Theoretical Introduction to Pulse Anodizing

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1. Abstract

This paper will give a short theoretic introduction to pulse anodizing, why pulse anodize, and what the advantages/disadvantages are.

After the introduction, the results from an earlier work will be shown and discussed. This work was to investigate and correlate conventional DC anodizing with three different pulse anodizing methods.

The anodic layers formed by the four methods were tested by various test methods, ASTM G85, Impedance test, Wear resistance (ISO 8251), Knoops hardness, Sealing test (ISO 3210) and a coloring test.

The last part of the presentation will briefly show how to implement pulse anodizing in a conventional anodizing line.

2. Introduction

2.1 Anodizing

Anodizing is the most common surface treatments of aluminum. By applying an anodic current or voltage in a sulphuric acid bath the natural oxide layer on the aluminum becomes thicker leading to a better corrosion and wear resistance. For decorative purposes, the oxide layer formed on the surface gives the possibility of coloring.

It has been known since 1932 that the aluminum oxide layer consists of a thin compact oxide layer, called the barrier layer, and a porous oxide layer, see figure 1a)[1]

This barrier layer has a thickness of around 0.1 − 2.0% of the total film thickness and is mostly affected by the concentration of the electrolyte and by the forming voltage. The current density has a negligible effect, and increasing the temperature of the electrolyte will only have a slight effect due to chemical dissolution[1].

As the formation of oxide continues in sulphuric acid, an arrangement of cells will be produced until finally a well-defined hexagonal cell pattern is apperent[1,2]. The pore and cell wall form the unit-cell as seen in figure 1a). Figure 1b) shows a plane view of the porous oxide layer.

The growth of the oxide layer is continuing from the bottom of the pores, more precisely in the barrier layer. This means that all the oxide has been a part of the barrier layer before becoming a porous oxide layer.

The anodizing process first introduced was the Bengough − Stuart process developed in 1923[1]. The anodic layer formed by this process consists of an oxide layer with pores having a very small diameter and therefore looking almost as a barrier oxide layer. In this process the electrolyte consists of 30 − 100 g/l chromic acid working at a temperature of 40°C and using current densities of 0.1 − 0.5 A/dm² with voltages from almost zero to 50 V. The coating thickness varies from 2 − 15 µm.
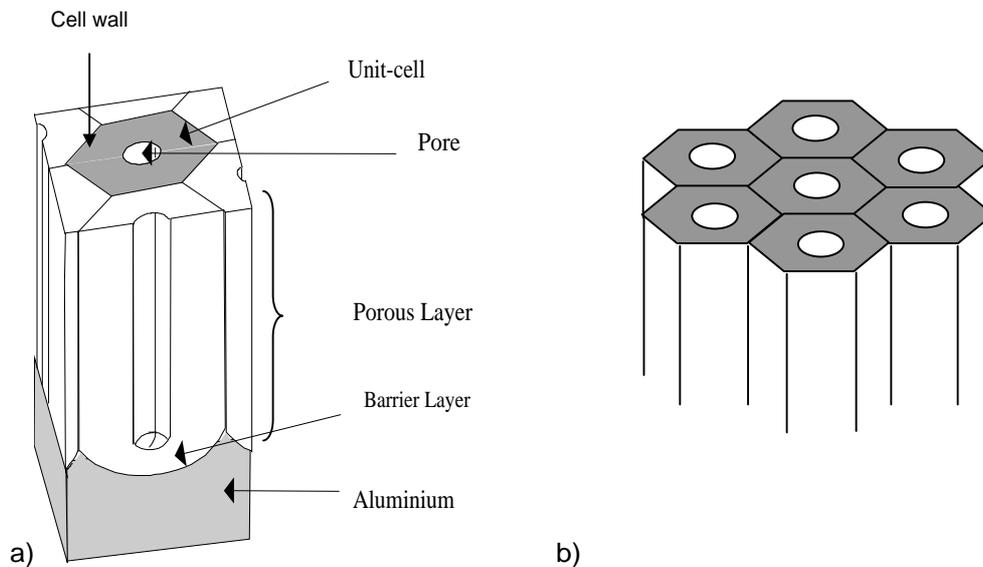
Figure 1, The hexagonal cell structure[1]

Another acid used for preparing porous oxide is phosphoric acid with a concentration of phosphoric acid around 10 − 12 wt%. The porosity of this oxide is very high with pore diameters of around 300 Å[1,3]. The thickness of the coating is never more than 1 − 2 μm. Phosphoric acid is used as pretreatment prior to adhesive bonding. In recent years this coating has been used as a nanostructural template onto which metal and semiconductors can be electroplated. These surfaces have been used as microelectrodes and as magnetic recording media[3]. The process is called the Boeing process because of its origin from this company.

2.2 Sulphuric acid anodizing

Turning to the sulphuric acid process much work has been done to understand this process. In the book Surface Treatment and Finishing of Aluminum and its Alloys by Wernick, Pinner and Sheasby[1] most of the work carried out until 1987 is compiled. Not only on sulphuric acid anodizing but also several other surface treatments. According to this reference the British Anodizing Association gives the following recommendations for architectural work. The temperature should be within 18 − 20°C ±1°C. The concentration of the electrolyte should be in the range of 160 − 185 g/l ±10 g/l using a current density of 1.4 − 2.0 A/dm² with sufficient electrolyte agitation. The voltage will normally be in the range of 17 − 21 V.

The thickness of the oxide layer varies with different applications of the coatings. Normally for outdoor use the thickness should be around 20 − 25 μm whereas for indoor use 10 − 15 μm is expected to be enough[1].

In the U.S.A. military specification, MIL-E-8625D (1985), the anodic oxide layer is divided into three groups. Type I, II and III, where type I is only chromic acid anodizing. Type II and III classifies the sulphuric acid anodizing into two groups, conventional coatings and hard anodic coatings. The hard anodic coatings be as thick as 50 μm. The thickness of the conventional formed oxide follows the British standard above.

It is a general assessment that the oxide film grows by field-assisted ion migration. The total rate of film growth is at any instant represented by the ionic current. The total ionic charge represents the amount of oxide formed and therefore the film thickness[1]. This can be expressed by the following equation:

$$i_+ = k \, dx/dt = \alpha e^{\beta F}$$

where i_+ is the ionic current density and F the field strength. X is the thickness and α, β, k are constants dependent on the process assumptions and t the time.

However, the thickness of the oxide layer will not continue to increase. For a certain thickness the dissolution will be as fast as the formation and therefore a constant thickness of the oxide layer is obtained. The thickness of the porous oxide layer will make the resistance of the total system so high that no current will flow through the pores (remembering the illustration of the porous oxide layer in the introduction).

For an oxide layer formed under recommended condition but with current densities different than those quoted above the following cell parameters are found, see table 1[4].

Table 1, Pore and cell diameters as a function of forming voltage[4].

