

Pulse Anodizing – An Overview

V. Raj, M. P. Rajaram,
G. Balasubramanian,
S. Vincent and
D. Kanagaraj

Central Electrochemical Research Institute,
Karaikudi-630 006, India

Dr. V. Raj has completed his B.Sc. (1988), M.Sc. (1991) and Ph.D. (1999) degrees in chemistry from Madurai Kamaraj University, Madurai. He has 10 years of experience in teaching and research and has worked as a lecturer, SN College, Madurai for one year. Since 1997, he has been working as a scientist at Central Electrochemical Research Institute, Karaikudi. His fields of interest are anodizing, electrochemical and chemical deposition, electrochemical and chemical polishing of metals. He has published 10 research papers and presented thirty research papers at national and international conferences.

Dr. D. Kanagaraj, senior scientist, obtained his B.Sc. and M.Sc. degrees from the University of Madras with specialisation in inorganic and analytical chemistry. He obtained his doctoral degree in industrial chemistry from Alagappa University, Karaikudi. He has been working as a scientist in Central Electrochemical Research Institute, Karaikudi since 1964. He has long experience in the field of anodizing and metal finishing, and has 15 patents and published more than 50 research papers in reputable national and international journals. He has developed improved technologies to Indian industries in the field of anodizing.

Sri S. Vincent obtained his B.E. degree from Madurai Kamaraj University, Madurai in Electrical and Electronics Engineering in 1989. He received his M.S. degree from BITS, Pilani in Electronics and Control Engineering in 1994. Presently he is studying for his Ph.D. He has been working in the Electrochemical and Electronics Instrumentation division of Central Electrochemical Research Institute, Karaikudi since 1982. His fields of interest are electrochemical instrumentation, microprocessor and computer based instruments. He has 10 patents to his name and published more than 30 research papers in reputable journals.

M. P. Rajaram and G. Balasubramanian are in the final year B.Tech. degree in Chemical and Electrochemical Engineering. Both are working on various projects related to electrochemical engineering and each has published 2 research papers.

*Corresponding author: Dr. V. Raj,
E-mail: alaguraj2@rediffmail.com.
Fax: +91-4565-427779, 427713

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SUMMARY – Anodizing is a versatile method used to prevent a metal from corrosion by forming an oxide coating over its surface. Various power supplies such as D.C., A.C. and A.C. superimposed on D.C. are used in industrial anodizing depending upon the different fields of application. For specific applications, especially for hard anodizing of aluminium containing high copper and silicon, the importance of the pulse current technique has been recognised. This paper reviews the entire history of pulse anodizing of metals such as aluminium, drawbacks of other existing power sources, advancement of pulse power sources and applications of pulse current techniques in various types of anodizing such as general pulse anodizing, pulse hard anodizing and pulse colour anodizing.

Keywords: Anodizing, Pulse current, Pulse Voltage, Duty Cycle and Frequency.

INTRODUCTION

Anodizing is one of the best methods of producing a protective coating on aluminium and its alloys. With the advancement in the use of aluminium from kitchenware to space applications, the demand for anodized aluminium is ever increasing. Thus, several anodizing techniques have been used to produce oxide films on aluminium alloys for use in different fields. The natural oxide film formed on aluminium will protect the metal under mild service conditions. However, by subjecting the metal to anodic oxidation, many desirable properties such as higher thickness, hardness, good corrosion resistance, higher abrasive and wear resistance can be imparted to the metal depending upon its end use. Generally for decorative and architectural applications, anodizing is carried out conventionally followed by colouring by chemical or electrochemical methods. For industrial and engineering applications, the oxide layer must be both thick and compact which can be done only by hard anodizing. The anodic process provides a suitable surface or base for subsequent electroplating, painting and colouring and also the nanoporous aluminium oxide films can be employed as templates for preparing nanomaterials.

TYPES OF POWER SOURCES USED IN ANODIZING

D. C. Anodizing

Bengough and Stuart^{1,2} introduced the process of anodizing in chromic acid electrolyte in 1923 using a voltage cycle for different time intervals using a D.C. power supply. Later on, in 1927, Gower and O'Brien³ developed sulphuric acid anodizing process containing 1.7 – 3.7 M sulphuric acid operated at 18–25°C using a current density of 1.2 – 1.8 A dm⁻² for 10–45 minutes using three-phase rectifiers. The oxalic acid process was patented by Kujirai *et al.*⁴, but it required the use of high voltage. In order to develop an oxide coating with specific properties for a given end use, addition of organic acids to sulphuric acid electrolyte has been reported. Some of these additives produce harder films but at relatively

higher anodizing voltages than the conventional anodizing voltage. Moreover the side products due to the decomposition of organic compounds may not be beneficial to anodizing and sometimes lead to the corrosion of the material subjected to anodizing.

A.C. Anodizing

In A.C. anodizing, the oxide film obtained is highly flexible and the hardness of the oxide film is inferior to that obtained with D.C. anodizing. Generally oxalic acid is used for A.C. anodizing to produce flexible oxide films on aluminium wires that are used for transformer windings. When sulphuric acid is used in A.C. anodizing, sulphur compounds will be deposited into the pores of the oxide film and hydrogen sulphide will be evolved. Further, it gives a non-uniform colour, therefore addition agents are used to prevent the deposition of sulphides in the oxide film that are responsible for the inferiority in the quality of the oxide film.

A.C. Superimposed D.C. Anodizing

In the case of aluminium alloys containing higher percentages of copper and silicon a better quality of coloured oxide coating could not be achieved by D.C. anodizing even with the addition of organic acids to the anodizing electrolyte. In the D.C. anodizing process, an initial passivity of the anode takes place due to polarisation which leads to heating of the anode surface during the formation of the thick hard anodic film. This problem is of more significance when attempting to anodize highly alloyed aluminium materials as ultimately the process ends with “burning”. By superimposing an alternating current in the form of a ripple on the direct anodizing current, the adverse effect of anode polarisation can be overcome to some extent. However the provision of the superimposed alternating current on the direct current requires relatively complicated, expensive and inflexible circuitry. In addition, the pattern of heating at the anode surface when the current density is increased cannot be resolved.

Pulse Anodizing

Anodizing using a pulse current technique can overcome all the above mentioned disadvantages that occur with other anodizing processes. Pulsing of the entire anodizing




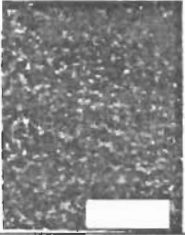

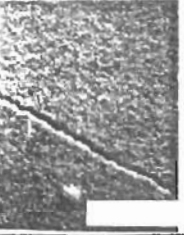


	DIRECT CURRENT		PULSE REVERSE CURRENT	
	0.5 A/dm ²	2.0 A/dm ²	$t_a=20$ A/dm ² , $t_c=0.1$ sec, $t_s=0.04$ sec $t=1.5$ A/dm ²	$t_c=1.5$ A/dm ²
NMF-water BATH				
DMF-water BATH				

Figure 1. SEM images of D.C. and pulse plated nickel deposits (After J. P. Celis et al. AESF 3rd International Symposium on Pulse Plating, 1986, 151)

pulse current not only decreases the anode polarisation but it also provides a cooling period between each interval of current flow at the anode surface. This permits higher current densities to be used without excessively increasing the reaction of the electrolyte on the anodic film. Pulsating anodizing current results in the production of relatively thick and hard anodized film which is carried out in a quicker work cycle than required by prior processes.

