

## EFFECTS OF ELECTROLYTE AND TI LAYERS ON STATIC AND DYNAMIC FRICTION OF ANODIZED ALUMINA

*T.Matijošius\**, *M.Gedvilas\*\**, *P.Gečys\*\**, *D.Vozgirdaitė\*\*\**, *S.Asadauskas\*<sup>1</sup>*

\* Tribology Laboratory, Center for Physical Sciences and Technology, Vilnius, Lithuania

\*\* Dept. of Laser Technologies, Center for Physical Sciences and Technology, Vilnius, Lithuania

\*\*\* Faculty of Chemistry and Geosciences, Vilnius University, Lithuania

**Abstract:** Static friction is important for many non-lubricated surfaces, especially when friction is intermittent. Coefficients of Friction (COF) were evaluated on industrial aluminum alloys 1050 and 6082, which were freshly anodized in sulfuric/oxalic or phosphoric acid electrolytes to 60  $\mu\text{m}$  coating thickness. Hard anodizing significantly reduced COF. Under 10 N load friction trends were nearly identical despite sliding velocity variation from 0.02 to 0.5 cm/s, while 1 N load led to higher static COF. Magnetron sputtering was used to deposit Ti layers. Static COF went down from over 0.4 to  $\sim$ 0.2 in 16 nm and 75 nm thick layers, while that of 2.3  $\mu\text{m}$  had no positive effect. Dynamic COF was also similarly reduced, suggesting possible industrial applications.

**Keywords:** Anodized alumina, Dynamic friction, Static friction, Ti sputtering.

### 1. INTRODUCTION

Alumina ( $\text{Al}_2\text{O}_3$ ) offers good mechanical, electrical and thermal properties leading to a wide range of applications. Anodization (electrochemical oxidation) is often used to produce hard porous alumina coatings of 1  $\mu\text{m}$  to 100  $\mu\text{m}$  or even higher thickness [1]. Improved hardness, anti-corrosion, paintability and other properties encourage the application of anodized alumina in aviation, electronics, automotive, food, marine industries and even in medicine. Hard anodizing (“Type III”) carried out in sulfuric acid-based electrolytes typically leads to thick  $\text{Al}_2\text{O}_3$  coatings with nanopore diameters less than 20 nm, whereas phosphoric acid-based electrolytes may produce coatings with large pore diameters exceeding 100 nm or more [2]. Despite better hardness, friction and wear rate of anodized  $\text{Al}_2\text{O}_3$  coatings is still very high, often above Coefficient of Friction (COF) of 1.0 [3]. Metal and polymer-based solid lubricants are sometimes used to reduce friction. However, the most popular lubricant is based on polytetrafluoroethylene (PTFE), capable of reducing COF to 0.2 or less [3] by forming a barrier layer.

Dry friction can be subdivided into static friction between initially stagnant surfaces and dynamic friction between continuously moving surfaces. Static friction is an important parameter of non-lubricated coatings, especially in industrial field where surfaces might undergo intermittent movements. Such regime is frequently encountered in traditional tribology segments, such as transport or industrial applications as well as high-tech areas, e.g. robotics (casings, frame, etc.), medical (dental braces, crowns, etc.), industrial (i.e. fasteners, railings) and many other areas. If static COF is greater than dynamic COF, it represents a barrier against slippage. This difference depends both upon the chemistry and the morphology of surfaces. The mechanical properties of material, surface roughness, mutual dissolution of materials, contact time, presence of the extraneous bodies in the contact zone might also influence static friction.

Recent study showed that nanothin Ti layers can significantly reduce dynamic COF on anodized alumina [4]. It remains unclear whether this effect extends into static COF. When Ti is coated using magnetron sputtering, three main layers are formed:  $\text{TiO}$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$  [5].  $\text{TiO}_2$  in anatase form is

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<sup>1</sup> Author for contacts: S. Asadauskas  
E-mail: asadauskas@chi.lt

stable, non-toxic, chemically inert, biocompatible and effective tribologically on implants, aerospace items and turbine engines. Anti-frictional Ti based layers increased wear resistance and reduced dynamic COF down to 0.15 under dry friction conditions [6]. Static friction tests might help in understanding the reasons of such effectiveness of nanothin Ti layers.