Current density [A/dm²]	Cell voltage [V]	Pore diameter [Å]	Porosity [number/cm²]	Cell diameter [Å]
1.0	14.5	145	81.3×10^9	400
2.5	17.8	160	61.1×10^9	460
5.0	19.6	180	45.2×10^9	535
8.0	23.5	215	41.7×10^9	585

As shown in the table the cell diameter will increase with increasing voltage, see figure 2. Hence the number of cells pr. square centimeter, the porosity, will decrease. At the same time the pore diameter will increase.
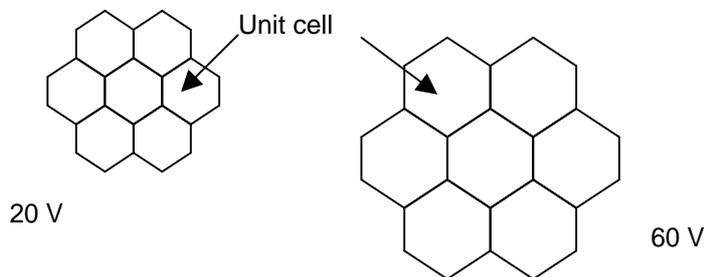

Figure 2, Schematic drawing of the cell size as a function of the voltage

The parameters, which usually are controlled during anodizing, are connected with the rectifier and the conditions of the anodizing electrolyte[5]. Typically the voltage or current will be controlled, while the chemistry of the electrolyte and the temperature of the electrolyte constant.

2.3 Hard anodizing

The main purpose of hard anodizing is to form a thick and dense oxide layer with a high wear resistance with thicknesses above 25 µm. A dense oxide layer is an oxide layer with narrow pores and very thick cell walls.

This can be done by using low electrolyte temperature and low concentration of the electrolyte in order to slow down chemical dissolution of the oxide layer. Therefore hard anodizing is usually carried out in 5 − 15 % (vol) sulphuric acid solutions with temperatures ranging from −5 to 5°C. Production of very thick coatings is usually done at high current densities. These factors involve very high voltages, which lead to high local temperatures therefore agitation of the electrolyte is most important[6]. Using very high current densities and at the same time having very high temperatures locally will enhance the possibility of burning as explained bellow.

These coatings are usually unsealed to maintain the wear resistance high but can be impregnated with different materials such as waxes and silicone[1]. Usually these coatings are used in the engineering industry for components such as pistons, cylinders and hydraulic gear.

The above has given information about the oxide layer formed by anodizing. Now it is important to realize how this formation takes place. As shown above interesting purposes can be fulfilled by formation of the porous aluminum oxide. The intention with next section is to give an understanding of the reactions at the aluminum surface during anodizing.

2.4 Formation of the porous oxide layer

Taken the formation of the porous oxide layer into consideration the two main reactions (1) and (2) only give a part of the history of forming aluminum oxide. Reaction (1) shows the formation of aluminum oxide and reaction (2) the chemical dissolution of the oxide layer in an acidic electrolyte, such as sulphuric acid.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \qquad (1)$$

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \qquad (2)$$
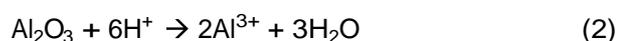
If this chemical dissolution should be the only dissolution process taking place it is difficult to explain the following; How can the chemical dissolution double as it should to keep a steady state for formation and dissolution when the rate of film growth is almost twice as high for a current density of 2 A/dm² than for 1 A/dm² for the same anodizing condition. This indicates that another dissolution process must take place beside reaction (2).

This process is called the field-assisted dissolution and is a result of concentration of the field across the barrier layer, and thus of the current, probably thermally enhanced through local Joule's heating. According to Thompson et al.[7] this dissolution mechanism is due to a weakening of the $Al - O$ bonds in the oxide lattice causing a dissolution at the film/electrolyte interface. These two dissolution mechanisms take place with very different rates. The field-assisted dissolution takes place with rates up to 300 nm oxide pr. minute whereas the chemical dissolution is much slower with rates up to 0.1 nm oxide pr. minute[7].

One must realize that the most important factor in aluminum anodizing is the behavior of the barrier layer. The electrical field across the barrier layer controls the dissolution rate of the oxide layer, as indicated by the big variation in dissolution rates. Turning to the growth, reaction (1), of aluminum oxide this process is purely field assisted. According to Anderson[8] the electrical field that is in the order of 10^7 volt/cm, is the main reason for the possibility of the ions to move through the barrier layer at all. Many considerations have been done to explain this formation process of aluminum oxide. The theory explained below gives a plausible explanation for this growth mechanism.

Solid aluminum is found as a fcc crystal lattice. When Al^{3+} ions leave this metal lattice vacancies are formed. These vacancies provide room for the ingress of oxygen ions from the adjacent oxide layer to continue the formation of aluminum oxide. The continued growth of the film is possible due to the very small radius of Al^{3+} which makes it easy for the ion to diffuse through the barrier layer under the influence of the electrical field present. The radius of Al^{3+} is 0.5 Å and that of O^{2-} is in the order of 1.3 Å. The size of the oxygen ions makes the movement of these ions possible only when there is sufficient space[8]. Hoar and Mott[9] suggested that the oxygen is transported not as O^{2-} but as OH^- which is much smaller. The H^+ ions found in the electrolyte may lead to the production of a hydroxyl ion instead of the oxygen ion according to reaction (3).

$$O^{2-} + H^+ \Leftrightarrow OH^- \qquad (3)$$
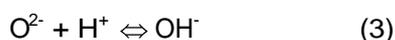
Under the influence of the high field, the hydroxide ions will move through the oxide to the interface metal/barrier layer. It will react with Al^{3+}, which is formed here and form aluminum oxide. If the oxide is formed by the hydroxide rather than the oxygen ions positive hydrogen ions will move back through the film and into the electrolyte.

This means that the continuous formation of oxide (1) is dependent on the ability of migration of aluminum and oxygen ions through the barrier layer as shown in figure 3. Takahashi et al.[10] show the migration of oxygen ions through the barrier layer into the interface area metal/barrier layer where the reaction takes place. They do not take into considerations if the oxygen ion is too big to migrate through the aluminum oxide lattice. They also postulate that chemical dissolution, reaction (2), will take place at the interface barrier layer/electrolyte at a rate keeping the thickness of the barrier layer constant as determined by the applied voltage[10].
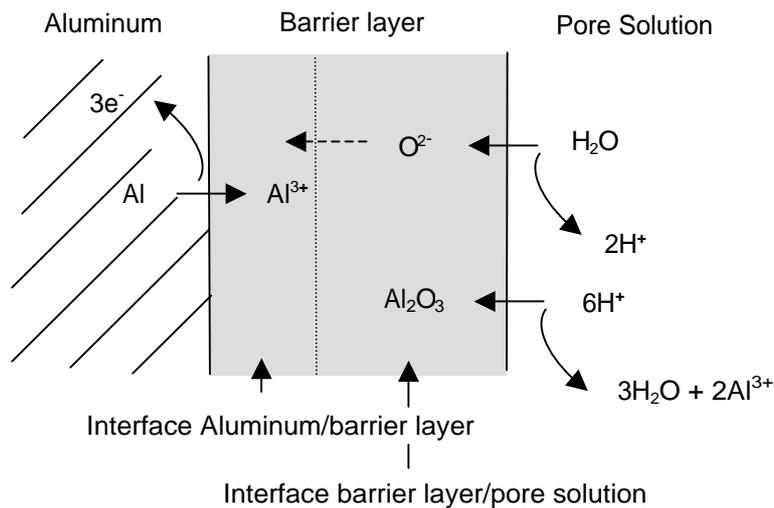
Aluminum   Barrier layer   Pore Solution

$3e^-$

O^{2-} H_2O

Al Al^{3+}

$2H^+$

Al_2O_3 $6H^+$

$3H_2O + 2Al^{3+}$

Interface Aluminum/barrier layer

Interface barrier layer/pore solution

Figure 3, The interfaces adjacent to the barrier layer[10].

