Article ID: 1003-6326(2005)06-1231-06

Tribological properties of solid lubricating film/ microarc oxidation coating on Al alloys①

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Abstract: A process for preparation of solid lubricating films on micro-arc oxidation(MAO) coating was introduced to provide self-lubricating and wear-resistant multilayer coatings for aluminum alloys. The friction and wear behavior of various burnished and bonded solid lubricating films on the as-deposited and polished micro-arc oxidation coatings sliding against steel and ceramic counterparts was evaluated with a Timken tester and a reciprocating friction and wear tester, respectively. The burnished and bonded solid lubricating films on the polished micro-arc oxidation coatings are superior to the as-deposited ones in terms of the wear resistant behavior, because they lead to strengthened interfacial adhesion between the soft lubricating top-film and the hard polished MAO sub-coating, which helps increase the wear resistance of the solid lubricating film on multilayer coating. Thus the multilayer coatings are potential candidates as self-lubricating and wear-resistant coatings for Al alloy parts in engineering applications.

Key words: Al alloy; micro-arc oxidation; aluminum oxide; multilayer; friction and wear behavior
CLC number: TG174 **Document code:** A

1 INTRODUCTION

The protection of aluminum alloys from wear by applying coatings of ceramic materials is currently of great interest[1]. A number of techniques have been applied to produce thick ceramic coating on aluminum components, including arc-discharge plasma, gas-flame spraying, vacuum deposition, and high temperature glass enameling[2]. However, most of these techniques require a high substrate temperature to provide adequate coating adhesion under high normal loads. The micro-arc oxidation(MAO) process, also called as micro-arc discharge oxidation(MDO) or plasma electrolytic oxidation(PEO) process, has been developed in Europe to provide modified surfaces with improved load support on aluminum, titanium, magnesium components, and protect them from severe wear and corrosion[3-14]. It has been known that the sparking reaction due to dielectric breakdown leads to the oxide ceramic deposition of material from an aqueous electrolyte. The resulting coatings have good wear and corrosion resistance, high microhardness, high insulation resistance and good adhesion with substrate, but have higher friction coefficient[15].

The above studies most emphasized on preparation technique, structure and characteristics of micro-arc oxidation coatings, but seldom studied on surface modification of self-lubrication ability of micro-arc oxidation coatings. Thus the multilayer coating is one of the main ways for improving the properties of self-lubrication and wear-resistant of micro-arc oxidation coatings on Al alloy with very wide application and promising market competition. A solid lubricating film can be conveniently formed on the micro-arc oxidation coatings to improve the friction-reducing ability of micro-arc oxidation coatings. However, the lubricating properties of the solid lubricating film are strongly dependent on the interfacial situation between the solid lubricating films and micro-arc oxidation coatings. Therefore, it is imperative to improve the lubricity of the micro-arc oxidation coatings by introducing proper top coatings.

In the present work, we try to introduce the burnished and bonded solid lubricating films on different micro-arc oxidation coatings for Al-based alloys, thus to provide good lubrication on micro-arc oxidation coatings.

2 EXPERIMENTAL

Ceramic coatings were deposited on LY12 Al alloy (Si 0.50%, Fe 0.50%, Cu 3.8%-4.9%, Mn 0.30%-0.90%, Mg 1.20%-1.80%, Zn 0.30%, balance Al; roughness $R_a = (4.2 \pm 0.6)$ μm) specimens with a 100 kW micro-arc oxidation equipment consisting of a potential adjustable AC power supply. The electrolytic solution is composed of 5 g/L

① **Foundation item:** Project(50271080) supported by the National Natural Science Foundation of China
Received date: 2005-01-06; **Accepted date:** 2005-08-30
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NaOH and 30 g/L Na_2SiO_3 in distilled water and the current density was controlled at 10^3 A/m^2[15]. The deposition process was stopped when the coating thickness comes to an appropriate value, thus the as-deposited coatings on the Al alloy specimens were obtained. The thickness of the micro-arc oxidation coatings was measured with a MINITEST 1100 microprocessor coating thickness gauge (Elektro-physik Koln) based on the eddy current technique. The as-deposited micro-arc oxidation coatings on aluminum alloys have two distinct regions, i.e. a loose brown outlayer region which is 40% thick of the as-deposited coating and consists predominantly of crystallographicalloy orientated γ-Al_2O_3 phase, and a dense black internal region consisting predominantly of α-Al_2O_3[15]. The whole loose outlayer was removed by SiC paper so as to obtain the polished coating samples. In this work, the surface roughness of the as-deposited coatings and polished coatings was (7.2 ± 0.4) μm and (2.8 ± 0.5) μm, respectively.

