技術論文

Friction Reduction Effect Through Alternative Lubricants on Aluminum Alloy Coated via Plasma Electrolytic Oxidation

プラズマ電解酸化処理したアルミニウム合金に対する代替潤滑油の摩擦低減効果

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要　　旨

昨今ますます関心が高まる環境保護の観点から，油圧機器においても技術革新が要求されている．材料技術において，有害物質による環境汚染対策には作動油を生分解性や無毒性を有する環境対応型作動油（EALs）へ代替する事，CO_2排出削減対策には鉄鋼系材料から軽量材料への転換が考えられる．ところが，鉄鋼に対する潤滑油は長年研究されてきているが，軽量化が期待できるアルミニウム合金に対する研究事例は圧倒的に少ない．例えば，プラズマ電解酸化（PEO）処理をアルミニウム合金に施すと飛躍的に耐摩耗性が向上するが，PEOとEALsの相互作用に関した系統的評価はなされていない．以上のようなEALおよびアルミ摺動部材の組み合わせを使用した油圧機器の開発が予想されることから，これらのトライボロジー特性を把握しておくことは意義のあることである．

本報では，EALs（代表的な摩耗防止剤を混合したポリアルキレングリコール（PAG）やTMPエステル）潤滑下における，PEO処理されたアルミニウム合金の摩擦摩耗特性について述べる．PEOに対するEALsの潤滑性は，ポリアルファオレフィンに最も広く使われる摩耗防止剤ZnDTPを添加した混合油より優れた結果が得られた．

Abstract

From the view point of the environmental protection, technical innovation for our hydraulic component is required as well. Focusing on material techniques, environmentally acceptable lubricants (EALs) and light weight material would be applied for new design hydraulics, in order to protect the environment against oil spill or leakage and to reduce CO_2 emissions. Many researchers have been studying lubricants on steel for many decades, however the lubrication research on light weight materials (e.g., aluminium alloy) is very limited. For example, novel surface treatments using plasma electrolytic oxidation (PEO) technique significantly improves wear resistance of aluminium alloys, however systematic study on the interaction of EALs lubricating aluminium alloy coated by PEO remained so far limited. Since a hydraulic system using PEO and EAL is expected, it is essential to investigate the tribological properties of such material combination.

In this paper, the friction and wear properties of an aluminium alloy coated by PEO under lubricating with EALs (polyalkylene glycol (PAG) or TMP-ester additivated with common anti-wear additive) are reported. The lubricity of the EALs on the PEO was better than polyalphaolefin with ZnDTP.

1 INTRODUCTION

Hydraulic fluids/lubricants are an element of mechanical parts and they are composed of base oil and various additives. The lubricating mechanisms have been studied for many decades mainly for frequent materials used in industries such as steel and cast iron. A well-known anti-wear additive is zinc dialkyldithiophosphate, which most effectively prevent wear of sliding parts[1]. Recently, due to the environmental issues, functional additives with low aquatic toxicities are required for environmentally acceptable lubricants (EALs) in order to develop new lubricant technologies[2)3)] with equivalent performance. In the aim of promoting and distinguishing EALs from "classic" lubricants, environmental labels are used (Fig. 1). In order to meet the environmental criteria, esters are commonly used as base oils, which are ready (ultimate) biodegradable and less toxic to aquatic species. Polyalkylene glycols (PAGs) are also used in specific applications and meet the eco-tox criteria. The functional and environmental profile of PAGs can be individually tailored through the backbone of the base oil molecule[4].

Fig. 1 Environmental labels

In mechanical parts, various materials are used like steel, aluminium alloys, titanium alloys, polymers and their composite materials, and so on. Except for steel, aluminium alloys are most commonly used light-weight material, which possesses excellent mechanical and physical properties for machine parts. However, aluminium alloys are soft and limited due to the poor wear resistance. When aluminium alloy is requested as sliding material, anodic oxidation processes can be applied. For further high wear resistance, the novel plasma electrolytic oxidation (PEO) represents an additional option. The PEO can increase surface hardness of aluminium alloys up to HV2000[5] by forming a dense and thin nano-crystalline alumina-type ceramic film. In general, alumina is chemically stable against most liquids, whereas it might specifically interact with polar molecules of lubricating oils due to its ionic bonding[6].

The aim of the present study was to investigate influence of EALs on aluminium based alloys to identify candidates for high loaded sliding parts under boundary lubricating condition. In this paper, the effect of formulated oils with typical anti-wear additives on tribological properties of PEO film on A6061 alloy will be discussed.