Investigations by a group at UMIST[7,11] give a more complete explanation of the formation of porous oxide, gathering the above explanations to a final well-founded theory. They conclude that "In all cases of film growth examined, Al^{3+} and O^{2-}/OH^- are mobile; the latter always develops solid film at the metal/film interface whereas the contribution of outwardly mobile Al^{3+} ions to film formation depends upon the specific conditions of anodic polarization"[7].

The initial stages of oxide growth correspond to a relatively uniform oxide thickness but by the egress of aluminum ions into the electrolyte penetrations paths will develop in top of the barrier layer. The local field will be concentrated in these penetration paths giving a field strength of up to about 2.1×10^7 V/cm [11]. Between these penetration paths there will be a decrease in field strength and hence a decrease in the field assisted dissolution rate. As a consequence of these variations in the field strength the interface aluminum/barrier layer will adopt the form of a fine scalloped structure. By concentration in the barrier layer of the electric field and the ionic current, beneath the major pores, a steady state porous anodic film is formed.

With these explanations of fundamental oxide formation in mind, the influence on the current and voltage behavior during anodizing will be considered.

The current - time curve obtained during the first 100 seconds of the anodizing will be as shown schematically in figure 4. Here the process is performed with constant voltage during the anodizing process.

Period a in figure 4 shows the formation of the first microns of oxide. In the beginning the current is high due to the fact that the current only passes through the metallic aluminum. Then the current starts to decrease because of the formation of a thin non-porous oxide layer. This oxide layer has a higher resistance than the metallic aluminum. The increase in thickness and therefore an increasing resistance result in a further decrease in the current in period b.

The tendency of the curve to turn upwards in period b is due to small imperfections (roughness) in the compact oxide layer. These small imperfections are formed by the concentration of the current in areas with thinner oxide than on the rest of the surface. According to Keller et al.[12] these areas with the small imperfection are the subgrain boundaries found on aluminum. They stated that these areas are the places where the initial formation of cells starts. The natural oxide film on either side of these subgrain boundaries is not as compact or uniform as on the rest of the surface. Therefore these areas offer less resistance to the current.
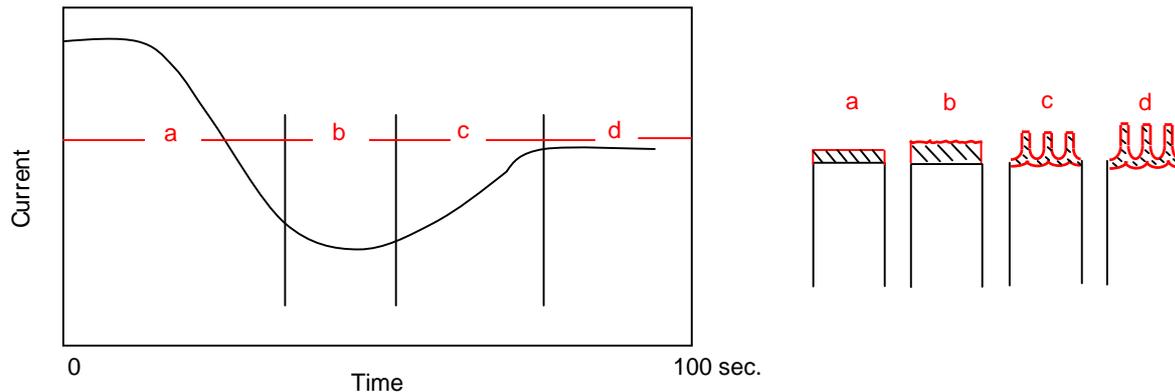

Figure 4, Current - time curve for a typical anodizing

Considering the formation of a single cell of oxide. At a single point the dissolution reaction is started, hence the oxide thickness is reduced and the current will start to flow to repair the damage. This will increase the temperature of the electrolyte and the solution will be more reactive and thus increase the rate of dissolution. This mechanism will perpetuate a pore once formed. According to Keller et al.[12] this mechanism could be halted. Therefore some pores will perpetuate and others will never get started.

Hence the current will concentrate on these small imperfections. This will increase the electrolyte temperature in these areas. Therefore the dissolution will increase and the oxide layer will become even thinner. The current will increase as seen in period c in figure 4. Now the formation of the porous oxide layer has started. In period d the current will reach a constant level where the rates of dissolution and formation of the oxide layer reach a steady state level.

2.5 Introduction to pulse anodizing

Pulsing between two values of direct current instead of using the same value during the whole process gives several possibilities for individual process conditions. A schematic diagram of square wave formed pulses is seen in figure 5. Many investigators have made suggestions of how these square wave pulses should be designed. Three different methods will be compared with conventional anodizing.

Another process type, which will only be mentioned briefly, is AC anodizing using alternating current with various frequencies instead of direct current. AC anodizing is not commonly used. This is due to the fact that AC anodizing requires higher voltage and about 50% more effective current than DC anodizing. This low efficiency is due to the cathodic period, where no oxide is formed. Another issue is the thickness of the film, since no film thicker than approximately 12 μm can be obtained[1].

Pulse anodizing using square wave-formed, low frequency pulses was invented by Yokoyama et al[13,14]. When dealing with low frequencies t_1 is often longer than t_2 with duration of pulses varying from 10 - 180 seconds. The voltages differ with the aluminum material and temperature of the solution. The current densities vary from 2 to 20 A/dm^2 and the preferred ratio is $i_2 = i_1 \times 0.75$. The magnitude of i_1 is dependent on the substrate.
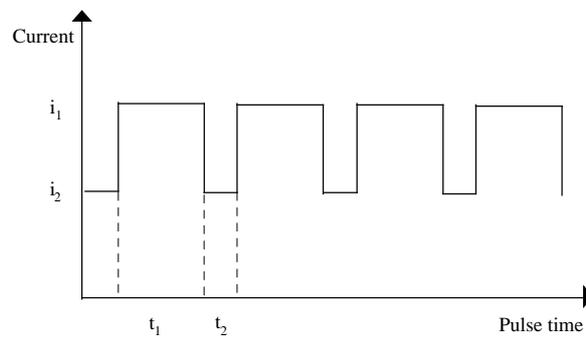
Figure 5, Schematic current - time curve for pulse anodizing showing the choice of parameters.

Yokoyama et al[13,14] have claimed that by pulsing between high and low voltage/current it is possible to increase wear resistance and corrosion resistance. They also show that they can improve the thickness uniformity and reduce the total time for the process. In addition, the low temperature used for making hard coatings can be raised and the maximum thickness can be increased.

The pulse time can differ significantly when square wave pulses are used. Pulses with high frequency in the order of kHz are described in many patents and articles, as invented for example by the Italian researcher Colombini[15].

The last method to be tested is the pulse reverse anodizing used by Okubo[16-18] in sulphuric acid. The pulse time is even shorter than the one Colombini claims to utilize and alternating anodic and cathodic pulses are used.