MoS_2 (purity 99%, size 0.76 μm, Shanghai Chemistry Industry Factory of China), irradiated polytetrafluoroethylene (PTFE, size 2 μm, Jinan Factory of Chemistry Industry of China), polyethylene wax and polytetrafluoroethylene (Polyfluo-150, size 3 μm, MICRO POWDERS INC of USA) particles were selected as the solid lubricants. The burnished films of the solid lubricants were obtained by reciprocal rubbing of the powders of irradiated PTFE and MoS_2 against the as-deposited or polished micro-arc oxidation coatings at a velocity of 0.2 m/s and pressure of 0.05 MPa for 20 m. The film thickness of PTFE is about 7.6 μm for as-deposited coating and 9.0 μm for polished coating, and that of MoS_2 is 0.8 μm for both coatings. The bonded solid lubricating films of irradiated PTFE and MoS_2 and polyfluo-150 wax were coated on the as-deposited or polished micro-arc oxidation coatings by spraying with air, and curing at 25 ℃ and ambient humidity of 65% for 6 d[16]. The resulting bonded solid lubricating films have polyurethane (PU) resin as the bonding agent, and the volume fractions of irradiated PTFE, MoS_2 and Polyfluo-150 are 40%, 45% and 30%, respectively. The thickness of the bonded solid lubricating film is about (55 ± 5) μm.

The friction and wear behaviors of the burnished and bonded films on different micro-arc oxidation coatings running against steel were evaluated with a ring-to-block tester (Jinan Tester Factory of China), using an AISI-C-52100 steel ring of 49.2 mm in diameter as the counterpart[16]. The ring rotated against a stationary block covered with the multilayer coatings at a speed of 0.75 m/s and 1.75 m/s, and a load of 200 N against the burnished films and 680 N against the bonded film. The sliding tests were also conducted on an RFT-Ⅲ reciprocating friction and wear tester, using a stationary LY12 Al alloy pin of 8 mm in diameter coated with the MoS_2 bonded film/MAO multilayer coatings sliding against blocks with a size of 70 mm × 19 mm × 10 mm, which were made of a mild steel, LY12 Al alloy, LY12 Al alloy with 100 μm nickel coating, and LY12 Al alloy with polished micro-arc oxidation (MAO) coating. The sliding amplitude was 50 mm, while a sliding speed of 0.50 m/s and contact pressure of 6 MPa were used. The frictional tests were all conducted in an ambient environment of about 40%-60% relative humidity. The failure of the solid lubricating films was accompanied by a sharp increase of the friction coefficient and friction noise which can be easily detected with eyes and ears. Then the wear life of the burnished and bonded films was calculated after dividing the sliding distance by the corresponding film thickness.

The phase composition of the burnished films was investigated using a D/Max-rB X-ray diffractometer equipped with a graphite monochromator (Cu K_α radiation). The wear scar morphology and corresponding elemental distribution of the bonded solid lubricating film were observed with a JSM-5600LV scanning electron microscope equipped with an energy dispersive spectrometer (EDX) operated at an acceleration voltage of 40 kV (Au deposited).