2 EXPERIMENTAL

2. 1 Lubricants

A polyalphaolefin (PAO), a polyalkylene glycol (PAG) and a trimethylolpropane ester (TMP) were used as base oils for test formulations used in this study. The same ISO viscosity grade (ISO VG46) was selected for all base oils.

Esters and polyglycols contain molecular oxygen. TMP has three ester bonds (-COO- in triesters), which are located mainly in the center of the molecule. In contrast, polyglycols have an "ether" link (C-O-C), e.g., an oxygen polarity, in each monomer of the whole backbone. Consequently, it is likely that the polarities of the ionic bonds of the alumina will interact with the polarities of the oxygenates in the backbones of the esters and polyglycols.

In order to investigate the effect of additives, a widely used anti-wear additive zinc dialkyldithiophosphate (ZnDTP) and an organic sulfur containing additive dibenzyldisulfide (DBDS) were selected and blended each by 1wt.-% into the three base oils to make 6 different

Table 1 Oil samples

Code	Base oil	+ZnDTP	+DBDS
PAO	PAO	-	-
PAG	PAG	-	-
TMP	TMP	-	-
PAO+Zn	PAO	+1wt.-%	-
PAG+Zn	PAG	+1wt.-%	-
TMP+Zn	TMP	+1wt.-%	-
PAO+S	PAO	-	+1wt.-%
PAG+S	PAG	-	+1wt.-%
TMP+S	TMP	-	+1wt.-%

additivated test formulations (Table 1).

2. 2 Plasma electrolytic oxidation coatings

A plasma electrolytic oxidation (PEO) coating was deposited on A6061-T6 by Keronite International Ltd. The thickness of the as-deposited film was approximately 45 µm. The polished disks were used for tribological tests. The surface roughness and thickness of the film after the polishing are listed in Table 2.

Table 2 Plasma electrolytic oxidation coating

Coating	Phases	Hardness [GPa]**	Thickness [µm]	Roughness Ra [µm]
PEO	α/γ-Al_2O_3* polished	6.9	32	0.30

*Characterization from XRD
** by Fischerscope at 1000 mN

2. 3 Friction and wear evaluation

A roller-on-disk oscillating tribo-test (SRV®) was made to evaluate friction and wear behavior, according to DIN 51834-4. The test condition is listed in Table 3. Specimens were ultrasonically cleaned with petroleum spirit. A roller made of bearing steel (SUJ2) was fixed with a holder, where the roller was deflected by 10° to the oscillating direction (Fig 2). Disk was made of A6061-T6 aluminium alloy coated by the PEO. Lubricant was dropped onto lower disk specimen and formed a meniscus at the edge of the roller. The normal load was controlled by electric motor. The averaged coefficient of friction (COF), maximum COF and several friction hysteresises were recorded during the test by a digital data acquisition system. After the test both upper and lower specimens were cleaned with the petroleum spirit. The wear scar on the roller was measured with an optical microscope and the disk with a profilometer.

Table 3 Test condition

Normal load [N]	50
Frequency [Hz]	50
Temperature [°C]	80
Test duration [min]	120

Fig. 2 Standard inclined roller in SRV® tribometer

3 RESULTS AND DISCUSSIONS

3. 1 Wear

Fig. 3 shows the result of wear evaluation by the standard inclined roller SRV® test in steel/PEO lubricated with the various oils.

The wear rates of SUJ2 rollers were in the order of 10^{-7}mm^3/Nm and one order of magnitude higher than that of disks due to the contact geometry. The lowest wear rate on roller was obtained for PAO+Zn. PAG base oil also showed comparatively low wear on roller. DBDS, as a sulfur carrier, tended to increase in all base oils the wear on roller.

The wear on the PEO disk was very low regardless of the lubricant type, especially extremely low wear rates of less than 10^{-8}mm^3/Nm were obtained when lubricated by TMP series.