When static friction is considered, usually surface topography and morphology becomes more important than in case of dynamic friction. Anodized aluminum surfaces have been thoroughly investigated, but mostly high purity aluminum was studied, whose nanopore arrays are highly uniform and symmetrical. Improvement of tribological properties of aluminum has always been important industrially [7]. Therefore, more attention has to be devoted to the nanopore distribution in industrial alloys. In this study, 1050 alloy was selected due to high Al contents, while 6082 was more corrosion resistant and anodization-friendly. Their anodizing in sulfuric and oxalic acid electrolyte resulted in 50-60  $\mu\text{m}$  coatings with  $\sim 5$  nm (1050) and  $\sim 20$  nm (6082) diameter nanopores, whose morphology were thoroughly evaluated microscopically [8]. Many other electrolytes are available for anodization of industrial Al alloys. In this study phosphoric acid electrolyte was also used and COF were evaluated on anodized coatings with and without Ti layers. Non-lubricated conditions under different loads and velocities were selected mostly focusing on static friction, which is very important in many commercial applications of anodized items.

## **2. EXPERIMENTAL**

Aluminum alloy 1050 (0.25% Fe; 0.08% Si with 99.67 wt.% purity) and Al alloy 6082 (1.1% Si; 1.02% Mg; 0.61% Mn; 0.54% Fe with 96.72 wt.% purity), whose sheet thicknesses were 1 mm and 2 mm from UAB SP MET (Lithuania) and Aleris (Germany) respectively, were used as substrates. Cleaning and degreasing was performed with laboratory grade solvent, while reagent grade salts and electrolytes were used in anodizing. Titanium target of 99.995% purity (Alfa Aesar) was utilized for deposition of Ti layers in magnetron sputtering.

### **2.1. Anodization**

Anodization was performed in aqueous phosphoric or sulfuric/oxalic electrolytes to produce  $\text{Al}_2\text{O}_3$  coatings from 10 to 60  $\mu\text{m}$  in thickness. Beforehand 1050 and 6082 Al discs were etched in an alkaline solution, cleaned in 30%  $\text{HNO}_3$  and rinsed in deionized (DI) water then submerged into constantly stirred electrolyte. Sulfuric/oxalic electrolyte was prepared from 175 g/L sulfuric acid + 30 g/L oxalic acid dehydrate + 55.5 g/L aluminum sulfate octadecahydrate. Phosphoric acid electrolyte contained 4%  $\text{H}_3\text{PO}_4$  in DI water. Coatings were periodically checked with CM-8825FN device (Guangzhou Landtek Instruments Co.) to obtain necessary thickness. After the anodization discs were submerged into stirred DI water for 3 rinse cycles of 10–30 s duration, dried at 50  $^\circ\text{C}$  for 30 min and stored in a desiccator for no longer than 50 h before tribotesting or magnetron sputtering. Caution was exercised to avoid any contamination of the anodized surfaces from fingerprints or oily surfaces. Fatty materials are known to bind strongly to alumina hydroxides [9], which might have a significant effect on friction, static COF in particular.