3 RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the burnished lubricating films on the as-deposited and polished micro-arc oxidation coatings. The solid lubricants in the multilayer coating show XRD

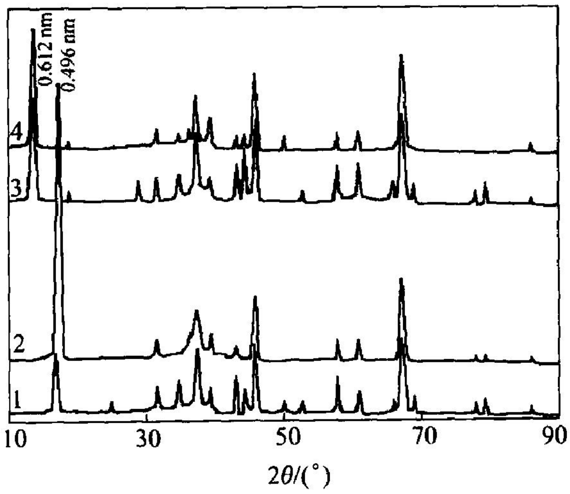

Fig. 1 XRD patterns of multilayer coatings
1 —PTFE film on as-deposited coating;
2 —PTFE film on polished coating;
3 —MoS_2 film on as-deposited coating;
4 —MoS_2 film on polished coating

peaks at 0.612 nm and 0.496 nm, which correspond to MoS_2 and PTFE, respectively.

Fig. 2 shows the friction coefficient and wear life of various burnished films on the as-deposited and polished micro-arc oxidation coatings when running against steel ring. It is seen that PTFE-burnished lubricating film records the lowest friction coefficient of 0.30, which is smaller than that of micro-arc oxidation coatings (0.6 ~ 0.7); and MoS_2 film has the longest wear life. The burnished films on the as-deposited micro-arc oxidation coating of 110 ~ 140 μm in thickness register the longer wear life because of the stronger bonding of the loose layer on the as-deposited coatings. Various burnished lubricating films on the polished micro-arc oxidation coatings show larger friction coefficients than those on the as-deposited coatings because they have more compact interlayer of α-Al_2O_3, other than the loose layer liable to erase off. The MoS_2 burnished film on the polished micro-arc oxidation coating of 60 ~ 70 μm in thickness records a wear life two times longer than that on the as-deposited coating with the corresponding thickness (110 ~ 140 μm). This is attributed to the compact and hard interlayer of the multilayers, which act to endure higher load and prevent the lubricant film from breakage.

The tribological properties of the bonded solid lubricating film on the polished micro-arc oxidation coating are presented in Fig. 3. It can be inferred that the wear life and friction coefficient of the bonded solid lubricating film against steel and ceramic show direct correlation. The wear life is shorter and the friction coefficient is larger when sliding against ceramic ring, as compared with sliding against steel ring.

The lower friction coefficient 0.15 and longer wear life 112 m/μm are observed for MoS_2/PU bonded solid lubricating film on the polished micro-arc oxidation coating of 60 ~ 70 μm in thickness against steel ring. Especially, the longest wear life 1 790 m/μm is observed for Polyfluo 150/PU bonded solid lubricant film on the polished coating at a load of 680 N and sliding speed of 1.75 m/s (Table 1). The wear life of MoS_2/PU bonded solid lubricating film on the as-deposited micro-arc oxidation coatings is only 40% that on the polished micro-arc oxidation coating (Table 1). This is attributed to

