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(54) METHOD FOR REACTIVE IMPREGNATION OF ANODIC ALUMINA COATING

(57) The aluminum anodization method is disclosed, which involves hard anodizing, drying off, impregnation with specific compounds and complete drying to obtain wear-resistant anodic alumina coatings. Impregnating compounds must react with the residual electrolyte within the nanopores of anodic coating to yield lubricious materials. The impregnating compound should have a molecular architecture of amphiphilic nature and a sufficiently small molecular size in order to penetrate into the nanopore. The molecules should also contain a functional group, capable of engaging into oxidation and/or hydrolysis reactions with the residual electrolyte. In addition, these molecules must have such alkyl chains, which would impart lubricating properties to the compounds, freshly formed by combining with the residual electrolyte within the nanopores. Molecules with phosphite, sulfide and/or ester functional groups and one, two or three alkyl chains assure the most effective interaction with the residual electrolyte and dramatically increase the wear resistance of anodic alumina coatings.

Processed by Luminess, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method of preparation of wear-resistant anodic coating on aluminum articles, such as bearings, casings, fasteners, frames, rails and similar.

BACKGROUND OF THE INVENTION

[0002] Articles made of aluminum alloys are often treated by anodizing to have their surfaces oxidized, which imparts hardness, higher corrosion resistance, better paintability and other advantages. Resultant anodic coatings contain porous, coarsely crystalline aluminum oxide, which often forms long vertical nanotubes, protruding continuously from the surface to the substrate. Capitalizing on the presence of hollow nanotubes, anodic coatings might be additionally treated after electrochemical oxidation to impregnate with dyes, then seal the nanopore openings and prevent the absorption of undesired materials from the environment. The anodic coating adheres strongly to the aluminum substrate, thus making the substrate more abrasion-resistant. However, due to the brittleness, roughness, residual internal stresses, and abundance of the nanopores, anodic coatings are not resistant to long-term mechanical stress of varying intensity, which results in premature wear and major damage to the coating.

[0003] When good wear resistance is important, a typical industrial practice involves hard anodizing (Type III) in an electrolyte, based on sulfuric acid, until a relatively thick anodic coating is produced - 10 to 100 μm or thicker. It is also important to select a suitable alloy, because not every alloy can be successfully anodized. Some of them, like those of 2000 series aluminum alloys have inclusions of various compositions, which respond to electrochemical reactions in a different manner and might severely distort the formation process of anodic coating. Others produce a distinct phase separation between the substrate and anodic coating, which makes the surface prone to cracking and crumbing. Industrially, aluminum alloys of 5000, 6000 and 7000 series are often selected for anodizing. After the anodization step sometimes a sealing step is performed. The anodic coating is immersed into a hot solution of alkali or some polymers, which leads to hydroxide buildup on the top of the nanopores. However, sealed hard anodic coating does not always provide sufficient improvement in friction and wear resistance, even at high thickness.

[0004] Therefore, the sealing stage might be replaced with the deposition of barrier lubricants on the surface of anodic coating. As one of the most effective techniques a polymeric barrier layer is formed by spraying/wiping a dispersion of fluoropolymers onto the anodized part or its portion, which needs resistance against friction and wear. Immersion into a fluoropolymer dispersion is also possible, followed by various procedures to remove excess liquid, such as dripping, shaking, blow-drying, wiping, etc. However, after treating with the fluoropolymer dispersion, the anodized parts must be heated to over 310°C. Such heating is needed for the continuous phase of the dispersion to evaporate and for the dispersed particles of fluoropolymer to congeal into a continuous layer. Concurrently, some polymer molecules can penetrate into the nanopores, but such penetration is limited, because their molecular size approaches that of the nanopore diameter. Another complication is the need to process the layer of fluoropolymer thermo-mechanically before it cools down, such as rubbing it with a cloth while hot. This might require many engineering issues to be resolved during the manufacture because manual operations might be difficult to eliminate.

[0005] Another major drawback is that extreme heat might affect the integrity of the anodized item, reducing the quality of anodic coatings because of the development of internal stresses and cracks due to thermal expansion. Energy losses might also be very significant. In addition, the appearance of the treated coating becomes glossy and usually much darker, unless the fluoropolymer dispersion contains some coloring pigments. More drawbacks of fluoropolymer coatings can become apparent in specific applications of anodized items.

[0006] Existing state-of-the-art to impart wear resistance on anodic alumina coatings mostly relies on the formation of a barrier layer on the surface. Although many inventions focus on a specific application of aluminum articles, some disclosures claim the treatment of generic anodic coatings.

[0007] US patent application No. US 10/426,788, publication No. US2003/0213698, discloses method of deposition of a polyester-PTFE mixture enriched with alumina particles on an anodic coating.

[0008] US patent No. US4,784,732, discloses a method covering electrochemical parameters for producing anodic coating, followed by the deposition of a barrier lubricant layer on the top.

[0009] US patent application No. US 10/995,527, publication No. US2005/0218004A1, discloses method of treatment of the anodic coating with nickel acetate or other Ni and Co salts, followed by the deposition of a PTFE layer. The function of the salts is to assure better adhesion between PTFE and the surface of anodic coating.