According to Wernick et al.[1] a cathodic reduction occurs in AC anodizing during the cathodic period. Similar arguments might apply to pulse reverse. The cathodic reduction is explained as the discharge of hydrogen ions that tend to destroy the oxide structure in the pores, or promote the chemical dissolution of the film. This could lead to an oxide layer with inferior properties compared with oxide layers formed by anodizing using a constant direct current.

Okubo[18] finds it evident that hydrogen gas is created in the interface between aluminum and the barrier layer destroying parts of the barrier layer oxide. According to Okubo[18] this destruction is one of the good part of using reverse pulse. The destroyed parts are the weak places in the barrier layer, which leads to microcracks. These microcracks will diminish the resistances of the barrier layer, hence the forming voltage will be less than in anodizing using a constant current. The rest of the oxide layer will consist of small cells, uniform and with big pore diameters.

One of the reasons for using pulse anodizing instead of conventional anodizing is a reduction in total treatment time and the possibility of avoiding burning and powdering problems. The next section will discuss these two destructive effects.

2.6 Burning and powdering

The interface between the barrier layer and the metal was described without considering the structure of this interface. Yokoyama et al.[13,14] claim that the interface is not smooth on a microscopic scale, as shown in the schematically drawing in figure 6. Metallic aluminum extends as many small projections into the barrier layer. During anodizing, the anodic current tends to concentrate on these projections giving an uneven growth and destruction of the oxide layer described as burning by the authors[13,14]. They explain the phenomenon as follows:

When the current density is high and the temperature of the electrolyte is low the balance between formation and dissolution is difficult to maintain. Hence the metallic needles will extend close to or even into some of the pores, see figure 6b). These metallic needles will transport the current easier than the aluminum

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oxide and give rise to a short circuit through the barrier layer in these pores. When the current density concentrates in these pores the temperature will raise at the bottom of the pores, see figure 7.
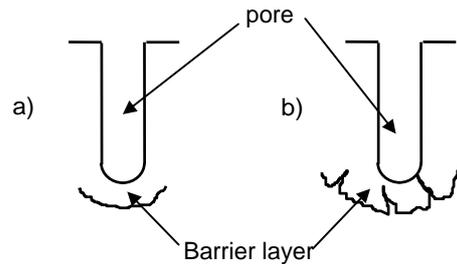

Figure 6, Schematic drawing of the interface between the barrier layer and the metal, a) low current density and high electrolyte temperature and b) high current density and low electrolyte temperature[13,14].

When the voltage U is maintained constant, we have by Ohm's Law:

$$U = R \times I.$$

In pores with metallic needles there will be a drastic increase in current, when $R \to 0$. The temperature will rise because of the effect $P = R \times I^2$.

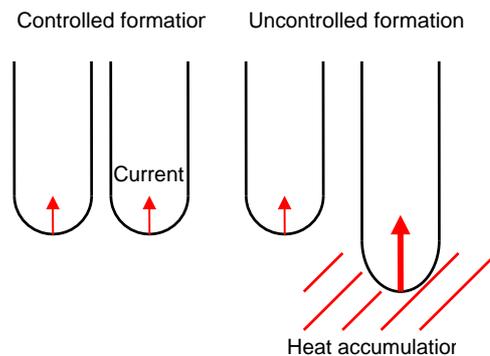In pores without metallic needles there will be a high resistance and only a small current flows.

Figure 7, Heat accumulation during uncontrolled formation of oxide

In pores with low resistivity formation of oxide will increase drastically. A thick oxide layer will be formed here and the temperature will increases due to Joule's heat, which will lead to an increase in the rate of chemical dissolution. Hence the oxide layer will be non-uniform and in some places the electrolyte even attacks the underlying aluminum.

To avoid burning the current density should be low. Hereby the chemical dissolution reaction (2), will be able to dissolve irregularities in the barrier layer. Hence anodizing will create a uniform oxide layer. However, lower current density means lower formation rate of the oxide, reaction (1), and hereby a longer treatment time to obtain a certain thickness of the oxide layer.

Powdering appears as a consequence of a prolonged treatment time. The acidic electrolyte will dissolve the aluminum oxide, reaction (2). Since the chemical dissolution is independent of the electrical field the attack on the oxide will happen everywhere on the surface, contrary to burning which is limited to certain areas.

Taking into consideration the variation in diameter from the top to the bottom of a single pore this can be explained. The cell width reported is almost 316 Å for a current density of 1.5 A/dm². Thus, as seen in table 2, anodizing for more than 60 minutes can give rise to a diameter at the top of the pore, which is wider than the cell diameter[2].

Table 2, Variation in diameter at the bottom and top of a pore depending on current density and anodizing time[2]

Current density [A/dm^2]	Anodizing time [min.]	Pore base diameter [Å]	Pore top diameter [Å]
1.0	30	120	159
1.5	30	120	182
1.5	60	120	246
2.5	30	120	208

Since the formation of oxide takes place at the bottom of the pores, the first formed oxide layer has been exposed to the electrolyte for a longer time than the rest. Hereby an etching of the oxide on the outer part of the oxide layer will take place, see figure 8. This results in an oxide, which will be powdered and soft.

Figure 8 shows three steps in the anodizing treatment. After a short time, as explained, the oxide will start growing. The structure will consist of regular cells. Continuing the formation of the oxide the outer part will start to dissolve chemically, after a while the top of the pore wall will be diminished.

This powdering effect is due to a combination of long treatment time and high concentration of the electrolyte. It can be prevented if a high current density can be applied and the concentration and temperature can be kept low.

Therefore to prevent burning it is advisable to[5]

- Decrease the current density
- Increase the temperature of the electrolyte
- Increase the concentration of the electrolyte

and to prevent powdering it is advisable to[5]

- Increase the current density
- Decrease the temperature of the electrolyte
- Decrease the concentration of the electrolyte

Aluminum before anodizing   Short term anodizing   Powdered oxide layer after long time of anodizing
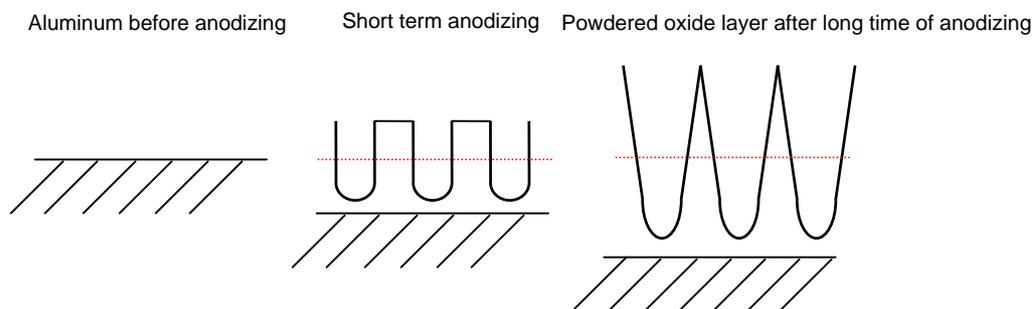

Figure 8, Schematical drawing of the powdering effect

If these criteria are compared, it is seen that in order to prevent burning, powdering will be favored and vice versa. By pulse anodizing both of these two phenomena can be reduced, as will be explained below and at the same time it will be possible to form a thick and dense oxide layer. Before going deeper into pulse anodizing the recovery phenomenon has to be described.