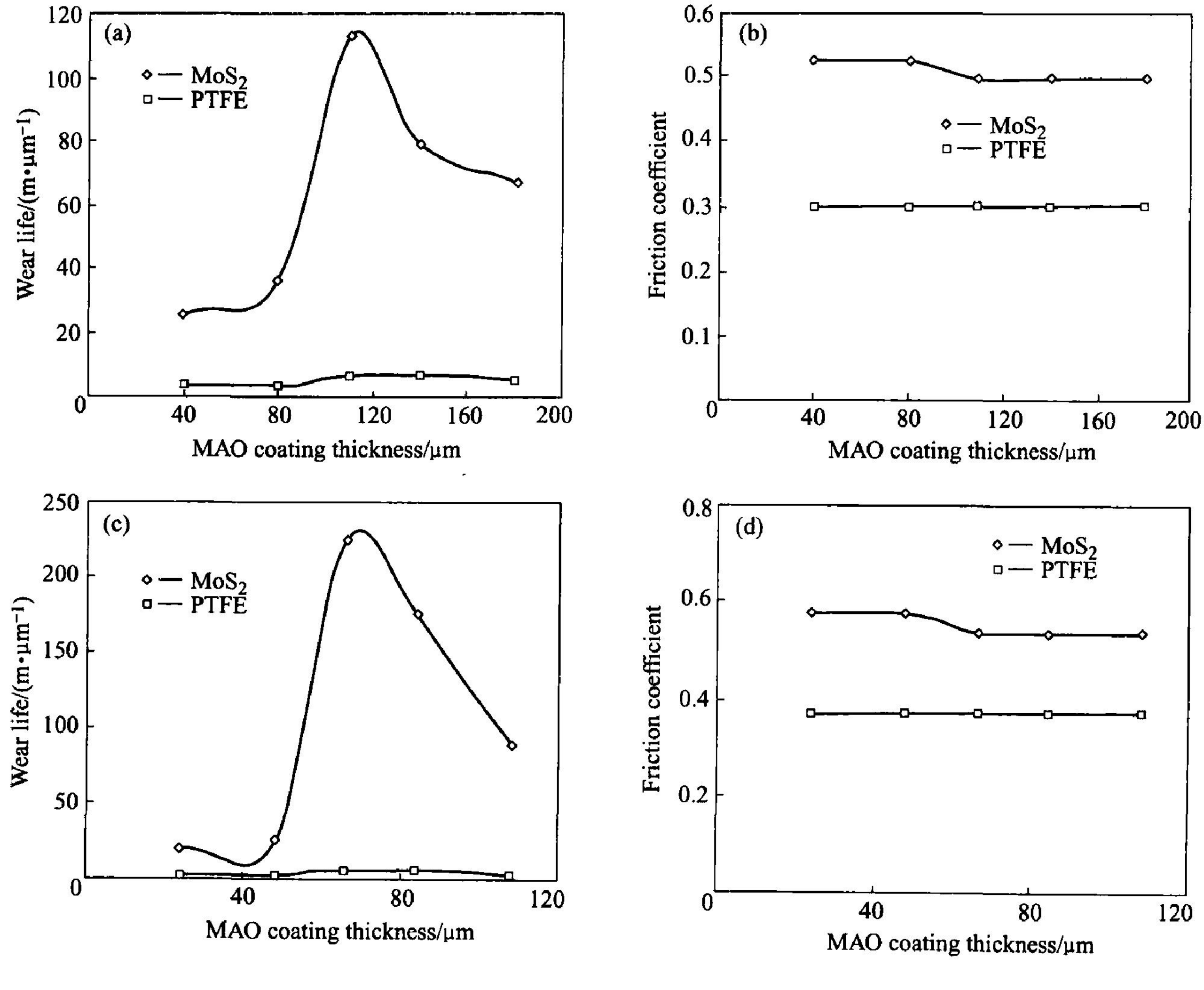

Fig. 2 Wear life and friction coefficient of burnished films on as-deposited coatings ((a), (b)) and polished coatings ((c), (d))
(Timken tester at 0.75 m/s, 200 N)