[0010] International patent application No. PCT/CN2018/097265, publication No. WO2019/128210A1, discloses a method comprising sonication of the anodic coating by immersion in a MoS_2 dispersion.

[0011] US patent application No. US10/910,767, publication No. US2005/0062317A1, discloses introduction of polymers, solid lubricants, or oils into the anodic coating.

[0012] US patent No. US3,567,597, discloses that molybdenum disulfide dispersion can be used during anodizing, i.e. may act as a component of the anodizing electrolyte.

[0013] Commonly to all disclosures related to friction reduction or wear resistance of anodic coatings, either the formation of barrier lubricant layers on the top of the coatings or the development of slippery liquid-infused porous surfaces (SLIPs) are described. The barrier layer formation is covered in detail by the patent literature, as discussed above.

[0014] Regarding SLIPs, silicones and fluoropolymers can be infused into the nanopores of 1000 series aluminum alloy, anodized in oxalic acid with subsequent etching in phosphoric acid as disclosed in Sakuraba, K. et. al. "Slippery Liquid-Infused Porous Surfaces on Aluminum for Corrosion Protection with Improved Self-Healing Ability" published in ACS Applied Materials & Interfaces, 2021, vol. 13, no. 37, pp. 45089-45096, Edition of American Chemical Society. Chen, L. et. al. "Enhancing tribological performance by anodizing micro-textured surfaces with nano-MoS2 coatings prepared on aluminum-silicon alloys" published in Tribology International, 2018, vol. 122, pp. 84-95, Edition of Elsevier, report tribological improvements of SLIPs formed by impregnating Molybdenum disulfide particles into relatively large nanopores on pure aluminum, anodized in phosphoric acid. Wu, D. et. al. "Durable lubricant-infused anodic aluminum oxide surfaces with high-aspect-ratio nanochannels" published in Chemical Engineering Journal, 2019, vol. 368, pp. 138-147, Edition of Elsevier, describe the vacuum-assisted infusion of a formulated lubricant itself into nanopores of 3003 series aluminum alloy, anodized by several techniques.

[0015] The present invention is dedicated to overcoming the above shortcomings and for producing further advantages over prior art.

SUMMARY OF THE INVENTION

[0016] The invention is a method for reactive impregnation of anodic alumina coating for making a low-wear anodized aluminum articles. Embodiments of the invention comprise four essential stages for producing wear-resistant anodic coatings.

[0017] According to the embodiments of the invention, during the initial anodization stage, an aluminum article is anodized in an acidic electrolyte to produce anodic coatings with open nanopores using conventional Type III or similar hard anodizing procedures. These procedures are well known to those skilled in the art. The obtained coating thickness is 5 - 100 μm and an internal diameter of nanopores is 5 - 50 nm. Alloys, electrolytes, and anodizing conditions (current density, temperatures, durations, etc.) are selected accordingly to achieve the declared characteristics of nanopores and capable to induce chemical reactions of impregnated compounds within the nanopores.

[0018] The blotting stage is the next step after anodizing when the fresh anodic coating is dried off. Actual blotting or wiping is optional and can be replaced by vibrating, heating, or blowing air. If the anodized surface is flat, like in laboratory specimens, simple blotting against a lint-free cloth is sufficient to achieve the needed extent of drying.

[0019] After the blotting stage the article has to be transferred to the impregnation stage without allowing its surface to dry out completely, i.e., the article is dried off so that it retains at least 10% of water by volume within the nanopores. The residual water along with the electrolyte makes it possible for the impregnated material to undergo hydrolysis and other reactions within the nanopores.

[0020] The impregnation stage covers the essential process of impregnating an anodized article with a liquid or liquefied material, which penetrates the nanopores of said anodic coating and reacts with the residual electrolyte and water. The impregnating media is liquid, therefore, if any solid compounds are employed, the temperature should be high enough to melt them. The liquid does not have to be fully homogeneous, it can constitute an emulsion or colloidal solution, or even have several liquid phases.

[0021] Drying stage involves heating and drying the impregnated anodic coating for two purposes: 1) to drive the reaction between the liquid and residual electrolyte within the nanopores and 2) to prevent nanopore sealing. Water evaporates on its own from the impregnated anodic coating.

[0022] Sequence of these stages and the parameters of the procedures are very important in producing successful wear-resistant anodic coatings.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0023] The following chapter describes specific cases of preferred embodiments of the invention which are intended as examples.

[0024] In the preferred embodiment, a low-wear coating is prepared in four stages, starting with an aluminum substrate. The substrate, surface for coating, can be pure aluminum or its cast, forged, rolled, or wrought alloy.

[0025] In the first stage, the anodization, surface for coating is prepared, type III Hard anodizing is carried out for the prepared surface and the anodized surface is rinsed with deionized water. The obtained coating thickness is from 5 to 100 μm and internal diameter of nanopores in the coating is from 5 to 50 nm.

