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Chapter 4

Plasma Electrolytic Oxidation Coatings on Lightweight Metals

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Additional information is available at the end of the chapter

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1. Introduction

Lightweight metals, e.g. aluminum (Al), magnesium (Mg), titanium (Ti) and their alloys are of great importance for applications in various machinery and transportation system, especially in aerospace and automobile products due to their high strength-to-weight ratio and superior physical and chemical performances. However, their poor tribological properties, such as low wear resistance, high friction coefficient and difficulty to lubricate, have seriously restricted their extensive applications.

In the past decades, various traditional surface treatments, such as physical vapor deposition [1-2], chemical vapor deposition [3], ion beam assisted deposition [4] and spraying [5], have been applied to metallic substrates to improve their generally poor tribological properties. However, most of the aforementioned methods involve high processing temperature, which may degrade the coatings and/or substrates. Here, a relatively novel technique, plasma electrolytic oxidation (PEO) treatment used to improve the tribological properties of lightweight metals was introduced.

1.1. The origin of PEO technique

Plasma electrolytic oxidation (PEO), also called micro-arc oxidation (MAO) [6], micro-plasma oxidation (MPO) [7], anodic spark deposition (ASD) [8] or micro-arc discharge oxidation (MDO) [9] in modern scientific literatures, is derived from conventional anodizing [10-11]. Anodizing is traditionally carried out using direct current (DC) electrolysis. The workpiece is made anodic in an acid electrolyte (sulfuric acid is most commonly used, but phosphoric, oxalic, chromic and other acids can be used, singly or in combination). Typically, the cell voltage is 20 to 80 V DC and the current density is 1 to10 A dm^{-2}, the process usually being controlled at a constant cell voltage. Plasma electrolytic oxidation (PEO) treatment usually

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carried out in high voltage condition which is introduced into the high-pressure discharge area from the Faraday region of traditional anodizing. The applied voltage is increased from tens of volts to hundreds of volts, which is the breakthrough of traditional anodizing. The voltage forms developed from DC to continuous pulse, and then to AC, resulting in corona, glow, spark discharge and even micro-arc discharge phenomenon in the surface of the samples [12]. The general comparison between conventional DC anodizing and PEO technique was shown in Table 1.

Properties	Anodizing	PEO technique
Cell voltage (V)	20-80	120-300
Current density (A/dm^2)	< 10	< 30
Substate pretreatment	Critical	Less critical
Common electrolytes	Sulfuric, chromic, or phosphoric	Neutral/alkaline (pH=7-12)
Coating thickness (μm)	< 10	< 200
Coating hardness	Moderate	Relatively high
Adhesion to substrate	Moderate	Very high
Temperature control	critical	Not so important

Table 1. General comparison between conventional direct current anodizing and plasma electrolytic oxidation coating technologies [12]

1.2. Process of PEO treatment

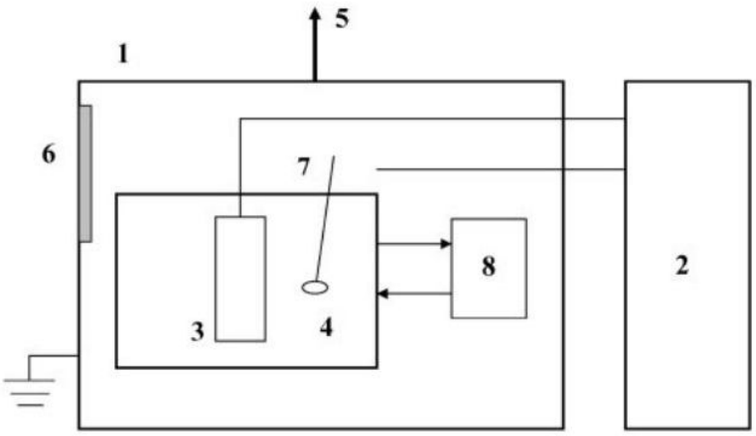
A typical equipment used for PEO treatment is shown in Figure 1. An enclosure (1) is mounted close to a high voltage AC power supply (2). The metal substrate to be PEO coated (3) is immersed in the electrolyte in a water cooled, insulated electrolyte tank (4) made of stainless steel and also serves as the counter electrode. The tank is insulated from ground and mounted in the safety interlocked enclosure (1), the latter being equipped with fume extraction facilities (5) and a window (6) to allow the PEO process to be viewed. The electrolyte is typically mixed (7) and recycled via a flow circuit containing a heat exchanger/chiller and a 50 to 100 mm filter (8) [12].

Before the PEO treatment, the samples should be ground and polished with abrasive paper, degreased ultrasonically in acetone and cleaned with distilled water. During the treatment, the samples are used as anode plates and immersed in the electrolyte which is cooled by a water cooling system and mechanically stirred by a mixer. After the treatment, the samples should be rinsed with distilled water and air dried [12].

1.3. Mechanism of PEO technique

When the samples of valve metals [13] or their alloys are placed in the electrolyte, the metal surface immediately generates a layer of insulating oxide film after the energization. The weak parts of the oxide film were broke down after the applied voltage exceeds a critical value,

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1. Insulated enclosure; 2. High voltage AC power supply; 3. Workpiece (light metal substrate); 4. Electrolyte holding tank and counter electrode (stainless steel); 5. Fume extraction vent; 6. Viewing window; 7. Electrolyte mixer; 8. Flow circulation via chiller and filter

Figure 1. Equipment used for PEO treatment [12].

resulting in the occurrence of micro-arc discharge phenomenon. The process of electrical breakdown of PEO involves many physical (such as crystallizing, melting, phase change at high temperature and electrophoresis, etc.), chemical (such as high-temperature chemistry, plasma chemistry) and electrochemical processes. A variety of models and hypotheses on the electrical breakdown of PEO process were created by many researchers to explain its causes. Therefore, the theory of electric breakdown also experienced different stages of development, such as thermal mechanism, mechanical effects and the mechanism of electron avalanche. The mechanism is so complex that, to date, no theory can give a complete and accurate explain of the whole PEO process. [14-15].

Recently, some studies have showed some basic processes of PEO treatment which involves: the formation of space charges in the oxide matrix; gas discharge generated in the pores of oxide; localized melting of the layer material; thermal diffusion; deposition of the colloidal particles; migration of negatively charged colloidal particles into the discharge channels; plasma chemical and thermochemical reactions, etc. [14-15].

1.4. Structures and compositions of PEO coatings

The PEO coatings generally consist of a porous top layer, compact intermediate layer and thin inner layer. The intermediate layer and inner layer are dense and adhered well to the substrate [12, 16]. The surface morphologies characterized with many micropores, microcracks and dimples [17]. Previous studies showed that the micropores were formed by molten oxide and gas bubbles thrown out of micro-arc discharge channels and the cracks resulted from the thermal stress due to the rapid solidification of the molten oxide in the relatively cold electrolyte.

The PEO ceramic coatings are composed of not only predominant substrate metal oxides (such as Al_2O_3, TiO_2 and MgO on Al, Ti, Mg and their alloys respectively)[12], but also more complex oxides and compounds which involve the components presented in the electrolytes (such as

Al_2O_3 on Ti6Al4V alloy in aluminate solution [18]; mullite on Al alloy in silicate solution [19]; MgF_2 on Mg alloy with KF in the electrolyte [20] and TiO_2 on Mg alloy in phosphate solution containing titania sol [21]).

