



Surface Treatment of Aluminium Alloy for Tribological Applications

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Abstract

Among various light-weight materials, aluminium alloy is the most typical material used for products at KYB. However, common aluminium alloys are not sufficiently wear resistant. This is problematic when such alloys are used for tribological application in mechanical parts.

Anodizing is typically used for surface treatment of aluminium. Plasma electrolytic oxidation (PEO) is more wear resistant than anodizing. The first step for designing machinery is to determine the substrate material. Therefore, the influence of substrate material on PEO film is discussed first in this report. The tribological properties of PEO films deposited on three different aluminium alloys are investigated.

In mechanical parts such as hydraulic shock absorbers, it is necessary to consider hydraulic oil. Our last report (KYB Technical Review, Vol. 51) described the tribological properties of PEO film lubricated with several hydraulic oils. In this report the tribological properties of the PEO film are further discussed using a wetting parameter from the view point of surface free energy.

makes aluminium a sustainable material.

However, aluminium as substrate material is likely to wear due to its lower hardness compared to steel, often presenting problems. Wear in mechanical parts in tribological interfaces leads to performance degradation or machinery failure. When sliding parts of a pump wear for instance, leakage through the interface between the contact part may increase, resulting in lower volume efficiency. Wear debris may also cause galling or seizure, leading to not only a pump problem but also system failure.

Therefore, what should be done first in order to use aluminium alloy for tribological applications is to improve the wear resistance of the alloy. It is also necessary to properly control the wear occurring in tribological applications since it always affects the mechanical efficiency and other performances. In other words, the tribological properties of the surface of aluminium alloy are very important. This report explains various tribological technologies related to surface treatment coating on aluminium alloy.

1 Introduction

With recent increasing environmental awareness, the demand for lighter components has become even more obvious. As an example, shock absorbers for automobiles can be reduced in weight to provide possible effects:

- Improved fuel economy and higher maneuverability with a lighter vehicle body, and;
- Greater ride quality with lower unsprung mass.

Lower weight design may be implemented by making the structure smaller or replacing the materials with lighter ones for instance. Typical light-weight materials include aluminium, magnesium, titanium and other alloys, as well as carbon fiber reinforced plastics and other similar resins. In particular, aluminium alloy is the first option to be considered since it is generally superior in cost, specific strength, corrosion resistance and thermal conductivity compared to magnesium and titanium. With its relatively lower melting point, aluminium can also be easily remolten for recycling. This excellent recyclability

2 Surface Treatment of Aluminium Alloy

2.1 Anodizing

Although surface treatment of aluminium may be done by plating or chemical conversion coating, anodizing is known to be the most typical method. Anodizing has been used from long ago as a means to increase resistance to corrosion and wear of aluminium substrate materials. In particular, hard anodizing can create coating highly resistant to wear with a high hardness.

In the anodizing process, passing an electric current through an electrolytic solution of sulfuric, oxalic or chromic acid with the material to be treated, serving as the anode, will grow the aluminum oxide film over the material surface. The thickness and quality of the film depend on the current density, the concentration and temperature of the electrolytic solution, and the time of the process. The film produced by anodizing is certainly an oxide of aluminium, but does not have a specific crystal structure. It is different in structure and hardness from

crystalline aluminum oxides such as the film produced by plasma electrolytic oxidation (α , γ -alumina) described later.

The anodized film has a microscopic structure as shown in Fig. 1¹⁾. A dense oxide layer called a "barrier layer" is produced over the surface of the aluminium substrate material. On top of the layer grows a cellular oxide layer consisting of hexagonal pillars. Each cell has a micropore in its center that penetrates down to just above the barrier layer. Unlike plating, anodizing provides an oxide film that grows due to the reaction of the substrate material. The cell size is approximately 300 nm, the micropore size is 10 to 30 nm, and the barrier layer size is approx. 150 nm, although the film configuration varies by the electrolytic solution and electrolysis condition used²⁾.

