

HARD ANODIC COATINGS ON ALUMINUM ALLOYS

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Summary

The review of the literature concerning hard anodizing of aluminium alloys was performed. The main features of the process was described as well as the influence of the anodizing parameters on the properties of hard anodic coatings. The most common industrial processes of hard anodizing applied for cast and wrought aluminium alloys were presented. The application of hard anodic coatings as well as the possibilities of improvement of their tribological properties were described.

Keywords: hard anodizing, abrasion resistance, aluminium alloys

Wytworzenie twardych powłok anodowych na podłożu stopów aluminium

Streszczenie

W artykule prowadzono analizę zagadnień dotyczących procesów wytwarzania twardych powłok anodowych o dużej odporności na zużycie ściernie. Przedstawiono charakterystykę anodowania twardego oraz wpływ parametrów tego procesu na właściwości powłok tlenkowych. Omówiono najczęściej stosowane procesy wytwarzania twardych powłok anodowych na podłożu stopów aluminium odlewniczych i do przeróbki plastycznej stosowanych m. in. w konstrukcjach lotniczych. Przedstawiono podstawowe zastosowania takich powłok tlenkowych oraz scharakteryzowano możliwości ulepszenia ich właściwości tribologicznych.

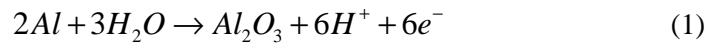
Słowa kluczowe: anodowanie twarde, odporność na zużycie ściernie, stopy aluminium

1. Introduction

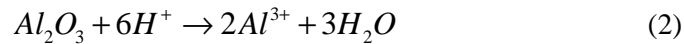
The worldwide production of aluminum has been increasing gradually for last 80 years and nowadays it is the biggest among non-ferrous metals [1]. Rapid growth of production of aluminium was observed since 1933 due to its high consumption in military industry, especially aircraft industry and subsequently in the transportation [2]. These applications stem from two important features of aluminum and its alloys: low density and ease of strengthening via appropriate heat treatment or cold working [3]. Aluminum, due to its strong affinity to oxygen and formation of a compact oxide layer onto its surface exhibits high corrosion resistance in air and water solutions in a pH range between 4 and 7 [4, 5]. However, aluminium alloys, especially with high content of copper undergo corrosion reactions easily.

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Anodizing is the method which is often applied to improve the corrosion resistance of aluminum alloys. Moreover, anodic coatings improve the adhesion of paints, may be easily colored and last, but not least, increase the wear resistance of the anodized part. Anodic oxidation is usually performed for the corrosion protection of aircraft, vehicles, boats, trains, buildings, household and office articles, electronics, in nanoscience and nanotechnology (porous anodic oxide membranes for sensors and templates for manufacturing of nanowires [6]). The process is known since 1923 (anodizing of Al-Cu alloys in chromic acid by Bengough and Stewart) [7]. The anodizing is an electrolytic process, the aluminum part, immersed in the electrolyte (usually acids *e.g.* sulfuric, orthophosphoric and oxalic), is the anode. The cathode is made of aluminum alloy, lead or stainless steel. The growth of anodic coating, which is composed of hydrated oxides: γ -Al₂O₃, γ' -Al₂O₃ and η -Al₂O₃, is the result of two processes. The first one is the electrochemical oxidation of aluminum with subsequent formation of oxide (overall equation (1)):



The other one is the chemical dissolution of the aluminum oxide according to equation (2):



They occur simultaneously during anodizing. The thickness of the coating is mostly influenced by the electrical charge passed through the metal/solution interface, temperature and chemical composition of the electrolyte. The last two factors determine the kinetics of dissolution of aluminum oxide. Thus, the coating is composed of two layers. The inner layer (called the barrier layer) is compact, but usually thin (tens to hundreds nm). The outer layer may be thick and porous (Fig. 1).

The dissolution power of the electrolyte determines not only the total thickness of the coating but also the thickness of the barrier layer and porosity of the coating [6–8]. The latter, in turn, determines the important properties of the anodic coating such as wear and corrosion resistance, adhesion of paints or dyeing ability. Therefore, the properties of anodic coatings may vary in a very wide range depending on the chemical composition of the solution, temperature, current density and voltage applied (Table 1).