2.7 The recovery effect

According to Wernick et al.[1] Murphy gives an explanation of the recovery effect as follows:

> If an anodizing voltage E_1 is quickly reduced to a lower value E_2, the current falls to a very low value and may take a considerable period amounting to minutes to attain the steady state condition characteristic of the second voltage: but if the voltage reduction is carried out slowly the recovery is very much quicker.

This recovery effect, as claimed by Murphy[1], is affected by:

1. The values of E_1 and E_2 as well as the differences E_1-E_2.
2. The rate of change of E from E_1 to E_2.
3. The concentration of the electrolyte in which the anodic coating at E_1 was formed.
4. The temperature of the electrolyte in which the recovery process occurred.
5. The treatment of the anodic coating between the time E_1 was switched off and E_2 applied. Drying of the film between formation and recovery approximately doubled the recovery time.

Murphy postulated that readjustment of the barrier layer to the new voltage E_2 is field assisted. Therefore the recovery effect should be dependent on field-assisted migration of protons out of the film and/or neutralization of protons by field assisted migration of anions into the film.

Several years later Takahashi, Nagayama, Akahori and Kitahara[10] presented their explanation of the recovery phenomenon. According to these authors the main features of the recovery effect can be explained by figure 9.

When the high voltage E_1 is applied, the current will reach a steady level i_1, stage 1 in figure 9. In this period the barrier layer will reach a thickness d_1 corresponding to the forming voltage E_1. The structure of the cells will also be controlled by E_1.
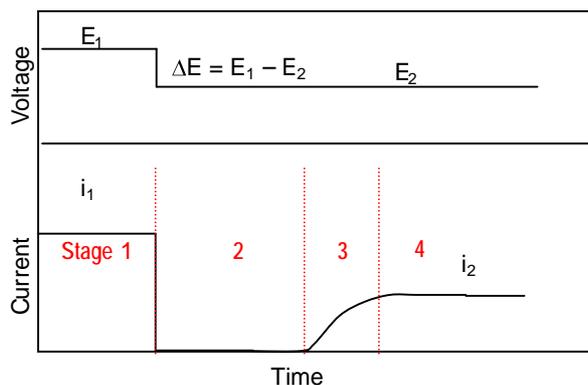

Figure 9, The recovery effect[10]

When the voltage is suddenly lowered to E_2 the current density will decrease drastically to a very small value as seen in stage 2. This small current density with values in the range of μA, corresponds to the very high resistance in the barrier layer d_1. The electrical field across the barrier layer in this period is very low. Hence the formation of oxide is almost zero and the field assisted dissolution also very slow. The main reaction in this period will be the chemical dissolution of oxide, reaction (2). This period is called the recovery period.

After a certain time, dependent on many factors such as alloying elements, concentration of the electrolyte, temperature and the value of ΔE, the thickness of the barrier layer has become thinner hereby increasing the electrical field across the barrier layer. Now the field-assisted dissolution and formation will take place

increasing the total dissolution rate as seen by the steep increase in current density during stage 3, due to a less resistance in the reduced thickness of the oxide layer.

After a while the current density will reach a steady level corresponding to the value of E_2, see stage 4. Now the barrier layer thickness has reached the value d_2 (less than d_1) that corresponds to the voltage E_2. The oxide will also adopt another dimension with smaller cells corresponding to E_2 and appearing beneath the oxide layer formed at E_1, see figure 10 below.

The dependency of the ΔE, as Murphy postulated, is confirmed by Takahashi et al.[10]. "The larger the value ΔE the longer is the recovery time t_2 beyond which the current increases steeply".

The structural change according to the different stages are as explained. In stage 1 the forming voltage has a value of E_1. Anodizing at this value will give a certain oxide structure a) in figure 10. Continuing treatment with this parameter will give a uniform oxide layer with an array of hexagonal cells of this size.

In stage 2 the forming voltage is abruptly decreased to a lower value E_2. This will make the electrical field across the barrier layer, which still has the thickness d_1, very small. This results in a zero formation rate of oxide. The dissolution will slowly increase during this period and the barrier layer will gradually diminish to an appropriate value, see figure 10 b).

In stage 3, the thickness of the barrier layer has reached a level where the field strength has increased enough and suddenly the current increases steeply. The new cells formed are smaller and with a barrier layer thickness d_2. In stage 4 the anodizing process continues at the current density i_2 creating a uniform oxide layer with characteristic array of hexagonal cells until the voltage is increased again.
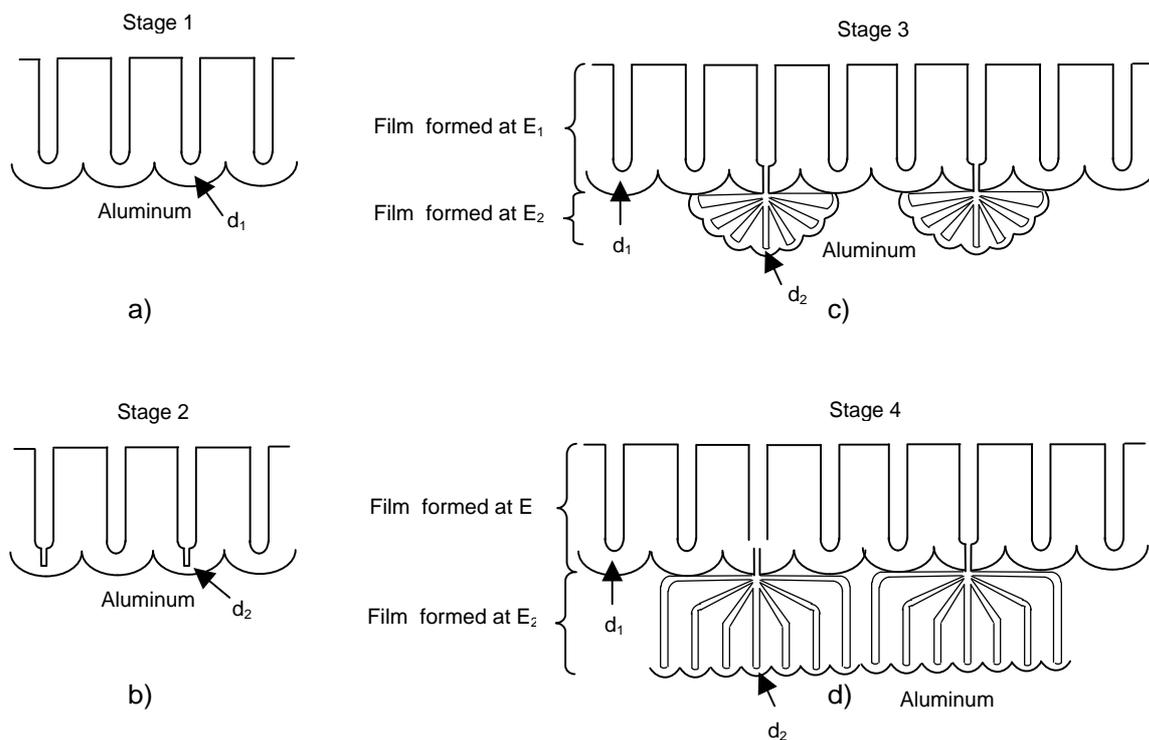

Figure 10, Schematic drawing of the structure of the oxide layer due to change in voltage[1,10].