As mentioned above, the anodized film has a porous structure consisting of unit cells with a micropore each. For this reason, the anodized film as it is normally provides poor resistance to corrosion. To solve the problem, sealing of anodic oxide coating is conducted to improve corrosion resistance. This process uses an electrochemical approach using water vapor, boiling water or nickel acetate to produce hydrate over the film surface, which covers the micropores. The sealing process, however, may slightly reduce wear resistance while improving corrosion resistance. It is thus needed to consider whether the sealing process should be selected or not and, if selected, discuss the process conditions, depending on the product application. Particularly for coating by hard anodizing with a focus placed on wear resistance, special consideration is needed in carrying out the sealing process.

The wear resistant anodized film may eventually cause failure originated in lower mechanical efficiency or higher friction when it is used for tribological applications, depending on the connecting part or tribological conditions. For the purpose of providing lubricity to the anodized film, an approach to composite molybdenum disulfide or fluorocarbon resin into the film is available. The composite film can thus have compatibility between wear resistance of the anodized film and lubricity. Still, the film hardness is normally around 400 to 500 HV. It cannot be said that the film is sufficiently resistant to wear compared to steel alloy.

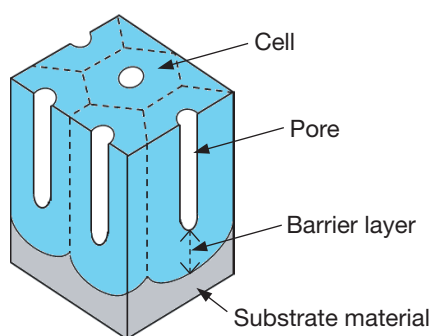


Fig. 1 Microscopic model of anodized film¹⁾

2.2 Plasma Electrolytic Oxidation (PEO)

This report focuses on PEO, with which higher film hardness can be obtained than the anodized film, in order to improve wear resistance of aluminium alloy. The principle of PEO was invented in Russia over one century ago. Development of the process has been promoted mainly in Europe since the 2000s. Recently, PEO technology has been commercialized in Japan as well. Thus PEO is a relatively new surface treatment method. Like anodizing, PEO can be applied, not only to aluminium alloy, but also to light metal. It can also be applied even to material that is difficult to be anodized.

While the oxide film produced by the aforementioned anodizing is a porous film with less crystallinity³⁾, that made by PEO has a crystalline structure mainly consisting of γ -alumina⁴⁾. The difference in processing method is that anodizing uses an oxidation reaction by normal electrolysis and PEO causes spark discharge in a process liquid with an even higher voltage to produce the oxide film. Furthermore, PEO creates a ceramic film with a dense, hard and stable structure, eliminating the sealing process needed for anodizing. Table 1 lists major differences between the two processes:

Table 1 Difference between anodizing and PEO^{3), 4)}

	Anodized film	PEO film
Electrolyte	Mainly acidic solution	Basic solution
Film composition	Amorphous alumina	Crystalline alumina (with variants depending on electrolyte)
Hardness	200 to 600 HV	Max. approx. 2000 HV
Film formation speed	Approx. 1 $\mu\text{m}/\text{min}$	Max. approx. 4 $\mu\text{m}/\text{min}$
Sealing	Necessary depending on application	Unnecessary

3 Tribological Properties of PEO Films

In consideration of using PEO films for tribological applications in mechanical parts, investigations were conducted on:

- Friction and wear characteristics of PEO films of different film thicknesses
- Wear characteristics of PEO films produced over different substrate materials

3.1 PEO Films with Different Film Thicknesses

The result of investigation on the friction and wear characteristics of PEO film samples with different film thicknesses (PEO_A, PEO_B and PEO_C films deposited on different processing times to be thinner in the order of PEO_A, PEO_B and PEO_C).

