7) against WC-Co and AISI 52100 counterfaces in dry sliding tests and seriously pitting corrosion due to many of the micro-holes in the coatings [12-13]. A low friction coefficient is usually required for sliding wear applications. Deposition of duplex Al_2O_3/DLC coatings on aluminum alloys for tribological applications using a combined micro-arc discharge oxidation and plasma immersion ion implantation techniques has also been developed, it demonstrates that the friction coefficient of this coatings can drastically decrease to a low and stable value (0.2-0.4) without the coatings spallation in the pin-on-disc test [14].

In this work, the TiN film prepared by the magnetron sputtering (MS) was deposited onto MDO treated Al-alloy coupons in which the alumina oxidation layer is thin. Microhardness measurements and pin-on-disk sliding wear tests were performed to evaluate the coating mechanical and tribological properties. Potentiodynamic polarization and salt spray tests were used to investigate the corrosion of the duplex coatings. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to observe and analyze the morphology and microstructures of the duplex coatings.

2. Experiment

Ground and polished disc samples (20 mm diameter, 5 mm thickness) of LY2 aluminum alloys which consisted of aluminum as a base and approximately 2.6-3.2% Cu, 2.0-2.4% Mg, 0.45-0.7% Mn and <0.8% impurity were subjected to micro-arc discharge oxidation in an alkaline aqueous electrolyte of primarily sodium tungstate and tri-sodium phosphate ($Na_2WO_4 \cdot 12H_2O$: $Na_3PO_4 \cdot 12H_2O$=1:12). The MDO treatment unit was developed by Southwestern Institute of Physics (SWIP), which consisted of an insulated electrolyte bath and a high pulse voltage power supply generating positive and negative pulses. One output of power supply was connected to the bath, and another to the sample immersed in electrolyte. The schematic diagram and typical voltage



(a) Schematic diagram of MDO device (b) Typical voltage waveforms

Fig. 1. The schematic diagram and typical voltage waveform.

waveform were shown in Fig. 1. A constant average current density on the sample surface was maintained by the control of the voltage pulses during the process. Electrolyte temperature was < 40 ℃. In our experiment, the average current density was 4 A/dm^2, the positive voltage was 350-500 V, the negative voltage was 15-200 V, the repetitive frequency was 1.25 kHz and the pulse width was 400 μs. The thickness of the oxidation layer of the samples was about 2 μm for 12 minutes under the mentioned conditions.

The deposition of TiN film on the treated samples was performed in the PSII-IM device at SWIP which described in detail elsewhere [15]. The titanium round plate sputtering target with the diameter of 90 mm was used to deposit the TiN film. During deposition, the working pressure was 8×10^{-2} Pa, the ratio of the argon and nitrogen pressure was 7:1, the sputtering current was 2 A, the substrate samples were biased with a DC potential of -200 V, the deposition time was 45 minutes, and the substrate sample temperature was < 200 ℃. The thickness of the TiN film was approximately 2 μm.

The processed samples were characterized for hardness, wear and corrosion. The Vicker's microhardness was measured with a HX-1000 micromet tester. A pin-on-dsic tribometer (CJS111) fitted with a 6.2-mm diameter ZrO_2 ball was used to determine the wear and friction properties of the samples in the laboratory ambient, at a load of 0.98 N and at a constant speed of 0.1225 m/s, and the depth of the wear track was detected by a profilometer (TYSYRF-3). The corrosion properties of the samples were investigated by potentiodynamic polarization and salt spray methods respectively. The polarization curves were depicted using potentiodynamic scanning method in 3.5% NaCl solution (PH=7) wherein the temperature was kept at 25℃ ± 1℃ during the measurement. A three-electrode system where Pt plate was as a auxiliary electrode, the sample was as a working electrode and Ag-AgCl plate was as a reference electrode, was adopted. The polarization potential scan began at -400 mV+E_{corr} (the free corrosion potential of a sample) and ended at 400 mV+E_{corr} with a fixed voltage scan rate of 20 mV/min. The conditions of the salt spray test were as follow: the temperature of salt spray at 35℃ ±2℃, 5 % NaCl and PH=6.5-7.2 in the salt solution, the constant spraying speed at1.2 ml/80 (cm^2.h). Film microstructure was characterized by glancing-angle (2°) X-Ray diffraction using the CuK_α line at 40 kV. The film morphology was observed by scanning electron microscopy (SEM).