[0026] If the anodic coating is thinner than 5 μm, the nanopores cannot provide a sufficient reservoir for the reaction with the impregnated material and residual electrolyte. If the anodic coating is thicker than 100 μm, the brittleness becomes excessive and the nanopores are too deep for the compounds, produced during the reaction to migrate into the friction zone. Nanopores of less than 5 nm might limit the penetration of impregnating compounds and chemical reactions with the residual electrolyte. On the contrary, wide nanopores from 50 nm to several hundred nanometers have insufficient mechanical resistance and load-carrying capacity leading to major surface damage and wear debris formation.

[0027] In the second stage, the blotting, the anodized surface is dried off to retain some deionized water within nanopores of obtained anodic coating. The anodic coatings retain at least 10% of original deionized water contents in nanopores before being immersed into impregnating liquid or liquefied material. Actual blotting or wiping is optional and can be replaced by vibrating, heating, or blowing air. If the anodized surface is flat, like in laboratory specimens, simple blotting against a lint-free cloth is sufficient to achieve the needed extent of drying.

[0028] In the third stage, the impregnation, the bloated anodized surface is soaked in liquid, molten or dissolved material, which contains amphiphilic compounds molecules of which are sufficiently small to penetrate the nanopore. For example, amphiphilic compounds may contain 50-100% wt. of molecules with one, two or three alkyl chains, whose chain length is from C6 to C24 with or without methyl or ethyl pendants or double bonds. Said molecules have a moiety or several such moieties, capable of oxidizing or hydrolyzing in the presence of residual acid within the nanopores of said anodic coatings.

[0029] The molecules should also contain a functional group, capable of engaging into oxidation and/or hydrolysis reactions with the residual electrolyte deionized water and electrolyte within the nanopores of obtained anodic coating. The residual water along with the electrolyte makes it possible for the impregnated material to undergo hydrolysis and other reactions within the nanopores. In addition, these molecules must have such alkyl chains, which would impart lubricating properties to the compounds, freshly formed by combining with the residual electrolyte within the nanopores. Molecules with phosphite, sulfide and/or ester functional groups and one, two or three alkyl chains assure the most effective interaction with the residual electrolyte and dramatically increase the wear resistance of anodic alumina coatings. If the coating is dried completely, the residual electrolyte will be consumed for the formation of salts, losing its effectiveness as a reagent or catalyst for oxidation and hydrolysis reactions. If the anodic coating is too wet, the penetration of the reactive compounds into the nanopores will be slower and the bath with impregnating materials will be contaminated excessively. The impregnation stage covers the essential process of impregnating the anodized article with a liquid or liquefied material, which penetrates the nanopores of said anodic coating and reacts with the residual electrolyte and water. The impregnating media is liquid, therefore, if any solid compounds are employed, the temperature should be high enough to melt them. The liquid does not have to be fully homogeneous, it can constitute an emulsion or colloidal solution, or even have several liquid phases. Solid particles, even if nanosized, are not likely to contribute to the reactions within nanopores. Most nanoparticles would be too large to migrate into the nanopores, but even if they are smaller than the internal diameter of the nanopore, they would still agglomerate and block the passage into the inner part of the nanopore.

[0030] Nevertheless, presence of nanoparticles in the impregnation solution is beneficial to wear resistance. The nanoparticles can adhere to the surface of anodic coatings and then participate in the subsequent processes in the friction zone. Impregnation of the anodic coatings with nanoparticle dispersions might lead to appreciable wear resistance. The continuous phase of such dispersion can still penetrate the nanopores and induce reactions with the residual electrolyte.

[0031] In the fourth stage, the drying, the impregnated anodic coating is completely dried to complete the reactions with the residual deionized water and electrolyte. Complete drying the impregnated anodic coating drive reaction between the impregnation material in liquid form and residual electrolyte within the nanopores and to prevent nanopore sealing. The compounds within the open nanopores are free to migrate into the friction zone thus reducing wear of the anodized aluminum surface.

[0032] If the impregnated article is stored under humid conditions, the excessive humidity is likely to result in hydroxide formation on the top of the nanopores. The hydroxides may seal the openings and it will become difficult for the compounds within nanopores to migrate into the friction zone.

[0033] As an example, preparation of an aluminum surface comprises etching the aluminum surface in an alkaline solution for example solution of 30 g/L NaOH + 25 g/L Na_3PO_4 + 75 g/L Na_2CO_3 for 45 s at 60 °C. After rinsing in deionized (onwards - DI) water the aluminum surface is cleaned for 1-2 min in 30% HNOs and rinsed in DI water again. Then the surface is fixed, for example into a titanium holder, and immersed into a continuously mixed H_2SO_4/oxalic a. electrolyte (175 g/L H_2SO_4 + 30 g/L $(COOH)_2 \cdot 2\ H_2O$ + 55.5 g/L $Al_2(SO_4)_3 \cdot 18\ H_2O$) for 70 min at 2 A/dm^2 anodic current density. For optimal anodization conditions, current density of 1.6 - 2.4 A/dm^2, electrolyte temperature of 14-16°C and duration of 67 to 73 min is retained. After anodization, the coating is preferably 60 ± 10 μm thick. The anodized surface is immersed into an ultrasonic bath and sonicated in DI water without heat for rinsing.