1.5. Influence factors for PEO technique

It is considered that the PEO treatment is a multifactor-controlled process, which is influenced by many factors, intrinsic or extrinsic. The compositions of substrate materials and electrolyte are considered to be intrinsic factors which play crucial role for the structure and composition of PEO coatings, while the extrinsic factors generally consist of electrical parameters, processing temperature, oxidation time and additives [14]. Herein, these influence factors for PEO technique will be introduced and discussed briefly.

1.5.1. Influence of substrate materials

The difference of substrate materials plays a crucial role in the components and properties of PEO coatings. The predominant compositions of the PEO coatings depend on the substrate materials, for example, the main content of coatings deposited on Al, Mg, Ti and their alloys are Al_2O_3, MgO and TiO_2 respectively. Therefore, the PEO coatings deposited on different substrate materials generally possess different properties. According to recent studies, the available coating thicknesses are around 300 μm on Al alloy, 150 μm on Mg alloy and 200 μm on Ti alloy respectively. The hardness value ranges for PEO coatings formed on different substrate materials are generally from 300 HV to 2500 HV on Al alloy, from 200 HV to 1000 HV on Mg alloy and from 300 HV to 1100 HV on Ti alloy [14-15].

1.5.2. Influence of electrolytes

The compositions of electrolyte greatly affect the properties of PEO ceramic coatings. Different electrolytes result in different growth rates, structures, phase compositions and element distribution of the PEO coatings [22-25]. Generally, the electrolytes used for PEO treatment are composed of acidic electrolytes and alkaline electrolytes. The acidic electrolytes including concentrated sulfuric acid, phosphoric acid and other salt solutions etc. are seldom used at present due to their great environmental pollution. While the alkaline electrolytes mainly consist of four systems including sodium hydroxide based electrolytes, silicate based electrolytes, phosphate based electrolytes and aluminate based electrolytes[14].

1.5.3. Influence of electrical parameters

The whole PEO process and the properties of ceramic coatings are greatly affected by electrical parameters including current modes, current density, current frequency, anodic voltage, cathodic voltage, duty cycle etc. Recently, the effects of electrical parameters on PEO coatings were investigated by many researchers as follows.

The effect of electrode distance on anode current and the influence of anode current on PEO process were investigated by C.B. Wei et al [26]. The PEO processes were carried out on 2024 Al alloy in the electrolyte of sodium silicate with other additives, keeping the anode and

cathode plates located face to face and separated by different distances. Results showed that the anode current was influenced by the distance between the electrodes and had a critical effect on the oxidation efficiency. The anode currents were found to decrease with larger distances. The current flowing through the front surface was higher than that through the back surface. The ball-on-disk tribological tests and corrosion tests revealed that the front surface has better tribological properties and higher corrosion resistance than the back surface.

R.O. Hussein et al. [27] studied the influence of different current modes on PEO plasma discharge behaviour and alumina coating microstructure. The PEO processes were carried out on pure 1100 aluminum using two different current modes of pulsed unipolar and bipolar in the electrolyte of Na_2SiO_3 (7 g/L) and KOH (1 g/L). It was found that the plasma temperatures vs. process time were different under different current modes. The plasma temperature spikes were believed to be caused by the strongest plasma discharges initiated at the interface between the oxide coating and substrate. Compared to the unipolar current process, the application of pulsed bipolar current resulted in reducing the high spikes on temperature profiles and the average plasma temperature. The aluminum oxide coating morphology and microstructure were also significantly different under different current modes. The bipolar current mode could improve the coating quality compared with the unipolar current mode, in terms of surface morphology and cross-sectional microstructure. A dense coating morphology could be achieved by adjusting positive to negative current ratio and their timing to eliminate or reduce the strongest plasma discharges and the high temperature spikes, thus resulting in the improvement of coating qualities.

Yue Yang et al. [28] investigated the effects of current frequency on microstructure and wear resistance of ceramic coatings embedded with SiC nanoparticles on Mg alloy produced by PEO. The PEO treatments were carried out on AZ91D Mg alloy in the electrolyte containing $NaAlO_2$ (20 g/L), NaOH (3 g/L) and SiC nanoparticles (2 g/L), with the current frequency fixed at 500 Hz, 700 Hz and 900 Hz respectively. Results revealed that with the increasing of current frequency, more SiC nanoparticles randomly dispersed on the surface. The thickness and growth rate of the coatings increased with the increasing of applied current frequency. Furthermore, the ceramic coating embedded with SiC nanoparticles formed at a current frequency of 900 Hz showed the finer microstructure, lower surface roughness and best wear resistance.

R.H.U. Khan et al. [29] studied the effects of current density on surface characterization of PEO treated Al alloy. The samples were fabricated by PEO process at different current density of 5, 10, 15 and 20 A/dm^2. It was found that the coating thickness increased with the increased current density. The largest coating thickness (40 μm) was obtained at 20 A/dm^2 current density, whereas a thinnest coating (3 μm) was formed at 5 A/dm^2. Furthermore, the relative content of α-Al_2O_3 tended to increase with increasing current density. Residual stresses in alumina coatings tended to decrease with the increased current density due to increased plasma microdischarge events which promoted stress relaxation through formation of microcrack network and thermal annealing in the coatings.

Ping Huang et al. [30] investigated the effects of different voltages on mechanical properties of titania prepared by PEO. The PEO treatment was carried out on pure titanium, in an aqueous

solution containing calcium salt and phosphate salt, using different voltages from 240 V to 450 V. Results showed that the composition of the PEO coatings was generally anatase and rutile, while at higher voltage of 400-450 V, a new $CaTiO_3$ phase appeared. The pore size of PEO coatings increased with the increase of applied voltage. The samples prepared at 240-350 V had much stronger bonding strength compared to that prepared at higher voltage. The elastic modulus and residual stress both increased with the increasing of applied voltage.

The effects of cathode voltage on structure and properties of PEO ceramic coatings formed on NiTi alloy were investigated by F. Liu et al. [31]. The PEO processes were carried out on nearly equiatomic NiTi alloy in a solution of sodium aluminate and sodium hypophosphite, using a constant voltage mode, with anodic voltage kept constant at 400 V and cathodic voltage controlled at 0, 10, 20, and 30 V respectively. It was found that, the thickness and surface roughness of PEO coatings increased with the increasing of cathodic voltage, the friction coefficient of PEO coatings against GCr15 steel ball also increased, while the bonding strength of the coatings to the substrate and the corrosion resistance of PEO coatings both decreased. The PEO ceramic coatings formed at various cathodic voltages on NiTi alloy were composed of γ-Al_2O_3 at the only crystalline phase. The crystallinity could be enhanced through increasing the cathodic voltages. As a whole, the cathodic voltage applied for PEO showed a negative correlation with the biocompatibility of the ceramic coatings.