An X-ray diffraction (hereinafter "XRD") analysis revealed that PEO_B and PEO_C, which both have relatively thinner film thicknesses, mainly contain γ -alumina and PEO_A, which is the thickest, contains α -alumina (Fig. 2). A film section sample was prepared from PEO_A and subjected to a Vickers hardness test. An optical microscope image and Vickers hardness distribution of the sample are shown in Fig. 3. In the figure, the hardest point appears in the film thickness region of several μm from the top surface.

The film hardness depends on the crystalline state of alumina. The hardest alumina is α -alumina. Since only the thickest PEO_A contains α -alumina, as revealed by the XRD analysis, the alumina crystalline state in the film is inclined. γ -alumina appears in the region close to the substrate material and α -alumina, which is the hardest among the alumina crystalline components, exists in the film thickness region of 20 μm and more from the surface (α -alumina has about 2000 HV hardness according to a literature⁵⁾). Note that the Vickers hardness, which is measured by making an indentation of a depth of several μm , slightly decreases at a film thickness very close to the surface. This is probably because the thickness area is very porous.

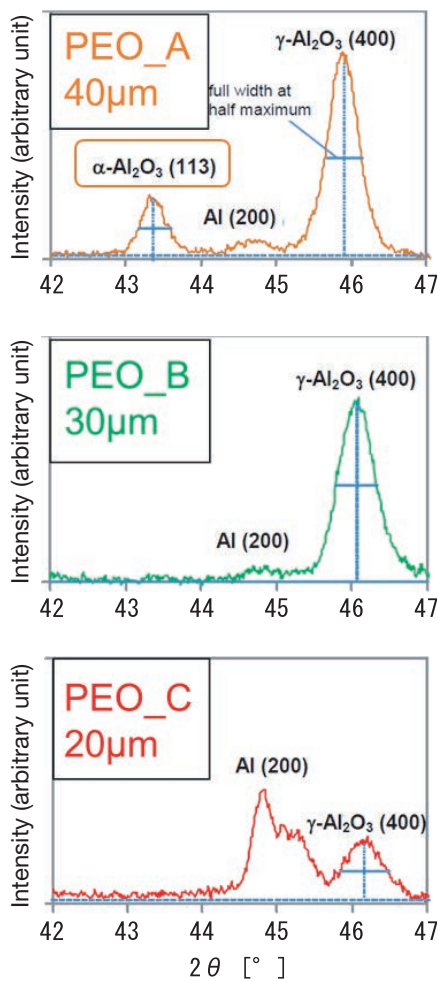


Fig. 2 XRD spectrum of PEO films with different film thicknesses

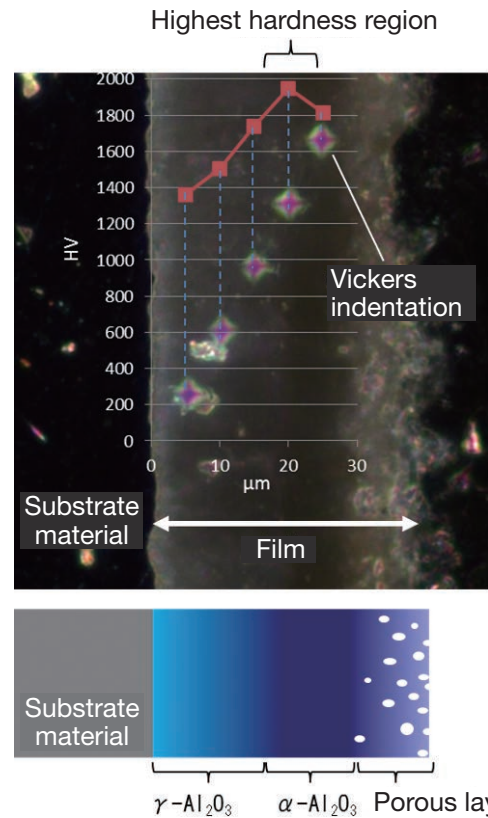


Fig. 3 PEO film section and Vickers hardness distribution

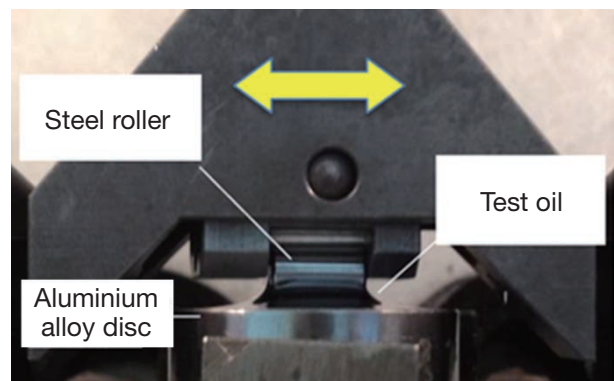


Fig. 4 Sliding test system

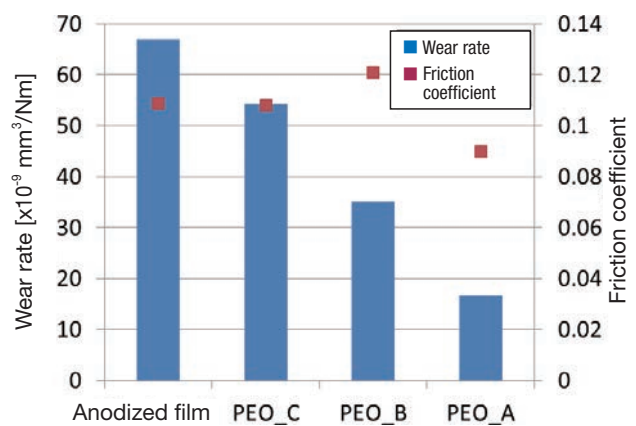


Fig. 5 Friction and wear characteristics of PEO and anodized films

The friction and wear characteristics of these PEO films were evaluated using the oscillating friction and wear testing machine (SRV tester) shown in Fig. 4. PEO samples were polished to smooth the top porous layer. A bearing steel roller was used as the counter material in such a manner that the two parts had line contact, which is similar to the tribological mode of the actual parts, rather than point contact. Polypropylene glycol (PPG) based oil was used as the lubricant, and PPG with additive was used for the anodized film that was used for comparison with the PEO films. The test was conducted under the conditions of a load of 50N, amplitude of +/-1 mm, a frequency of 50 Hz, test temperature of 80°C and sliding time of 2 hours.