3. Experimental

The samples used were panels, electrolytically degreased in an alkaline degreaser (15g/l NaCN, 15g/l Na$_2$CO$_3$, 60g/l NaOH) at 5V. Etched in a 60 g/l NaOH solution at 60°C and then in a 50 (v/v)% nitric acid solution at 20°C. The anodizing electrolyte was a 15 wt% sulphuric acid solution at the temperature 20 °C ± 1 °C with air agitation.

The software program CAPP (Computer Aided Pulse Plating) was used to make the pulse waveforms and coupled to an AXA 25V/20A rectifier. The eight sets of anodizing parameters used for the experiments were as follows, see table 3:

Table 3, Anodizing parameters for the various experiments.

Method	i$_1$	i$_2$	i$_{aver}$	t$_1$	t$_2$	t$_{total}$
Conventional*	2.7 A/dm^2	-	2.7 A/dm^2	-	-	24.7 min
Low frequency*	2.9 A/dm^2	2 A/dm^2	2.7 A/dm^2	60 sec	20 sec	24.7 min
High frequency*	3 A/dm^2	2 A/dm^2	2.7 A/dm^2	0.250 sec	0.1 sec	24.7 min
High frequency, reverse*	2.85 A/dm^2	2.85 A/dm^2	2.7 A/dm^2	0.071 sec	0.004 sec	24.7 min
Conventional, optimum	2 A/dm²	-	2 A/dm²	-	-	34 min
Low frequency, optimum	4 A/dm²	1 A/dm²	3.4 A/dm²	120 sec	30 sec	20 min
High frequency, optimum	2.6 A/dm²	2 A/dm²	2.43 A/dm²	0.250 sec	0.1 sec	28 min
High frequency, reverse, optimum	2 A/dm²	2 A/dm²	2 A/dm²	0.071 sec	0.004 sec	38 min

The parameters chosen to be held constant in the first experiment were the total process time and the average current density, designated by * in table 3.

The optimum conditions for the four methods were performed to see if these conditions were showing another result than the one using constant process time and average current density.

The samples were sealed in boiling water for 60 minutes corresponding to 3 min/μm. The total amount of coulomb was ~4080 C for each sample resulting in a thickness of ~22 μm.

The Electrochemical Impedance Spectroscopy was carried out on a Gamry Instrument, FAS1 Potentiostat/Galvanostat/ZRA using the software program CMS 100. The cell was consistent of a Standard Colomel Electrode (SCE) as reference electrode and titanium net plated with IrO$_2$, Permascand, as counter electrode. The electrolyte was a 3.5 wt% K$_2$SO$_4$. The results presented were measured at the potential +240 mV vs. reference electrode and a fixed amplitude of $\Delta E =$ 10 mV in the frequency range of 10 mHz $\leq$ f $\leq$ 65 kHz.

The abrasive wear test was a reciprocating test in accordance with the international standard ISO 8251, which is a wear test especially designed for abrasive wear measurements on anodized aluminum.

The tested part of the surface was 12 mm wide by 30 mm long and the diameter of the abrasive wheel was 50 millimeter. The test sample makes 40 reciprocal movements (cycles) per minute, giving a test time of 10 minutes per 400 wear cycles. After this the abrasive tape on the wheel was changed to give a fresh abrasive tape for every double stroke.

The wear W is presented as the number of wear cycles needed to remove 1 μm of the coating. The number of cycles was 1200 for most of the test. Except for the first wear test, performed on the old wear machine, where 1600 cycles were tested.

The hardness measurements were carried out by Knoop measurement.

The sealing test according to ISO 3210 was followed closely, except for the first degreasing step. This step was omitted due to the fact that these panels were tested immediately after finishing the anodizing and sealing process. The weight lost was measured at a calibrated weight, $\pm$ 0.1 mg.

The coloring electrolyte was a $SnSO_4$ solution used at room temperature, Alficolor S1, CANDOR Sweden past by from SAPA, Vetlanda. The only agitation was the movement of the sample during the coloring process. The coloring process was divided into three steps:

1. 60 seconds standby in the coloring electrolyte
2. 24 seconds with 20V applied
3. 330 seconds with alternating voltage, $\pm$ 20V

The color of the samples was measured on a MacBeth, Coloreye 3000, by Henkel against a standard HX30+/HX30- from SAPA, Vetlanda. When the samples were completely dry, measurement of the color difference on the color computer (CIElab, 10° observer, specular component included, UV in) using the original standard as reference (HX 30+ and HX 30-) was carried out.

3.1 Results

3.1.1 Acetic acid test
The five samples of each method showed no distinct corrosion attack on the surface after 1000 hour. Comparing the samples by the naked eye a matt finish is found on the sample after 100 hours in AAS. Though the rating, according to ASTM B537, depends on pits and none of the samples show pits.

3.1.2 Impedance test
The early studies of AC-impedance on the panels show a distinct variation in resistance of the porous layer R_p. The method using low frequencies has a resistance R_p which is almost 10 times higher than for conventional anodizing and anodizing using high frequencies, see table 4. It was not possible to obtain any impedance results of the oxide layer formed by reverse pulses using high frequencies.

Table 4, Results from the impedance test

Method	R_p	C_p
Conventional*	2802 Ohm	3.69 μF
Low frequency*	29403 Ohm	3.9 μF
High frequency*	2800 Ohm	1.4 μF
High frequency, reverse*	-	-

One of the reasons for not obtaining any impedance results from this method could be, according to the explanation about the barrier layer formed by this method. Believing that the barrier layer has been destroyed by the discharge of the hydrogen ions. The structure of this layer will influence the small alternating current used during the impedance test, so no results can be obtained.

The high resistance of the oxide layer formed by low frequencies could be due to the morphology of the porous oxide layer. According to Yokoyama et al[13,14] this structure will increase the corrosion resistance compared to the uniform structure with parallel pores. This seems to be true regarding the values of R_p. The R_p found for the high frequency pulse oxide layer has the same value as the R_p for the conventional formed oxide layer. This could indicate that the morphology of the oxide layer does not have the same sandwich structure as the low frequency oxide layer. One of the explanations is that the time of the base pulse, which is 100 milliseconds, is too short. This period with low current is not long enough to utilize the low voltage to make pores with smaller diameter and a thinner barrier layer and thereby will the pores presumably be of another structure, as claimed by Colombini[15].
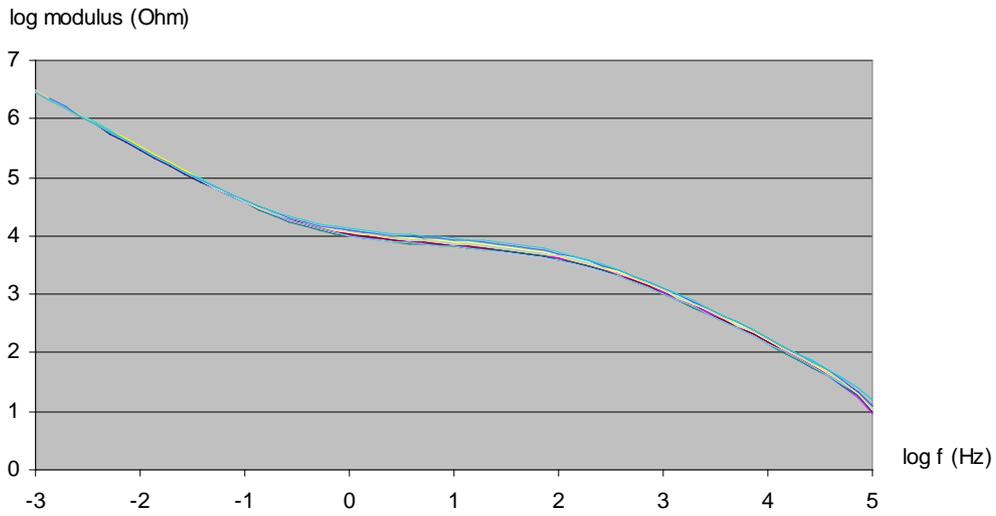
log modulus (Ohm)

Figure 11, Bode plots of the last tests anodized by the four methods, optimum on cylinders.

