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• **HAYASHI, Kazuo**
Sano-shi, Tochigi 327-0103 (JP)
• **KOYAMA, Yuji**
Tokyo 101-0044 (JP)

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(71) Applicant: **IDX Co., Ltd.**
Sano-shi, Tochigi 327-0103 (JP)

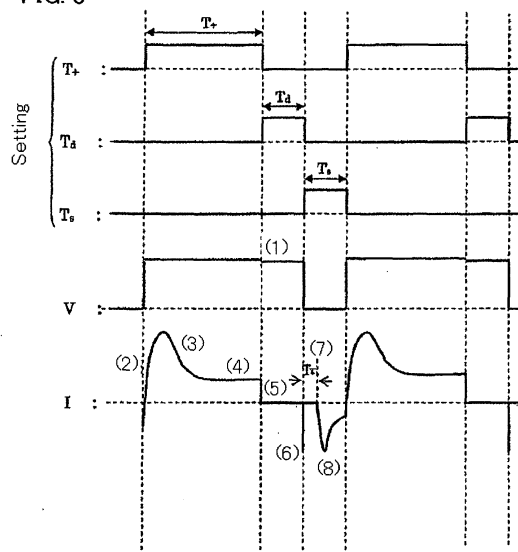
(74) Representative: **Hall, Matthew Benjamin**
Frank B. Dehn & Co.
St Bride's House
10 Salisbury Square
London
EC4Y 8JD (GB)

(72) Inventors:
• **ODAJIMA, Hiromichi**
Tokyo 101-0044 (JP)

(54) **METHOD FOR ANODICALLY OXIDIZING ALUMINUM ALLOY AND POWER SUPPLY FOR ANODICALLY OXIDIZING ALUMINUM ALLOY**

(57) In a method for anodizing an aluminum alloy to form an anodic oxide film on a surface of the aluminum alloy using pulsed electric power, a short circuit is formed, after application of a positive pulse voltage, between an anode for anodic oxidation and a cathode for anodic oxidation for a short-circuit duration of not longer than 15 μ s during non application of the pulse voltage. The pulsed electric power has a waveform having a cycle composed, in the order, of a pulse voltage application duration (T_+), a dead time (T_d) and a short-circuit duration (T_s). Then, no or almost no negative current is allowed to flow, and the film formation rate can be increased to improve productivity.

FIG. 3



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Description

TECHNICAL FIELD

- 5 **[0001]** The present invention relates to a method for anodizing an aluminum alloy and to a power supply for anodizing an aluminum alloy.

BACKGROUND OF THE INVENTION

- 10 **[0002]** Conventionally, anodizing of an aluminum alloy is carried out in a bath containing an aqueous solution of sulfuric acid, oxalic acid, phosphoric acid or the like to form an oxide film or coating on a surface of the aluminum alloy for the purpose of increasing the hardness, wear resistance and corrosion resistance of the surface or coloring the surface. An anodic oxide film has a dense barrier layer and a porous layer both composed of Al_2O_3 .

- 15 **[0003]** As methods of applying electric power to obtain a film with desired properties, a direct current anodizing method, a periodic reverse electrolyzing method, a method using superimposed direct current on an alternating current, a pulse anodizing method and so on have been reported (Kinzoku Hyomen Gijutsu (Metal Surface Technology) 39, p.512 (1988), Journal of Aluminum Finishing Society of Kinki, No.1334, p.1 (1988), Japanese Unexamined Patent Application Publication No. 2000-282294, Japanese Unexamined Patent Application Publication No. 2004-35930).

- 20 **[0004]** When a high voltage is applied to supply a large current in order to achieve a high film formation rate in a direct current anodizing method, a large amount of Joule heat is generated in the barrier layer to cause a defect called "burning of anodic oxide coating" on the oxide film. Thus, it is difficult to form a thick anodic oxide film on a molded aluminum product and an aluminum die-cast product, containing a large amount of Si, Cu or Fe and having poor electrical conductivity, within a short period of time by a direct current anodizing method.