[0034] Afterward in the blotting stage the anodized surface is soaked off from excess water droplets and dried off to retain some moisture in nanopores before the impregnation stage, i.e., the article is dried off so that it retains at least

10% of water by volume within the nanopores.

[0035] In a particular embodiment of the invention, sheet of aluminum alloy 6082 of 96.72% wt., where contents of the alloy are 1.10 wt.% Si, 1.02 wt.% Mg, 0.61 wt.% Mn, 0.54 wt.% Fe, and sheet of aluminum alloy 7075 of 87.39% wt., where contents of the alloy are 7.74 wt.% Zn, 2.80 wt.% Mg, 2.08 wt.% Cu, with a thickness of 1.5 ± 0.5 mm were used for coating. The aluminum alloy sheets were laser cut to produce 16 ± 1 mm outside diameter (OD) discs from these sheets and subject them to surface preparation and subsequent anodizing. The anodized discs were immersed into 170 W ultrasonic bath, model VTUSC3 Velleman, Belgium, and sonicated at full power for 5 to 10 min in DI water without heat for rinsing. The discs in the blotting stage were placed onto lint-free absorbent paper to soak off the excess water droplets and to dried off to retain some moisture in nanopores before the impregnation stage, i.e. the article is dried off so that it retain at least 10% of water by volume within the nanopores. Employed anodization parameters and established properties of the obtained coatings are listed in Table 1.

Table 1. The main anodization parameters, i.e., electrolyte composition, processing characteristics, etc., and measured properties of obtained anodic coatings before subsequent impregnation stage of sheet of aluminum alloy 6082 and sheet of aluminum alloy 7075.

Anodization parameters	Values		Anodic coating properties	Values
Sulfuric acid	175 g/L		Nanopore density on 6082	1040±120 pores/μm^2
Aluminum sulfate	55 g/L		Nanopore density on 7075	1290±100 pores/μm^2
Oxalic acid	30 g/L		Avg nanopore ID on 6082	20 nm
Current density	2 A/cm^2		Avg nanopore ID on 7075	15 nm
DC voltage	15 V		Roughness, Ra on 6082	1.49 ± 0.14 μm
Temperature	15°C		Roughness, Ra on 7075	1.13 ± 0.13 μm
Achieved thickness	60 μm		Hardness on 6082	4.8 ± 0.5 GPa
Duration	60 min		Hardness on 7075	4.1 ± 0.4 GPa

[0036] During the blotting stage the discs were dried off, i.e. the article is dried off so that it retain at least 10% of water by volume within the nanopores, before immersing them into any of the materials, used for impregnation, except for polytetrafluoroethylene (PTFE). The latter needed full drying during this stage to obtain the anodic coating.

[0037] The anodized discs with PTFE layers were used as a control material for assessing the tribological performance of anodic coatings, impregnated in claimed liquids. For producing the PTFE layers, the fluoropolymer-based DryFilm RA/IPA dispersion from DuPont (USA) was employed. This dispersion is among the state-of-the-art commercial PTFE dispersions, which are frequently used on commercial anodized items to build a top barrier layer of low friction and good resistance to wear. Impregnation with PTFE was based on procedures often employed industrially in anodizing plants, utilizing fully dried anodic coatings. The dispersion contained 25% wt. PTFE particles, suspended in isopropanol by auxiliary surfactants (CAS N° 65530-85-0, 24938-91-8 and 9002-84-0). The dispersion was agitated well before each use to achieve full homogeneity and applied as is.

[0038] As opposed to the partial drying in the blotting stage, the discs for impregnating with PTFE were fully dried by storing them in a desiccator for at least one day. The dry anodized discs were immersed for 15 minutes at room temperature into the said PTFE dispersion without agitation, then removed and suspended vertically in the air for 30 min. Afterwards, a thermo-mechanical process was performed to improve the adherence of the polymer to the anodic coating. The specimens were placed in an inclined position into the crucibles and moved into the tube furnace, model RS 80/500/11, Nabertherm GmbH, Germany, at 305-310°C for 10 min curing with a circulation of N_2 gas for optimal temperature distribution, then cooled to 100°C within 60 min in the furnace. Afterwards, the crucibles were taken out from the furnace, the discs removed and some of them were manually rubbed with a lint-free cloth for 5-10 seconds before cooling below 90°C. Then the anodized discs with PTFE layers were placed into the desiccator until tribological tests.

[0039] During the impregnation stage the discs with dried off, i.e. the article is dried off so that it retain at least 10% of water by volume within the nanopores, anodic coatings were immersed into a heated liquid or liquefied material. A series of materials were tested as immersion media. Technical grade oleic a. of 70% purity was acquired from StanChem (Poland), dilauryl sulfide of 98% purity, methyl oleate of 90% purity and stearic a. of 95% purity from Sigma (USA), trilaurin of 98% purity, dilauryl succinate of 94.8% purity and triisodecyl phosphite of 96.5% purity from TCI (Japan) and trilauryl phosphite from Dover Chemical (USA). The materials were melted (if necessary) and the dried off anodized discs were immersed for 1 hour at 90°C without agitation in order for the compounds to penetrate into the nanopores of the anodic coating. Afterwards, the impregnated discs were suspended in an oven at 90°C for at least one hour to ensure that any excess liquid would drip off and only a negligible amount would remain on the surface. The specimens were inspected visually to ensure a homogeneous surface without any agglomerations of distinct particles, discolorations, or discontinuities.