Fig. 5 shows the result of friction and wear evaluation. The anodized film for comparison showed the highest wear rate in spite of the lubricant with additive being used. All the PEO films showed a lower wear rate than that of the anodized film. Moreover, PEO_A containing α -alumina particularly showed low friction and wear.

From the above, it has been verified that PEO films have different crystalline structures depending on the film thickness and the differences affect the friction and wear characteristics.

3.2 Influence of PEO films

In considering actual product design, the first step is to select a substrate material. The substrate material influences the properties of the surface treated film and, of course, the tribological properties. The following describes the results of investigation on the tribological properties of PEO processed samples deposited on three different substrate materials.

PEO_A is a sample produced on wrought aluminum alloy material. PEO_A' and PEO_A'' are samples made on cast aluminium alloy materials with different chemical compositions (Fig. 6). The microstructure of these three substrate materials indicate that there is a difference in distribution of crystallized intermetallic compounds (particles scattered over the substrate materials) among the three samples.

For PEO, the film grows as the surface layer of the substrate material is dissolved into the electrolyte, as seen in anodizing. This is the reason why the film may

have different compositions depending on the substrate material, thereby showing different mechanical and other physical properties. Particularly for castings, silicon (Si) contained in the substrate material is also distributed in the film. In Fig. 7 giving the results of component analysis by the Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDX), slightly pale blue parts distributed in the film enclosed by a yellow line represent Si. The values appearing under the sample name indicate the Vickers hardness of the film section, representing the average hardness of the film including the distributed Si phase. This suggests that PEO_A with the highest film hardness is expected to be most resistant to wear.