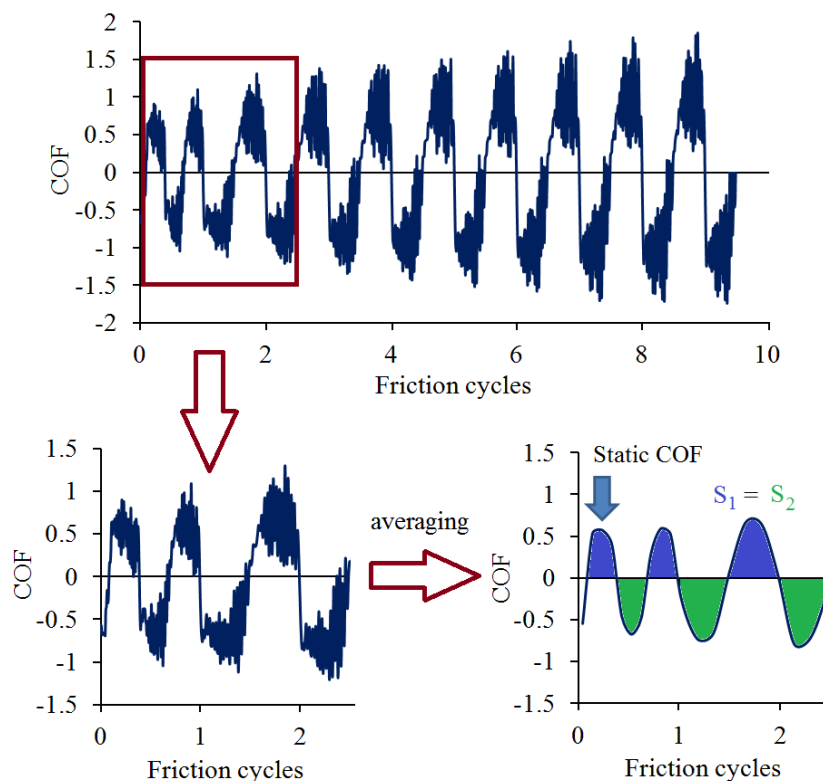
### **2.2. Magnetron sputtering**

Deposition of Ti layers of 16 nm, 75 nm and 2.3  $\mu\text{m}$  thickness was performed during a previously reported study [4]. Briefly, anodized Al specimens were processed in DC/RF magnetron sputtering device Univex 350 (Leybold Vacuum Systems). Before deposition chamber was vacuumized for 16 h to achieve 250  $\mu\text{Pa}$  base pressure. Ti layers were sputtered at 250 mPa pressure of Ar gas maintaining constant substrate temperature at 12  $^\circ\text{C}$ . Duration, current and voltage of sputtering were optimized to produce a needed thickness of Ti layers: 6 nm (15 min, 100mA, 421 V), 75 nm (30 min, 200 mA, 420 V) and 2.3  $\mu\text{m}$  (30 min, 400 mA, 375 V). A rotary holder with 6 specimens was rotating during the sputtering at 18 rpm to assure homogeneous deposition of Ti layers.

### **2.3. Tribological tests**

Pin-on-Disc Tribometer (Anton Paar TriTec SA) was used for friction tests in ball-on-plate reciprocating linear configuration with 6 mm OD corundum (99.8%  $\text{Al}_2\text{O}_3$ , grade G16, roughness Ra

0.025  $\mu\text{m}$ , hardness 2100 HV) balls (Ceratec) under 1 N or 10 N loads, 2 cm/s velocity and 8 mm cycle length [4]. At 2 cm/s velocity each friction cycle contained  $\sim 100$  data points of recorded friction force. Friction values stayed similar within most of the reciprocal motion, usually covering over 90% segment [1]. The average dynamic COF was determined by the built-in software from the central 80% segment of the path. The results were reported as COF variation with progressing number of friction cycles. Static COF was measured using 100 Hz data collection rate for improved sensitivity. COF data at such high collection rate is strongly affected by surface roughness and debris particles [10, 11]. Therefore, fluctuations of COF curve were smoothed by averaging every 15 data points to get a representative segment of initial 10 friction cycles, Fig. 1. In the segment, the line of COF=0 was established with equal aggregates of 'negative' and 'positive' areas under the peaks. Static COF was determined at the maximum of the first full friction cycle.