An example of the improvement in coating that can be obtained by using pulse plating is shown in Figure 1 where Ni deposits produced by this process show superior properties to those obtained by D.C.

DEVELOPMENT OF PULSE EQUIPMENTS

About four decades ago, in 1960, Miller⁴ used unidirectional current pulses for anodizing aluminium and its alloys with a frequency of 60 Hz. Initially the pulse current anodizing was done manually with the time interval in minutes and complicated, large phase shifting and pulsing circuits were used. In 1970, The Seionics Corporation⁶ used both positive and negative current pulses adjustable to achieve different values that are sensed and used to maintain automatically the values for anodizing of aluminium alloys. The authors used the ratio of negative to positive current of about 1:3 for obtaining thick and hard oxide coatings. Moreover additional means were used to improve throwing power eliminating negative current and using capacitors or inductors to prolong decay of positive pulse. Permaloy Corporation⁷ carried out anodizing of aluminium alloys with average direct positive voltage interspersed with applied peak pulses of higher level positive current voltage and with a waved pattern. The power supply

system has a capacity of $I_a = 1000$ A and $I_p = 5000$ A. This process is not an On-Off type but pulses are superimposed on a D.C. current. It can be applied to anodizing of aluminium alloys to form thick oxide coating. Polf⁸ used a special three-circuit pulse rectifier from which the output power was distributed to the three anode bars over the anodizing tank for hard anodizing of aluminium and its alloys. It was possible to increase the hardness as there is a voltage drop between the three work holding bars and, because of the difference in current wave form, there is an interaction of current from one bar to the other.

In 1974 Seisako^{9,10} patented an electrolytic treatment apparatus for the colouring of anodized aluminium alloys which contains a pulse generator placed between the electrodes and connected to ammeter for detecting the final current to the by-pass circuit. The by-pass circuit is a key element between the electrodes which generate a signal to control the by-pass. This circuit has more complications and exhibited a lower efficiency. Later the author designed another apparatus which has a by-pass circuit between the electrodes connected to a semiconductor device. Kondo et al.^{11,12} designed an electric cell equipped with an electronically controlled

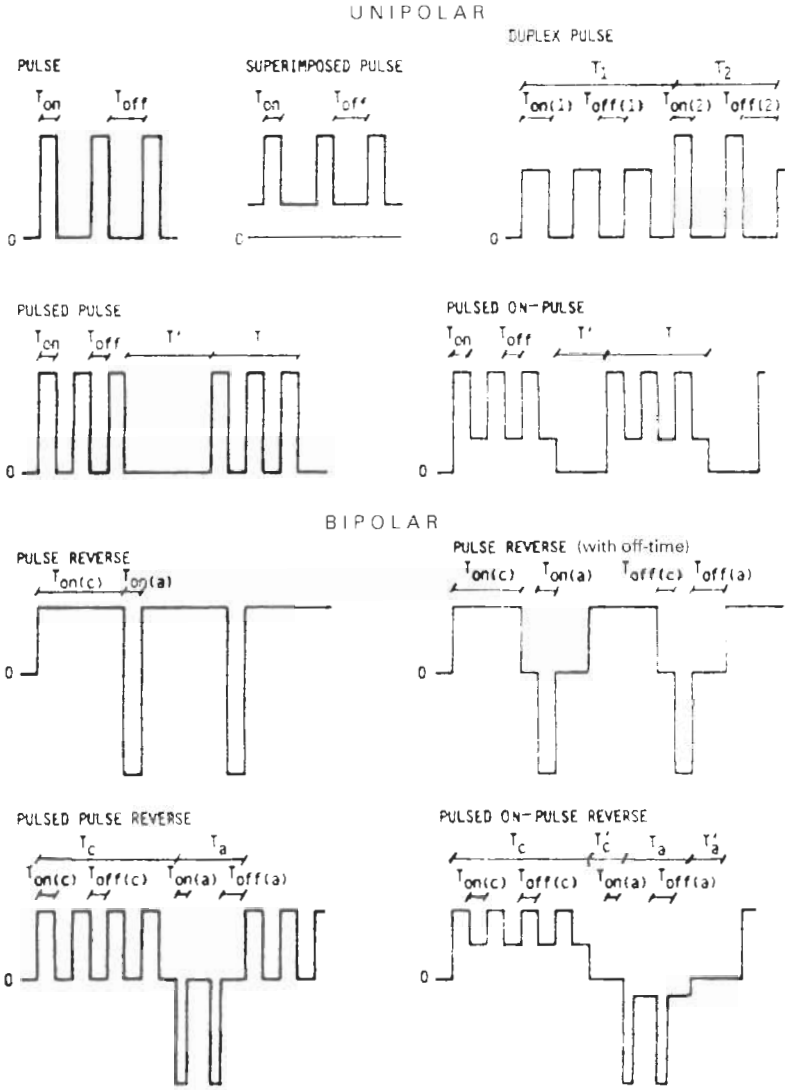


Figure 2. Diagram showing various types of pulses possible (Adapted from J. Cl. Puppe, AESF 3rd International Symposium on Pulse Plating, 1986, 6)

switching device that bridges the electrodes for colouring of anodized aluminium. The switching device that allows the precise control of pulse characteristics is controlled by a signal from an electric current detector. The author devised equipment for colouring aluminium with good colour reproducibility. Here the D.C. source for supplying pulse current was equipped with a device for regulating the pulse characteristics and another device for regulating the peak voltages. Sugiyama *et al.*¹⁴ designed an apparatus for electrolytic colouring of anodized aluminium and its alloys. By passing the current through the impedance connected parallel to the cell, the characteristics of pulsed potential were achieved. The current loss can be significantly lowered by regulating the by-pass current.

In 1982, Okubo¹⁵ carried out anodic oxidation of aluminium alloys with a D.C. rectangle inverter by the current inversion method. Chuo Seisakusho Ltd¹⁵ designed an apparatus for the pulsed D.C. anodizing of aluminium. This apparatus is useful for colouring anodized aluminium, and a pulsed D.C. voltage can be supplied to both electrodes. Scheineder *et al.*¹⁶ constructed a pulse generator, which was appropriate for the production of simultaneously doped Al_2O_3 layers. This pulse generator was distinguished by polar and bipolar operating modes with continuously controllable voltages up to 380V and current up to 60 A with pulse durations from 200 milliseconds to 30 seconds.

In 1986, our group¹⁷ fabricated a microprocessor unit to carry out pulse anodizing of aluminium and its alloys to produce thick and hard oxide coatings. The pulse unit consists of a programmable D.C. power supply unit, a microprocessor unit, a 16-bit D/A converter and other interfacing chips. Using software, the following functions of output were varied: (i) type and magnitude of pulse current, (ii) steady state D.C. current, (iii) period, (iv) number of pulses and (v) temperature of the bath. The advancement of the microprocessor, the personal computer allows easy program modification and the operation of many units from a centralised location. The main advantages of user interface include reduced energy and labour consumption. Colombini¹⁸ used pulsed rectifiers to compare the anodizing of aluminium in 1.94 M sulphuric acid at 20°C by applying a current density of 1-2.5 A dm⁻² using conventional rectifiers. The pulse rectifiers with a pulse level 1.5 times higher than the base level had weight losses lesser than conventional rectifiers with sliding brush control or SCR control.