3. Results and discussion

The Vicker's microhardness at a load of 200 g are shown in Table I, the microhardness for both of the MDO and duplex MDO/MS coated samples are greater than for the untreated sample. However, the microhardness for the coated samples are much lower than that of the pure alumina or alumina+TiN composite ceramic, since for 200 g load the indenter (several micrometers of indention depth of the micromet tester) is basically probing the soft aluminum substrate.

The coefficient of friction results obtained from pin-on-disc tests for the LY12 Al-alloy substrate, MDO and duplex MDO/MS coated samples are shown in Fig. 2. After an initial short period with the sharp increase of the friction coefficient for LY12 Al-alloy substrate, the friction coefficient is slowly increased up to the value of 0.9. For MDO coated sample, the friction coefficient sustains at a low value of approximately 0.18 in the initial time of 35 minutes, then starts to slowly increase and reach the value of approximately 0.35 within the duration of test. The friction coefficient for the MDO/MS treated sample is almost constant at

Table I. The Vickers microhardness at a load of 200 g.

Samples	Un-treatment	MDO treatment	MDO/MS treatment
Microhardness (HV)	78	115	150

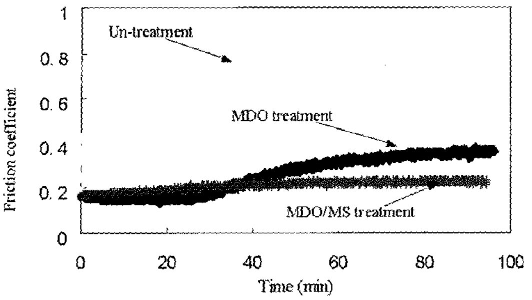


Fig. 2. Friction coefficients in Lab. ambient from pin-on-disc tests.

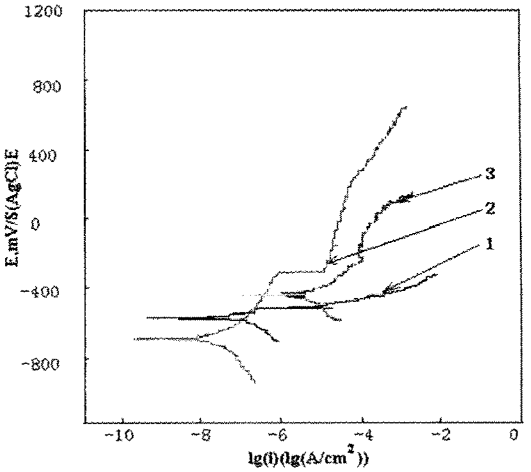


Fig. 4. The polarization curves acquired from potentiodynamic polarization: 1-un-treatment, 2-MDO treatment, 3-MDO/MS treatment.

the value of approximately 0.2 in the overall test. The cross-section profilograph of the wear track is depicted in Fig. 3 after 180 minutes in the test. It clearly shows that the wear track is the biggest with the depth of 12 μm and width of 1.2 mm for the LY12 Al-alloy substrate, and the smallest with the depth of 1.6 μm and width of 0.3 mm for the MDO/MS treated sample. No visible debris could be found under optical microscopy. This represents that wear resistance for the MDO/MS treated sample is the best for all samples.