[0040] For tribological measurements, a Micro-PoD TR-20 M63 tribometer (Ducom Instruments Europe B.V., Netherlands) was employed by utilizing a ball-on-disc rotational configuration. As a stationary part, two types of 6 mm OD balls were used: 1) bearing steel 100Cr6 (96.5% purity, grade G100, hardness ~800 HV and roughness Ra 0.100 μm) and 2) corundum Al_2O_3 (99.8% purity, grade G16, hardness ~2900 HV and roughness Ra 0.025 μm) from RGP International Srl (Italy). The balls were fixed into the holder and pressed under the 50 ± 0.5 N load by a pneumatic piston against the coated specimen, mounted on a rotary part. The rotational motion of 500 rpm was maintained with a 5 ± 0.5 mm radius resulting in a circular track length of 31.4 mm in one revolution, a so-called friction cycle. The average dynamic COF value was calculated automatically as the ratio between friction force and normal load using Winducom 2010 software. The results were presented as COF changes with progressing friction in terms of number of cycles. To ensure good reproducibility, each sample was tested 2 or more times at given conditions and the most representative runs were selected for the comparison between samples. Tribotest duration was either automatically limited due to excessive torque because of an increase in COF or stopped after average friction exceeded COF = 0.6 for more than 1000 friction cycles. The COF variation throughout the course of the measurement was inspected and the threshold was established by determining the number of friction cycles (i.e. revolutions), after which friction and wear rate began to continuously increase much faster. This threshold coincides with the beginning of severe abrasion; hence it is considered as an abrasion onset.

[0041] In order to demonstrate the advantages of the proposed reactive impregnation, a series of industrially-widespread comparative materials were impregnated onto the said anodic coatings and tested for the abrasion onset. The anodized discs with PTFE layers were used as the basis of comparison. Four traditional lubricity additives, Zinc dialkyl dithiophosphate (ZDDP), alkyl phosphite, oleic acid and dialkyl pentasulfide, were used as the comparative material for impregnation. It was expected that once within the nanopores, these compounds might react with the residual electrolyte through hydrolysis, oxidation, soap formation and possibly other mechanisms. Although these lubricity additives are initially liquid, after such reactions they should form solids or bond to the inner walls of nanopores sufficiently strongly without exiting to the surface under ambient conditions. Therefore, the anodic coating should still be considered as dry coating, despite the impregnation with the aforementioned lubricity additives. Rapeseed oil, trilaurin and dialkyl sebacate were also included as comparative materials to represent esters, which can hydrolyze within nanopores. A fully formulated synthetic engine lubricant 0W-40 in compliance with API SM certification was tested as the comparative material for impregnation. Since the major constituent, over 80% wt., of 0W-40 was a poly alpha olefin basestock, i.e., an alkane, it was not likely to hydrolyze or oxidize to any significant extent. Admittedly, some additives in 0W-40 could react with the residual electrolyte in the nanopores of anodic coating. However, the remaining basestock would be able to resurface and such anodic coating, which was impregnated with unreacted liquid lubricant, could not be considered as a dry surface. After impregnation, a significant portion of 0W-40 lubricant would reside on the top, implying liquid lubrication conditions and rendering the anodic coating visually inferior. Two other comparative oils, squalane and squalene, which are often used to simulate lubricant basestocks, also showed liquid lubrication trends and inferior appearance. In this embodiment, the tribological performance of 0W-40, squalane and squalene is provided for reference, but not included in the Exhibits as a comparison, because they cannot be used for producing dry anodic coatings. Anodic coatings with these oils act as slippery liquid-infused porous surfaces (SLIPs) and lead to liquid lubrication regime. They release fluids not only in the friction zone, but also during storage, albeit to a lower extent. They also release some volatiles, generate odors, collect dust, stain clothing and produce other workmanship issues. So, they cannot be used for producing dry anodic coatings.

[0042] Two alloys, which represented 6000 and 7000 aluminum series, were used for anodization, and testing the tribological effects of the proposed reactive impregnation. Anodic coatings on 6082 and 7075 alloys were produced in the same manner, achieving nanopore diameters of 20 nm and 15 nm respectively and the thickness of anodic coating at 60 μm, see Table 1. Then the impregnated discs were subjected to tribotesting against steel and corundum balls. The measured values of abrasion onset are listed in Table 2.

Table 2. Wear resistance of anodic coatings, impregnated in industrially-widespread comparative materials, by determining their abrasion onset - number of friction cycles at 500 rpm, 50 N, room temp.. Most representative duplicate runs are shown.