Yuming Tang et al. [32] studied the influences of duty cycle on the bonding strength of Mg alloy by PEO treatment. The duty cycle varied in the range of 10-40% with positive and negative cycle remained equal. It was revealed that the higher duty cycle increased the coating porosity and slightly decreased the thickness of the oxide coating. The PEO coatings mainly consisted of MgO and $MgSiO_3$. And the relative content of MgO in the coatings increased while the content of $MgSiO_3$ slightly decreased with the increase of duty cycle. Furthermore, as the duty cycle increased, the lap-shear strength of the bonding joints increased. The highest lap-shear strength (24.50 MPa) was obtained under the duty cycle of 40%. The reason was attributed to the larger porosity and enhanced mechanical interlocking effect.

1.5.4. Influence of processing temperature

The electrolyte temperature can greatly affect the PEO process. If the temperature is too low, the oxidation process becomes weak, resulting in less thickness and lower hardness of the PEO coatings. If the temperature is too high, the dissolution of oxide film will be enhanced, and thus cause the coating thickness and hardness to decrease significantly. Therefore, the processing temperature should also be studied and generally controlled in the range of 20-40℃.

H. Habazaki et al. [33] investigated the effects of different electrolyte temperatures on formation and characterization of wear-resistance of PEO coatings on Ti alloy. The PEO processes were carried out on Ti-15-3 alloy in the electrolyte of $K_2Al_2O_4$ (0.15 mol/L), Na_3PO_4 (0.02 mol/L) and NaOH (0.015 mol/L), at different electrolyte temperatures between 278 K and 313 K. Results showed that at the lowest temperature of 278 K, the yielded PEO coating contained higher concentration of α-Al_2O_3 phase in addition to the Al_2TiO_5 major phase, exhibited lower porosity, uniformity and density, and thus showed more improved wear resistance, compared to that formed at higher temperatures.

1.5.5. Influence of oxidation time

With the increasing of oxidation time, the coating thickness increases, while the growth rate decreases. Different oxidation time can result in different coating qualities, such as thickness, roughness, adhesion, hardness, wear resistance and corrosion resistance etc.. Therefore, the oxidation time for PEO treatment should be investigated and optimized.

Yanhong Gu et al. [34] studied the effect of oxidation time on corrosion behavior of PEO coatings on Mg alloy in simulated body fluid. The samples were fabricated on AZ31 Mg alloy in aqueous solution of sodium phosphate (30 g/L), using applied DC voltage of 325 V, current density of 150 mA/cm^2 and pulsed frequency of 3000 Hz, with 1, 3, 5 and 8 min different oxidation time. Results showed that the coatings mainly consisted of Mg, MgO, $MgAl_2O_4$ and $Mg_3(PO_4)_2$, and the oxidation time had very little influence on the phase compositions. The diameter of the micropores in the PEO coating surface increased with increasing oxidation time. The coating thickness increased with increasing oxidation time until 5 min (20 μm). The sample coated at 5 min showed the thickest layer with a relatively smooth and uniform microstructure with fewer micropores, compared to the other PEO oxidation times. When the oxidation time, however, was increased to 8 min, the coating thickness decreased and the coating surface became rough. The porosity decreased with increasing oxidation time until 5 min (4.40%), and then increased to 6.28% for an oxidation time of 8 min. As a whole, the PEO coating produced at 5 min had the smallest corrosion current density and the largest electrochemical impedance, resulting in the highest corrosion resistance, due to the compact, smooth and uniform morphology of coating surface with lower porosity.

1.5.6. Influence of additives

Employing different additives in the electrolyte can greatly affect the PEO process, and thus resulting in different properties of the coatings. For example, Jun Liang et al. [20] studied the effect of KF in Na_2SiO_3-KOH electrolyte on the structure and properties of PEO coatings formed on Mg alloy. It was found that the addition of KF contributed to increase the electrolyte conductivity, decrease the work voltage and final voltage in the PEO process and change the spark discharge characteristics. Furthermore, the addition of KF resulted in a decrease of pore diameter and surface roughness, an increase of the coating compactness and the changes in the phase compositions as well. The hardness and wear-resistance of the coating also enhanced due to the addition of KF.

2. Tribological properties of PEO coatings

Employing PEO technique to form ceramic oxide coatings on Ti, Mg, Al and their alloys can significantly enhance the mechanical and tribological properties, such as high hardness, superior wear resistance and good adhesion to the substrate. In recent years, investigations on the phase composition, mechanical and tribological properties of PEO coatings on Ti, Mg, Al and their alloys were done by many researchers. However, the tribological performances of PEO coatings are not only affected by the intrinsic properties of PEO coatings, but also affected

by many extrinsic factors, such as sliding loads, sliding speed, counterpart materials, lubricated conditions, temperature and humidity etc. Herein, the sliding loads are emphasized and classified into three levels: low loads (0-5 N), medium loads (5-50 N) and heavy loads (above 50 N). And then, the friction and wear behaviors of different PEO coatings in different conditions will be introduced and discussed under different load levels.

2.1. Friction and wear behavior of PEO coatings under low loads

The microstructure, mechanical and tribological properties of PEO coatings formed on Ti6Al4V alloy were studied by Y.M. Wang et al [35]. A nanoindentation test showed that the hardness and elastic modulus were about 8.5 GPa and 87.4 GPa for the compact region of the PEO coating, and about 4 GPa and 150 GPa for the Ti6Al4V substrate. The hardness and elastic modulus were mainly constant in the compact region within 33 μm, and decreased remarkably beyond 33 μm to the outer surface. A sheer test showed that the adhesion strength between coating and substrate was about 70 MPa. The tribological behaviors of untreated and PEO coated samples were evaluated by a pin-on-disk tribometer under the normal loads of 0.3, 0.5, and 1 N, with a sliding speed of 0.05 m/s or 0.15 m/s, using SAE52100 steel ball as counterpart material. Results of friction and wear tests showed that the friction coefficient of PEO coating against steel was as low as 0.2-0.3 at loads not more than 1 N and sliding cycles within 2500 times, and gradually increased at the later stage of wear test due to the oxidation and materials transfer wear mechanism.

The investigations of structure, composition, mechanical and tribological properties of PEO coatings formed on AM60B Mg alloy in silicate and phosphate electrolyte have been done by Jun Liang et al. [36] The samples were fabricated in the electrolyte containing Na_2SiO_3 (10 g/L), KOH (1 g/L) or Na_3PO_4 (10 g/L), KOH (1 g/L). The coating formed in silicate electrolyte is composed of periclase MgO and forsterite Mg_2SiO_4 phases while MgO and a little of spinel $MgAl_2O_4$ are the main phases of the coating formed in phosphate electrolyte. Generally, the forsterite Mg_2SiO_4 has a greater hardness than that of the MgO. Therefore, the coating formed in silicate electrolyte exhibits a higher microhardness than that formed in phosphate electrolyte. The friction and wear properties of the PEO coatings were evaluated on a reciprocal-sliding UMT-2MT tribometer in dry sliding conditions under a load of 2 N, using Si_3N_4 ball as counterpart material, with a siding speed of 0.1 m/s and sliding amplitude of 5 mm. The wear life of PEO coatings formed in two different electrolytes was compared with the thin coatings and results showed that the wear life of coating formed in silicate electrolyte is about four times as long as that of coating formed in phosphate electrolyte. The uncoated Mg alloy has a friction coefficient of about 0.3 and exhibits a high wear rate of 3.81×10^{-4} mm^3/Nm. While for both the oxide coatings, the friction coefficients are in the range of 0.6-0.8 and the wear rates are only in the range of $3.55\text{-}8.65\times10^{-5}$ mm^3/Nm. These evidences demonstrate that the PEO coatings formed on Mg alloy in both electrolytes have greatly enhanced the wear resistance but exhibit higher friction coefficients compared with the uncoated Mg alloy. Furthermore, the oxide coating formed in silicate electrolyte has a higher friction coefficient but exhibit a better wear resistance than that formed in phosphate electrolyte. It also suggests that the structure and phase composition of coatings are indeed the dominant factors which influence the mechanical property and friction and wear behaviors of PEO coatings.