**Figure 1.** Scheme for determination of static COF

Two or more friction tests were performed on different specimens to ensure good reproducibility of results, selecting the most representative run for comparing different samples.

#### 2.4. Microscopy and profilometry

Scanning Electron Microscopy (SEM) images were obtained using Helios NanoLab 650 (FEI) at 50.000 $\times$  and 150.000 $\times$  magnification. Cr layers of 1.5–2 nm in thickness were applied on all specimens in order to obtain the necessary electrical conductivity on the nanoporous surface by using a magnetron sputtering device Quorum Q150T ES (Judges Scientific Plc). Calculations of nanopore diameter, density and porosity were described previously [4]. Briefly, the latter represented a % ratio of nanopore openings to remaining surface area.

Surface roughness of alumina and Ti specimens was measured by contact profilometer SurfTest SJ-210. Visualization was obtained with Image Plus software using 2  $\mu\text{m}$  diamond tip needle

#### 2.5. Statistical analysis

Statistical analysis of tribological, surface roughness and nanopore measurements is presented as mean  $\pm$  standard deviation. In tribological experiments static COF were evaluated at least from 3 measurements. Average roughness (Ra) was calculated from 20 values using 2 or more specimens.

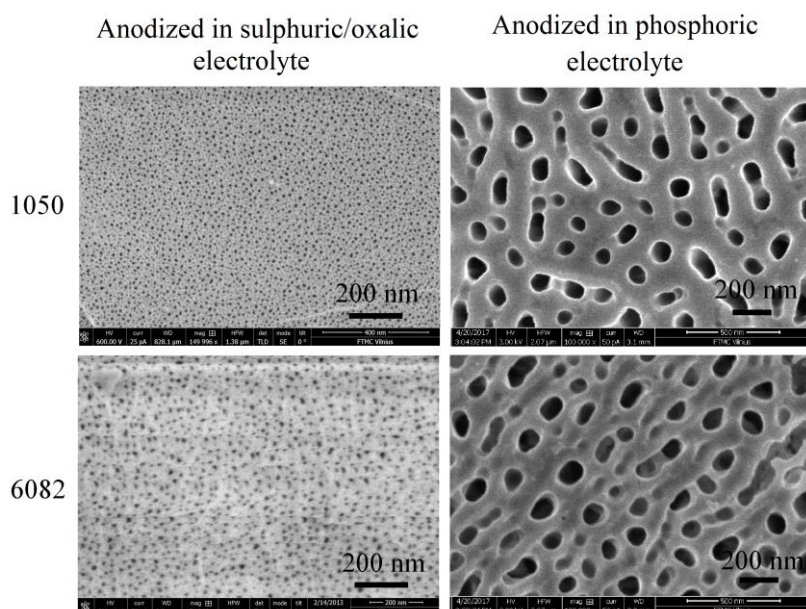
Nanopore density was calculated from 4 random areas to obtain the average, meanwhile the nanopore diameters were determined from 10 measurements.

### 3. RESULTS AND DISCUSSION

Two Al alloys: commercially pure 1050 alloy of 99.67 wt.% and 6082 of 96.72 wt.% purities was chosen as substrates for tribological measurements. Unlike chemically pure Al (>99.99 wt.%), the alloys are more recognized industrially not only for low price, but also for their physical-mechanical properties. Both of them offer good corrosion resistance, but 1050 provides improved plasticity and formability, whereas heat treatable 6082 substrate has better mechanical resistance most likely due to Si and Mg alloying additives along with higher strength.

#### 3.1. Alumina surface characterization

In this study, Al alloy discs were anodized using a “hard anodizing” (Type III) procedure in sulfuric/oxalic electrolyte for hard coatings and phosphoric electrolyte for soft coatings forming self organized nanopore arrays. Coating thickness, surface nanotopography and porosity depended very significantly on electrolyte, Fig. 2.