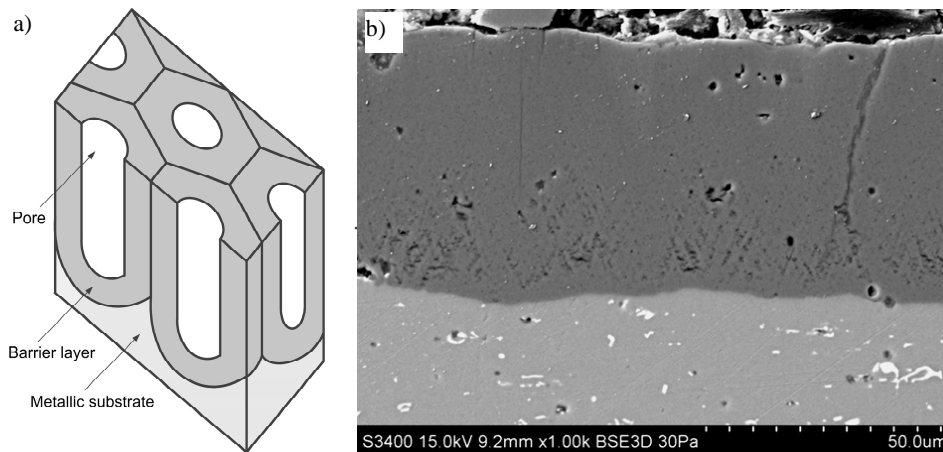


Fig. 1. The morphology of the anodic coating: a) schematic representation, b) microstructure of the coating on AA 6061 – T6 alloy

Table 1. Major applications and properties of anodic coatings on aluminium and its alloys [5]

Application	Main feature	Coating morphology	Thickness	Electrolyte
Electrical (electrolytic capacitors)	Compactness	Compact (barrier layer)	< 500 nm	Boric acid, borax
Architectural	Corrosion resistance, dyeing ability	Porous (sealed or dyed and sealed)	10 – 60 μm	Sulfuric acid, chromic acid, oxalic acid
Engineering applications	Wear resistance, hardness	Porous (less than for architectural applications)	15 – 200 μm usually > 51 μm	Sulfuric acid, oxalic acid

The anodic coatings are often dyed with organic dyes or inorganic pigments. In order to improve the durability of the coatings they are sealed *i.e.* pores are closed by hydration of the aluminum oxide in deionized hot water, hot potassium dichromate solution, sodium silicate, water solution of inorganic salts of nickel and cobalt, zirconium, chromium(III), titanium, cerium and yttrium. Sometimes, non-toxic inorganic corrosion inhibitors are also applied (*e.g.* tungstates, vanadates, molybdates) [9].

The oxide coatings in wide range of thickness are commercially produced onto aluminium part. However, the chemical composition of the anodized alloys affects the properties of the oxide significantly. The higher content of alloying elements, the worse quality of the oxide coating *i.e.* worse corrosion and wear resistance as well as homogeneity. It is especially true for the copper-rich alloys.

2. Main features of hard anodic coatings

The term “hard anodizing” indicates a process of production of anodic coating for engineering applications. Their primary characteristic is high abrasion resistance or hardness and thickness [10]. The well-known classification of anodic coatings is presented in military specification MIL-A-8625F [11]. Hard anodic coatings on aluminum alloys are classified as coating type III. The range of thickness allowed is between 12.7 and 114 μm whereas the typical value is 51 μm .

However, it should be noted here that thick not necessarily means hard. Anyway, the thickness of the anodic coating is the result of the trade-off between the rate of its growth, governed by the Faraday law, and rate of its dissolution. The former depends on the applied current density, the latter on the chemical composition and the temperature of the electrolyte. Thus, the increase of the thickness of the coating is best achieved using solutions where the rate of dissolution of the Al_2O_3 is low, *i.e.* at low temperatures (below 5°C) and high current density (around 3 $\text{A}\cdot\text{dm}^{-2}$) [5–8]. The comparison between the thicknesses of the coating obtained in the conventional process in sulphuric acid solution and hard anodized (Alumilite Hard Coating) for various aluminium alloys is presented in Fig. 2.