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2.2. Friction and wear behavior of PEO coatings under medium loads

P. Bala Srinivasan et al. [37] studied the dry sliding wear behaviour of PEO coatings with different thickness of 10 μm and 20 μm on cast AZ91 magnesium alloy. The samples were fabricated by PEO treatment in silicate based electrolyte containing Na_2SiO_3 (10 g/L) and KOH (10 g/L). The dry sliding wear behaviour of the untreated Mg alloy, PEO coated specimen A and B was assessed on a ball-on-disc oscillating tribometer, under three different loads of 2N, 5N and 10N, with an oscillating amplitude of 10 mm and at a sliding velocity of 5 mm/s for a sliding distance of 12 m, using an AISI 52100 steel ball of 6 mm diameter as static friction partner. For the uncoated Mg alloy, the friction coefficients were fluctuating in the range of 0.24-0.40 under different loads. For the 10 μm PEO coating, the friction coefficient reached to a steady value of about 0.78 under 2 N load, dropped to around 0.35 after a sliding distance of about 4 m under 5 N load, while dropped in a very short time under 10 N load. For the 20 μm PEO coating, the friction coefficients did not drop at all loads and remains steady. Moreover, the friction coefficient showed lower value with an increase in load (0.8 at 2 N, 0.68 at 5 N and 0.62 at 10 N). The uncoated Mg alloy under all loads and the 10 μm PEO coating under 5 N and 10 N loads all showed high wear rates. While the 20 μm PEO coating under all loads and the 10 μm PEO coating under 2 N load all showed much lower wear rates. The results indicated that the thickness of coatings played a crucial role in enhancing the wear resistance. At higher initial stress levels, the deformation of the substrate causes the cracking and flaking-off of the coating, especially when it is thin. Under such circumstances the increased thickness of PEO coating provided a better load bearing capacity, thus resulting in a superior wear resistance.

M. Treviño et al. [38] investigated the wear of coatings on Al 6061 alloy fabricated by PEO treatment in Na_2SiO_3-KOH electrolyte. The coatings with different thickness of 100, 125 and 150 μm were fabricated and characterized. Composition analysis showed that the coatings consisted of a combination of oxide phases such as mullite, α-Al_2O_3, γ-Al_2O_3 and amorphous alumina. It was suggested that the presence of α-Al_2O_3 phase presented the greatest wear resistance compared with other phases such as mullite, γ-Al_2O_3 and amorphous alumina which were highly vulnerable for the conditions studied. No difference was detected for the different coatings in hardness values which were of 1556±11 HV_{50} compared with that of 109±3 HV_{50} for the substrate. The tribological properties were evaluated by a pin on disc test machine, with a sliding distance of 1 km and a constant linear speed of 13.76 m/min, using 10, 20, 30 and 40 N different normal loads for each coating thickness. Friction and wear tests showed that the friction coefficient changed along the tests, and the weight loss depended on both the thickness of the coatings and the loads applied during the test. The wear mechanisms were suggested to be adhesion and abrasion by hard particles. The thinnest coating of 100 μm exhibited better resistance to wear and showed the friction coefficients which exhibited a continuous increase independently of the applied loads. The friction coefficients for the coating of 125 μm remained constant when loads of 10 and 20 N were used, and reduced their values once a certain distance was achieved when tested with 30 and 40 N. The friction coefficients for the coating of 150 μm were found to increase under a load of 10 N, to remain fairly constant with loads of 20 and 30 N and to reduce their value once a distance of around 500 m was achieved with a load of 40 N. The reduction of friction coefficients for the coatings of 125 μm and 150 μm suggested that

the coatings were completely removed under the loads of 30 N and 40 N resulting in contact with the alloy substrate which was probably lubricated by wear debris generated.

2.3. Friction and wear behavior of PEO coatings under heavy loads

Chen Fei et al. [39] studied the tribological performance of PEO ceramic coatings fabricated on Ti6Al4V alloy in the electrolyte containing Na_2SiO_3 (10g/L), Na_2CO_3 (4g/L) and EDTA-2Na (5g/L). Coatings with a thickness of 10 μm were formed and polished to remove the prominent ceramic particles of the outer surface in order to reduce the effect of roughness on tribological behavior. The tribological behaviors of unpolished coating, polished coating and untreated Ti6Al4V alloy were evaluated on a ball-on-disk tribometer under the dry sliding conditions, using balls of SAE52100 steel as counterpart materials, with normal load of 100 N, rotation speed of 1000 rpm, sliding speed of 0.42 m/s and sliding time of 10 min. For the untreated Ti6Al4V alloy, the long-term friction coefficient is about 0.4, and the worn surface that sliding against steel revealed that the dominant wear mechanism is extensive abrasive and adhesive wear. For the unpolished PEO coating, the friction coefficient exhibited a high value of about 0.5, and the wear track showed severe abrasive wear, also accompanied by severe adhesive wear from the steel counter surface leading to material transfer on the coated surface. The porous surface of the unpolished PEO coatings is very rough due to the scraggy ceramic products. Unlike sliding that usually leads to plastic shearing in materials, the impact caused by the ceramic asperities on the surface results in catastrophic failure, such as cracking and crushing of the contact regions, which leads to faster material removal and the production of the sharp ceramic debris fragments. In contrast, for the polished coating, the friction coefficient exhibited a relatively low and stable value, almost remaining constant at 0.2. As the outer surface was polished to remove the prominent ceramic particles, the initial contact conditions were changed from a rough ceramic/steel to a smooth ceramic/steel mating surface. Therefore, the cracking and crushing of prominent ceramic regions due to great vibrations were eliminated. Results showed that the worn surface was relatively smooth, accompanied with fine debris embedded in the edges of contact regions. The good antifriction properties are attributed to the microstructure of the coatings which are mainly composed of rutile and anatase TiO_2. TiO_2, especially the rutile-type, is known as a potentially low friction and wear reducing material.