For the purpose of determining the wear resistance of the films over different substrate materials in particular, a friction and abrasion test was conducted. To accurately evaluate the wear, an alumina ball was used as the counter material to accelerate the wear in the SRV test. Synthetic hydrocarbon poly- α olefin base oil was used as the lubricant. The test was conducted under the conditions of a load of 20N, amplitude of +/-0.5 mm, frequency of 50 Hz, test temperature of 25 +/-2°C, and sliding time of 20 minutes.

Fig. 8 shows the wear rate of the films. Contrary to the expectations, among the films subjected to the investigation, PEO_A'', with the lowest film hardness, showed the highest resistance to wear. The sample showing the second highest wear resistance was PEO_A'. This is probably because the presence of Si in the film influenced resistance to wear. Since all the samples except PEO_A contain Si in their substrate materials, the deposited films may have a chemical composition, including Si, highly resistant to wear.

With the idea that microhardness around the contact surface influences wear resistance, nano-indentation hardness (hereinafter "nano-hardness") of the film surface was measured. With the indentation depth of the indenter during nano-hardness measurement fixed to 50 nm, the hardness in the submicroscopic contact projected area (indentation area) was determined. Fig. 9 shows the nano-hardness and the elastic modulus of the films. PEO_A'' with the lowest film hardness is distributed in the highest nano-hardness region. The result for PEO_A' is also

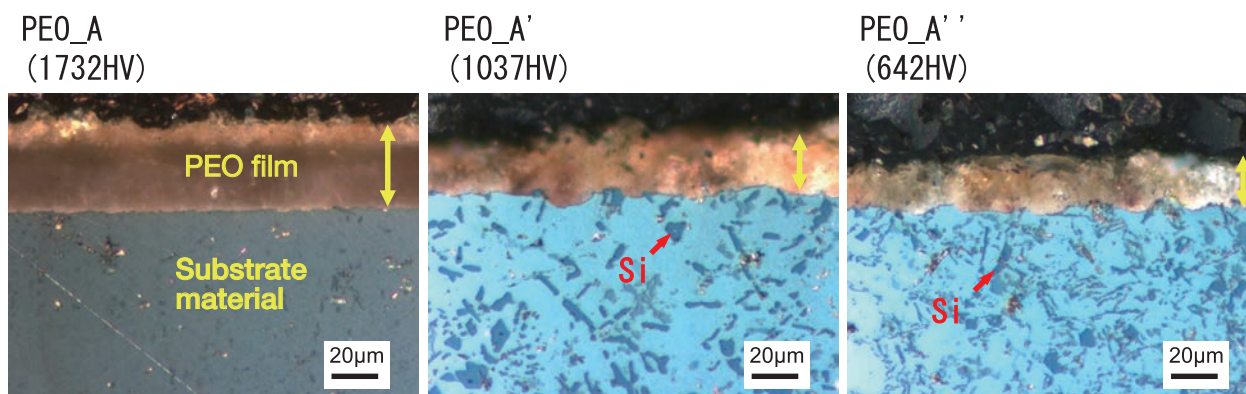


Fig. 6 Sections of PEO films deposited on different substrate materials and their Vickers hardness (HV)

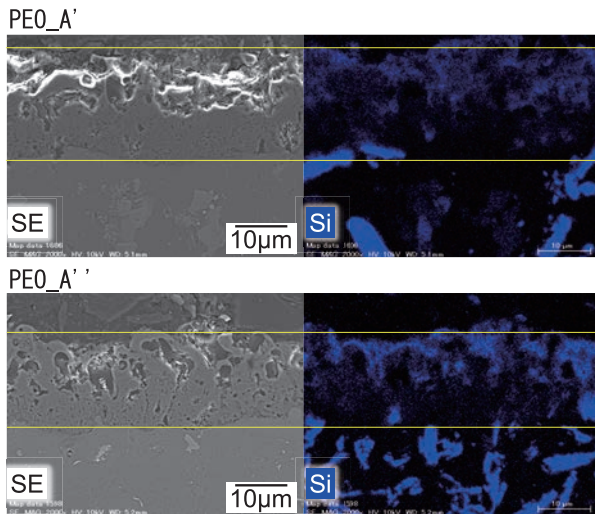


Fig. 7 SEM/EDX analysis on cross section of PEO film deposited on cast materials (left: SEM image, right: EDX mapping image)

included in the figure for reference purposes, although the measurements are not necessarily accurate since the sample is relatively porous.