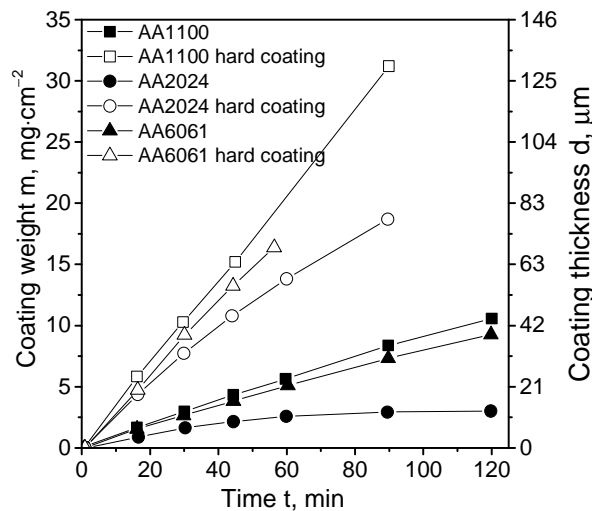


Fig. 2. Weight and thickness of anodic coatings produced on three aluminium alloys in the conventional Alumilite and Alumilite Hard Coating Process (data calculated on the basis of [7])

According to MIL-A-8625F specification, abrasion resistance of hard anodic coatings should be determined using a Taber Abraser Test. In brief, the wheels

made of an abrasive material (denoted as CS-17) revolve on the anodic coating (60 rpm) for 10 000 cycles. The wear index, which is the weight loss in milligrams per 1000 cycles, is then calculated [12].

The wear index for the alloys having the copper content below 2% should be lower than 1.5, for the copper-rich alloys (over 2%) in turn should not exceed 3.5. In principle, hard anodizing should not be applied to aluminium alloys with the content of copper over 5% or silicon over 8% [11]. The abrasion resistance is also determined by using other methods such as Abrasive Jet Test or Abrasive Wheel Test [10].

The abrasion resistance is related to the weight of the coating *i.e.* the higher weight of the coating (lower porosity), the higher its wear resistance. According to MIL-A-8625F the former should be over $0.18 \text{ g}\cdot\text{cm}^{-2}\cdot\text{mm}^{-1}$. It is determined in the destructive manner *e.g.* anodic coating is dissolved in the hot water solution of H_3PO_4 containing CrO_3 [13]. However, there are attempts to replace chromate ions with a non-toxic inhibitor of corrosion of aluminum alloys in acidic solution [14,15].

The corrosion resistance should be determined in the salt spray test, according to ASTM B117 [16]. The high thickness of the hard coating not necessarily improves the corrosion resistance. What is more, anodic coatings, contrary to standard coatings, are not sealed after anodizing since it worse the abrasion resistance.

3. Hard anodizing processes

The first analysis of preparation hard anodic coatings on aluminum were performed just after World War II (1946 – 1948) in Germany, United Kingdom and Soviet Union. The types of electrolytes applied were: oxalic and sulphuric acid. Nowadays, still H_2SO_4 in wide concentration range is most frequently applied in the production of hard anodic coatings [7].

The well-known procedure of production of hard anodic coatings is called the M.H.C. (Martin Hard Coat) process. In the case of pure aluminium, the coatings as thick as $150 \mu\text{m}$ are obtained in 15% H_2SO_4 at 0°C . The current density is in the range between 2 and $2.5 \text{ A}\cdot\text{dm}^{-2}$ [7]. This process is suitable for the alloys containing less than 3% of copper and 7.5% of silicon. The alloys with high content of copper are especially difficult to anodize, since Cu forms intermetallic phases with aluminium and other alloying elements (*e.g.* CuAl_2 , AlCuMg , AlCuNi) which does not undergo oxidation. These phases dissolve in the acidic solution and increase the concentration of copper in the bath. The silicon in the cast alloys, which is a component of eutectic mixtures, undergoes oxidation slightly. However, Si in the form of Mg_2Si phase in wrought alloys is not detrimental [17,18]. It should be noted here that cast alloys are usually more difficult to anodize than wrought alloys. The former usually contain high content of alloying elements, which are present in the form of intermetallic compounds.