Jun Tian et al. [40] investigated the structure and antiwear behavior of PEO coatings on 2A12 Al alloy. The samples were fabricated by PEO treatment in the electrolyte composed of Na_2SiO_3 (30g/L), NaOH (5g/L), with current density controlled to below 10^3 A/m^2. The as-deposited coatings were polished with SiC paper to remove 20%, 30%, 40% and 50% of the whole thickness of the coatings as polished coating samples. The results of structural and phase composition analysis showed that the PEO coatings on Al alloys showed two distinct layers, i.e. a porous outer layer consisting predominantly of γ-Al_2O_3 and a dense inner layer consisting predominantly of α-Al_2O_3. The inner layer α-Al_2O_3 has better antiwear ability compared with the outer layer γ-Al_2O_3. Therefore, with the increasing of the coating thickness, the antiwear life of the outer layer becomes smaller than that of the inner layer. The results of friction and wear tests showed that the polished coating mainly composed of α-Al_2O_3 registered a lower wear rate of 3.00-5.00×10^{-6} mm^3/Nm in reciprocating sliding against ceramic counterpart at a

speed of 0.33 m/s and a contact pressure of 2 MPa. The antiwear life of the polished coating reached 2500 m at a speed of 1.25 m/s and a load of 300 N, and the friction coefficient was more than 0.45 against the steel ring in a Timken tester which was a little lower than that of the out layer registering more than 0.47.

The aforementioned studies revealed that the PEO ceramic coatings can sharply increase the wear resistance and decrease the wear rate, compared to the uncoated substrates. However, the PEO coatings normally exhibit higher friction coefficients which can cause not only the wear of sliders, but also the wear damage of counterpart materials in many tribological applications. Thus, it is necessary to fabricate the PEO coatings with both good wear resistance and low friction coefficient.

3. Improvements of tribological behavior of PEO coatings

In order to further improve the tribological properties of the PEO-treated lightweight metals, many attempts to reduce the friction coefficient of the PEO coatings have been made. Herein, three main developments in improvement of tribological properties of PEO coatings are reviewed, which can be categorized as (1) liquid lubrication, (2) duplex coatings and (3) composite coatings.

3.1. Liquid lubrication for improving the tribological behavior of PEO coatings

As there are many micropores, microcracks and dimples on the surface of the PEO coatings [17], these pores, cracks and dimples can act as reservoirs for oil lubricants, which may result in a positive effect to the tribological performance of PEO coatings under boundary-lubricated conditions.

Studies on the wear resistance of PEO coatings on 2024 Al alloy under oil-lubricated condition were done by Tongbo Wei et al. [41]. The friction and wear tests were carried on an MRH-3 ring-on-block tester, at a ring linear speed of 2.60 m/s and normal loads from 300 N up to 1400 N, using AISI-C-52100 steel rings and aluminum rings covered with polished PEO coatings as counterpart. Commercial 4838 lubricating oil was used as the lubricating medium. Friction and wear test showed that the friction coefficient of polished coatings was within 0.020-0.060 under oil-lubricated condition which was reduced to about 1/10 compared with that under dry sliding condition registering within 0.20-0.35, and the wear rate of polished coating was within $1.00\text{-}8.50\times10^{-9}$ mm^3/Nm which was reduced to be about 1/1000 compared with that under dry sliding condition registering within $1.00\text{-}2.00\times10^{-6}$ mm^3/Nm. The polished coatings showed excellent wear-resistance in oil-lubricated sliding against steel and Al_2O_3 ceramic ring and can endure a sliding distance as large as 18.7 km at loads as high as 1400 N.

Fei Zhou et al. [42] investigated the friction characteristic of PEO coating on 2024 Al alloy, sliding against Si_3N_4 balls, in water and oil environments, at different normal loads and sliding speeds. Results showed that, with the increasing of normal load and sliding speed, the friction coefficient of the PEO/Si_3N_4 tribopair in water and oil decreased from 0.72 to 0.57 and 0.24 to

0.11 respectively. The wear mechanism of the PEO coatings changed from abrasive wear in air to mix wear in water, and finally became microploughing wear in oil.

M.H. Zhu et al. [43] investigated the fretting wear behaviors of PEO coating on LD11 Al alloy sealed by grease. It was found that the friction coefficient of the sealed PEO coating under all test parameters were greatly lower than that of the PEO coating. At the same time, there was a longer stage with low friction coefficient that can be observed in the friction coefficient curves for all test conditions of the sealed PEO coating. It was clear that the sealed PEO coating presented an obvious lubricating action during the fretting wear processes. In partial slip regime, the damage of the two coatings was very slight, and the porous structure was still intact even after 104 cycles. The fretting wear mechanisms of the two coatings in slip regime were main abrasive wear and delamination, but higher proportion of the traces of relative sliding was presented on the scars of the sealed PEO coating. As a conclusion, the sealed PEO coating exhibited a better resistance for alleviating fretting wear and lengthening service life than that of the PEO coating.

The fretting wear behaviour of PEO coatings formed on Ti6Al4V alloy under oil lubricated conditions was studied by Yaming Wang et al. [44]. The fretting wear tests of PEO coatings were conducted on a PLINT fretting fatigue machine under unlubricated and oil lubricated conditions (smear and oil bath lubrication), using 52100 steel ball as vibrated counterpart material and with a small reciprocating amplitude of 60 μm. The results showed that in unlubricated condition, the friction coefficient rapidly increased up to 0.8-0.9 and maintained relatively stable. In smear oil lubricated condition, the friction coefficient showed an obvious higher value within 0.18-0.43 in the range of about 2500-6700 cycles. While in oil bath lubricated condition, the friction coefficient reduced significantly to a low and stable value of 0.15 in the long-term fretting test. This indicated that the coatings with oil lubrication lowered the shear and adhesive stresses between contact surfaces, and consequently alleviated the possibility of initiation and propagation of cracks in the inner layer of the coating or titanium alloy substrate.

3.2. Duplex coatings for improving the tribological behavior of PEO coatings

Employing liquid lubricants may improve the tribological properties of the PEO coatings. While in rigid and severe working conditions, such as high vacuum, high temperature, chemical and radioactive environments, liquid lubricants often do not function [45]. Furthermore, liquid lubricants may contaminate the workpieces. Therefore, some multi-step preparation methods combined with the PEO process are employed to fabricate PEO-based duplex coatings on the metallic substrates. The duplex coatings are formed by one of the post treatments (mainly including impregnation, spraying and chemical/physical vapour deposition) on the yielded PEO ceramic coatings. These duplex coatings can sharply decrease the friction coefficient and improve the wear resistance. Herein, some successful applications for the duplex coatings were introduced briefly.

3.2.1. Impregnation

Because the PEO ceramic coating is formed on the metal surface via a series of localized electrical discharge events, there are many micropores left in the coating [17]. This provides

the probability to deposit small sized solid lubricant particles into these micropores to form a binary coating [46]. Herein, a simple and effective method of vacuum impregnation was introduced. In this method, the PEO coating samples are immersed into water-based solid lubricant suspension, and put into a vacuum oven. When deposited for a set time, the samples are heated for a period of time in high temperature for solidification. The solid lubricant particles can impregnate into the micropores of the PEO ceramic coating under the vacuum. With the increasing of deposition time and heat treatment, a compact top film covering the PEO ceramic coating is formed for anti-friction purpose.