Compound	6082 - corundum	6082 - steel	7075 - corundum	7075 - steel

(continued)

Compound	6082 - corundum	6082 - steel	7075 - corundum	7075 - steel
None	3; 4	6; 12	2; 3	3; 7
PTFE	720; 900	210; 280	490; 550	550; 800
PTFE rubbed	90; 100	200; 220	170; 250	250; 400
Zinc di-2-EH dithiophosphate	400; 480	1900; 2500	570; 630	2000; 2200
Oleic a. FAN-719	1000; 1100	3800; 4500	400; 480	3800; 4500
Squalane $C_{30}H_{62}$	58; 78	16; 100	5000; 6500	35; 50
Squalene $C_{30}H_{50}$	45; 56	510; 800	3000; 3400	24; 40
Mobil 0W40 4M1	2500; 3200	6300; 6700	6000; 6500	3000; 3600
2-ethylhexyl sebacate 10E	2100; 2300	2000; 2600	1800; 2500	1800; 2200
Rapeseed oil OR6	1300; 1500	1300; 1600	1200; 1600	340; 380
2EH phosphite E58	490; 500	290; 300	730; 780	670; 1400

[0043] The results show that PTFE layers and impregnating compounds significantly improve the wear resistance of anodic coatings. Plain anodic coatings withstand only several friction cycles until severe abrasion begins. The PTFE layers increase the wear resistance by nearly two orders of magnitude, which agrees well with their industrial recognition. The poorer performance of thermo-mechanically processed surfaces appears somewhat counterintuitive because it is colloquially considered that such treatment should improve the adhesion of PTFE layer to the anodic coating. However, the tribotesting conditions are quite severe, leading to relatively fast deterioration of the barrier layer. Therefore, the adhesion strength might not have a significant effect on wear resistance under these tribological conditions. Thermo-mechanical processing is likely to reduce the thickness of the PTFE layer, hence leading to faster deterioration of the barrier.

[0044] Squalane is often employed to simulate paraffinic mineral oil as lubricant basestock, but its performance as an impregnating compound is not as effective on anodized 6082 discs as the PTFE layers. Squalene, which has six double bonds, performs nearly as poorly as fully saturated squalane. Their wear resistance clearly exceeds that of PTFE layers only on anodized 7075 discs against corundum. It remains unclear why squalane and squalene become much better under the latter conditions. Since 7075 has 7.74% Zn, additional catalytic effects could take place and induce reactions, which could not take place in 6082 alloys. Nevertheless, squalane and squalene strongly suggest that typical lubricant basestocks, such as poly alpha olefins or mineral oils, would not be capable to dramatically improve wear resistance. Although their discs operated under a liquid lubrication regime, it was not sufficient to clearly outperform PTFE layers. On the other hand, liquid lubrication was very helpful for the anodized discs, impregnated in a fully formulated 0W-40 lubricant. These discs showed improved wear resistance, which appeared an order of magnitude better than PTFE layers.

[0045] Not all basestocks should be viewed as inappropriate for impregnating the anodic coatings. Synthetic ester basestocks or vegetable oils, which are also used for lubricants, might undergo hydrolysis within the nanopores of anodic coatings. Their ester linkages are hydrolyzed into carboxylic acids and alcohols. These carboxylic acids are likely to form soaps, resulting in solid materials. Tests with 2EH sebacate and rapeseed oil show that anodized discs, impregnated in any of the two, last much longer before the abrasion onset than PTFE layers. It should be noted that hydrolysis of sebacate and rapeseed oil leads to the formation of 2EH alcohol and glycerol, respectively. These are liquid at room temperature, so they should migrate to the surface and provide conditions for the liquid lubrication regime. Therefore, these esters should not be considered as impregnation materials for obtaining dry anodic coatings.

[0046] Typical Anti Wear additives, used by lubricant manufacturers, are developed to improve wear resistance under various lubrication regimes. There isn't any dominating compound for reducing wear of alumina. Oleic acid, ZDDP and 2EH-phosphite are widely used to reduce wear of steel. The former two improve wear-resistance of the anodic coatings during the tribotests against steel counter-body but appear to be less effective against the corundum. The performance of the 2EH-phosphite does not appear significantly better than that of PTFE layers.

[0047] These results show that a conventional approach by those skilled in the art does not lead to such wear resistance of dry impregnated anodic coatings, which would significantly exceed the resistance imparted by PTFE layers. Impregnation with traditional lubricants or their basestocks does not produce dry anodic coatings, while impregnation in traditional lubricity additives does not demonstrate a significant improvement over PTFE layers. Thus, a series of molecules with alkyl chains and functional groups, which are prone to oxidation and/or hydrolysis, were tested as impregnating materials, as shown in the Exhibits.

[0048] The following exhibits are only examples and should not be interpreted to restrict the scope of the invention. The information presented comprises particular features in which the exhibits differ, but all exhibits follow method steps for reactive impregnation of anodic alumina coating even though not recited entirely.