Often they do not undergo oxidation and dissolve or are incorporated to the coating. The surface finish is also very important – the anodic coating on a non-machined, rough area of the cast is very thin.

In order to achieve good quality of the coatings on cast alloys, the concentration of acid should not be too high. Otherwise rough surface will be obtained.

For aluminium alloys that are difficult for anodizing, more sophisticated electrolytes are applied. Many organic and inorganic additives are introduced to the bath in order to improve the quality of the coatings. They inhibit burning of anodic coatings and reduce its dissolution rate [7,19]. A good example is the Sanford process. The solution contains sulphuric acid (7%), methyl alcohol (7%) to decrease the freezing point of the solution, peat extract (3%), and small additions of surfactants (0.02% of nonyl alcohol and 0.02% of polyethylene glycol). Temperature of anodizing is equal to -10°C , current density in the range from 1.1 to $2.2\text{ A}\cdot\text{dm}^{-2}$ [5,7]. The mixture of sulphuric acid-nitric acid was also employed for processing of Cu-rich alloys. Application of nitric acid (or nitrates such as ammonium nitrate, aniline nitrate, cupric nitrate) decreases the voltage during anodizing. The similar effect was obtained in the mixture of sulphuric acid – hydrochloric acid [7].

Since CuAl_2 phase may be oxidized to some extent in the oxalic acid, it is sometimes applied in the anodizing of copper-rich alloys. For instance 3 - 5% $(\text{COOH})_2$ at $3 - 5^{\circ}\text{C}$, current density between 1 and $2\text{ A}\cdot\text{dm}^{-2}$ [5]. In general, wide range of concentration of oxalic acid is allowed *i.e.* from 1 to $100\text{ g}\cdot\text{dm}^{-3}$. Also mixtures of oxalic acid and formic acid were used *e.g.* $80\text{ g}\cdot\text{dm}^{-3}$ of $(\text{COOH})_2$ and $80\text{ g}\cdot\text{dm}^{-3}$ of HCOOH [7]. Another possibility is the mixture of sulphuric and oxalic acid with inorganic additives such as CaF_2 and $\text{Cr}_2(\text{SO}_4)_3$. Tartaric acid based electrolytes have been developed in Japan, sulphonic acids in Germany [7].

The current density applied in the hard anodizing process is several times higher than in the conventional process. The typical value is $2.5\text{ A}\cdot\text{dm}^{-2}$. Anodizing is rather performed at the constant current density than constant voltage, since when the thick coating is produced, the voltage grows up for instance from initial value around 20 V to over 100 V, depending on the chemical composition of the alloy, electrolyte and its temperature. The current density should slowly increase from 0 to the target value at the origin of the process. On the one hand it was observed that in the case of alloys difficult to anodize (*e.g.* cast alloys) the decrease of the current density often improves the quality of the coatings. Sometimes special electrical programs are applied such as d.c. steps for 2024 alloy [19,20]. On the other hand increasing current density usually improves the abrasion resistance of anodic coating produced on wrought alloys. Therefore, pulsed d.c. current is sometimes used. Very high current density (2 – 5 times higher than in d.c. process) is applied for certain period of time (from milliseconds to seconds) and is followed by a period where much lower or even no current

passes through the part. The large amount of generated heat is then easily dissipated.

Application of pulsed d.c. current facilitates obtaining coatings without burned corners or edges and is particularly useful for the alloys that are difficult to anodize [7,19].

The processing of difficult aluminum alloys is easier, when the alternating current is superimposed on the direct current. It enables working with lower voltage which means two serious benefits. The first one is the lower risk of the burning during the process, the other one is lower refrigeration capacity necessary. The well-known commercial example of the process where a.c. superimposed on d.c. current is applied is the Hardas process. Initially it was done in the oxalic acid, however later it was substituted with sulphuric acid. Another commercial method using the a.c. superimposed on d.c. current is the Sanford process [5,7]. Regardless of the the direct or alternating current is applied, good electrical contact must be provide. It should be made of aluminum *e.g.* AA 5083 or AA 6063 alloys, preferably the same alloy that is anodized. It is especially important when cast alloys are anodized. Titanium is very often applied for electrical contacts. It should be noted here, that only one alloy can be anodized in one operation [7,19].