Zhijiang Wang et al. [47] investigated the properties of a self-lubricating Al_2O_3/PTFE duplex coating formed on LY12 Al alloy by PEO treatment combined with vacuum impregnation of PTFE. In their work, the PEO coating samples were immersed into water-based PTFE suspension, and putted into a vacuum oven (less than 5×10^{-3} torr). When deposited for a set time, the samples were heated for 24 h at 200℃. Results showed that the PTFE powder particles with the size in the range of 100-170 nm could deposit into the PEO ceramic coating and covered the rough and porous surface. Tribological tests showed that the friction coefficient and wear mass loss of the Al_2O_3/PTFE duplex coating decreased sharply. As the cracks and micropores of the PEO coating were filled by solid lubricant, PTFE could form a lubricating film on the frication surface of the steel ball when the steel ball which worked as counter material slided against the coating. With increased sliding distances, the solid lubricant provided continuous supply due to the abundance of PTFE lying in the micropores of the PEO coating. At the same time, the PEO coating could play the role as the wear-resistant substrate to support soft PTFE polymer. As a result, the friction coefficient of the self-lubricating coating could remain at a constant with minimal weight loss during the long-term sliding.

3.2.2. Spraying top coatings

The porous feature of the PEO coating opens a good way to introduce solid lubricant into micropores or depositing on the surface of coating. And the presence of pores affords an effective mechanical keying between solid lubricant topcoat and the PEO layer. Spraying is a simple, effective and low cost method as a post treatment to apply solid lubricant on PEO coating to form a self-lubricating duplex coating. The PEO ceramic coating serves as underlying loading layer and solid lubricant top layer plays the roles as friction reducing agent.

Y.M. Wang et al. [48-49] have successfully prepared a self-lubricating duplex coating on Ti6Al4V alloy by PEO treatment combined with spraying graphite process. The spraying graphite process forced on the surface of the PEO coating was carried out using a self-made spraying gun with 4 atmosphere pressure, followed by solidification at 180℃ for 15 min. Results showed that the surface of PEO coating was characterized by micropores of different size and shape and covered by graphite lubricant exhibiting a special shape of plate. The duplex coating exhibited good antifriction property, registering friction coefficient of about 0.12, which is 5 times lower than that of the PEO coating sliding in the similar condition.

C. Martini et al. [50] have successfully fabricated a self-lubricating duplex coating on Ti6Al4V alloy by PEO treatment combined with spraying PTFE process. The PTFE topcoat deposited by spraying a solvent-based aerosol suspension proves to be beneficial in terms of both friction

and wear resistance, particularly in an intermediate (30-50N) load range. The friction coefficient of duplex coating reduced from 0.8-1 to 0.2-0.3, which is attributed to the anti-friction properties of PTFE.

3.2.3. CVD/PVD to form top films

Chemical vapour deposition (CVD) and physical vapour deposition (PVD) techniques are well known to deposit hard coatings such as TiN, CrN and DLC etc., for providing surfaces with enhanced tribological properties in terms of low friction coefficient and high wear resistance. In recent years, attempts have been made to introduce CVD or PVD coatings on components of machines and engines. However, in practice TiN-, CrN- or DLC-coatings on alloys of light metals formed by various CVD/PVD methods often exhibit limited tribological performance due to the elastic and plastic deformation of the substrates under mechanical loadings, which can result in eventual coating failure, since the coatings are usually too thin to support the heavy loads and protect the substrates in the contact conditions [51]. Deposition of thick (e.g. >10 μm) CVD/PVD coatings usually results in high compressive stresses, and thus low adhesion [52].

Employing PEO technique can deposit thick ceramic coatings which exhibit high hardness, superior wear resistance and excellent load-bearing capacity. However, these PEO coatings generally exhibit high friction coefficients which can limit the wear resistance and cause the wear damage of counterpart materials. Therefore, a multi-step preparation of duplex coatings by PEO and CVD/PVD can integrate the advantages of excellent load-bearing capacity of PEO coatings and low friction coefficient of CVD/PVD coatings. In recent years, successful applications of these methods were done by some researchers as follows.

Samir H. Awad et al. [53] studied the tribological properties of duplex Al_2O_3/TiN coatings on 2A12 Al alloys deposited by a combined plasma electrolytic oxidation (PEO) and arc ion plating (AIP) technique. The thickness of the Al_2O_3 coatings and TiN coatings were 30-40 μm and 3-5 μm, respectively. The tribological properties were evaluated by ring-on-ring tests at speeds of 0.75 and 1.25 m/s, under loads of 98, 300, 500, and 800 N, using a GCr15 bearing steel ring as rotated counterpart material. Results showed that the duplex coatings possessed very high hardness and wear resistance, and their mechanical and tribological properties were better than those of single TiN coatings, single PEO coatings and the uncoated Al alloy substrate. The Al2O3 intermediate layer played a crucial role in providing the load support essential to withstanding sliding wear at high contact loads.

X. Nie et al. [54] investigated the tribological performances of duplex Al_2O_3/DLC coatings on Al alloy fabricated by a combined PEO and PI^3 (plasma immersion ion implantation) technique. The alumina ceramic coatings with a thickness of 50-60 μm were formed on BS Al-6082 aluminum alloy by PEO treatment and DLC coatings with 2-5 μm thickness were deposited on top of the PEO coatings. All the duplex alumina/DLC coatings exhibited a hardness of over 2000 HK_{10g}. The tribological properties of Al alloy, alumina coating on Al alloy, DLC coating on Al alloy and duplex alumina/DLC coatings on Al alloy were evaluated by pin-on-disc tribological tests, under a 10 N normal load, 0.1 m/s sliding speed and 50% RH, using SAE 52100 bearing steel (BS) or WC-Co (WC) balls as counterpart materials. Both the untreated Al

alloy substrate and the PEO alumina coating gave a high friction coefficient of above 0.7 against both counterpart materials. Both the alumina and alumina/DLC duplex coatings exhibited excellent wear resistance, registering the wear rates in a low range of 1.4-1.9×10^{-6} mm^3/Nm siding against WC-Co. Only the alumina/DLC duplex coatings provided a low and stable friction coefficient in a low range of 0.1-0.22. Whereas the single DLC coating on Al alloy failed quickly only at 25 m sliding distance due to its low load bearing capacity.

The tribological properties of duplex PEO/DLC coatings on Mg alloy formed by a combined plasma electrolytic oxidation and filtered cathode arc deposition technique were investigated by Jun Liang et al. [55]. The DLC film deposited on PEO coating was not uniform due to surface roughness of interface. The friction and wear properties of the uncoated Mg alloy, the polished PEO coating, single DLC film on Mg alloy and the duplex PEO/DLC coating were evaluated on a reciprocating ball-on-disk UMT-2MT tribometer, under a load of 2 N, with a sliding speed of 0.1 m/s and sliding amplitude of 5 mm, using Si_3N_4 ball as counterpart material. For the uncoated Mg alloy substrate, the friction coefficient varied in the range of 0.2-0.4 accompanied by severe oscillation. Severe wear and seizing were observed. Even for the DLC deposited Mg alloy substrate, the tribological behavior did not improve significantly. The DLC film failed quickly at around 350 s after starting the sliding test, due to the low load-bearing capacity of soft substrates. The polished PEO coatings showed a very high friction coefficient of around 0.7-0.8. But the deposition of DLC film on PEO coatings improved the dry friction behaviors significantly. The friction coefficient of the duplex PEO/DLC coating remained steady and less than 0.2, independently of the nonuniformity of coating surface.