The investigation above has revealed that one of the reasons why PEO_A'' showed the highest resistance to wear was the high nano-hardness of the surface. However, it is necessary to determine the reason for the high nano-hardness of PEO_A'' in further film analysis in future.

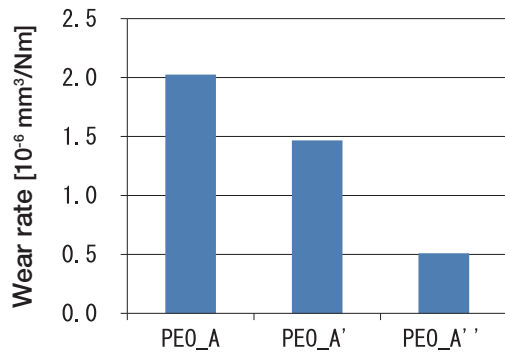


Fig. 8 Wear resistance of various PEO films

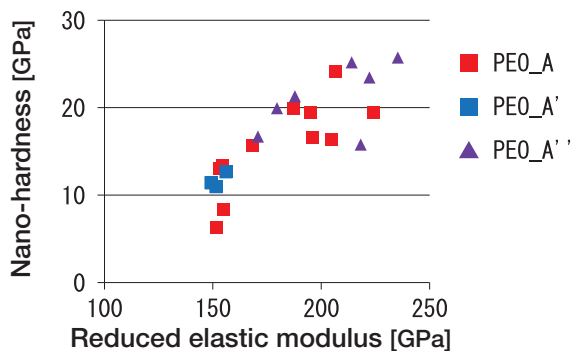


Fig. 9 Nano-hardness and Reduced elastic modulus of various PEO films

4 Lubrication Parameter for PEO Films

In relation to the effect of lubricants as mentioned in the previous section, the use of environmentally acceptable lubricants has been recently expanding. The base oil of environmentally acceptable lubricants is biodegradable ester or polyglycol, rather than mineral oil as seen in conventional lubricants. The tribological properties of lubricants depend on the type of base oil and additives. Then the influence of hydraulic oil on friction and wear characteristics of PEO film has been investigated and reported in a previous KYB Technical Review⁶⁾.

It has been revealed by numerous studies on tribology that the tribological properties of lubricants are governed by the chemical structure of their base oil. Specifically, Van der Waals forces or hydrogen bonding strength by the functional group of molecules in the base oil decides the surface contact behavior, namely wetting (the ability of a liquid to maintain contact with a solid surface). Wettability is one of the factors of the tribological properties. Surface wettability is an intrinsic property of each combination of oil and surface that is decided by their own surface free energy. In other words, there should be an interrelation between the coefficient of friction and the wetting of lubricated interacted surfaces. Wetting is expected to be one of the effective indexes in selecting and designing lubricants.

As lubricant, synthetic hydrocarbon poly- α olefin base oil (PAO), polypropylene glycol (PPG) and unsaturated fatty acid trimethylolpropane ester (TMP) were used. All these oils have a viscosity of ISO-VG46. 1 wt% dibenzyldisulfide (DBDS) was added to these base oils as an extreme-pressure agent or anti-wear additive to make a blend oil each. Another blend oil, commercially available ester oil (hereinafter "commercial oil E") was used as well. These base oils and blend oils were dropped on the PEO_A film and evaluated through an SRV test. (The same test condition as that for 3.1 was applied).