Prior to performance of polarization voltage scan, the samples were immersed in the solution for 30 minutes. The polarization curves acquired from potentiodynamic polarization method are plotted in Fig. 4. The free corrosion potential of the MDO coated sample is higher than that of the Al-alloy substrate, but lower than that of the duplex MDO/MS coated sample. The free corrosion current for the Al-alloy substrate is linearly increased with the applied voltage due to the dynamic solvation process. But the free corrosion current density for the coated samples are significant reduced at the same applied voltage in compared with that of the Al-alloy substrate, this represents the lower corrosion rate of the coated samples, furthermore, the passive process for the coated samples is also observed. The passive process makes the coated samples raise the free corrosion potential. It also observed that the pitting corrosion occurs for the coated samples since there are many of micro-holes in the coatings. The salt spray test indicates that the corrosion occurs in 48 hours, 312 hours and 504 hours for the Al-alloy substrate, MDO and duplex MDO/MS coated samples respectively. This results confirm the conclusion of the electrochemical measurement.

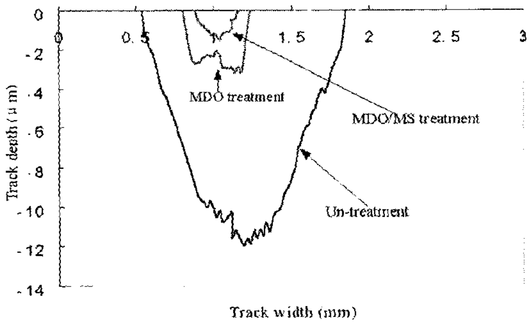
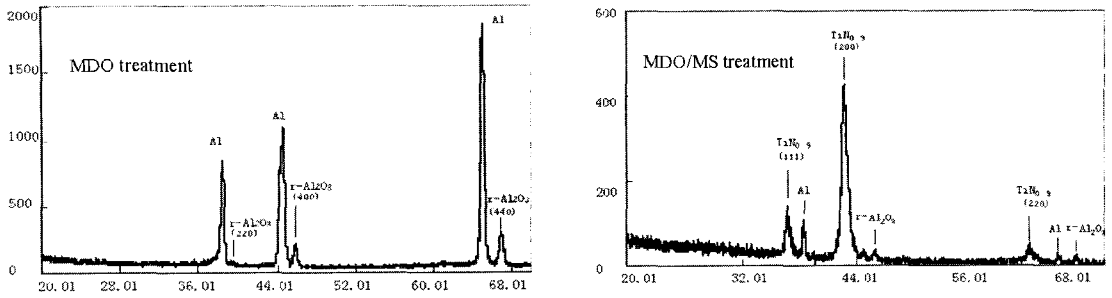


Fig. 3. The cross-section profilograph of the wear track after 180 minutes in the test.

Figure 5 shows the X-ray diffraction patterns of the MDO and duplex MDO/MS coated samples. The γ-Al_2O_3 (440, 400, 220) peaks are dominant and no α-Al_2O_3 peak is detected for the MDO coated sample. The $TiN_{0.9}$ (220, 200, 111) peaks are observed besides γ-Al_2O_3 peaks for the duplex MDO/MS coated sample. It shows that the pure $TiN_{0.9}$ film was deposited by magnetron sputtering without rich titanium in the coats.

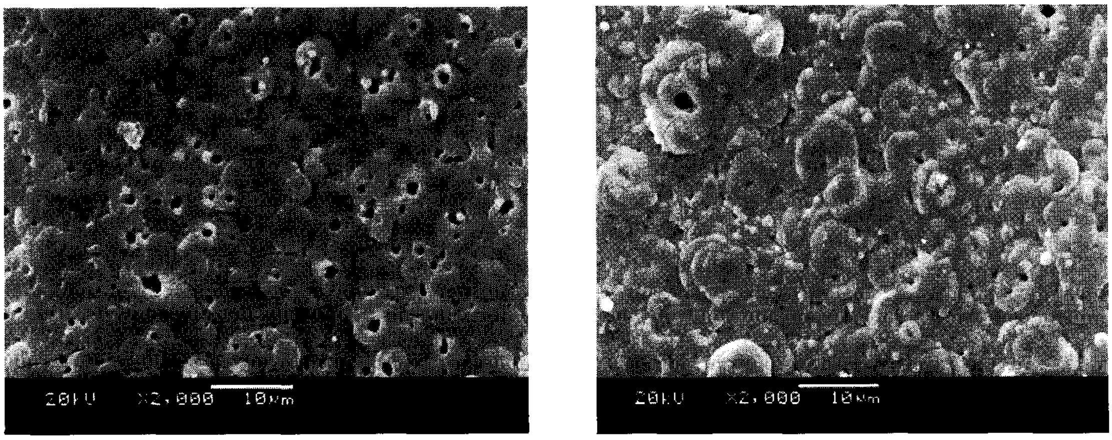
The SEM photographs for the MDO and MDO/MS coated samples are shown in Fig. 6. Many of micro-pores in a maximum diameter of several micrometers are