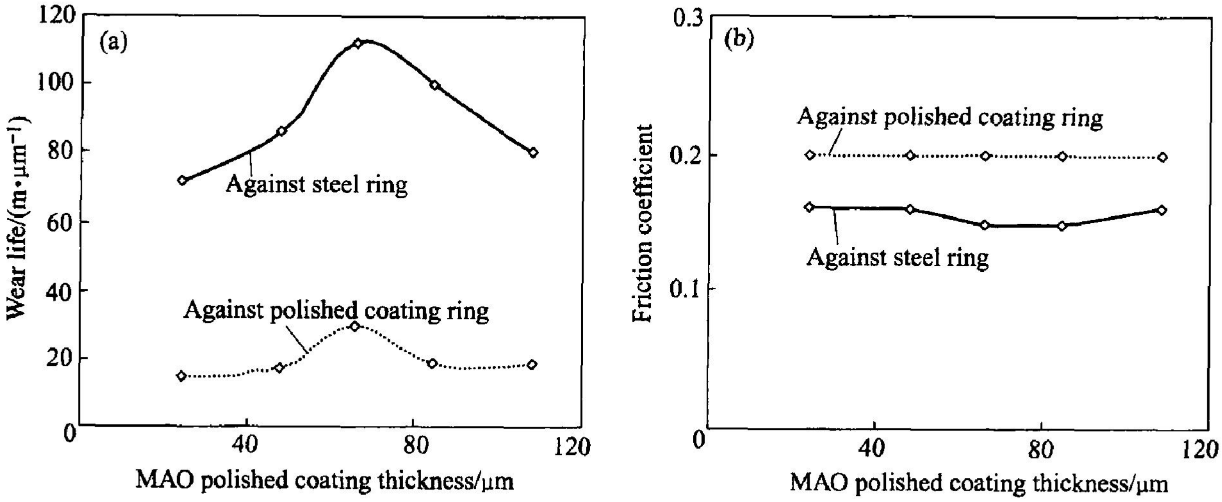

Fig. 3 Wear life(a) and friction coefficient(b) of bonded film on different polished coatings (Sliding speed 1.75 m/s, load 680 N)

Table 1 Wear life and friction coefficient of bonded lubricating film on MAO coatings (Timken tester, against steel ring, speed 1.75 m/s, load 680 N)

Multilayer	Wear life/ (m • μm^{-1})	Friction coefficient
Ployfluo-150/PU on 110 μm as-deposited coating	755	0.21
Ployfluo-150/PU on 60 - 70 μm as-deposited coating	1 790	0.20
MoS_2/PU on 110 μm as-deposited coating	44	0.16
MoS_2/PU on 60 - 70 μm polished coating	110	0.15

the different structures of the as-deposited and polished micro-arc oxidation coatings. Namely, the as-deposited coatings have loose outlayer which is not strong enough to support the load applied to the top self-lubricating coatings; while the polished micro-arc oxidation coatings are more compact and are able to support load by the hard sub-interlayer of α-Al_2O_3. Subsequently an extended wear life of the multilayer coating composed of the soft lubricating top-film and the hard micro-arc oxidation sub-layer is obtained.

Fig. 4 shows the SEM photographs and the corresponding Al distribution of the wear scar on the multilayer of bonded lubricant film/polished coating. Plastic deformation is visible near the edge of the wear scar (zone along arrow *c*) and the original coating surface (zone along arrow *d*). The broken zone of the bonded solid lubricating film (arrow *a*) records a higher content of aluminum ((b) in Fig. 4), which is attributed to the sub-aluminum oxides. The coexistence region of film and sub-aluminum oxides near the broken zone

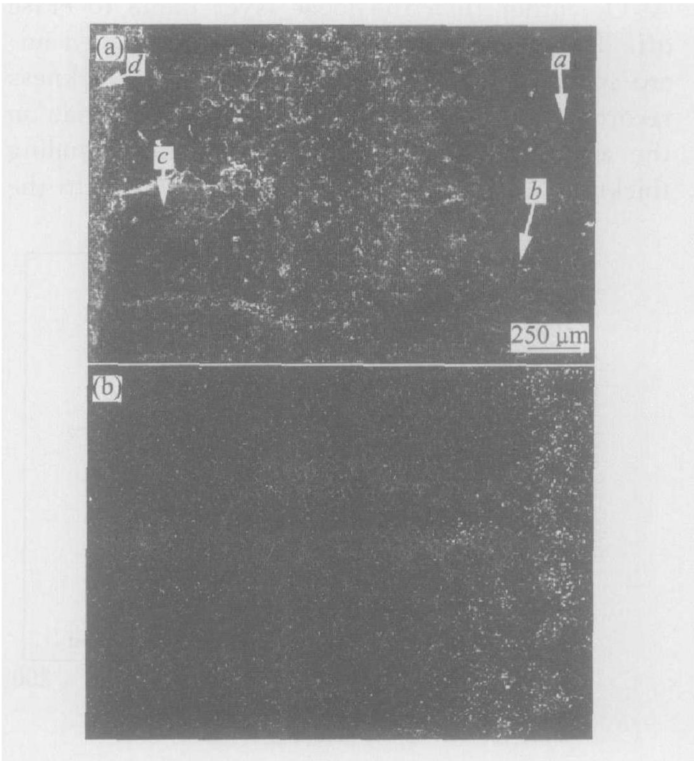

Fig. 4 SEM morphology of wear scar(a) and corresponding Al distribution(b) of MoS_2/PU bonded solid lubricating film on polished coating of 60 - 70 μm in thickness (Timken tester, against steel ring, speed 1.75 m/s, load 680 N)

(zone along arrow *b*) indicates that the bonded solid lubricant film and the hard α-Al_2O_3 sub-layer have strong interfacial bonding.