For many years, pulse rectifiers with silicon controlled rectifier were used. As these cannot meet the need of faster rise and fall times, and higher pulse rates, linear series pass power supplies were used. These are very versatile and can be configured as either voltage or current source. However, much of the energy is dissipated and the power supply efficiency is less than 50% and is highly complex. To overcome this disadvantage, switch mode power supplies were used. These had increased bandwidth and were more compact, but for higher output transformer losses increased and the rapid change of current

levels imposed severe damage on semiconductors. These considerations limit their uses to a maximum of 250 KW.

In 1994, Colombini¹⁹ studied the effects of current wave residues on the properties of anodized aluminium oxide coatings. He recommended that rectifiers for hard anodizing be fitted with a smoothing filter comprising inductance and mutually compatible capacitors. Juhl *et al.*²⁰ compared four different pulse anodizing processes for anodizing AA 6063 aluminium alloy. Over the years, various waveforms were suggested, some squared pulse and others sinusoidal. Pulse time was another parameter varied between milliseconds and minutes. Colombini *et al.*²¹ discussed the advantages of computerised pulse rectifiers for hard anodizing of aluminium and its alloys. These can be used with printing devices to print out directly the V/I diagrams and the different pulse parameters.

In 2000, Rasmussen²² applied a plurality of pulses for hard anodizing of aluminium. The pulses have a pattern that has three magnitudes. He used a first magnitude of about 6 A dm⁻² and a third magnitude of 1 A dm⁻². The duration of the high magnitude portion of the pulse was 30 seconds and those of the zero magnitude and third magnitude portions of the pulse were about 10 seconds. Recently, Wen²³ invented an intelligent, high capacity and high speed reverse current pulse power supply which can be used for hard anodizing of aluminium and its alloys. The pulse power supply consisted of a power supply unit and measurement displaying unit. The power supply unit comprised a rectifying circuit and control circuit. A high power semiconductor auto-switch was used as the primary switch device. Close-loop feed back PWM real time control was adopted for controlling anodizing bath current and voltage separately. The pulse parameter adjusting system was formed from computer software.

Table I summarises the chronological development of the equipment used and Figure 2 and Table II illustrate examples of pulse regimes and conditions used for anodizing processes.

PULSE ANODIZING

In 1960 Miller¹ patented the pulse current anodizing with unidirectional current pulses of repetition frequency of 60 pulses per second in a 2 M sulphuric acid + 0.079 M oxalic acid bath at a temperature of 38° - 42°F (-4 - 6°C) and a current density of 20 A dm⁻² for a period of about 10 minutes. The time interval between the pulses was approximately 3 times that of the pulse width. A film of thickness 50-87.5 µm was obtained. The current recovery effect during pulse anodizing of aluminium was observed by Murphy *et al.*²⁴. Kazuo *et al.*²⁵ carried out the anodizing of aluminium alloy in sulphate solution using an interrupted current ratio of 1:1 with a pulse time of 30-60 seconds. The power required for anodizing was also reduced. The effect of pulse rates on voltage, average time, coating ratio and coating thickness were studied for various alloys. Murdock Inc.²⁶ patented the anodizing of aluminium using current pulsing,

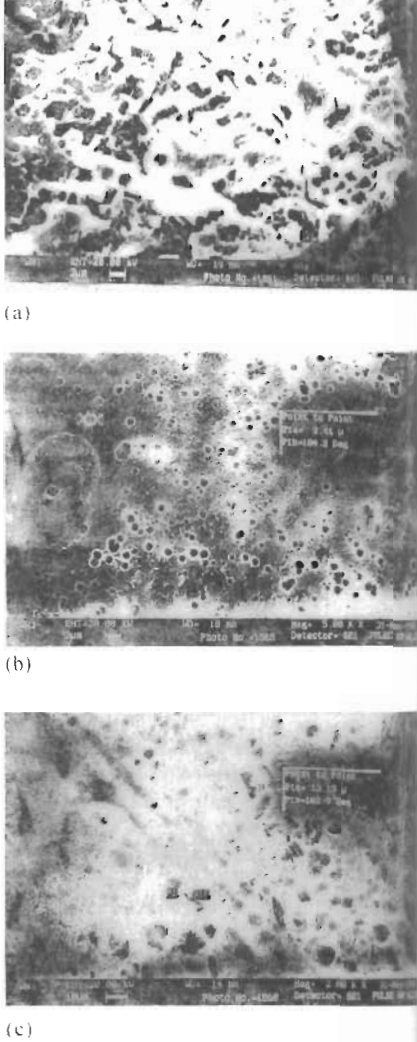


Figure 3 SEM images of pulse anodized aluminum at C.D. of 2 A dm⁻² 80% duty cycle and frequency 0.1 Hz, formed from 15% sulphamic acid at 30°C. (a) AA1100 alloy (b) AA1204 alloy (c) A16061 alloy

the amplitude of which is carried at frequency approximately 1/60 of the pulse rate. In 1972, Permaloy Corp.² patented the process of anodizing of aluminium alloy with average direct positive voltage interspersed with applied peak pulses of higher-level positive current/voltage such that time from average current peak current was greater than the time from peak current back to the average current.

In 1977, Takahashi *et al.*²⁷ anodized AA1100 aluminium alloy in 2.8 M sulphuric acid at 10°C using base and peak voltages of 0 and 35 V respectively with a pulse width of 48 ms to give a 30 µm oxide film. Macos *et al.*²⁸ produced an anodic oxide film on indium antimonide semiconductor surfaces using constant frequency pulses of varying amplitude. The thickness of the oxide film can be increased from 0.12-0.2 µm by applying pulse current instead of D.C. anodizing. The film growth under pulse conditions is time independent. The effect of pulse current parameters on roughness of anodic surface in electrochemical machining of steel and carbon alloy surfaces was studied by Orlov *et al.*²⁹ Some general laws covering the relationship between surface roughness and pulse parameters were also given. The decrease in

Table I. Time line inventions and discoveries on the technology of pulse anodizing.

Inventions	Year
A.C. superimposed on D.C.	1956
Pulse anodizing-manually operated	1960
Pulse superimposed on D.C.	1972-74
Pulse Silicon controlled rectifier (3-circuit)	1974-76
Pulse rectifier (by pass circuit)	1976-77
Electronically controlled pulsed on D.C.	1977-78
Pulse voltage	1979
D.C. Rectangular inverter voltage (switch mode)	1982
Microprocessor based pulse	1986
PC based pulse	1994
Squared pulse	1995-96
Computer controlled pulse	1998
Plurality	2000

surface roughness at significant current density was attributed to the increased effect of depassivation of anodic surface on pause time. Baba *et al.*³⁰ studied the pulse anodizing of aluminium in an oxalic acid bath, and its colouring mechanism.