The friction coefficient at test end is shown in Table 2. For base oil comparison, the friction coefficient was higher in the order of PAO, PPG and TMP. DBDS showed an effect of reducing the friction coefficient for all the base oils. It was verified that the commercial oil E showed

Table 2 Friction coefficient of lubricants for PEO_A

Lubricant	Friction coefficient		
	Base oil	Base oil + DBDS	—
PAO	0.113	0.089	—
PPG	0.090	0.081	—
TMP	0.079	0.062	—
Commercial oil E	—	—	0.080

a lower friction coefficient than any of the PAO or PPG oils.

For wettability evaluation, a Drop Shape Analyzer DSA100 made by Krüss in Germany was used to measure the contact angle of a droplet on a solid surface. The surface free energy of a liquid or solid has a relationship with the contact angle that can be expressed in the following Young's equation:

$$\cos\theta = \frac{\sigma_s - \sigma_{sl}}{\sigma_l} \quad (1)$$

where θ is the contact angle, σ_s is the surface free energy of the solid, σ_l is the surface free energy of the liquid, and σ_{sl} is the interfacial energy of the solid and the liquid.

Now the focus has been placed on the work of adhesion W_A as a wettability parameter. The work of adhesion W_A represents work consumed by the liquid to form an interface over the solid surface. In other words, it may be recognized as necessary work to remove the liquid from the solid surface. The energy before adhesion is the sum of the surface free energy of the solid and that of the liquid ($\sigma_s + \sigma_l$). The energy after adhesion is the interfacial energy σ_{sl} by the solid-liquid interaction. Therefore, Equation (2) holds:

$$W_A = \sigma_s + \sigma_l - \sigma_{sl} \quad (2)$$

The interfacial energy σ_{sl} can be expressed in the equation:

$$\sigma_{sl} = \sigma_s + \sigma_l - 2 \left(\sqrt{\sigma_s^d \sigma_l^d} + \sqrt{\sigma_s^p \sigma_l^p} \right) \quad (3)$$

where σ_s^d indicates the surface free energy dispersion of the solid, σ_s^p the surface free energy polarity of the solid, σ_l^d the surface free energy dispersion of the liquid and σ_l^p the surface free energy polarity of the liquid. For detailed calculation of the surface tension of the liquid and of the surface free energy of the solid, published works were referred to^{7), 8)}.

The surface tension of oils (surface free energy of liquids) σ_l was determined using the pendant-drop method. The dispersion term σ_l^d and polarity term σ_l^p were determined using the sessile drop method on dimethyl polysiloxane.

The surface free energy of the solid σ_s was determined using the Owens, Wendt, Rabel and Kaelble methods. Equations (1) and (3) can be modified to obtain the equations:

$$\frac{\sigma_l (\cos\theta + 1)}{2 \sqrt{\sigma_l^d}} = \sqrt{\sigma_s^p} \frac{\sqrt{\sigma_l^p}}{\sqrt{\sigma_l^d}} + \sqrt{\sigma_s^d} \quad (4)$$

If $y = a \cdot x + b$

$$x = \frac{\sqrt{\sigma_l^p}}{\sqrt{\sigma_l^d}}, \quad y = \frac{\sigma_l (\cos\theta + 1)}{2 \sqrt{\sigma_l^d}}$$

$$a = \sqrt{\sigma_s^p}, \quad b = \sqrt{\sigma_s^d}$$

Using three or more types of reference liquid with a known surface tension, the contact angle was measured to plot the measurements using the linear equation $y = a \cdot x + b$. $\sqrt{\sigma_s^p}$ and $\sqrt{\sigma_s^d}$ can be determined as slope a and intercept b . Therefore, the solid surface free energy polarity and dispersion terms can be determined according to $\sigma_s^p = a^2$ and $\sigma_s^d = b^2$ respectively.

The resultant surface free energy of the PEO film (PEO_A) and lubricants are shown in Table 3. These values were used to calculate W_A using Equations (1) and (2). Results are shown in Table 4.