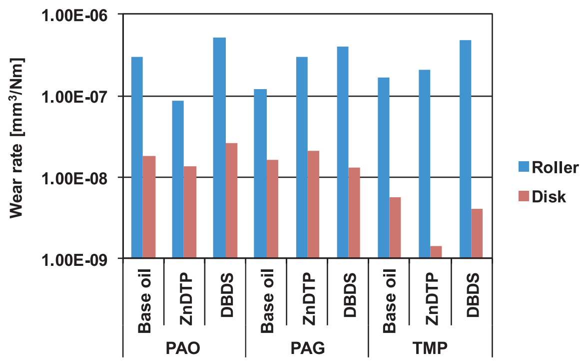
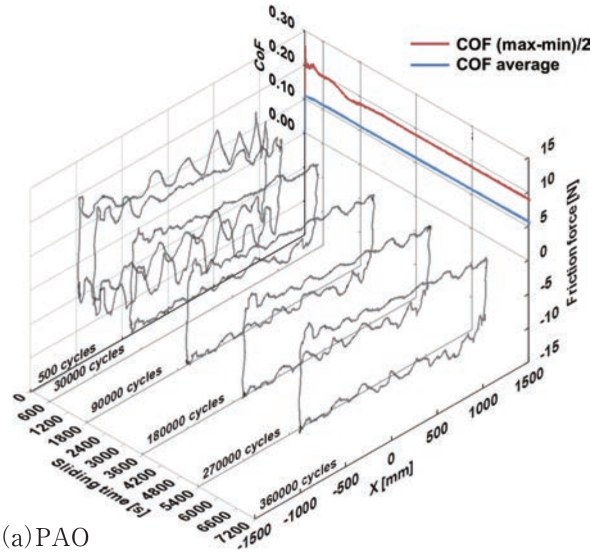


Fig. 3 Wear rate of PEO coatings

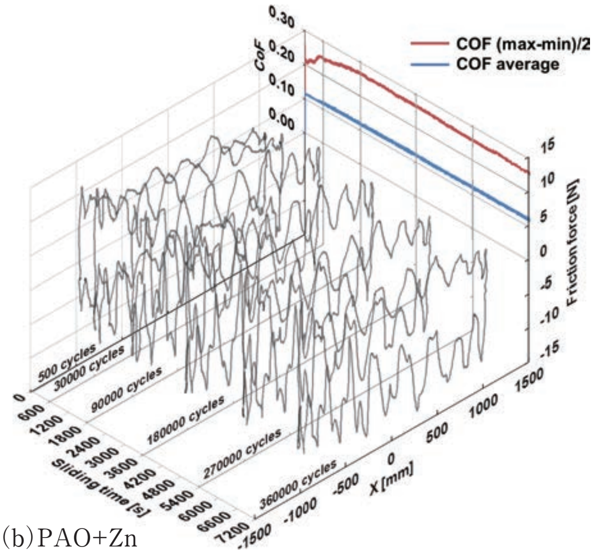
3. 2 Friction behavior

Friction behavior was much more influenced by the additives. Fig. 4 to Fig. 6 show the evolution of COF as function of stroke position (as hysteresis) over sliding time for PAO, PAG and TMP blended oils, respectively.

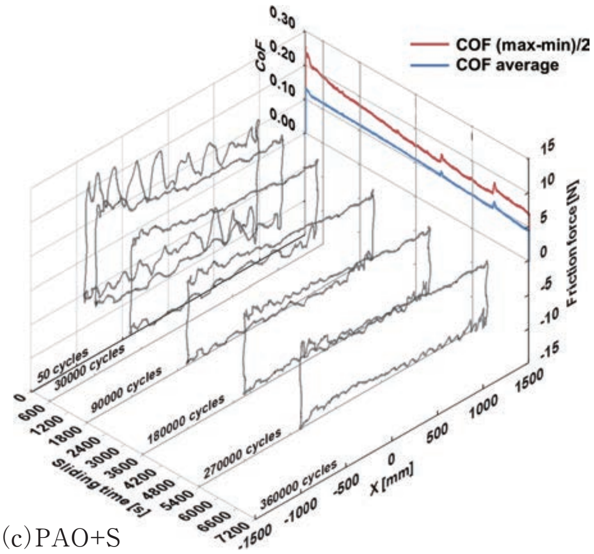
The COF of PAO base oil was initially approximately at 0.11 and slightly increased by sliding time. ZnDTP increased friction for PAO and PAG (average COF of 0.12 and fluctuated friction hysteresis), but did not influence friction