In 1982, Yokoyama *et al.*³¹ anodized various aluminium alloys in sulphuric acid and oxalic acid baths. They described the advantages of pulse anodizing regarding hardness, thickness, power consumption, sale and production rate with respect to the conventional D.C. anodizing. By the use of electron microscopy they suggested a mechanism for the processes occurring during the recovery period. They observed that pulsing from a higher to lower voltage increases corrosion resistance, abrasion resistance, thickness and uniformity and reduces the total anodizing time and cooling cost. Mita *et al.*³² anodized aluminium in 0.05 M borax added to a 0.5 M boric acid or 9.08 M phosphoric acid bath, using a synthesised pulse wave by chopping a D.C. constant voltage source using a microcomputer and power transistor. When

the off-time was changed from 25 to 50 milliseconds, the barrier layer was chemically dissolved and no capacitance current was observed at the start of oxidation in 1 M sulphuric acid even when the current wave form for each pulse, every 25 milliseconds, was stored in the wave memory. Okubo¹⁴ studied pulse anodizing of aluminium AA2014, AA2017, AA2024 and KS-21 aluminium alloys with a D.C. rectangle inverter with pulse frequency ranging from 0.033 to 500 Hz in 6.67 M sulphuric acid and 0.79 M oxalic acid in order to improve the characteristics of anodic coatings. The peak current density was fixed at 4 A dm⁻² and duty cycle varied from 50-100%. Hardness, coating ratio and thickness of the coatings were found to increase by the current inversion method with 10 - 20 Hz and higher duty cycle. Yoshiumura Research Lab³³ anodized aluminium in an alkali bath using the current recovery method and studied the influence of electrolysis time and pulse width on thickness of oxide coating.

In 1984, Matsushita Electric Industrial Co.

Ltd³⁴ patented a process for pulse anodic treatment of aluminium foil at a frequency of 5-100 Hz and duty cycle of 40-95% in a bath containing Cl⁻ ions sulphuric acid or oxalic acid, thereby forming an oxide film with simultaneous etching of foil. Huang³⁵ applied a series of pulse galvanostatically for the study of the anodizing of aluminium in sulphuric acid. Application of 2-step pulses showed a better coating efficiency and formed better oxide films. Different oxide formation mechanisms were observed for 3 potential ranges obtained from the log I-E curves. From the magnitude of the critical current coating, the efficiency of different systems were compared.

Our group¹⁷ used microprocessor controlled pulse power source for anodizing of aluminium and its alloys, compared both D.C. anodizing and pulse anodizing in sulphuric acid at a temperature of 20°C with frequencies ranging from 300 Hz for a period of 30 minutes. The maximum oxide film thickness of 45 µm was obtained by passing a current of 720 C. The pulse frequency of 125 Hz. The group studied the influence of 'On' and 'Off' time frequency of the pulse on the properties of the oxide coating and reported that pulse anodized aluminium yields better quality oxide film than that of D.C. anodized aluminium. Mita *et al.*^{36, 37} anodized ADC 12 aluminium alloy die castings in a sulphuric acid bath with concentration 1-5 M with a duty cycle of 50-100 milliseconds at temperatures ranging from 30°C. The current wave was varied from anodic to cathodic forming a barrier film to cathodic forming a porous film. When aluminium was pulse anodized in 0.3 M trisodium phosphate with addition agents such as 0.1 M sodium tartrate and 0.2 M potassium fluoride at porous film forming waveforms, the oxide film was lustrous and non-powdery. The authors anodized Al-Si alloys containing 12% silicon using pulse waves in sulphuric acid as electrolyte with a constant voltage of 5-40 V. They studied the relationship between increase of silicon content and the current density. The current density capacity at 4 A dm⁻² reached a maximum value when the aluminium alloy contained 4-6% silicon. Okubo *et al.*¹⁴ anodized aluminium with pulse current having a negative current component in a 2.5 M sulphuric acid bath at a pulse frequency of 13.3 Hz reversing cycle and a duty cycle ranging from 76-100% and studied the effect of duty cycle on the properties of the oxide film. They found that hardness, coating ratio and thickness improved for duty cycle of 95%. The coating grew faster at current densities of 2-6 A dm⁻² and the pores were uniform and small in size. They investigated the anodizing of aluminium in oxalic acid solution including the effect of temperature. Thick coatings could not be obtained at high negative current densities. They controlled current densities and decreased temperatures, hardness of the coating increased. At 10°C and current density 4 A dm⁻² and an anodizing time of 30 minutes the hardness of the coating was 600 Hv. Here they observed the cell size to be uniform and pores were divided into branches.

Table II. Conditions of pulse anodizing process (current density 1, 2 and 3 A dm⁻²)

Duty cycle	Frequency /Hz	On /s	Off /s
20%	0.01	20	80
	0.1	2	8
	1	0.200	0.800
	10	0.020	0.080
	100	0.002	0.008
40%	0.01	40	60
	0.1	4	6
	1	0.400	0.600
	10	0.040	0.060
	100	0.004	0.006
60%	0.01	60	40
	0.1	6	4
	1	0.600	0.400
	10	0.060	0.040
	100	0.006	0.004
80%	0.01	80	20
	0.1	8	2
	1	0.800	0.200
	10	0.080	0.020
	100	0.008	0.002

In 1989, Titanium alloys were anodized for 60 minutes in aqueous sulphuric acid – phosphoric acid solutions at 0–10°C with pulse frequency of 1 Hz, current density of 500 mA dm⁻², and potential range 180–200 V by Kocich⁴⁰. The resulting titanium oxide layers were 40–45 µm thick and were compact. The pores obtained had an average pore density of 105–106 mm⁻² and a diameter of 0.1–1 µm. The Al³⁺ and Cr³⁺ species were uniformly distributed and Zr³⁺ and Fe³⁺ showed concentration extremes. Columbin⁴¹ used pulse current technique in the anodizing of aluminium for improved oxide film formation. He also observed increased corrosion resistance and more efficient sealing. To examine the effects of anodizing voltage and temperature Okubo *et al.*^{42, 43} formed anodic coatings on aluminium in 1 M chromic acid by pulse current with negative component. When the negative current was high, thick coatings could not be obtained but the coatings had uniform large grain size. The author investigated the anodizing of aluminium using pulse current with negative current density in various baths such as 2.8 M sulphuric acid, 0.4 M oxalic acid and 1 M chromic acid using a frequency of 13.3 Hz. Cells and pores of films obtained in sulphuric acid were uniform in size and the size was not significantly influenced by the anodizing conditions. However, in oxalic and chromic acid baths the pores were branched and the degree of branching increased with increase of duty cycle. Cell and pore size were uniform. The microstructure of the film formed in chromic acid was similar to that of oxide film formed in oxalic acid.

In 1993, Rasmussen *et al.*^{44–47} obtained a hard and thick oxide film on AlMg₃ and AlSi₃ alloys by applying high current density at room temperature and at elevated temperature. The interactions between pulse parameters were studied using multiple regression analysis and it was confirmed by online monitoring of current-potential response during anodizing. The author studied the anodizing of AlMg₃ alloy in 2.8 M sulphuric acid and AlSi₃ in 1.3 M sulphuric acid at a temperature of 11°C. The results were compared with D.C. anodizing at a temperature of 5°C. The greatest hardness was achieved for AlSi₃ at pulse periods of 70 and 30 seconds. The alloys can be pulse anodized without scratches up to a current density of 3 A dm⁻². He also studied pulse anodizing of AlMg₃ and AlSi₃ alloys in 2.8 M sulphuric acid at 4°C to improve the initial wear resistance of the coating. Incorrect pulse current and amplitude led to decrease in wear resistance. The author also anodized aluminium using superimposed D.C. pulse at a rate of 6 pulses per second in sulphuric acid/oxalic acid baths and obtained oxide film of thickness 25–300 µm.