Very important parameter which must be carefully controlled during hard anodizing is temperature. Usually it is around 0°C which is much below the value for classical anodizing. During hard anodizing, large amount of heat must be dissipated, thus appropriate refrigerating capacity must be ensured. On the one hand, dissolution of aluminum in the acidic solution is exothermic. On the other hand, the resistivity of the coating increases during anodizing. The thicker coating is, the higher voltage is required to ensure the target current density. Thus, the intensive agitation of the solution must be ensured. Insufficient agitation as well as improper electrical contact or too high starting voltage lead to obtaining burned coatings. The tendency for production of burned coatings may be reduced by increasing the dissolution power of the electrolyte (*e.g.* increasing concentration of acid and temperature) as well as application of organic and inorganic additives [7,19].

4. Properties of hard anodic coatings

The properties of hard anodic coatings are strongly dependent on the chemical composition of the alloy and the anodizing process itself. By definition, hard coatings should be wear resistant. The abrasion resistance is affected by concentration of acid, temperature and current density. In general, decreasing concentration of acid increases the abrasion resistance of the coating [5]. It was observed that variation in the current density at low temperature range (from 0 to -5°C) does not influence the abrasion resistance significantly. However, between 10 and 20°C the decrease of the current density leads to pronounced deterioration of the abrasion resistance.

It is caused by increasing porosity of the coating. The best combination of these two variables is high current density and low temperature [7,10].

The best abrasion resistance is obtained on pure aluminium, the higher content of alloying elements, the more significant its deterioration is. Good abrasion resistance is also characteristic for Al-Mg-Si and Al-Zn-Mg wrought alloys. Increasing content of copper in the alloy (over 2%) deteriorate wear resistance significantly. The hardness and corrosion resistance are affected in the same manner. The weight loss obtained from the Taber abrasion tests for anodized AA6061 – T6 alloy are in the range between 7 and 12 mg after 10 000 cycles, no matter if sulphuric acid or the mixture of sulphuric and oxalic acid was applied during anodizing. It was also observed that increasing thickness of the coating in the range between 25 and 57 μm decreases the wear loss during abrasion [7,10]. It should be noted here however, that usually coating thickness has no significant impact on the abrasion resistance up to approximately 76 μm . Above this value, deterioration of the wear resistance may occur [11].

The hardness of the coatings onto AA6061 – T6 alloy correlates well with the wear resistance, however it was not necessarily observed for the coatings on other aluminium alloys. Hard anodized aluminum (MHC process) is more wear resistant than hard chrome plate or cyanide hardened mild steel, although its hardness is half of the hardness of steel and chrome plate. Therefore, the measurements of hardness cannot substitute the wear tests [7,10].

On the 2024 alloy in turn, the strong influence of the concentration of sulphuric acid on the abrasion resistance was observed. The anodizing process should be performed in the solution containing over 250 $\text{g}\cdot\text{dm}^{-3}$ of H_2SO_4 [7]. The abrasion resistance of the coatings produced in the solution containing 300 $\text{g}\cdot\text{dm}^{-3}$ of H_2SO_4 with some organic additives (Sanford process) exceeds the requirements of MIL-A-8625F standard (weight losses from the Taber test in the range between 7.3 and 12 mg were obtained after 10 000 cycles). Similar results were achieved in the low voltage process where a.c. component was superimposed on d.c. These results may be explained in terms of the high coating mass per surface area [21].

Abrasion resistance of the anodic coating depends also on its hardness and friction coefficient. The latter is dependent on the roughness of the coating. Generally speaking, it is increased by hard anodizing by 0.25 – 0.5 μm for wrought alloys and 1.25 – 2.5 μm for castings. Therefore, the surface before anodizing should be as smooth as possible [7,19].

The anodizing process affects the mechanical properties of the part and it should be taken into account during the designing. The ultimate tensile strength and elongation of the hard anodized part is deteriorated when compared to the part uncoated. However, the most pronounced adverse effect of the hard coating was observed on the fatigue strength. The fatigue limit is lowered considerably at high stress.