(a)

(b)

Fig. 5. X-ray diffraction patterns at glancing angle 2° for the treated samples.



(a) MDO treatment

(b) MDO/MS treatment

Fig. 6. The SEM photographs for the treated samples.

randomly distributed on the surface of the MDO coated sample. Plasma chemical interactions in multiple surface discharges result in a uniform porous coating growing in both directions from the substrate surface and these discharge passages also result in the multiple micro-holes left in the coats. Some of the micro-pores go thoroughly into the surface of the substrate Al-alloy material, the other are not. For the MDO/MS coated samples, most of the micro-pores are fully covered by the TiN coats, the others are partly capped by the TiN coatings due to their large diameters. But the surface morphology for the MDO/MS coated sample is not improved in comparison with that of the MDO coated sample at all. Fig. 7 shows the morphology of pits on the Al-alloy substrate, MDO and MDO/MS coated samples in 3.5% NaCl solution (PH=7) after electrochemical measurement stops. The pitting holes are regular, small and deep for the treated samples, but the pitting holes are irregular, big and shallow for the Al-alloy substrate. It discloses that the corrosion processing is preferentially passed into the Al-alloy substrate where the pits initiation occurs on the coat surface for the treated samples, and the corrosion is aggressively developed along the boundary of the aluminum grains for the Al-alloy substrate sample.

4. Conclusions

The TiN film by magnetron sputtering, with good adhesion onto the MDO alumina thin layer, has been successfully produced. The Vicker's microhardness is increased from HV 78 to HV 150. The friction coefficient is low at a value of 0.2, and stands this