E. Arslan et al. [56] studied the tribological performances of duplex titania/DLC coatings deposited on Ti6Al4V alloy using combined PEO and CFUBMS (closed field unbalanced magnetron sputtering). The thickness of PEO coating and DLC coating were about 10 μm and 6 μm respectively. The tribological properties were evaluated by a pin-on-disk tribometer (Teer-POD2), under a load of 2 N, at a speed of 100 rpm, a relative humidity of 45% and room temperature, using Al_2O_3 balls as counterpart materials. For the PEO coatings, the friction coefficient was considerably high, approximately above 0.45, and fluctuated, and the wear tracks were quite broad and rough with debris. For the single DLC coatings, the friction coefficient increased abruptly after 420 seconds due to severe failure caused by their low load bearing capacity. While for the duplex PEO/DLC coatings, the friction coefficients were much more stable, and approximately at 0.1. These results indicated that the duplex PEO/DLC coatings exhibited better tribological behaviors than the PEO and DLC coatings deposited on lightweight metals substrate.

3.3. Composite coatings for improving the tribological behavior of PEO coatings

The duplex coatings fabricated by the aforementioned methods can sharply decrease the friction coefficient and wear rate. However, these coatings are generally comprised of two layers: an inner PEO ceramic layer and an outside solid lubricant layer. When the outside layer is worn through, the tribological properties will be back to its original level. M. Aliofkhazraei et al. have successfully fabricated TiO_2/Al_2O_3 [57] and TiO_2/Si_3N_4 [58-59] nanocomposite coatings by PEO treatment on pure titanium. The PEO processes were carried out in the

electrolyte of sodium-silicate (15 g/L), sodium-phosphate (2 g/L) and potassium hydroxide, adding Al_2O_3 or Si_3N_4 fine nanopowder. It was found that due to the incorporation of Al_2O_3 or Si_3N_4 nanoparticles in the coatings, the wear resistance and hardness of TiO_2/Al_2O_3 and TiO_2/Si_3N_4 nanocomposite coatings both increased significantly. However, the friction coefficients were still high or even higher, which could easily cause the wear damage of counterpart materials.

Recently, an alternative approach to obtain PEO coatings with low friction property was to introduce low friction materials into the coating by modifying the electrolytes with the solid lubricants additives. In this approach, solid lubricant particles, such as graphite, PTFE, MoS_2, WS_2 etc. are added into the electrolyte and dispersed with mechanical stirring to form a suspension. During the PEO process, solid lubricant particles can move from the electrolyte to the surface of the specimen, and be adsorbed on the surface, then be embedded into the ceramic coating.

It is important for this approach that solid lubricant particles should be sufficiently and uniformly dispersed in the electrolyte. So sufficient and constant mechanical stirring is inevitable. What's more, if necessary, a dispersant (such as acetone, ethanol etc.) is used to wet and disperse the solid lubricant particles. A kind of anionic surfactant (e.g. Sodium dodecyl sulfonate, etc.) is also used as additive to help the solid lubricant particles to be negatively charged and be suspended in the electrolyte. But the quantity of added dispersant and surfactant should be controlled and optimized. Too much additive can greatly affect the original properties of electrolyte and the whole coating process, resulting in low qualities of the coatings, such as nonuniformity, high roughness, poor adhesion to the substrate, less thickness, more inclination to breakdown and burn out, etc. However, lower concentration of additive can't wet and disperse the solid lubricant particles in the electrolyte sufficiently. So the specific and accurate quantity of additives should be decided by different coating processes.

It is generally considered that the embedding of solid lubricant particles into the ceramic coating matrix depends on concentration diffusion and electrophoretic deposition. The embedding of particles may be recognized by the adsorption of particles on the surface of the specimen, so higher concentration can help to enhance the adsorption rate, thus lead to more particles embedded into the ceramic coating. To be negatively charged are beneficial to the electrophoresis of particles in the electrolyte, thus resulting in more particles incorporated into the ceramic coatings. On the other side, the concentration of solid lubricant particles in the electrolyte and the quantity of solid lubricant particles incorporated into the coating should also be controlled and optimized. Too higher concentration of particles in the solution may greatly affect the original properties of electrolyte, causing poor qualities of the coatings. Too much solid lubricant particles incorporated into ceramic coatings may cause the destruction of the original coating structure and less ceramic component which plays the role as wear-resistant substrate, resulting in poorer qualities and lower wear resistance of the coatings.

It is also considered that the embedding of nanoparticles into the PEO coatings depends on current density, frequency, duty cycle and coating time. M. Aliofkhazraei et al. [58-59] investigated the effects of concentration, current density, frequency, duty cycle and coating

time on the embedding of Si_3N_4 nanoparticles into TiO_2 coatings. Results showed that the wear mass loss rate decreased with the increasing of relative content of Si_3N_4 in the coatings. And the relative content of Si_3N_4 in the coatings increased by increasing of concentration, frequency and coating time, while it decreased by increasing of duty cycle and current density.

Up to now, some researchers have successfully incorporated solid lubricant particles (such as graphite, PTFE, MoS_2, etc.) into the PEO ceramic coatings formed on Al, Mg and Ti alloys. In the friction and wear process, the ceramic oxide coating plays the role as wear-resistant substrate while solid lubricant particles act as friction reducing agent during the sliding. Compared with the single PEO coatings, the yielded self-lubricating composite coatings can sharply decrease the friction coefficient and wear loss during the long-term sliding. Furthermore, the wear damage of counterpart materials can also be reduced greatly due to lower friction coefficient.

Xiaohong Wu et al. [60] have successfully incorporated graphite into Al_2O_3 ceramic coating fabricated on 2024Al alloy by PEO technique in a graphite-dispersed sodium aluminate electrolyte. The thickness of the composite coating produced was in the range 22±1 μm. Ball-on-disk tribological tests showed that the self-lubricating composite coating formed in the electrolyte containing 4g/L graphite exhibited a lowest friction coefficient of 0.09, under a normal load of 1 N, with a sliding time of 8 min and linear sliding speed of 0.08m/s, using a ball of Si_3N_4 as counterpart material.

Ming Mu et al. [61] have also successfully incorporated graphite into TiO_2 ceramic coating fabricated on Ti6Al4V alloy by PEO technique in a graphite-dispersed phosphate electrolyte. The tribological evaluation was carried out on a ball-on-flat UMT-2MT tribometer, under a constant normal load of 2N, with a frequency of 5 Hz, an oscillating amplitude of 5 mm and a sliding time of 30 min, using AISI52100 steel balls as counterpart materials. And the results of friction and wear tests showed that the friction coefficient of the PEO coating reduced from nearly 0.8 to about 0.15 and the wear resistance improved significantly under dry sliding conditions, due to the presence of the graphite particles in the coating. The specific wear rate of PEO/graphite composite coating decreased significantly, which registered to be around 8.6×10^{-6} mm^3/Nm, compared with that of the uncoated alloy and pure PEO coating, which registered to be 5.2×10^{-5} mm^3/Nm and 1.7×10^{-5} mm^3/Nm respectively. The worn surface of uncoated alloy showed typical features of abrasive and adhesive wear, which resulted in high wear rate. For the pure PEO coating, the main forms of wear damage were suggested to be abrasive wear and detachment of the TiO_2 coating which made its friction coefficient and wear rate high. While for the PEO/graphite composite coating, the worn surface appeared quite smooth and showed no evidence of appreciable detachment of the coating. It was deduced that the graphite particles in the coating could be exposed to the wear track and then smeared on the contact surfaces which acted as solid lubricants in dry sliding wear condition, making the friction coefficient low throughout the sliding test. And consequently, the abrasive wear and detachment of the coating was effectively reduced.