In 1995, Mita *et al.*⁴⁸ anodized ADC 12 aluminium alloy die casting and 99.87% pure aluminium in sulphuric acid and boric acid/sodium tetraborate solution at constant pulse voltage with 25 milliseconds On-time and 1–100 milliseconds Off-time. ADC 12 alloy in sulphuric acid solution had better charging properties than those formed in boric acid/sodium tetraborate solution. Juhl *et al.*²⁰ compared the different pulse parameters using

four different waveforms in the anodizing of extruded AA 6063 aluminium alloys. The advantages and disadvantages of these different waveforms were discussed. The throwing power of oxide layer varied for different waveforms, but their wear resistances were the same. Bei *et al.*⁴⁹ compared the oxide films formed by pulsed and constant current anodizing and studied the relation between oxidation time and current consumed.

In 1997, Azzouz *et al.*⁵⁰ anodized AA 1050 aluminium alloy by continuous and pulse potentials in 0.1 M sodium chloride or 0.1 M sodium hydroxide baths and polarisation resistance (R_p) measurements were carried out. R_p was found to be high for pulse anodized aluminium in both baths. Large and small cells were obtained at high and low potentials respectively. M. Sakairi *et al.*⁵¹ used pulsed AD-YAG laser to investigate the destruction and deformation of barrier oxide films on aluminium in neutral borate solution. The thickness of the film at the laser-irradiated area was proportional to the applied potential. Meng *et al.*⁵² found that by pulse anodizing of AILD31 aluminium alloy with a pulse rate of 100 pulses per second at 25–30°C, microhardness decreased from the inner to the outer part. He obtained a thickness greater than 80 µm and a hardness greater than 400 Hv. McGinnis *et al.*⁵³ used the pulsed current anodizing method for fabricating patterned porous silicon *p-n* junction light emitting diodes.

Our group^{54–55} used pulse current technique to produce uniform thick and hard oxide coatings on AA1100, AA6063 and AA2024 aluminium alloys at room temperature in 5–15% sulphamic acid electrolyte with addition agents such as 0.01 M magnesium sulphate, 0.005 M aluminium sulphate and 0.01 M sodium sulphate at current densities ranging from 1–3 A dm⁻² and various duty cycles ranging from 40–90% at the pulse frequency of 0.01 Hz. The appearance of the samples is shown in Figure 3. The influence of current density, duty cycle and addition agents, bath compositions, anodizing time and voltage on the properties of the oxide film such as thickness, hardness, breakdown voltage, coating ratio and corrosion resistance has been studied in detail and the pulse anodizing conditions optimised. The increase in duty cycle and current density increases the quality of the oxide film and maximum values were obtained for 70–80% duty cycle and at 2 A dm⁻². Among the addition agents used, magnesium sulphate was found to be the best. Also, the properties of the oxide films formed by pulse anodizing were found to be far better than those obtained by D.C. anodizing.

Shih *et al.*⁵⁶ studied the anodic oxidation of aluminium in mixed acid using pulse current of 80% duty cycle at a temperature of 20°C for a time of 50 minutes. Baths of 1.9 M sulphuric acid with 0.24 M nitric acid, 1.9 M sulphuric acid with 0.19 M boric acid and 1.9 M sulphuric acid were compared. Hardness was found to increase for boric acid addition and thickness was found to increase on nitric acid addition. Grover *et al.*⁵⁷ studied the luminescence of porous silicon formed by pulsed anodizing as a function of duty cycle and concentration of hydrofluoric acid.

Rasmussen²² patented the process of anodizing of aluminium alloy (3% Cu, 9.5% Si, 1% Mg) and aluminium alloy (4.5% Cu, 17% Si) using pulses of magnitude 6 and current density 1 A dm⁻² in an electrolyte of 3 M sulphuric acid at 10–15°C with on-time 30s and off-time 10 s.

Recently, our group^{58–60} studied the pulse anodizing of AA1100 aluminium alloy in oxalic acid electrolyte at 30°C and the influence of the pulse parameters on the properties of the oxide film in order to assess the quality of the oxide coating. The pulse anodizing of AA1100 aluminium alloy in sulphamic acid electrolyte at various pulse frequencies ranging from 0.01 to 100 Hz at constant duty cycle of 75% has been studied and the results showed that the properties of the oxide film improve with pulse frequency and maximum values were obtained at 100 Hz. A comparative study on the corrosion behaviour of D.C. and pulse anodized AA2024 aluminium alloy using electrochemical impedance spectroscopy has also been carried out.

PULSE HARD ANODIZING

In order to reduce or avoid burning problems that occur normally in D.C. anodizing and to hard anodize the aluminium alloys containing a high percentage of Cu and Si, more complex power supplies with biased, pulsed or interrupted current are used. Most of the work has been done using A.C. superimposed on D.C. power sources. In practice, the hard anodizing process is controlled by anodizing time and current density, keeping the concentration of electrolyte and temperature constant. The current density is adjusted according to the particular alloy composition and should be maintained at a constant level by raising the voltage as the film thickness increases. Finally, the current is reduced gradually as switching it off suddenly may adversely affect the adhesion of coating. The magnitude of A.C. component requirement varies with alloy composition. A hard anodizing process using superimposed A.C. on D.C. was first carried out by Jenny⁶¹ to increase the film thickness and to produce hard and non-porous oxide coatings on aluminium and its alloys. Kazuo *et al.*²⁵ studied the hard anodic oxide coating on aluminium and its alloys and also the effect of interrupted current during anodized oxidation. Tyukina *et al.*⁶² found that use of superimposed A.C. on D.C. improved the properties of thick oxide coatings formed on aluminium alloys with more Cu content. A wide range of different waveforms including full wave and half wave rectified D.C., interrupted current, superimposed current and pulsed current were examined by Ikuta *et al.*⁶³ who found that pulsed current produced harder coatings than D.C. particularly when using a ratio of 4:1 between high current level (4 A dm⁻² for 30 s) and low current level (2 A dm⁻² for 7.5 s).

Woods⁶⁴ patented a pulse hard anodizing process in 2.35–5.63 M sulphuric acid baths containing 0.1–0.2 M sodium lignosulphonate as stabiliser. This process can be used to hard anodize aluminium alloys containing greater than 5% copper to obtain thick dense oxide

coating without physical deterioration of the object. An oxide film of thickness of 50 μm was obtained in 6 minutes for a voltage of 36 V and a current density of 1.4 A dm^{-2} . Sanfords⁶⁵⁻⁶⁶ suggested the use of D.C. voltage modulated by a sinusoidal A.C. voltage of normal frequency at low voltage with a D.C. component and a superimposed A.C. component. He developed a special power supply that generates superimposed A.C. voltage waveform. These processes allow the use of low anodizing voltage compared with that of conventional hard anodizing by employing a low concentration of electrolyte at high temperature. It has been suggested by Lerner⁶⁷ that not more than 20 V D.C. is required at temperature from 4 to 10°C for producing hard coatings if A.C. superimposed on D.C. power source is used.