**Figure 2.** SEM nanotopography of Al surfaces after anodization in sulfuric/oxalic and phosphoric electrolytes.

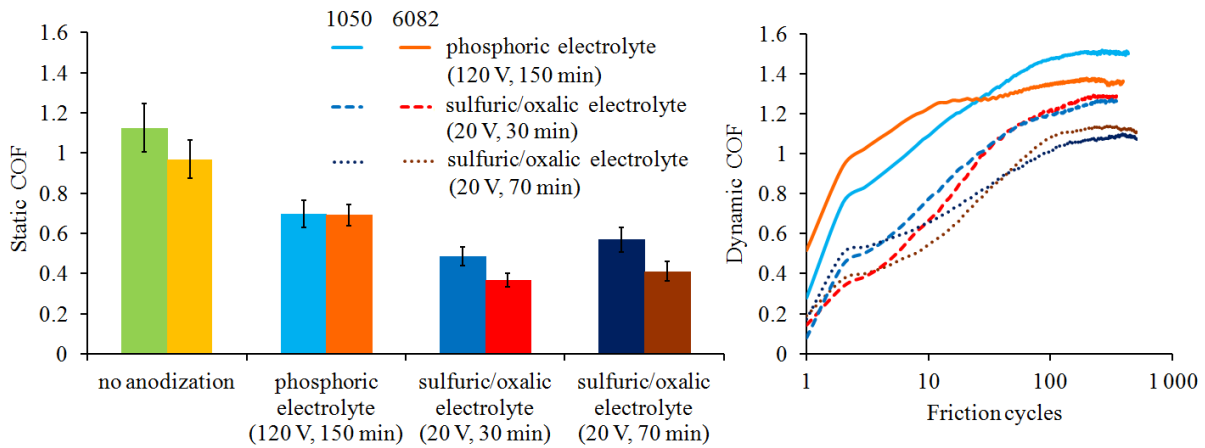
SEM data showed that nanopore diameter was at least 8 times larger after anodization in phosphoric electrolyte, despite much thinner coatings, see Table 1. Moreover, nanopores of anodized 6082 alloy were at least twice as wide as those in 1050 with four times higher porosity obtained in sulfuric/oxalic electrolyte. Higher porosity also was obtained after anodization of 6082 in phosphoric electrolyte, while nanopore diameter appeared similar to that of 1050. Variation of porosity and nanopore diameter might affect tribological tendencies, therefore, static and dynamic COF were measured on the obtained surfaces of different nanotopography.

**Table 1.** Characteristics of anodized coatings and their nanopores.

Electrolyte	Al alloy	Coating thickness, $\mu\text{m}$	Nanopore diameter, nm	Nanopore density, pores/ $\mu\text{m}^2$	Porosity, %
Sulfuric/oxalic (70 min at 20 V)	1050	$59 \pm 2$	$6.5 \pm 1.3$	$1560 \pm 110$	5.5
	6082	$56 \pm 2$	$15.0 \pm 2.2$	$1040 \pm 121$	22.5
Phosphoric (150 min at 120 V)	1050	$7 \pm 1$	$110 \pm 23$	$22 \pm 2$	26.4
	6082	$6 \pm 1$	$119 \pm 14$	$25 \pm 2$	38.5

### 3.2. Friction tendencies of anodized alumina coatings

Only freshly anodized discs were tested for better understanding of friction phenomena. Surface anodization in sulfuric/oxalic as well as in phosphoric electrolyte significantly reduced static COF, see Fig. 3. In case of sulfuric/oxalic anodization, COF went down from nearly 1.0 to about 0.4 under 1 N load. For 6082 alloy the friction reduction was particularly evident, possibly affected by alloying additives, which increase hardness and mechanical strength. Static COF did not appear to depend on anodizing duration in sulfuric/oxalic electrolyte.