The friction and wear mechanism of the multilayer coatings on Al alloy is schematically illustrated in Fig. 5. For the lubricating film/as-deposited coating, breakage of the loose layer of the as-deposited coating is easily caused under normal load, then shorter wear life of the multilayer coatings is observed in the presence of micro-cracking and abrasion. On the contrary, for the lubricating film/ polished MAO coating multilayer, the compact sub-layer of α-Al_2O_3 has ability to resist abrasion, and it helps to support the load applied to the self-lubricating top-layer as well, thus an extended wear life of the multilayer coatings is obtained. In other words, the intermediate loose layer of the as-deposited MAO coating is harmful to sustain the friction and wear behavior of the multilayer coatings, because it is liable to deform and detach in the sliding process.

The wear life of the MoS_2/PU bonded solid lubricating film on the polished coating of 60 - 70 μm in thickness against steel and ceramic hard pairs is drastically increased (Fig. 6), and the incorporation of the boned solid lubricating film gives a much smaller friction coefficient between 0.08 and 0.09. When sliding against mild steel and ceramic blocks, it is observed that transfer film of the bonded solid lubricant is formed on the counterpart surfaces (Fig. 7), thus a decreased friction and wear is obtained.

In summary, the compact and hard interlayer of MAO coating is able to prevent the solid lubrica-

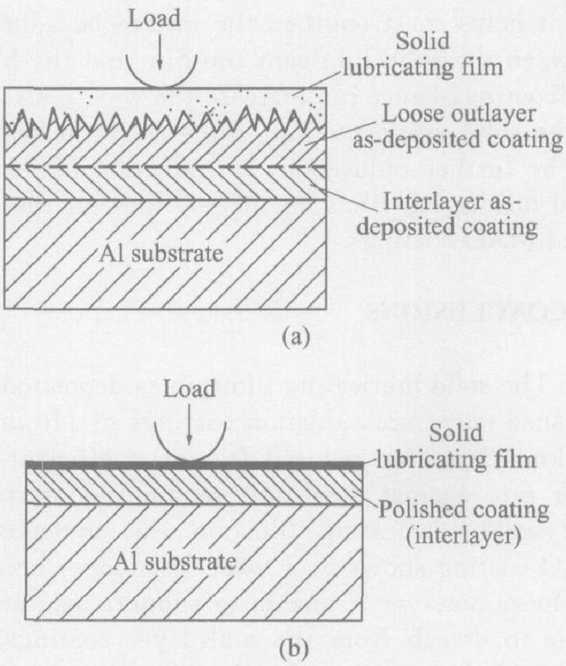

Fig. 5 Schematic dagrams of wear mechanism on solid lubricating film/ as-deposited MAO multilayer coating (a) and solid lubricating film/ polished MAO multilayer coating (b)