Figure 11 shows the result of all the samples anodized by the four different methods. It is evident that no variation is found in this test method despite the variation in pulse parameters.

3.1.3 Wear test

Figure 12 shows the wear resistance of the various methods from table 3. The best wear performance was found by conventional anodizing using 2.7 A/dm². Comparing this value with the one seen for the conventional, optimum anodized samples using 2 A/dm² a lower wear resistance of the oxide layer formed by the optimum parameters was found. This is due to a longer treatment time for the latter method.
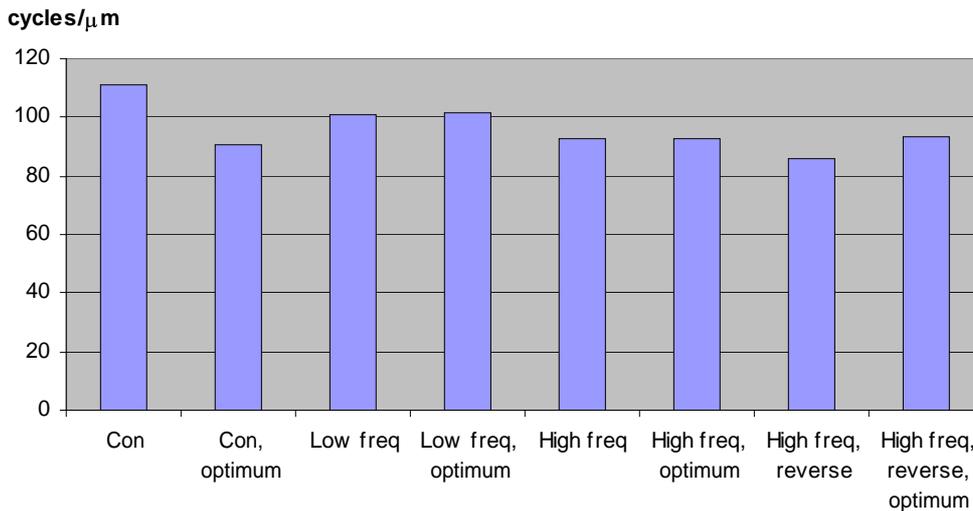

Figure 12, Diagram showing the wear resistance of the oxide layer formed by the four methods

The two bars showing the wear resistance of the low frequency anodizing are almost identical. Indicating that this method is independent on the current density used which could be possible due to the sandwich structure. The two methods using high frequencies results in a less wear resistance than for the two other methods.

The pulse methods using only anodic pulse, low and high frequency, showed no distinct variation in wear resistance for the * and the optimum parameters, see figure 12. Indicating that the optimum values of these parameters were not found. These optimum parameters were chosen from literature[13,14,15] and from advises obtained during conversation with some of the factories using the two methods.

3.1.4 Hardness test

The results shown in figure 13 indicate that the hardest oxide layer is found on the samples conventional and low frequency anodized with optimum conditions. The values are the average of the measurements of 15 indentations on three samples.

The very low value of the high frequency reverse anodizing can be due to the anodic treatment time, which is 38 minutes for this method resulting in an increased exposure of the oxide layer to the acid. Though also the conventional anodizing have a long treatment time (34 min.) but this value is not as low as the one for high frequency reverse. The rest of the methods show almost identical values.
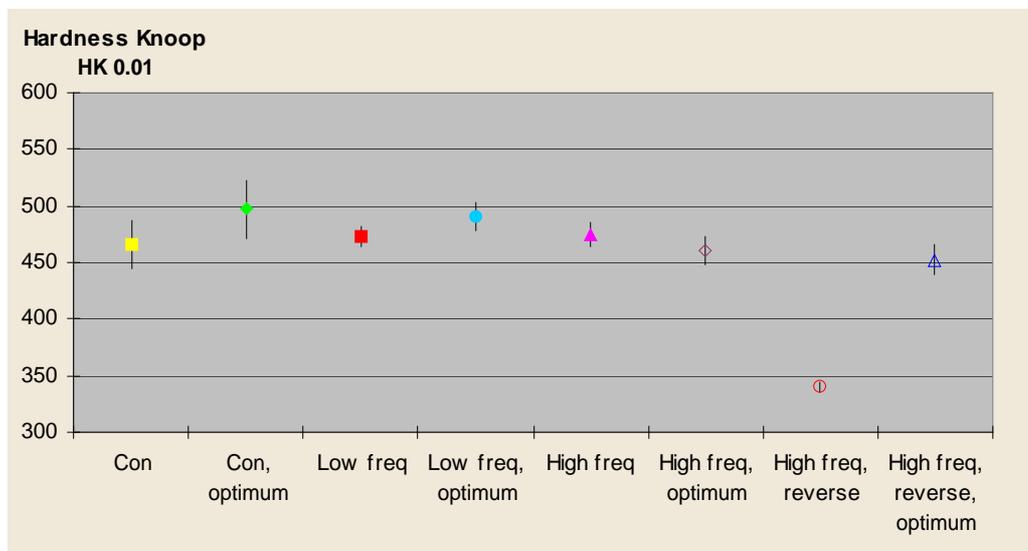

Figure 13, The Knoop hardness of the various anodizing treatments.

3.1.5 Sealing test

In figure 14 the results from the sealing test are found. The weight loss of the sealed oxide layer gives an indication of how well the oxide layer has been sealed. Normally the weight loss should be less than $25 - 30$ mg/dm² to pass. To test if different structures of the oxide layer would give a variation in the sealing quality this test was done on samples anodizing with optimum conditions. It is evident that a very small variation is found in the diagram in figure 14. The three methods, conventional, high frequency and high frequency reverse have almost the same weight loss. The low frequency samples show a minor increase in weight loss compared to the other three. This can be due to the expected sandwich structure of the oxide layer, which could be more difficult to seal properly.