(a)PAO

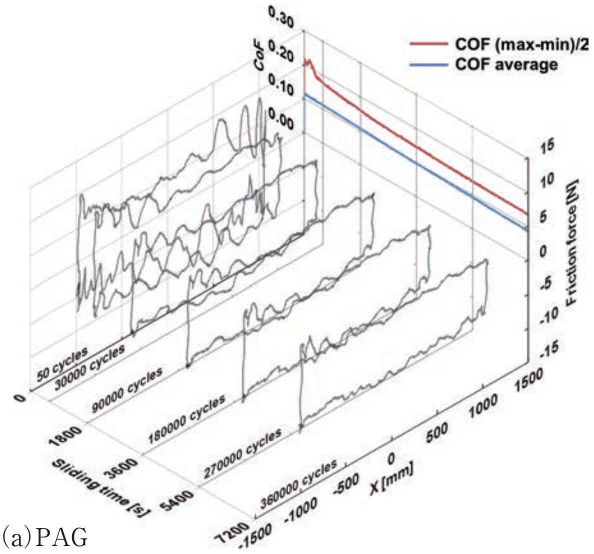


(b)PAO+Zn

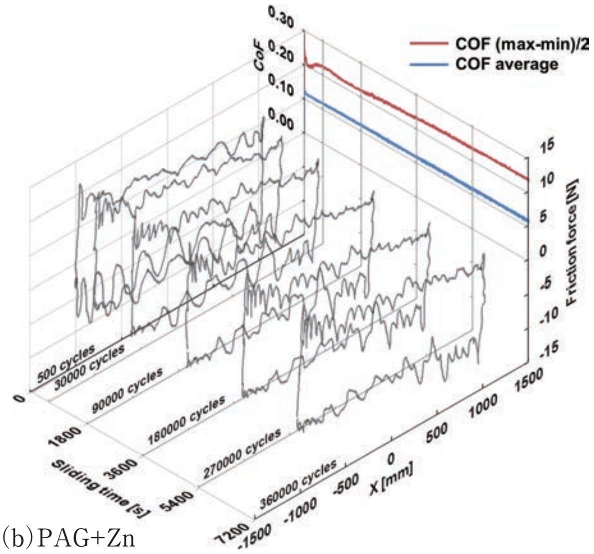


(c)PAO+S

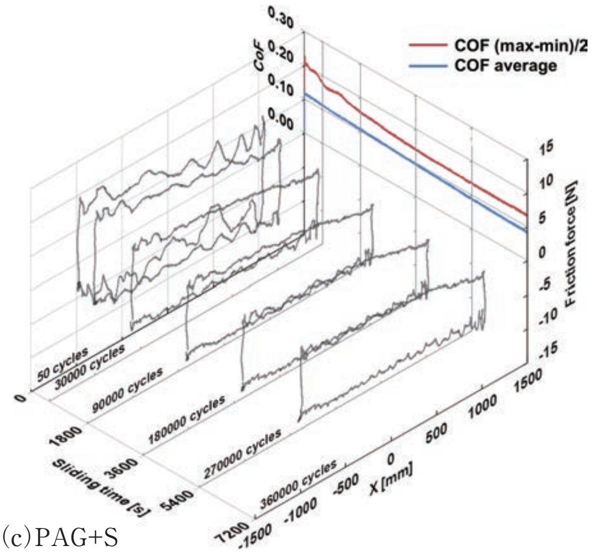
Fig. 4　Friction behavior of PAO blended oils