- 25 **[0005]** It is said that a pulse electrolysis method including the periodic reverse electrolyzing method is better than a direct current anodizing method to form a desired oxide film free of a defect called "burning of anodic oxide coating" within a short period of time with high productivity. For example, it is reported in Kinzoku Hyomen Gijutsu, 39, p.512 (1988) that an oxide film can be formed at a high rate by a periodic reverse electrolyzing method in which a negative current is intermittently supplied to a sulfuric acid bath at an oxidation voltage lower than that used in a direct current anodizing method. It is reported in Journal of Aluminum Finishing Society of Kinki, No.1334, p.1 (1988) that when
30 aluminum A1080P (JIS H4100) was subjected to electrolysis by a periodic reverse electrolyzing method in a bath containing 20 wt % sulfuric acid and 10 g/L oxalic acid at 20°C for 65 minutes under the conditions involving a frequency of 13.3 Hz, a current density of 4 A/dm² and a duty of 95 %, an aluminum anodic oxide film with a thickness of 92 μm (1.4 μm/min) was obtained. In these methods, however, since a voltage having a frequency in the order of 10 Hz is applied, the film formation rate cannot be increased in the case of an aluminum die-cast product containing a large
35 amount of alloy elements. In addition, since a positive voltage and a negative voltage must be applied, a power supply having a complicated bipolar structure is required.

- [0006]** Japanese Unexamined Patent Application Publication No. 2000-282294 discloses that an aluminum anodic oxide film with a high heat resistance and a corrosion resistance can be formed on an aluminum alloy surface by a method using superimposed direct current on an alternating current under such an electrolysis condition that the AC
40 component does not contain a negative component and the AC component is at least 5 % of the level of the DC component. However, the current density suitably employed is as low as 0.1 to 2 A/dm². With such a current density, the film formation rate is so low as to cause problems of low productivity and high cost. In addition, the power supply system required for this method is also complicated since both an AC power supply and a DC power supply are required.

- [0007]** Japanese Unexamined Patent Application Publication No. 2004-35930 suggests, as a technique which can
45 increase the formation rate of an aluminum anodic oxide film for the purpose of improving productivity, a method in which a sine wave current with a high frequency of 200 to 5000 Hz (preferably 600 to 2000 Hz) on which a DC current is superimposed is supplied to a sulfuric acid aqueous solution bath. That is, a high-frequency sine wave with a frequency of 1000 Hz and a voltage of ± 20 V on which a DC voltage of 19.8 V was superimposed was supplied to aluminum alloy ADC12 (JIS H5302) in a 10% sulfuric acid aqueous solution at 17°C for an electrolytic treatment period of 20 minutes,
50 thereby obtaining an anodic oxidation film with a thickness of 22 μm (growth rate: 1.1 μm/min). It is reported that the current density obtained five minutes after the start of electrolysis was 13.8 A/dm². However, the method is still disadvantageous in that the frequency is limited to 200 to 5000 Hz and in that, since a sine wave is used, the amount of current which can be supplied per unit time is smaller as compared to a rectangular wave. In addition, the power supply system required for this method is also complicated since both an AC power supply and a DC power supply are required.

- 55 **[0008]** Japanese Unexamined Patent Application Publication No. 2006-83467 discloses a method for forming an anodic oxide film having cells which have grown in random directions relative to a surface of aluminum or aluminum alloy and thus have no orientation for the purpose of improving the corrosion resistance and impact resistance. In one specific method using an alloy containing impurities such as silicon, a step of applying a plus voltage and a step of

removing electric charge are repeated. The plus voltage is applied for 25 to 100 μs (5 to 20 KHz in terms of frequency) at a time. During the step of removing electric charge, the application of the plus voltage is stopped and a short circuit is formed between the anode and cathode or a minus voltage is applied across the anode and the cathode. It is shown that when a minus voltage is applied, such a minus voltage is applied for the same time period as that for which the plus voltage is applied. The reason why electric charge is removed is as follows. Namely, when an electric charge is accumulated, the resistance substantially increases so that a high voltage must be applied in order to obtain a constant current value. As a result, the before-mentioned defect called "burning of anodic oxide coating" occurs.