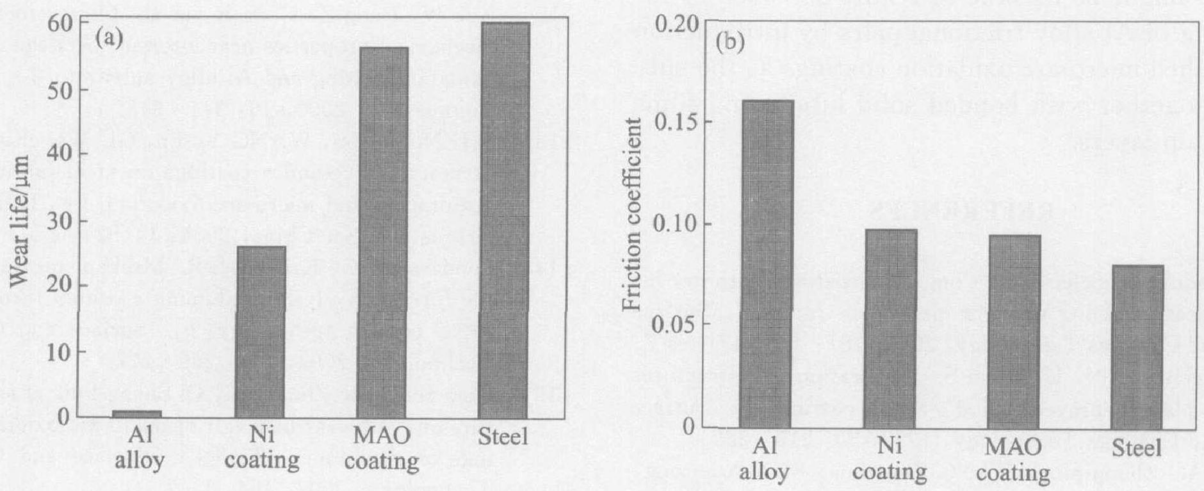

Fig. 6 Wear life (a) and friction coefficient (b) of MoS_2/PU bonded solid lubricating film on polished coating pin against various blocks

(Reciprocating tester, sliding speed 0.50 m/s, contact pressure 6 MPa)

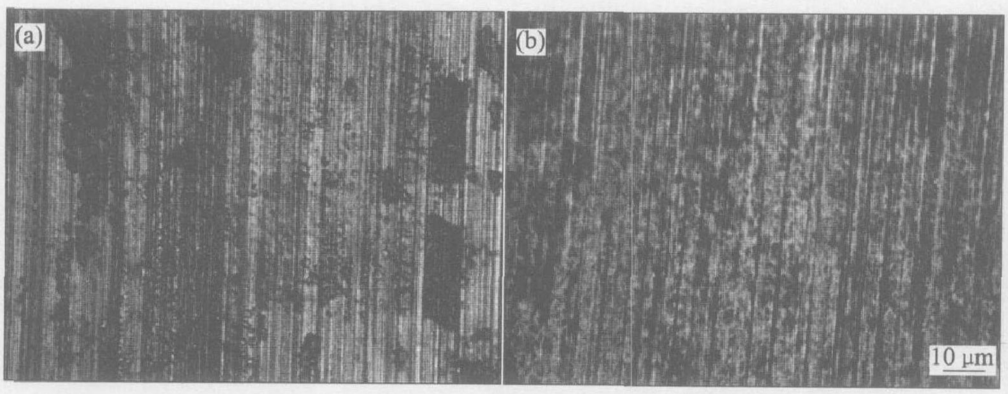

Fig. 7 Optical micrographs of transfer films formed on surface of MAO ceramic block (a) and steel block (b) of MoS_2/PU bonded solid lubricating coating

ting film from damage by supporting heavy load, and it helps to strengthen the interfacial adhesion between the solid lubricant top-film and the MAO sub-coating, hence can increase the wear resistance of the solid lubricant film. Moreover, the friction can be further reduced by introduction of bonded solid lubricating films as the top-film on the polished MAO coatings.

4 CONCLUSIONS

The solid lubricating films on as-deposited and polished micro-arc oxidation coatings of 110 μm in thickness register reduced friction coefficient and wear rate against steel and ceramic counterpart. The solid lubricating film on the as-deposited MAO coating shows poor wear resistance, because the loose outlayer is unable to support load and is liable to detach from the multilayer coatings. In other words, the interfacial adhesive mechanism changes from soft top-film/hard sub-layer to soft top-film/weakened intermediate loose layer/hard sub-layer, and the weakened intermediate loose layer is harmful to maintain the friction and wear behavior of the multilayer coatings on Al alloy. Thus it might be feasible to realize satisfactory lubricating of Al alloy frictional pairs by introduction of polished micro-arc oxidation coatings as the sub-layers together with bonded solid lubricating films as the top layers.

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(Edited by YANG Bing)