EXAMPLE 1

[0049] The discs of 6082 and 7075 alloys were anodized in the electrolyte of sulfuric and oxalic acids, rinsed with water, blotted with a lint-free paper cloth and suspended in the air at room temperature. Within 36 hours after anodization, when the discs retained at least 10% of original water contents, they were immersed into dilauryl succinate at 90°C for 1 hr and suspended in the air at 90°C for 1 hr. After cooling and storing at room temperature for at least 16 hrs, tribotests were performed against corundum balls. The discs of 6082 and 7075 alloys with dilauryl succinate recorded the averages of 3 200 and 6 700 cycles before abrasion, much better than discs with PTFE layers, which recorded 810 and 520 cycles respectively. Tribotests were also performed against steel balls. The discs of 6082 and 7075 alloys with dilauryl succinate recorded the averages of 9 300 and 40 200 cycles before abrasion, whereas those with PTFE layers averaged 250 and 680 respectively. The impregnated coatings appeared dry because lauryl and succinate moieties, which were formed due to hydrolysis of dilauryl succinate, were reacted into solid compounds within the nanopores after oxidation and saponification.

EXAMPLE 2

[0050] The discs of 6082 and 7075 alloys were anodized in the electrolyte of sulfuric and oxalic acids, rinsed with water, blotted with a lint-free paper cloth and suspended in the air at room temperature. Within 36 hours after anodization, when the discs retained at least 10% of original water contents, they were immersed into trilauryl phosphite at 90°C for 1 hr and suspended in the air at 90°C for 1 hr. After cooling and storing at room temperature for at least 16 hrs, tribotests were performed against corundum balls. The discs of 6082 and 7075 alloys with trilauryl phosphite recorded the averages of 2 400 and 11 500 cycles before abrasion, much better than discs with PTFE layers, which recorded 810 and 520 cycles respectively. Tribotests were also performed against steel balls. The discs of 6082 and 7075 alloys with trilauryl phosphite recorded the averages of 5 150 and 89 800 cycles before abrasion, whereas those with PTFE layers averaged 250 and 680 respectively. The impregnated coatings appeared dry because lauryl and phosphite moieties, which were formed due to the hydrolysis of trilauryl phosphite, were reacted into solid compounds within the nanopores after oxidation and saponification. Impregnation with trilauryl phosphite delivers much more wear resistance compared to tri-isooctyl phosphite. Lauryl chains are much more beneficial to the lubricating properties of the compounds in the friction zone, compared to shorter chains of isooctyl, which also include ethyl pendants.

EXAMPLE 3

[0051] The discs of 6082 and 7075 alloys were anodized in the electrolyte of sulfuric and oxalic acids, rinsed with water, blotted with a lint-free paper cloth and suspended in the air at room temperature. Within 36 hours after anodization, when the discs retained at least 10% of original water contents, they were immersed into methyl oleate at 90°C for 1 hr and suspended in the air at 90°C for 1 hr. After cooling and storing at room temperature for at least 16 hrs, tribotests were performed against corundum balls. The discs of 6082 and 7075 alloys with methyl oleate recorded the averages of 1 000 and 2 100 cycles before abrasion, being better than discs with PTFE layers, which recorded 810 and 520 cycles respectively. Tribotests were also performed against steel balls. The discs of 6082 and 7075 alloys with methyl oleate recorded the averages of 3 400 and 33 200 cycles before abrasion, whereas those with PTFE layers averaged 250 and 680 respectively. The impregnated coatings appeared dry because methanol, which was formed due to hydrolysis of methyl oleate, was volatilized from the coating, while oleic acid was reacted into solid compounds within the nanopores after oxidation and saponification. Methyl oleate performs much better as a material for impregnation compared to oleic acid, which does not undergo hydrolysis.

EXAMPLE 4

[0052] The discs of 6082 and 7075 alloys were anodized in the electrolyte of sulfuric and oxalic acids, rinsed with water, blotted with a lint-free paper cloth and suspended in the air at room temperature. Within 36 hours after anodization, when the discs retained at least 10% of original water contents, they were immersed into dilauryl sulfide at 90°C for 1 hr and suspended in the air at 90°C for 1 hr. After cooling and storing at room temperature for at least 16 hrs, tribotests were performed against corundum balls. The disc of 6082 and 7075 alloys with dilauryl sulfide recorded the averages of 590 and 1 500 cycles before abrasion, being comparable or better than discs with PTFE layers, which recorded 810 and 520 cycles respectively. Tribotests were also performed against steel balls. The discs of 6082 and 7075 alloys with dilauryl sulfide recorded the averages of 20 300 and 2 900 cycles before abrasion, whereas those with PTFE layers averaged 250 and 680 respectively. The impregnated coatings appeared dry because lauryl and sulfide moieties, which were formed due to the hydrolysis of dilauryl sulfide, were reacted into solid compounds within the nanopores after oxidation and saponification.