Jie Guo et al. [62] tried to introduce PTFE nanoparticles suspension into the electrolyte to fabricated a PTFE-containing multifunctional PEO composite coating on AM60B Mg alloy. The samples were fabricated by PEO treatment in the electrolyte containing Na_3PO_4 (10.0 g/L),

KOH (1.0 g/L), with the addition of 3 vol.% PTFE nanoparticles suspension (10 wt%). In the PTFE-dispersed suspension, a nonionic surfactant (octylphenol polyoxyethylene ether, with the addition of 1-2 vol.%) and an anionic surfactant (sodium dodecyl sulfonate, with the addition of 2-4 vol.%) were used for PTFE nanoparticles dispersion and surface charge adjustment. Results showed that such PTFE-containing composite coating exhibited superior corrosion resistance, excellent self-lubricating property and better hydrophobic property when compared with pure PEO coatings. The PTFE-containing PEO coating exhibited a low and stable friction coefficient of less than 0.2 and low wear rate.

Recently, Ming Mu et al. [63] have once again successfully incorporated MoS_2 into TiO_2 ceramic coating fabricated on Ti6Al4V alloy by PEO technique in MoS_2-dispersed phosphate electrolyte. The electrolyte was prepared using Na_3PO_4 (20.0 g/L), KOH (2.0 g/L) in distilled water, with addition of MoS_2 particles (20.0 g/L), ethanol (100 ml/L) and an additive (0.5 g/L). Results showed that the TiO_2/MoS_2 composite coating exhibited improved tribological properties compared with the TiO_2 coating under dry sliding condition, which reduced the friction coefficient from 0.8 to about 0.12 and decreased the wear rate from 1.7×10^{-5} mm^3/Nm to 5.5×10^{-6} mm^3/Nm. It also should be noted that the TiO_2/MoS_2 composite coating showed better tribological property than the PEO/graphite composite coating under the same conditions.

From above studies, it is clear that the approach to prepare self-lubricating composite coating was much more effective than the duplex approaches in practice, for the PEO coatings contained low friction materials could be obtained by only one step. Besides, the coatings were expected to integrate the advantages of wear resistance of the PEO coating and low friction property of solid lubricants.

4. Concluding remarks

Plasma electrolytic oxidation (PEO) is a relatively novel technique that can be used to form metallurgically bonded ceramic coatings on some valve metals [13], such as Ti, Mg, Al, Nb, Zr and Ta etc. PEO process is now widely used to improve the surface performances of nonferrous metals by virtue of its high effectiveness, more convenience, economic efficiency and environmental performance. Moreover, the PEO ceramic oxide coatings deposited on light metals and their alloys generally exhibit superior wear resistance, large thickness, high microhardness and good adhesion to substrates. Therefore, in many tribological applications, employing PEO treatment to deposit ceramic coatings on surface of light metals can greatly improve the wear resistance, decrease the wear rate, enhance the wear life and reduce the wear damage of workpieces, thus resulting in good economic efficiency. However, it is necessary to realize the following conclusions about the tribological properties of PEO coatings.

Firstly, the thickness of the coatings plays a crucial role to possess a better wear resistance. For at high stress levels, the deformation of the substrate under loading/sliding can cause the cracking and flaking-off of the thin coatings, and thus result in severe failure. So higher thickness of PEO coating can provide a better load bearing capacity and thus possess superior wear resistance and enhanced wear life.

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Secondly, the components of the PEO coating also greatly affect the friction and wear performances of the coating. It is found that the relative content of α-Al_2O_3 phase in PEO coatings on Al alloy, Mg_2SiO_4 phase in PEO coatings on Mg alloy and rutile phase in PEO coatings on Ti alloy plays a crucial role in presenting higher wear resistance of PEO coatings.

Thirdly, as the PEO ceramic coatings generally consist of a porous outer layer and a compact inner layer, in many tribological applications, the PEO coatings are polished with abrasive papers to remove the porous outer layer and get a higher hardness and a lower roughness. It is found that the polished PEO coatings generally exhibit improved friction and wear behaviors than the original PEO coatings and the untreated alloy substrates.

And last but not least, although the wear resistance has significantly enhanced, the PEO coatings deposited on the alloy substrates generally exhibit high brittleness and high friction coefficient which have seriously restricted their extensive applications. For the ceramic coatings are hard to bear heavy impingement and mechanical deformation due to their high brittleness. Furthermore, the high friction coefficient of ceramic coatings can easily cause the wear damage of counterpart materials. Therefore, overcoming the challenges of improving the toughness and reducing the friction coefficient of PEO ceramic coatings is of great significance which can bring about broad application prospect in tribology.

In recent years, many researchers have done a lot of work to reduce the friction coefficient of PEO ceramic coatings. The successful methods include employing liquid lubricants, introducing post treatment such as spraying, vacuum impregnation, PVD and CVD to form a self-lubricating duplex coating and one-step preparation of self-lubricating composite coating. However, none of the methods is so perfect in applications.

Employing liquid lubricants can decrease the friction coefficient of PEO coatings and consequently reduce the wear damage of counterpart materials. The wear resistance and wear life of the PEO coatings can also be enhanced in liquid lubricated conditions, ascribed to the anti-wear ceramic coatings and friction-reducing liquid lubricants. However, employing liquid lubricants may contaminate the workpieces, especially in precise instruments. Furthermore, in rigid and severe working conditions, such as high vacuum, high temperature, chemical and radioactive environments, liquid lubricants often do not function.

The duplex coatings produced by multi-step preparations can not only decrease the friction coefficient and wear rate sharply, but also avoid the shortcomings of liquid lubricants. However, these coatings are generally comprised of two layers: an inner PEO ceramic layer and an outer solid lubricant layer. When the outer layer is worn through, the tribological properties will be back to its original level. Moreover, the coating processes are too complicated and generally employ high temperature which may degrade the coatings and/or substrates.

As for the composite coatings, the solid lubricant micro- and nanoparticles are embedded in the ceramic coatings and play a role as friction-reducing agent during the whole sliding time before complete removal of the coatings. The coating process is simple and convenient, but according to recent studies, the thicknesses of yielded composite coatings are only in the range of 13-23 μm, which are far less than that of the original PEO coatings. As a result, the load

bearing capacity and wear life of the composite coatings will be limited due to the low coating thickness.

Therefore, a high quality coating is still worth investigating, which has a lower friction coefficient and wear rate, a longer wear life, good mechanical properties and with a simple, cheap, effective fabricating method. More improvements should be done for the PEO technique which is of great significance in different tribological applications.

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