(a)PAG

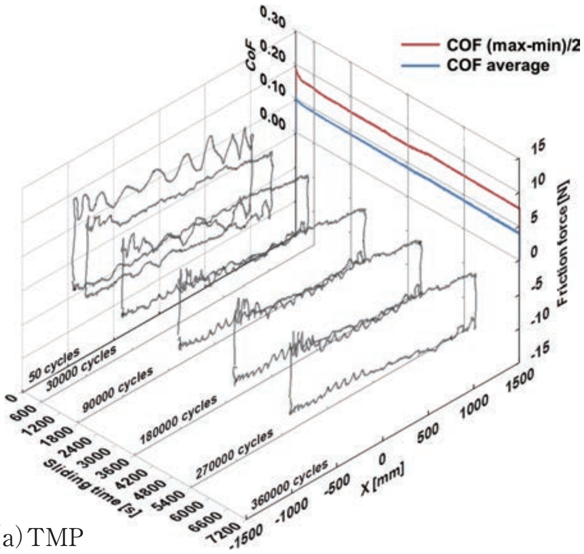


(b)PAG+Zn

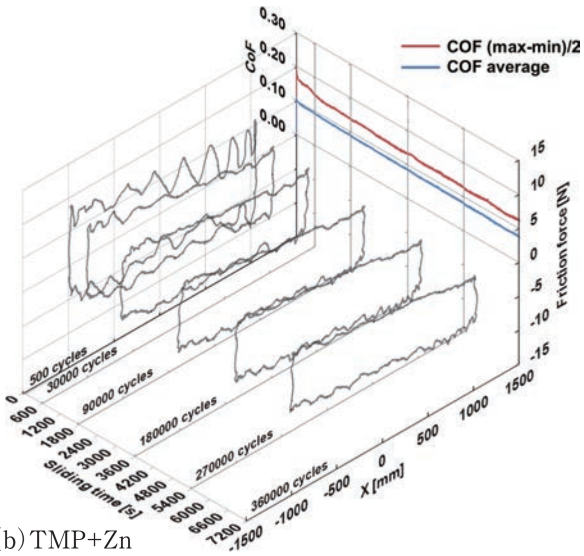


(c)PAG+S

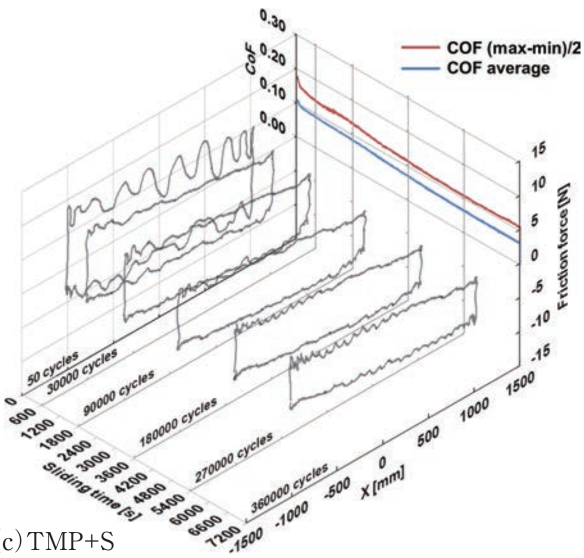
Fig. 5　Friction behavior of PAG blended oils



(a) TMP



(b) TMP+Zn



(c) TMP+S

Fig. 6 Friction behavior of TMP blended oils

in TMP. DBDS had a friction reduction effect for all base oils after rubbing for 2 hours, but initial COFs were higher than that of the base oils.

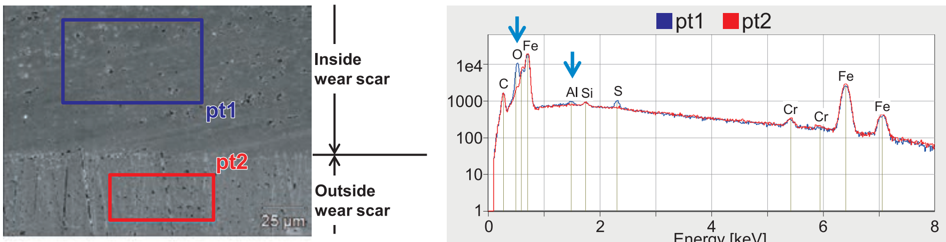
The lowest COF at test end was found with TMP+S combination. TMP+S showed 45% lower friction in comparison to PAO+Zn (reference). Furthermore, a positive effect with regard to friction behavior could also be achieved by oil formulation of PAG+S which showed 30% lower friction than the reference oil.

3.3 Tribochemistry of the blended EALs in SUJ2/PEO system

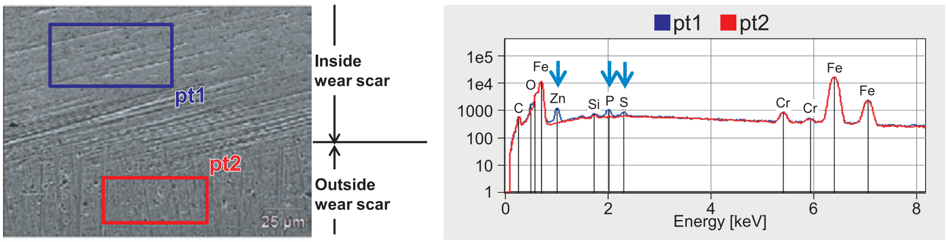
The anti-wear mechanisms of ZnDTP and DBDS have been studied by many researchers in hydrocarbon base oils, such as mineral oil and PAO for steel/steel tribosystem. Tribochemical reaction will build tribofilms composed of complex reaction products from additives and surface oxides. The tribofilm will protect the sliding surface and improve wear resistance and may reduce friction. In order to produce tribofilms, additive must initially adsorb onto the surface. When a polar base oil is used as carrier fluid, the base oil and the additive will compete with each other. Consequently, base oils with higher polarity showed different wear and friction behavior by use of steel/PEO in the present study.

Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDX) analysis on wear scar was conducted to understand the mechanism. Tribofilms from ZnDTP can be detected through zinc, phosphorus and sulfur, whereas the metal-free DBDS only through sulfur. These elements are not present either in the tribomaterials or the base oils.