The low frequency experiments show the poorest sealing quality according to the test. Looking at the standard deviation, illustrated by the vertical lines in the diagram, it seems evidently that the four methods is almost identically. Taken the procedure of the test method into considerations it seems clear that variations seen in the diagram are infinitesimal. The reproducibility of the various steps are very much dependent on the temperature in the room where the test is made. Also the time between the various steps is a source of error.
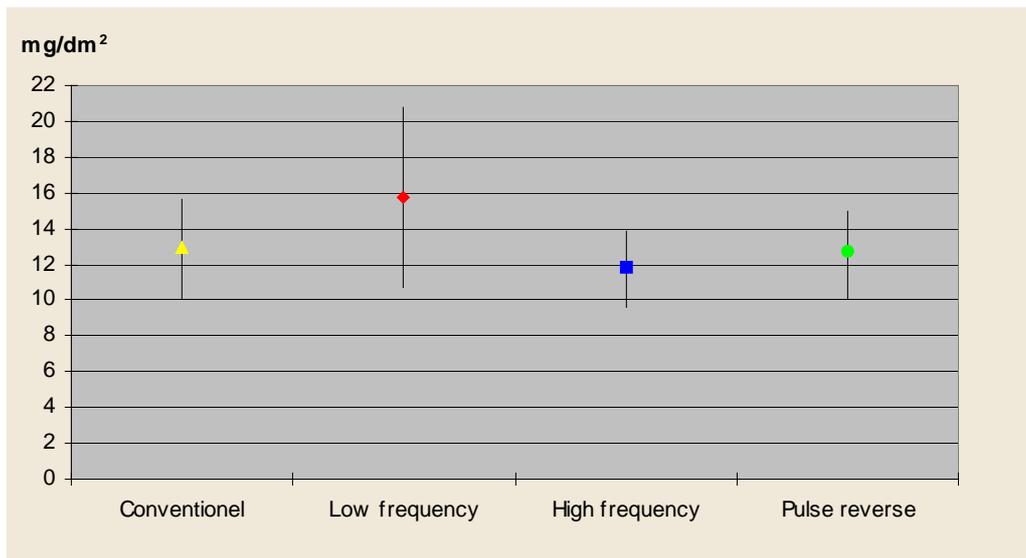

Figure 14, The results from the sealing test, ISO 3210

In the testing procedure performed in the laboratory the oven was place in another room with another temperature. Bringing the samples back and forward could make a small difference in dryness of the sample. The weight reductions between each step are in the range of $1 - 2$ mg, resulting in a test, which is very sensitive.

3.1.6 Electrolytical coloring
By visually inspection it was found that the low frequency samples showed a lighter performance of the color than the rest of the electrolytically colored samples. By the coloring inspection method used the ΔE value is the most important one.

These values of the colored samples are found in table 5. A small value of ΔE indicates values near the standard. It seems like from these values in table 5 that the low frequency samples are the one nearest the standards, both regarding the HX30+ and HX30-.

A visual look at the samples gives another impression. Here the low frequency samples show a lighter appearance than the rest. The color method is not designed for colored anodic oxide layers but to measure the color of paints. Paints are less transparent making this measuring method more suitable for measuring paints than colored oxide layers.

Table 5, ΔE values of the colored samples

Sample	ΔE, against HX 30+	ΔE, against HX 30-
Conventional, optimum		
KON 5-14X	2,4	7,0
KON 5-15	1,7	5,2
KON 5-16	2,6	7,2
KON 5-17	3,9	8,8
KON 5-18	2,3	6,7
Low frequency, optimum		
NAG 5-14	1,5	6,2
NAG 5-15	1,2	5,5
NAG 5-16	1,3	5,1
NAG 5-17	1,1	5,5
NAG 5-18	1,4	6,3
High frequency, optimum		
COL 5-13	2,4	6,8
COL 5-14	1,8	5,6
COL 5-15	1,7	4,9
COL 5-16	1,9	6,1
COL 5-17	2,1	6,1
High frequency, reverse, optimum		
OKU 5-14	2,3	6,9
OKU 5-15	2,0	6,6
OKU 5-16	3,1	7,9
OKU 5-17	2,8	7,5
OKU 5-18	2,5	7,2

3.2 Discussion

The present work is an extensive study of pulse anodizing on the extruded 6063 alloy. The pulse anodizing methods investigated were: low frequency, high frequency and high frequency, reverse pulse anodizing. These three methods were compared with conventional anodizing.

The four anodizing methods were all investigated by optimum conditions and conditions using constant average current density during a constant treatment time. All samples were sealed except in very special occasions.

To obtain an expanded understanding of pulse anodizing of the 6063 alloy, the recovery phenomenon was investigated. The time of recovery, when pulse anodizing the 6063 alloy, was found for various parameters of E_1 and E_2. It is important to be aware of that the barrier layer has time to recover.

Turning to the comparison of the four methods:

The AAS test:	no difference
The impedance test:	no difference
The wear resistance test:	conventional* and low frequency* show a minor increase
The Knoop hardness test:	conventional, optimum and low frequency, optimum show a minor increase, high frequency, reverse* a decrease
The structure of oxide layer:	no difference
Sealing test:	low frequency shows a minor decrease
Coloring test:	visually low frequency show a minor variation compared to the three other methods

The final conclusions of the comparison must be that: when anodizing a 6063 alloy to a thickness of 20 μm, non of the four methods indicate a superior behavior. The only reason for choosing pulse anodizing when maximum thickness of the oxide layer is 20 μm will be the shorter treatment time of the anodizing process. The decrease in time can be up to 10 − 15 minutes depending on the parameters chosen. Though it is important to realize that coloring of the anodic oxide layers made by low frequency will give a lighter performance than with rest of the methods. Therefore it is necessary to compensate for this by a few seconds longer in the electrolytic coloring bath.

4. How to implement pulse anodizing

In order to implement pulse anodizing in the conventional shop, a few but very important aspects have to be considered.

First of all the shop must acquire a considerable amount of theoretical knowledge about the principles of pulse anodizing. This is not merely to gain basic understanding of the process, but indeed necessary in order to obtain the expected advantages of pulse anodizing during the daily production.

Secondly, something that almost always needs to be changed when implementing pulse anodizing, is the rectifier[19]. The rectifier should have the possibility of giving current densities ranging from 2 − 20 A/dm^2, also for conventional anodizing in order to obtain the time reduction for the process. The rectifier must be coupled to a monitor showing the online current − voltage curve as the process progress.

Finally, when using pulses for conventional anodizing, sealing should not be made a bottleneck. Therefore it is often necessary to install an extra sealing tank.

Having made the necessary investments in knowledge and equipment, the task of managing the process begins. It is important to find the recovery period by using voltage control test. This should be done with different alloys but also with different customer products.

Vigorous agitation must be used during pulse anodizing, primarily to maintain the temperature low in the electrolyte and in the growing oxide layer. Often air is used for cooling but this has some disadvantages, such as a high fume level and a reduction of the conductivity of the solution due to the non-conducting nature of the air bobbles. Using the electrolyte for agitation through flow eductors, will give a better uniformity of the temperature and it is possible to direct them at the work.

The advantages of pulse anodizing are numerous, most important the time reduction per load, which can often be reduced by as much as 25% or more.

A more uniform oxide layer, will also be found, with the possibility of being able to hard anodize difficult alloys with a higher wear resistance of the hard anodized oxide layer. Turning to hard anodizing it is mostly the time reduction again which give the very hard and dense oxide layer.

Using current control when pulse anodizing a more even oxide layer is formed from one load to another, given better coloring results.

The advantages of pulse anodizing are there to pick and the fruits are big and ripe, but they are not hanging on the low branches of the tree.

5. Acknowledgement

SkanAluminum, Oslo, Norway

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