Table 3 Surface free energy (at 80°C)

Solid	σ_s	σ_s^d	σ_s^p
PEO_A	40.65	38.08	2.57
Lubricant	σ_l	σ_l^d	σ_l^p
PAO base oil	23.47	17.45	6.02
PAO + DBDS	24.26	20.48	3.78
PPG base oil	25.28	17.70	7.58
PPG + DBDS	25.43	19.23	6.20
TMP base oil	27.32	20.54	6.78
TMP + DBDS	27.30	22.51	4.79
Commercial oil E	25.87	21.09	4.78

Table 4 Work of adhesion of lubricants and PEO films

Lubricant	W_A		
	Base oil	Base oil + DBDS	—
PAO	59.42	62.09	—
PPG	60.75	62.10	—
TMP	64.28	65.57	—
Commercial oil E	—	—	63.69

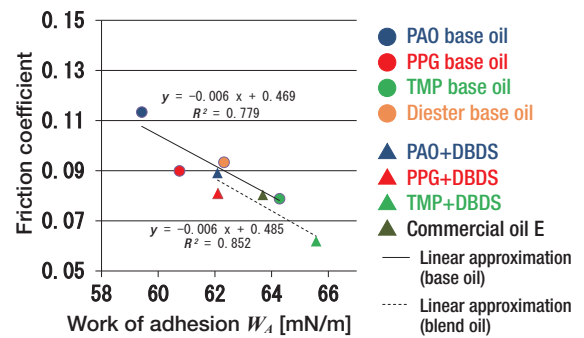


Fig. 10 Correlation between work of adhesion and coefficient of friction of lubricants for PEO_A

Fig. 10 plots the correlation between the friction coefficient and work of adhesion W_A . With the focus placed on the base oils only, the figure indicates that the higher the work of adhesion W_A is, the lower the friction coefficient is. (Another type of base oil (diester) has been added to increase reliability). On the other hand, the base oils with DBDS additives have a tendency of showing higher W_A and lower friction coefficient.

Although it is still necessary to continue verification using more types of solids and liquids in future, the work of adhesion W_A , which is one of the wetting parameters derived from the surface free energy, is correlated with the friction coefficient and can be used as an effective measure in selecting lubricants for a solid surface.

5 Concluding Remarks

This report has introduced plasma electrolytic oxidation (PEO) as one of the possible breakthrough measures for applying aluminium alloy to tribological applications of mechanical parts. This Technology Explanation mainly covers tribological technologies related to surface treatment of aluminium alloy. KYB is committed to continuously addressing product application, contributing to implementation of lighter KYB products with higher added values.

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References

- 1) Keller, F., M.S. Hunter, and D.L. Robinson: Structural features of oxide coatings on aluminum, *Journal of the Electrochemical Society* Vol. 100 Issue. 9, pp. 411-419, (1953).
- 2) Japan Aluminium Association: *Aluminium Handbook*, 8th edition (2017).
- 3) The Japan Institute of Light Metals: *New Edition, Aluminium Technology Handbook* (1996).
- 4) Yerokhin, A.L., et al.: Oxide ceramic coatings on aluminium alloys produced by a pulsed bipolar plasma electrolytic oxidation process, *Surface and Coatings Technology* 199. 2, pp. 150-157, (2005).
- 5) Taylor, E. Wilfred: Correlation of the Mohs's scale of hardness with the Vickers's hardness numbers, *Mineralogical Magazine* 28. 206, pp. 718-721, (1949).
- 6) NAKASE Takuya: Friction Reduction Effect Through Alternative Lubricants on Aluminium Alloy Coated via Plasma Electrolytic Oxidation, *KYB Technical Review No.51* (Oct. 2015).
- 7) D.K. Owens, and R.C. Wendt.: Estimation of the surface free energy of polymers, *Journal of applied polymer science* 13. 8, pp. 1741-1747, (1969).
- 8) D.H. Kaelble: Dispersion-Polar Surface Tension Properties of Organic Solids, *The Journal of Adhesion* 2. 2, pp. 66-81, (1970).