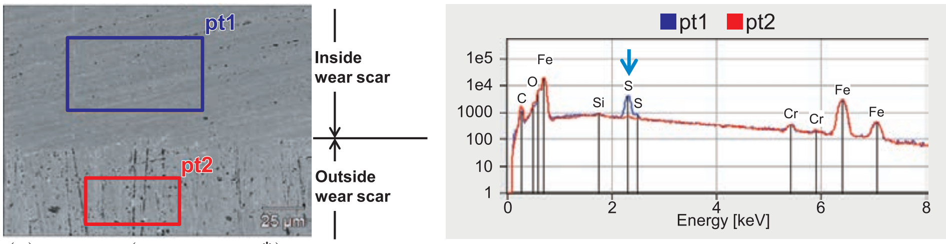
Observing the wear track of the SUJ2 roller lubricated with PAO base oil (Fig. 7 (a)), micro-damage and oxidation were detected which can be the evidence of the relative high friction and adhesive wear. This may cause seizure when more severe contact condition is applied. The addition of ZnDTP into PAO prevented such micro-damage by tribofilm formation containing Zn, P and O, whereby the friction value was at the highest level. Smooth sliding surfaces with sulfur containing film were yielded by PAO+S. Additionally, the friction was reduced.



(a)PAO(COF=0.112*)



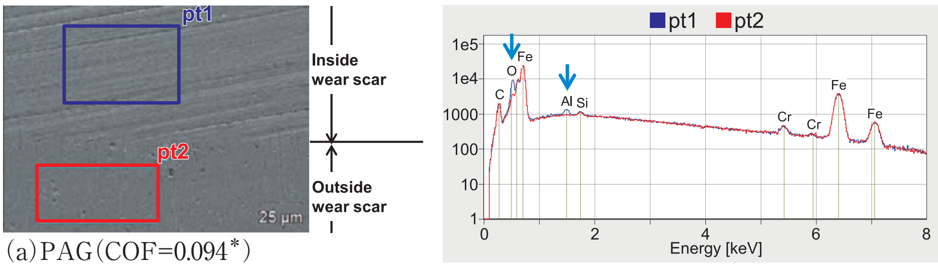
(b)PAO+Zn(COF=0.117*)



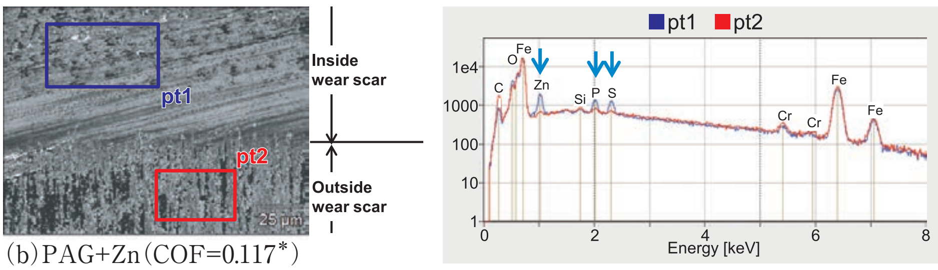
(c)PAO+S(COF=0.089*)

*The averaged COF at test end

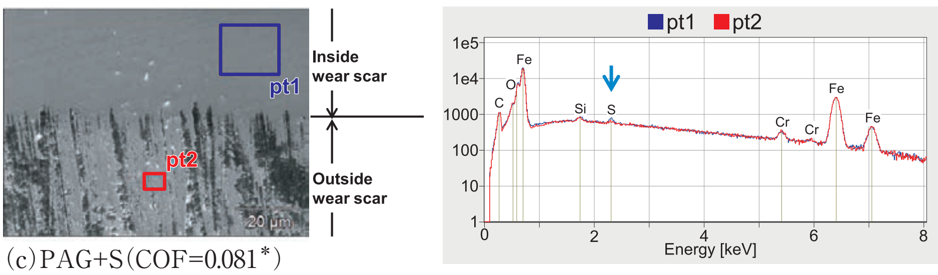
Fig. 7　SEM image and EDX spectrum on SUJ2 roller lubricated with PAO blended oils



(a)PAG(COF=0.094*)