**Figure 3.** Influence of anodization at 15 °C in phosphoric (150 min at 120 V) and sulfuric/oxalic (30-70 min at 20 V) electrolytes on static and dynamic friction under 1 N load (left bars – 1050, right bars – 6082)

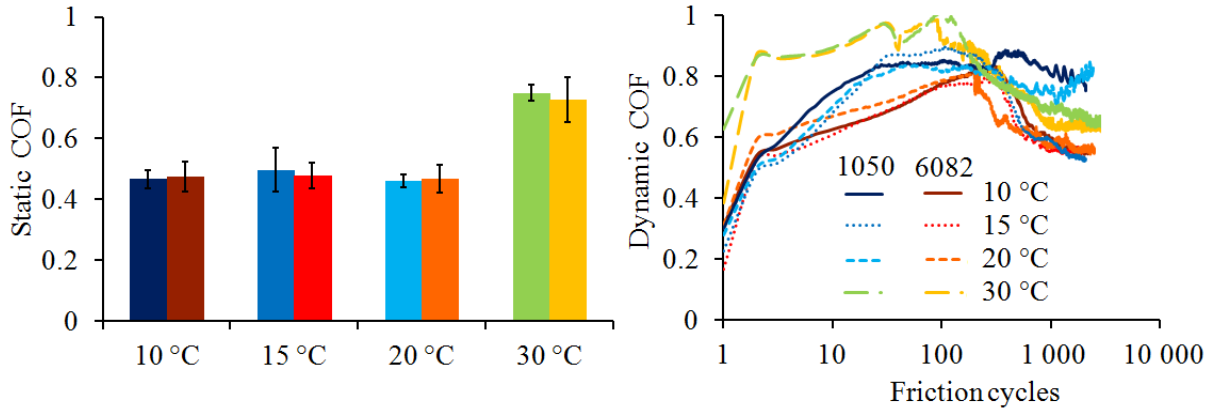
Higher surface porosity and softer coatings produced in phosphoric electrolyte resulted in static COF ~0.7, still significantly lower than COF of surfaces before anodization. Aluminum phosphates are also formed during the latter process, in contrast to sulfuric/oxalic electrolyte anodization. Therefore, it could be expected that friction reduction in coatings, anodized in phosphoric electrolyte, would be more significant, because many phosphates act as anti-wear additives in various coatings and lubricants. Nevertheless, surface porosity and other morphological properties seemed to play a more important role.

Dynamic friction of discs after sulfuric/oxalic anodization was lower than that of phosphoric, in agreement with static COF trends. The latter coating still showed lower dynamic friction than that of surfaces before anodization [4]. Consequently, anodization itself can be considered a means to reduce friction, static COF in particular. However, friction and wear of alumina coatings is still quite high in general, leading to abrasion and wear debris formation after just 100 friction cycles under 1 N load.

**Table 2.** Roughness Ra (µm) of untreated Al surfaces and coatings, anodized at 15 °C.

Al alloy	No anodization	Phosphoric (120 V, 150 min)	Sulfuric/oxalic (20 V, 30 min)	Sulfuric/oxalic (20 V, 70 min)
1050	0.99 ± 0.09	1.01 ± 0.11	0.78 ± 0.09	0.86 ± 0.09
6082	1.28 ± 0.08	1.42 ± 0.19	1.47 ± 0.06	1.49 ± 0.14

Surface roughness of untreated and anodized Al alloys was evaluated by profilometer. Studies showed that independently of electrolyte Ra varies between 0.8-1.5 µm, Table 2. Despite somewhat higher surface roughness static COF is lower in case of sulfuric/oxalic electrolyte, suggesting that COF might be more strongly influenced by other parameters and possibly chemical characteristics.