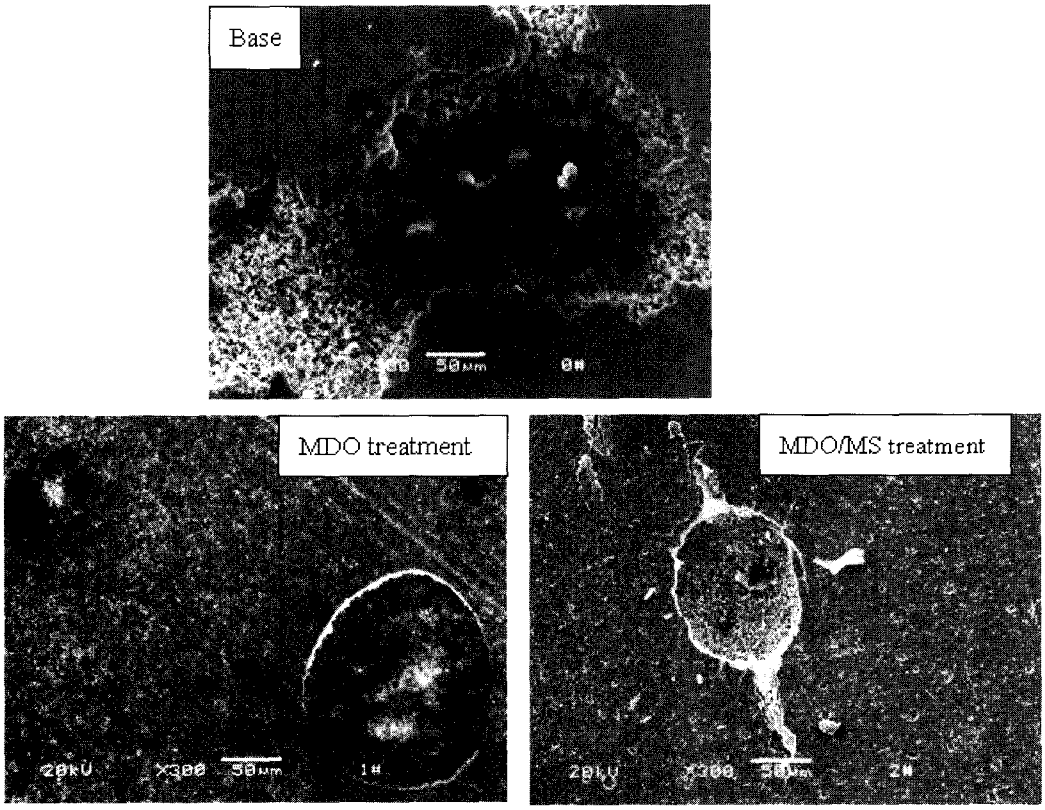


Fig. 7. The morphology of pits obtained from the SEM after electrochemical measurement.

low value for a long time in the pin-on-disc wear test. The potentiodynamic polarization measurement indicates that the MDO/MS coated samples have the highest free polarization potential (-350 mV) and lowest corrosion current as well as a passive regime. For salt spray test, there is the longest time (504 hours) for the corrosion resistance of the MDO/MS coated samples. The SEM morphology discloses that the pitting corrosion is the prominent form of the corrosion for the treated samples. Moreover, The alumina grains and TiN film produced on the coated samples as well as the micro-holes in the MDO/MS coats partly or fully covered by the TiN films are accounted for the improvement of the corrosion resistance.

Acknowledgement

This work is financially supported by China National Science Foundation (NSF) grant 90205001.

References

[1] Kato R, Diao D F and Tsuysumi M., *Wear of Materials*, New York, ASME (1991).

[2] Pin Feng, Yanfi Gang, and Linshan Zeng, Surface Technology (in Chinese) **28**(6), 20 (1999).

[3] Pin Feng, Linshan Zeng, and Yanfi Gang, Surface Technology (in Chinese) **29**(1), 25 (2000).

[4] Penghui Zhao, Yu Zhuo, and Jinmao Zhao, Corrosion Science and Protection Technology (in Chinese) **15**(2), 82 (2003).

[5] Shuyin Li, Huang Wang, Li Mao et al, Surface Technology (in Chinese) **29**(4), 9 (2000).

[6] X. B. Zhou, De Hosson J Th M., Acta Metall Mater. **42**(4),1155 (1994).

[7] D. S. Richerby and A. Matthews (eds.), *Advanced surface coatings: A Handbook of Surface Engineering*, (Blackie, Glasgow 1991).

[8] Xiaoyan Zeng, Zengyi Tao, beidi Song et al., Material Science and Engineering **13**(4), 8 (1995).

[9] A. A. Voevodin, A. L. Yerokhin, V. V. Lyubimov et al., Surface and Coatings Technology **86-87**, 516 (1996).

[10] Bailin Di, Surface Technology (in Chinese) **24**(1), 1 (1995).

[11] Hongbo Zho, Qingshan Kong, Jiuqi Shang, Materials Protection (in Chinese) **28**(7), 21 (1995).

[12] X. Nie, A. Leyland, H. W. Song, and A. Yerohkin, Surface and Coatings Technology, in press.

[13] P. A. Dearnly, J. Gummersbach, H. Weiss, et al., Wear **225-229**, 127-134 (1999).

[14] X. Nie, A. Wilson, A. Leyland, and A. Matthews, Surface and Coatings Technology **121**, 506 (2000).

[15] Zhenkui Shang, Man Geng, and Honghui Tong, China Nuclear Science and Technology Report, CNIC-01204, SIP-0102.