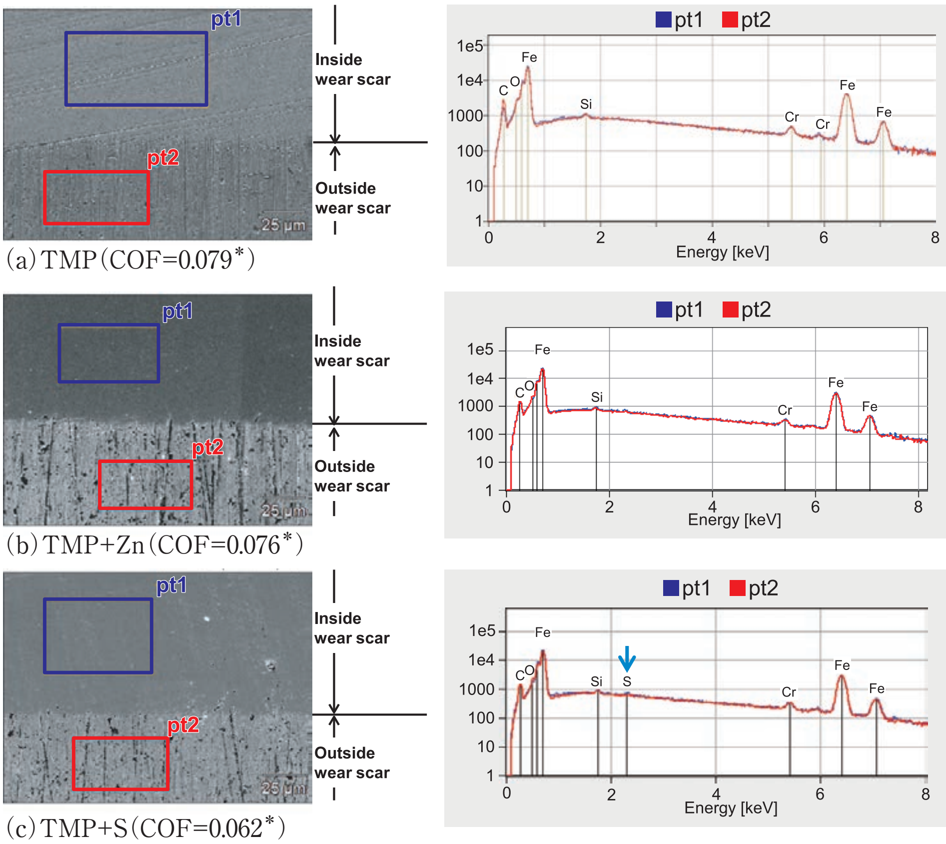
(b)PAG+Zn(COF=0.117*)



(c)PAG+S(COF=0.081*)

*The averaged COF at test end

Fig. 8　SEM image and EDX spectrum on SUJ2 roller lubricated with PAG blended oils



(a) TMP (COF=0.079*)

(b) TMP+Zn (COF=0.076*)

(c) TMP+S (COF=0.062*)

*The averaged COF at test end

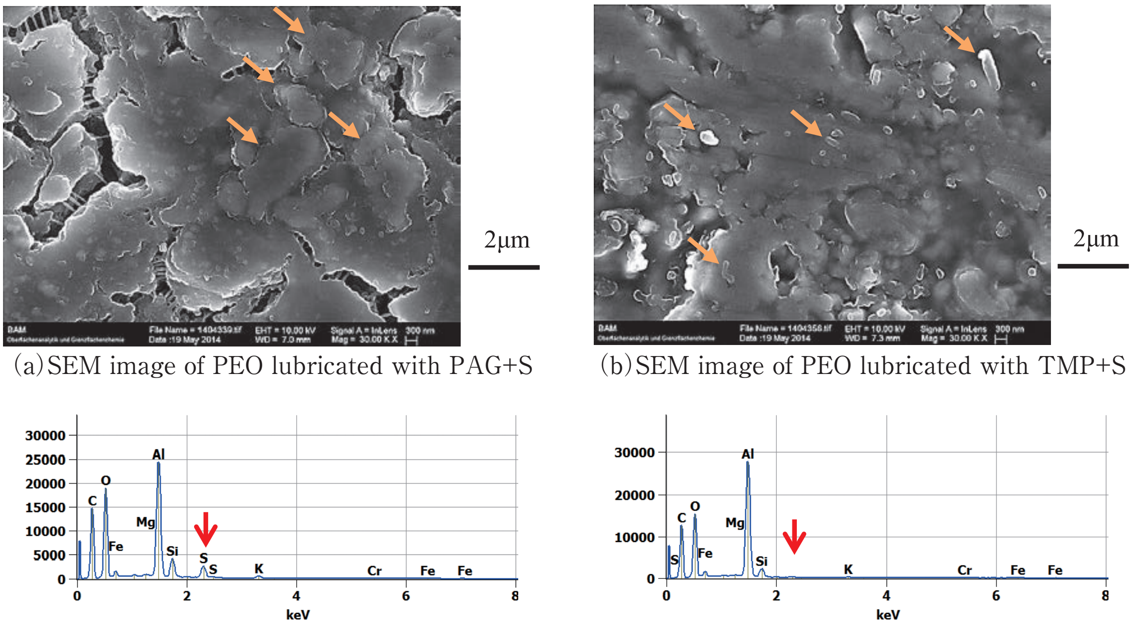
Fig. 9 SEM image and EDX spectrum on SUJ2 roller lubricated with TMP blended oils