EXAMPLE 5

[0053] The discs of 6082 and 7075 alloys were anodized in the electrolyte of sulfuric and oxalic acids, rinsed with water, blotted with a lint-free paper cloth and suspended in the air at room temperature. Within 36 hours after anodization, when the discs retained at least 10% of original water contents, they were immersed into isolauryl pentasulfide at 90°C for 1 hr and suspended in the air at 90°C for 1 hr. After cooling and storing at room temperature for at least 16 hrs, tribotests were performed against corundum balls. The discs of 6082 and 7075 alloys with trilauryl phosphite recorded the averages of 1 800 and 3 800 cycles before abrasion, much better than discs with PTFE layers, which recorded 810 and 520 cycles respectively. Tribotests were also performed against steel balls. The discs of 6082 and 7075 alloys with isolauryl pentasulfide recorded the averages of 1 000 and 5 200 cycles before abrasion, whereas those with PTFE layers averaged 250 and 680 respectively. The impregnated coatings appeared dry because isolauryl and sulfide moieties, which were formed due to the hydrolysis of isolauryl pentasulfide, were reacted into solid compounds within the nanopores after oxidation and saponification.

EXAMPLE 6

[0054] The discs of 6082 and 7075 alloys were anodized in the electrolyte of sulfuric and oxalic acids, rinsed with water, blotted with a lint-free paper cloth and suspended in the air at room temperature. Within 36 hours after anodization, when the discs retained at least 10% of original water contents, they were immersed into trilaurin at 90°C for 1 hr and suspended in the air at 90°C for 1 hr. After cooling and storing at room temperature for at least 16 hrs, tribotests were performed against corundum balls. The discs of 6082 and 7075 alloys with trilaurin recorded the averages of 4 000 and 6 300 cycles before abrasion, much better than discs with PTFE layers, which recorded 810 and 520 cycles respectively. Tribotests were also performed against steel balls. The discs of 6082 and 7075 alloys with trilaurin recorded the averages of 7 000 and 4 400 cycles before abrasion, whereas those with PTFE layers averaged 250 and 680 respectively. The impregnated coatings appeared dry because glycerol and lauric acid, which were formed due to the hydrolysis of trilaurin, were reacted into solid compounds within the nanopores after oxidation and saponification.

[0055] It should be noted, that in combination of materials selected from trilauryl phosphite, dilauryl sulfide, methyl oleate, dilauryl succinate, isolauryl pentasulfide and trilaurin any of the mentioned materials exceeds 5% wt. each.

Claims

1. Method for reactive impregnation of anodic alumina coating comprising anodizing aluminum surface in an acidic electrolyte to produce anodic coatings with open nanopores **characterized in that**

    a surface for coating material is selected from pure aluminum or its cast, forged, rolled or wrought alloy,
    anodized coating is formed having thickness of 5 - 100 μm and an internal diameter of nanopores of the coating 5 - 50 nm,

        wherein surface of the anodized coating is rinsed with deionized water,
        wherein the anodized surface is dried off to retain at least 10% deionised water by volume within the nanopores of the obtained anodic coating,

    the open nanopores of the anodized surface are penetrated by a material in liquid form comprising amphiphilic compounds for reacting the impregnating material with the residual deionized water and electrolyte within the nanopores of the anodized coating,
    reaction between the impregnating material in liquid form and residual electrolyte within the nanopores is driven by completely drying the impregnated anodic coating for preventing nanopore sealing.

2. Method of claim 1, wherein said material in liquid form comprising amphiphilic compounds contains 50-100% wt. of molecules with one, two or three alkyl chains, whose chain length is from C6 to C24 with or without methyl or ethyl

pendants or double bonds.

3. Method of claim 2, wherein said molecules have a moiety or several such moieties, capable of oxidizing or hydrolyzing in the presence of residual acid within the nanopores of said anodic coatings.

4. Method of claim 3, wherein said polar moieties are phosphite, sulfide, or ester.

5. Method of claim 4, wherein said phosphite is trilauryl phosphite.

6. Method of Claim 4, wherein said sulfide is dilauryl sulfide.

7. Method of claim 4, wherein said ester is methyl oleate.

8. Method of claim 4, wherein said ester is dilauryl succinate.

9. Method of Claim 4, wherein said ester is isolauryl pentasulfide.

10. Method of Claim 4, wherein said ester is trilaurin.

11. Method of claim 4, wherein a combination of materials is selected from any claims 5-10 and any of the aforementioned materials exceeds 5% wt.

12. Method according to any one previous claims, wherein anodization conditions are current density - 1.6 - 2.4 A/dm^2, electrolyte temperature - 14-16°C and anodization duration - 67 to 73 min.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 16 8208

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	DE 21 37 052 A1 (BEREDAY SIGMUND) 5 April 1973 (1973-04-05) * page 4, paragraph 2 - page 40, paragraph 2 * -----	1-12	INV. C25D11/24 ADD. C25D11/06
A	TADAS MATIJOSIUS ET AL: "Determination of the dye penetration rate in porous aluminum oxide using Raman spectroscopy", COLORATION TECHNOLOGY, WILEY, HOBOKEN, USA, vol. 135, no. 4, 8 May 2019 (2019-05-08), pages 275-282, XP072248090, ISSN: 1472-3581, DOI: 10.1111/COTE.12404 * page 276, left-hand column, paragraph 2 - page 276, right-hand column, paragraph 1 * -----	1-12	
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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	6 September 2023	Crottaz, Olivier

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
L : document cited for other reasons
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

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