In 1987, Tu and Huang⁶⁸ compared pulsed D.C. and pulsed A.C. power sources with frequency of 60 Hz. They obtained better results for pulsed D.C. Maximum hardness of 467 VPN was obtained with the current density of 10 A dm^{-2} , above which hardness dropped. Hardness and roughness were better at sulphuric acid concentration of 0.94 M than at 2.8 M concentration. Oxalic acid addition increased oxide formation, especially at a temperature of 10°C. Use of higher voltage increased microhardness except for very high voltages. Chialvo *et al.*⁶⁹ pulse anodized rhodium electrodes to form an hydrous oxide layer that after electroreduction yielded reproducible surfaces with a large increase in the active surface area. The square pulse wave was applied with changing pulse parameters at a temperature of 30°C. This increase in surface area was related to the formation of oxide film studied under different experimental conditions. Using pulse current, Columbini⁷⁰ studied the hard anodizing of aluminium in sulphuric and chromic acid baths and observed the increase in the hardness and abrasion resistance of the oxide coating. The influence of superimposition of pulse current over direct current on the hard anodizing of aluminium and its alloys was studied by Narahsimhan *et al.*⁷¹ using sulphuric acid and oxalic acid electrolytes over a frequency of 50 to 300 Hz. Among different pulse rates, 250 pulses per second was found to be the best. Higher pulse rates were more suitable than the lower pulse rates. Pulse current superimposed on D.C. gave uniform, flawless oxide compared with pulse current from zero to peak.

Our group⁷² compared the pulse anodizing of AA2014, AA1351, and AA1725 aluminium alloys in 1.5 M sulphuric acid containing 0.08 M oxalic acid at a pulse rate of 250 pulses per second, and On and Off-ratio of 1:3, and obtained the thickness and corresponding coating ratio for the alloys. Al-Mg alloy gives higher thickness than the copper containing alloys. A mechanism correlated with copper was also proposed for the differences in the thickness obtained for these alloys. In 1991, Ponten *et al.*⁷³ used pulse voltammetry to examine the anodizing of silver microelectrodes in perchlorate, hydroxide, cyanide, and chloride media. The products of anodizing were detected by reverse pulse voltammetry. In 1994 Rasmussen⁴⁶ studied the pulse hard anodizing of AlMg₃ and AlSi₂Mg alloys at

11°C in sulphuric acid and found that pulse anodizing increases the wear resistance. Incorrect pulse timings and amplitude led to decrease in wear resistance. Li *et al.*⁷⁴ hard anodized LD2, LC4 and ZL108 aluminium alloys by the use of overlapping pulse current. They suggested that no linear relationship was found between hardness and wear resistance. Ping⁷⁵ compared hard anodizing using D.C. with superimposed A.C. and square wave pulse in sulphuric acid, oxalic acid and tartaric acid. The results of using various power supplies were also compared. In 1996, Rasmussen⁷⁶ studied the initial and post wear resistance of hard pulse anodized aluminium with pulse time ranging from 65 to 100 s in a sulphuric acid bath. The wear resistance was found to increase if pulse anodizing was performed in dicarboxylic acids instead of sulphuric acid. Meng³² carried out pulsed hard anodizing of Al LD31 aluminium alloy at 25–30°C and analysed the microstructure of the anodic oxide film using long cycle (100 s) pulsed current; he obtained a hardness above 400 Hv. Zhang *et al.*⁷⁷ obtained an oxide film of hardness about 400 Hv by oxidation of aluminium by A.C. pulsed potential in 2 M sulphuric acid 0.25 M oxalic acid, 8–12 g dm^{-3} sulphates and 1–4 $\text{cm}^3 \text{dm}^{-3}$ additives at a current density of 2–3 A dm^{-2} for positive pulse and 0–1 A dm^{-2} for negative pulse under air agitation. In this process film was formed at a rate of 1 $\mu\text{m min}^{-1}$.

PULSE COLOUR ANODIZING

Aluminium and its alloys have been coloured after anodizing either by chemical methods (organic dyeing and inorganic pigmentation.) or by electrochemical methods (electrolytic colouring by D.C. and A.C.). Also, coloured coatings can be formed simultaneously during anodizing (integral colour anodizing). However, these methods have many problems. In the organic method, if the coloured materials are exposed to sunlight, fading of colour will take place. In inorganic pigmentation, colour matching from batch to batch will vary and inconsistency in the finished product will occur. Integral colour anodizing is much more costly and only a specific colour can be produced on a particular alloy. Electrolytic colouring exhibits poor throwing power and needs proper configuration and positioning of electrode to achieve uniformity of colour. In order to overcome the problems encountered with the above processes, an attempt was made to prepare various coloured oxide coatings on aluminium and its alloys in a single bath by applying short pulses, called pulse colour anodizing. In 1966, Fair⁷⁸ patented the process of pulse colour anodizing of aluminium alloys in sulphuric acid, chromic acid and oxalic acid electrolytes. Square wave pulses are applied with make-break ratio of 1:5 and a make period of 1–100 ms. The Scionics Corporation⁶ patented the process of integral colour anodizing of aluminium using both positive and negative pulse components in organic acid electrolytes. For better results of the production of thick dyeable hard coatings and conventional coatings of light integral colour shadings, the ratio of negative current to positive current should be preferably

greater than 3%. Additional use of capacitors are discussed to improve the throwing power and improve the prolong decay of positive pulses.

In 1974, Riken Light Metal K.K.⁷⁹ produced amber coloured coatings on aluminium by treating it cathodically in sulphuric acid and etching for 5–10 minutes before applying pulse current. S. Kimura *et al.*^{80,81} studied the effect of pulse characteristics and other electrical conditions on colouring of anodized aluminium using pulsed current in sulphuric acid electrolyte. A brown colour was obtained at 30 V and current density of 2 A dm^{-2} at duration of 2–5 s. They also proposed a mechanism for colouring anodized aluminium using pulsed current. Takahashi *et al.*^{82,83} treated aluminium in 1–2 M sulphuric acid solution using a pulse width of 30–50 ms, period:width ratio of 3:5, peak current density of 10 A dm^{-2} and average current density of 4 A dm^{-2} and obtained amber coloured coatings. Pitting was observed in 0.5 M sulphuric acid. The authors pulse treated aluminium plates with sulphuric acid and obtained a brown colour. Adding oxalic acid to sulphuric acid required less current and shorter time. They suggested that pulse height and width had little effect on colour but did affect growth rate. Batrakov *et al.*⁸⁴ anodized titanium alloys at 80–200 V and current density 10–80 A dm^{-2} to obtain solid wear resistant anodic coatings.