It was expected, that due to the polarity of PAG and TMP, the PEO sliding surfaces were to protect against wear. Fig. 8 (a) shows that PAG base oil lubricated the surface better than PAO base oil, as less or no micro-damage was observed on the wear track of the SUJ2 roller. TMP ester provided much smoother sliding surface as shown in Fig. 9 (a). For this reason, PAG and TMP are also used as lubricant additives in combination with base oils offering insufficient lubricity.

Both blended PAG oils formed tribofilms, but in contrast to blended TMP less additive elements were found within the wear scar. In Fig. 8 (b) shows the EDX spectrum of PAG+Zn. Zinc, phosphorus, sulfur and slight oxygen-level were detected nearly in the same range found for PAO+Zn. For PAG+S, a small amount of sulfur was detected.

Considering Fig. 9 (b) and (c) it would appear that any tribofilm for two blended TMP was not observed by EDX analysis on the sliding surface of the SUJ2 roller. Thus, the TMP base oil probably has very strong interaction onto surface of metal and metal oxide. In terms of wear, TMP itself proper lubricated the PEO surface resulting in extremely low wear. It is known that esters can form anti-wear aluminium soap on alumina rubbing surface[7].

Fig. 10 compares FE-SEM images of the wear tracks on PEO lubricated with PAG+S and TMP+S. Sulfur and iron were detected for PAG+S, while no sulfur but only small amount of iron was detected for TMP+S. Pad-like tribofilm can be observed for PAG+S as shown in Fig. 10 (a) (recognized as relative white contrast arrowed in the image). This might be compounds containing iron and sulfur, as these elements were detected by EDX (Fig. 10 (c)). On the other hand, TMP+S did not form such a solid tribofilm, only sub-micron size particles (arrowed in Fig. 10 (b)) were observed. These particles might be the soap-like triboreaction products mainly caused by TMP base oil, containing no sulfur (Fig. 10 (d)). These films formed on rubbing surface probably reduced the friction.



(a) SEM image of PEO lubricated with PAG+S　(b) SEM image of PEO lubricated with TMP+S

(c) EDX spectra on PEO lubricated with PAG+S　(d) EDX spectra on PEO lubricated with TMP+S

Fig. 10　SEM image and EDX spectrum on wear track of PEO coating

4　CONCLUSION

In this paper, the influence on the tribological properties of PEO by EALs was investigated compared with PAO formulations[8]. The following conclusions can be drawn.

(1) On PEO sliding against steel, the base oil type significantly influenced the friction and wear behavior.

(2) PAO had the highest level of COF when either base oil or ZnDTP blended PAO was used, whereas DBDS had friction reduction effect. Hydrocarbon-base oil needs to be additivated with anti-wear additive to protect sliding surfaces.

(3) PAG base oil lubricated the steel well and also PEO comparable to PAO. Both formulations with ZnDTP and DBDS formed tribofilms. PAG+Zn showed similar high friction as PAO+Zn. DBDS reduced the friction by forming sulphur containing solid tribofilm on PEO.

(4) The best tribological performance on PEO was obtained with TMP regardless of the formulation.

(5) The different influences of the tested formulations on the tribological properties of PEO can be interpreted by chemistry of the backbone type of the base oil. The polarities of PAG and TMP strongly influenced the friction and wear in steel/PEO tribosystem, while PAO has no polar part in the molecule.

5　ACKNOWLEDGMENTS

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Abbreviations

COF(s): Coefficient of friction(s)
DBDS: Dibenzyldisulfide
EAL(s): Environmentally acceptable lubricant(s)
PAG(s): Polyalkylene glycol(s)
PAO: Polyalphaolefin
PEO: Plasma electrolytic oxidation
FE-SEM: Field Emission Scanning Electron Microscopy
EDX: Energy Dispersive X-ray Spectroscopy
SRV®: Schwingung-Reibung-Verschleiß
TMP: Trimethylolpropane-(Ester)
XRD: X-ray Diffraction
ZnDTP: Zinc dialkyldithiophosphate

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2005年入社．技術本部基盤技術研究所材料研究室．博士（工学）．主にトライボロジーに係る材料技術開発に従事．