It was observed that deterioration of the mechanical properties is less pronounced when the a.c. current is superimposed on the d.c. current during

anodization. The influence of the coating thickness on the fatigue limit is insignificant [7,22].

The fatigue strength of the anodized element depends on the internal stresses in the coating. Whereas compressive stress increases the resistance to fatigue failure, tensile stress facilitates the formation of cracks and decrease the fatigue limit. The sign and magnitude of the stress depend not only on the difference in the molar volumes of the oxide and metal but also on the surface preparation and anodizing conditions (chemical composition of the electrolyte and current density). It was observed that in thin coatings obtained at low current density compressive stress is observed. The higher coating thickness and current density, the magnitude of the compressive stress decrease. At certain point, the transition from compressive to tensile stress was observed [6,7].

It should also be noted that hard anodic coatings are good electrical and heat insulators. The resistivity of the thick coating (50 μm) is comparable to that of glass and porcelain. Good heat resistance of the thick coatings enables withstanding short exposures to temperature over 2000°C [7].

5. Application of hard anodic coatings

The number of applications of hard anodized aluminium is growing. Depending on the desired properties of the coating they are applied in the different fields. Since they are erosion, impingement, abrasion and scratch resistant, such products as valve bodies, piston crowns, pumps and impellers, guide rails, pneumatic cylinders, low loaded bearings, hand-rails or moving walkways made of aluminium alloys are hard anodized [7].

For certain applications *e.g* in aircraft industry the abrasion resistance of hard anodic coatings should be further improved. It is often realized via impregnation of the hard anodic coatings with polytetrafluoroethylene, graphite or molybdenum disulphide. It decreases the value of friction coefficient significantly. For instance, for the coatings impregnated with teflon its reduction from *c.a.* 0.25 to 0.13 may be achieved [5, 17-19]. What is more, polytetrafluoroethylene ensures good corrosion resistance and hydrophobicity of the surface. The term “impregnation” suggest introduction of polytetrafluoroethylene particles into the pores of the anodic coating. However, since the particles in commercially available polytetrafluoroethylene suspensions are bigger than the pores size, the weakly-bounded polytetrafluoroethylene coating on the Al_2O_3 is rather formed [23]. The impregnation process may be realized by simple immersion of the element in the polytetrafluoroethylene suspension. Better quality of the coatings may be achieved, when the migration of the particles to the coating is forced with the electric field (electrophoresis) or ultrasonic waves [24–28].

Molybdenum disulphide in turn may be synthesized in the pores of the anodic coating during electrochemical treatment of the anodized element. It is performed in the diluted aqueous solution of tetrathiomolybdate. These anions diffuse into

the pores of the coating and decomposes to molybdenum trisulphide during anodic polarization. Subsequently appropriate heat treatment is performed to obtain molybdenum disulphide [29,30].

Due to relatively good corrosion resistance, hard anodized aluminium elements are applied in the marine environment (*e.g.* torpedoes). Thanks to good electrical and heat resistance, heat sinks and heating elements are also produced from the hard anodized aluminium [7].

Summary

The hard anodizing process is practised more and more often nowadays. In many applications hard anodic coatings are alternatives to hard chromium coatings. The former when compared to the latter are cheaper to apply, give better oil retention and last but not least, their production is more environmentally friendly. However, they cannot be used on all aluminium alloys [7]. The further development in this area will probably be observed now, because since April 2016, the application of chromium(VI) ions in industry is restricted with the REACH regulation. However, it should be noted here, that the plasma electrolytic oxidation (PEO) emerges as a potential replacement of hard anodizing. This process is more environmentally-friendly (non-aggressive electrolyte is employed) and offers higher hardness and abrasion resistance of the coatings when compared to hard anodizing. What is more, anodizing of the multi-component alloys (*e.g.* with high content of copper) is easier [31–33]. However, the cost of the rectifier may be significantly higher when compared to the lower-voltage power sources for hard anodizing.

Acknowledgment

Project no. UOD-DEM-1-557/001, co-financed by the European Union under the European Regional Development Fund within the Innovative Economy Operational Program and Foundation for Polish Science (FNP) are gratefully acknowledged.

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Received in February 2017