Fukasawa *et al.*⁸⁵ anodized aluminium in 0.24 M oxalic acid with or without pulse current of 10 to 10 kHz. The cathodic part of pulse current was said to play an important role in colouration. Intensive colouration was obtained at 1000 Hz and a mechanism of built-in current related with electronic current was proposed. Takahashi *et al.*⁸⁶⁻⁹⁰ obtained integral colouring for the pulse anodized aluminium sample in 2.8 M sulphuric acid bath, and suggested that the colouring of the film was attributed mainly to the flow of current rather than to the nature of the electrolyte, when the voltage for electrolysis was above a definite value. The optimum Off-time and On-time ratio is 1:5 with current density of 6 A dm^{-2} and a pulse width of 50 ms with 30 V at a temperature of 10°C. The authors pulse treated AA6063 aluminium plates in 1.5 M sulphuric acid containing 10 wt % glycerol at a temperature range of 11–20°C using pulses with 16 ms width and 48 ms period. The peak voltage used was 38–39 V and the average current density was 2.4–1.6 A dm^{-2} . For a period of 30 minutes, yellowish grey colour coatings with NBS value 26 and thickness 54 μm were obtained. They also used pulse current with 16 ms pulse width, 48 ms period, peak voltage of 36.5 to 37.5 V and an average current density of 2–1.1 A dm^{-2} to treat AA6063 aluminium alloy. The electrolyte used was sulphuric acid containing 20 g dm^{-3} of Al^{3+} . 48 μm thick, yellowish grey coatings with NBS 28.1 were obtained for a period of 30 minutes. In 1978 the authors electrolytically coloured aluminium alternatively by applying pulsed positive D.C. potential and obtained bright yellowish brown coatings. They also anodized aluminium in 0.94–3.75 M sulphuric acid using a pulse of 2 s On-time and 3 s Off-time for two minutes

at a current density of 1.5 A dm⁻² at 5–20°C. The resultant light yellowish oxide film consisted of two porous layers separated by a barrier layer. Riken Light Metal Industries Inc.⁹¹ carried out anodizing in a metal salt bath using a periodic pulsed potential of changing polarity and this anodic oxide was further treated in the same bath, using the same potential and a by-pass On-Off circuit which promotes current discharge at zero applied voltage. This enhances the colouring effects.

Baba²⁹ attempted integral colouring in pulse anodizing in oxalic acid using negative and positive voltages. The film decreased in L-value at higher voltages. The L-value decreased further at higher negative voltages and the film was dark in colour. A mechanism was proposed for the luminescence of anodized aluminium. The relationship between electroluminescence and photoluminescence was predicted to be an inverse one. Azzouz *et al.*⁹² prepared coloured anodic films using squared potential pulses of range 15–30 V in sulphuric acid. They correlated the evolution of oxide layer by an electric equivalent circuit. The optical properties of the anodic film were explained by superimposition of different size cells.

ADVANTAGES OF PULSE ANODIZING

1. Pulse current technique can be used for all types of anodizing such as normal anodizing, hard anodizing and colour anodizing.
2. Better quality of oxide coating can be obtained compared to D.C. anodizing.
3. All properties of oxide coating such as thickness, hardness, coating ratio, breakdown voltage, corrosion resistance, abrasion resistance and weather resistance *etc.* will be enhanced.
4. Burning of oxide film that normally occurs during the initial stage of D.C. anodizing can be avoided.
5. 25–30% reduction of power consumption can be obtained by the use of pulse anodizing rather than D.C. anodizing.
6. Anodizing time can also be minimised because the same quality of oxide coating can be achieved in lesser time if pulse current is passed instead of D.C.
7. Hard anodizing of aluminium alloys containing higher percentage of Cu or Si, that are normally very difficult to anodize, can be easily carried out.
8. Self-colour can be generated simultaneously during anodizing by applying pulse current.
9. The amount of cooling can also be minimised because during pulse anodizing, the heat produced is dissipated effectively and uniformly throughout the bulk of the electrolyte and so it requires somewhat lesser amount of cooling compared to D.C. anodizing.

REFERENCES

1. G. D. Bengough and J. M. Stuart, British Patent, 223, 994, 1923.
2. G. D. Bengough and J. M. Stuart, British Patent, 223, 995, 1923.
3. C. H. R. Gower and S. O' Beren, British Patent, 290, 901, 1927.
4. T. Kujirai and S. Ueki, U.S. Patent, 1,735,509, 1926.
5. M. A. Miller, U.S. Patent, 2,920, 018, 1960.
6. The Scionics Corp. Northridge, Calif., U.S. Patent, 3,708, 407, 1970.
7. Permaloy Corp. Ogden, Utah. U.S. Patent, 3, 857, 766, 1972.
8. G. H. Poll, *Prod. Fin.*, 1972, **36**(6), 84, 89.
9. Chuo Seisakusho K K., Jap. Patent, 51/4 032, 1974.
10. Chuo Seisakusho K K., Jap. Patent, 51/4 034, 1974.
11. M. Kondo, M. Kitagawa and T. Takahashi, Japan Kokai, 77 88, 553, 1977.
12. M. Kondo and T. Takahashi, Japan, Kokai, 77 88, 233, 1977.
13. N. Sugiyama, T. Sato, M. Takahashi, H. Kanamori, Y. Hirayama, M. Miama, T. Takahashi, K. Wada, K. Kanada and I. Hara, Jap. Tokyo Koho, 79 14, 581, 1979.
14. K. Okubo, *J. Met. Fin. Soc. Japan*, 1982, **33**, 219.
15. Chuo Seisako Ltd., Jap. Tokyo Koho JP, 82, 26, 357, 1982.
16. H. G. Scheineder, G. Marx, W. Krysmann, P. Kurze, H. G. Treiber and S. Koenig, *Exp. Tech. Phys.*, 1982, **30**(2), 179.
17. D. Kanagaraj, V. L. Narasimhan, S. Vincent, S. Chandrasekharan and S. Birlasekaran, *Bull. Electrochem.*, 1986, **2**, 597.
18. C. Columbini, *Trans. Inst. Met. Fin.*, 1988, **66**, 142.
19. C. Columbini, *Galvanotechnik*, 1994, **85**, 790.
20. A. D. Juhl, M. E. Benzon and P. Moeller, *Proc. AESF 83rd Annual Tech. Conf.*, 1996, 859.
21. C. Columbini and M. Leoni, *Galvanotechnik*, 1998, **89**, 1865.
22. J. Rasmussen, U.S. Patent, 6, 113, 770, 2000.
23. Y. Wen, *Diandu Yu Huanbao*, 2000, **20**, 30.
24. J. F. Murphy and C. E. Michelson, *Conference on Anodizing of Aluminium, ADA*, Nottingham, 1961.
25. I. Kazuo, F. Akio and T. Kazuhiko, *Inst. Phys. Chem. Res.*, 1962, **38**, 635.
26. Murdock Inc., U.S. Patent, 3, 418, 222, 1968.
27. T. Takahashi and J. Saitoh, *Plat. Sur. Fin.*, 1977, **64**(7), 36.
28. E. Macas, U. S. Mashtakov, O. V. Snitko and V. I. Chaikin, *Electrochimica*, 1977, **13**(3), 431.
29. B. P. Orlov and L. V. Lel'kora, *R. Zh. Mash.*, 1980, **11B**, 196.
30. N. Baba and I. Mizuki, "Advanced Metal Finishing Technology in Japan" 1980, p.87.
31. K. Yokoyama, H. Konno, H. Takahashi and M. Nagayama, *Plat. Surf. Fin.*, 1982, **69**(7), 63.
32. I. Mita and K. Miazawa, *J. Met. Fin. Soc. Japan*, 1982, **33**, 165.
33. Yoshimura Res. Lab., *Kunki Aruminyumu Hyomen Shori Kenkyukai Kaishi*, 1982, **93**, 6.
34. Matsushita Electric Industrial Co. Ltd., US Patent, 4,671 858, 1984.
35. H. J. Huang, *Proc. Nat. Sci. Council Republ. China, Part A, Phys. Sci. Eng.*, 1985, **9**(1), 5.
36. I. Mita, *Kenkyu Hokoku, Tokyo-Toritsu Kogyo Gijutsu Senta*, 1988, **18**, 69.
37. I. Mita and H. Miyasaka, *Kuzoku Hyomen Gijutsu*, 1988, **39**(6), 323.
38. K. Okubo S. Toba and Y. Sakura, *J. Met. Fin. Soc. Japan*, 1988, **39**(9), 512.
39. K. Okubo and Y. Sakura, *J. Met. Fin. Soc. Japan*, 1988, **39**(11), 751.
40. J. Kocich, G. Janak, J. Sevcikova, P. Guba and V. Valo, *Koroze Ochr. Mater.*, 1989, **33**(3), 43.
41. C. Columbini, *Finishing*, 1989, **13**(11), 38.
42. K. Okubo, S. Suyama and Y. Sakura, *Hyomen Gijutsu*, 1989, **40**, 579.
43. K. Okubo, S. Suyama and Y. Sakura, *J. Surf. Fin. Soc. Japan*, 1989, **40**, 1366.
44. J. Rasmussen, M. Eis and P. Moeller, *Proc. 80th AESF Annual Tech. Conf.*, 1993, 905.
45. J. Rasmussen, *Galvanotechnik*, 1994, **85**, 1841.
46. J. Rasmussen, *Galvanotechnik*, 1994, **85**, 2176.
47. J. Rasmussen, *Galvanotechnik*, 1994, **85**, 1477.
48. I. Mita, Togashiva and S. More, *J. Surf. Fin. Soc. Japan*, 1995, **46**(10), 960.
49. H. Bei and Z. Zhu, *Diandu Yu Huanbao*, 1996, **25**, 164.
50. N. Azzouz, K. Belmokre and J. Pagetti, *Entropie*, 1997, **33**, 207.
51. M. Sakairi, Y. Ohira and H. Takahashi, *Proc. Electrochem. Soc.*, 1998, **97**(26), 463.
52. H. Meng, J. S. Wu, W. B. Hu, and L. Liu, *Shanghai Jiaotong Daxue Xuebao*, 1999, **33**, 808.
53. S. Mc.Ginnis, P. Sines and B. Das, *Electrochem. Solid State Lett.*, 1999, **2**, 468.
54. D. Kanagaraj, S. Vincent, V. Raj and S. V. K. Iyer, *J. Electrochem. Soc. India*, 1999, **48**, 222.
55. D. Kanagaraj, *Ph.D. Thesis*, Alagappa University, Karaikudi, 2000.
56. H. H. Shih and S. L. Tzou, *Surf. Coat. Technol.*, 2000, **124**, 278.
57. R. Grover, K. L. Narasimhan and D. K. Sharma, *J. Porous Mater.*, 2000, **7**, 377.
58. D. Kanagaraj, V. Raj, S. Vincent, B. Prasannakumar, A. Senthilkumar and S. Venkatakrishna Iyer, *Bull. Electrochem.*, 2001, **17**, 28.
59. D. Kanagaraj, V. Raj, S. Vincent and S. V. K. Iyer, *Bull. Electrochem.*, 2001, **17**, 523.
60. S. Mohan, D. Kanagaraj, V. Raj, S. Vincent, N. G. Renganathan and S. Raman, *Proc. Electrochem. Soc.*, 2001 (in press).
61. A. Jenny, "The Anodic Oxidation of Aluminium and its Alloys", 1940, p.133.
62. M. N. Tyukina, N. N. Ignatov, F. P. Zulivalov and N. D. Tomashov, *Zhur Priklad Khim.*, 1963, **36**, 338.
63. R. Ikuta, S. Ueda and S. Koizumi, *J. Met. Fin. Soc. Japan*, 1974, **25**, 499.
64. Woods, U. S. Patent, 3,857,766, 1974.
65. Sansfords Process Corp. U. S. Patent, 4, 128, 461, 1978.
66. Sansfords Process Corp. U. S. Patent, 4, 133, 725, 1979.