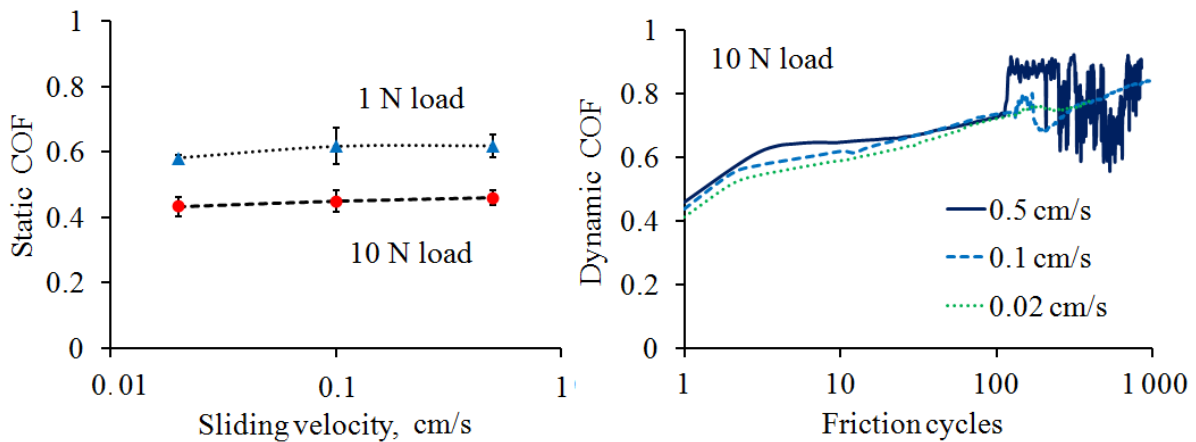
**Figure 4.** Influence of anodization temperature in sulfuric/oxalic electrolyte on static COF (left bars – 1050, right bars – 6082) and dynamic friction of anodized discs under 10 N load.

Properties of coatings and surfaces were also varied by setting different electrolyte temperatures for anodization. Changing anodization temperature from 10 °C to 30 °C did not significantly affect coating thickness, which remained about 60 μm. Surface roughness did not change very far from its values before anodization, Table 3. However, anodization at 30 °C produced coatings with much higher friction, as compared under higher load of 10 N, Fig. 4. Most likely this can be explained by the fact that coating, anodized at 30 °C, was much softer than in case of 10–20 °C. It can also be observed that under 10 N load static and dynamic COF remain quite similar between the alloys, while static friction differences under 1 N load are more pronounced. This is in agreement with the expectation that surface hardness affects friction more significantly under lower loads.

**Table 3.** Influence of anodization temperature in sulfuric/oxalic electrolyte on resulting surface roughness Ra (μm). See Table 2 for Ra values before anodization.

Al alloy	10 °C	15 °C	20 °C	30 °C
1050	0.79 ± 0.05	0.86 ± 0.09	0.63 ± 0.09	0.85 ± 0.06
6082	1.54 ± 0.08	1.49 ± 0.14	1.52 ± 0.09	1.13 ± 0.07

Influence of load and sliding velocity was analyzed as well, Fig. 5. Static COF was much lower under 10 N than under 1 N load. In addition to the surface hardness effects, this might also be related to the reduction of surface contact area. In contrast to load, sliding velocity had no influence on static or dynamic friction. However, under higher sliding velocity heat is dissipated less effectively, which might cause surface wear and abrasion to take place sooner, as evident from friction curves, Fig 5.