67. M. Lerner, *Plat. Surf. Fin.*, 1983, **70**(8), 60.
68. G. C. Tu and L. Y. Huang, *Trans. Inst. Met. Fin.*, 1987, **65**, 60.
69. A. C. Chialvo, W. E. Triaca, and A. J. Arvia, *J. Electroanal.Chem.*, 1987, **237**, 237.
70. C. Columbini, *Finishing*, 1988, **12** (1), 34, 38.
71. V. L. Narasimhan, S. Vincent and D. Kanagaraj, *Bull. Electrochem.*, 1989, **5**, 505.
72. D. Kanagaraj, S. Vincent and V. L. Narasimhan, *Bull. Electrochem.*, 1989, **5**, 513.
73. M. Ponten, Y. Oster and Janet, *J. Electrochem. Soc.*, 1991, **138**, 1.
74. S. Li, S. Duan, X. Duan and C. Zhou, *Cailiao Baohu*, 1994, **27**(3), 6.
75. R. Y. Ping, *Electroplat. Pollut. Contr.*, 1994, **14**(4), 22.
76. J. Rasmussen, *Proc. AESF. 83rd Annual. Tech. Conf.*, 1996, 995.
77. X. S. Zhang, W. Zhang, H. Zhang and W.Xiang, *Cailiao Baohu*, 1999, **32** (2), 15.
78. R.W. Fair, British Patent, 1, 090, 840, 1966.
79. Riken Light Metal KK., Jap. Patent, 1974, 51/8 131, 1974.
80. S. Kimura, T.Takahashi, T. Nagano. K. Nada, Y. Suzuki and S. Ohkuma, *Aruminyumu Hyomen Shori Kenkyu Chosa Hokoku*, 1974, **80**, 28.
81. S. Kimura, T. Takahashi, T. Nagano, K. Nada, Y. Suzuki and S. Ohkuma, *Aruminyumu Hyomen Shori Kenkyu Chosa Hokoku*, 1974, **80**, 30.
82. T. Takahashi, K. Wada, Y. Suzuki and S. Ohkuma, *Aruminyumu Hyomen Shori Kenkyu Khora Hokoku*, 1974, **86**, 43.
83. T. Takahashi and Y. Suzuki, *Aruminyumu kenkyu kaishi*, 1976, **108**, 47.
84. V. P. Batrakov, L. N. Pivovarova, A. S. Pivovarova and G I. Ivanov, U.S.S.R, 534, 525(1976)
85. H. Fukasawa, T.Yoshina, N. Baba and J. Mizuki, *Kinzoku Hyomen Gijutsu*, 1977, **28**(7), 369.
86. T. Takahashi and J. Saitoh, *Plat. Surf. Fin.*, 1977, **64**(7), 36.
87. T. Takahashi, M. Ikeyaga and M. Ozaki, Japan Kokai, 77, 58,026, 1977.
88. T. Takahashi, M. Ikeyaga and M. Ozaki, Japan Kokai, 77, 58,027, 1977.
89. T. Tahakashi and M. Ikegaya, Japan Kokai, 78, 55,420, 1978.
90. T. Takahashi and M. Ikegaya, Japan Kokai, 78, 55,421, 1978.
91. Riken Light Metal Industries Inc., Jap. Tokkyo Koho JP, 8021,116.
92. N. Azzouz, C. Morel, G. Messin and J. Pagetti, *Interfinish-92, Int. Congr. Surf. Finish*, 1992, **2**, 510.