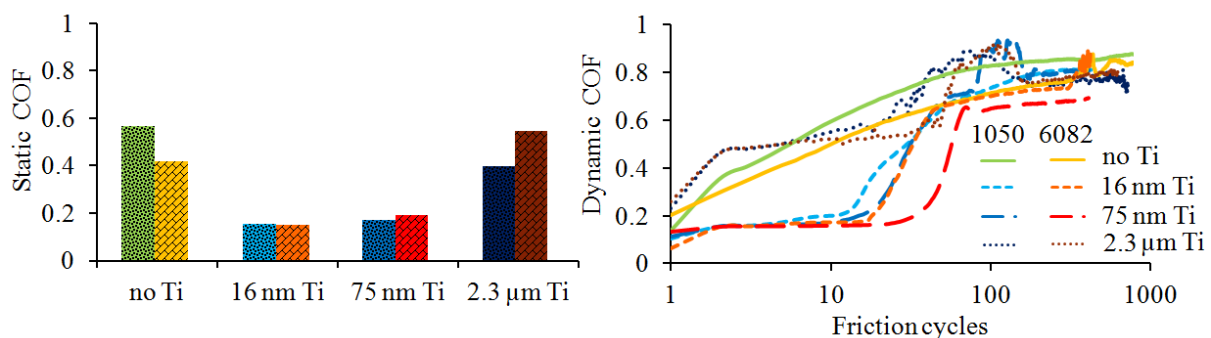


**Figure 5.** Influence of sliding velocity and load on friction of 6082 alloy after anodization in sulfuric/oxalic electrolyte (20 V, 70 min)

### 3.3. Influence of Ti layers on tribology of anodized alumina

Magnetron sputtering was employed for depositing Ti layers of 16 nm, 75 nm and 2.3  $\mu\text{m}$  on discs, anodized in sulfuric/oxalic electrolyte at 15 °C to 60  $\mu\text{m}$  thickness. Phosphoric anodization was not studied further, because obtained coatings did not seem industrially appealing due to their low thickness. Static and dynamic friction of Ti-deposited surfaces was measured under 10 N load, Fig. 6.

Results show that nanothin Ti layers (i.e. those of 16 nm and 75 nm thickness) significantly reduce static and dynamic friction, bringing COF below 0.2. Thickness of 75 nm was the most effective, maintaining quite low COF  $\sim 0.2$  for 20 cycles on 1050 alloy and 60 cycles on 6082. Surprisingly, 2.3  $\mu\text{m}$  Ti layers were much less effective with COF above 0.4. Deposition of Ti layers had only a minor effect on the surface roughness, despite some changes in Ra values: 0.8–1.1  $\mu\text{m}$  for 1050 and 1.4–1.7  $\mu\text{m}$  for 6082. Consequently, roughness cannot be related to the observed tribological effectiveness of nanothin Ti layers. Another explanation suggests that a Ti layer might transform into a quasi-fluid state [12]. Such layer might undergo material transfer within the wear track, dissipating the excess energy and assuring significantly lower friction [13, 14].



**Figure 6.** Effect of Ti layer thickness on static and dynamic friction under 10 N load after anodization in sulfuric/oxalic electrolyte (20 V, 70 min), (left bars – 1050, right bars – 6082).

More research is necessary to explain such effectiveness of nanothin Ti layers on reduction of static and dynamic friction of anodized alumina. Nevertheless, it must be noted that COF below 0.2 is highly desirable in many applications of anodized items and currently PTFE is the most popular means to achieve such friction reduction. The latter approach is often problematic, because it requires heating of the anodized coating to over 300 °C and post-processing, such as rubbing. Therefore, the effectiveness of nanothin Ti layers promises valuable means to replace PTFE coatings, leading to significant tribological improvements of existing anodized articles and very likely new applications in both high-tech areas and traditional industries

## 4. CONCLUSIONS

1. Hard anodizing in sulfuric/oxalic electrolyte may significantly reduce static and dynamic COF on industrial Al alloys. Anodization in phosphoric electrolyte provides less improvement in friction reduction, despite reputation of phosphates as anti-wear additives.
2. Anodization at higher temperatures, such as 30 °C, increases surface porosity and reduces friction resistance compared to coatings obtained by hard anodizing.
3. Nanothin Ti layers on coatings, anodized in sulfuric/oxalic electrolyte, effectively reduce static and dynamic friction down to 0.2. However, 2.3  $\mu\text{m}$  Ti layers have no positive effect on friction reduction.

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