[0009] In this method, however, since the film formed is reduced by electrolysis when a minus voltage is applied, the film growth rate cannot be improved. Also, it has been found that a negative current with a large negative current density flows, when a short circuit is formed between the anode and the cathode. For example, when the positive current density was 18 A/dm² under an anodizing condition, the negative current density was 12.8 A/dm². Thus, there still remains a room for improvement to increase the film growth rate.

SUMMARY OF THE INVENTION

[0010] The present invention has been made in view of the above problems, and it is, therefore, an object of the present invention to provide a method for anodizing an aluminum alloy and a power supply for anodizing an aluminum alloy capable of increasing the film formation rate and improving productivity without developing a defect called "burning of anodic oxide coating" by suppressing or preventing a negative current when anodizing of an aluminum alloy is carried out by a pulse electrolysis method.

Another object of the present invention is to provide a method for anodizing an aluminum alloy and a power supply for anodizing an aluminum alloy capable of further increasing the film formation rate to improve productivity by setting a frequency of pulse voltage that allows a maximum current to flow when the pulse voltage is applied.

[0011] For the purpose of accomplishing the above objects, the present invention provides the following inventions.

[1] A method for anodizing an aluminum alloy to form an anodic oxide film on a surface of said aluminum alloy using pulsed electric power, characterized in that, after application of a positive pulse voltage, a short circuit is formed between an anode for anodic oxidation and a cathode for anodic oxidation for a short-circuit duration of not longer than 15 μs during non application of the pulse voltage.

[2] A method for anodizing an aluminum alloy as recited in [1] above, wherein said short-circuit duration is not shorter than 1 μs and not longer than 15 μs .

[3] A method for anodizing an aluminum alloy as recited in [1] above, wherein said short-circuit duration is not shorter than 1 μs and not longer than 5 μs .

[4] A method for anodizing an aluminum alloy as recited in [1], [2] or [3] above, wherein said pulsed electric power has a waveform having a cycle composed, in the order, of a pulse voltage application duration (T_+), a dead time (T_d) and a short-circuit duration (T_s).

[5] A method for anodizing an aluminum alloy as recited in [1], [2] or [3] above, wherein said pulsed electric power has a frequency of 8 to 35 KHz.

[6] A method for anodizing an aluminum alloy as recited in [1], [2] or [3] above, wherein said pulsed electric power has a frequency of 10 to 30 KHz.

[7] A method for anodizing an aluminum alloy as recited in [4] above, wherein said pulsed electric power has a frequency of 8 to 35 KHz.

[8] A method for anodizing an aluminum alloy as recited in [4] above, wherein said pulsed electric power has a frequency of 10 to 30 KHz.

[9] A power supply for anodizing an aluminum alloy for use in a method for anodizing an aluminum alloy to form an anodic oxide film on a surface of said aluminum alloy using pulsed electric power, comprising a pulsed electric power generating section configured to generate such pulsed electric power that, after application of a positive pulse voltage, a short circuit is formed between a terminal connected to an anode for anodic oxidation and a terminal connected to a cathode for anodic oxidation for a short-circuit duration of not longer than 15 μs during non application of the pulse voltage.

[10] A power supply for anodizing an aluminum alloy as recited in [9] above, wherein said pulsed electric power generating section is configured to generate pulsed electric power which provides a short-circuit duration of not shorter than 1 μs and not longer than 15 μs .

[11] A power supply for anodizing an aluminum alloy as recited in [9] above, wherein said pulsed electric power generating section is configured to generate pulsed electric power in which the short-circuit duration is not shorter than 1 μs and not longer than 5 μs .

[12] A power supply for anodizing an aluminum alloy as recited in [9], [10] or [11] above, wherein said pulsed electric power generating section is configured to generate pulsed electric power

having a waveform composed, in the order, of a pulse voltage application duration (T_+), a dead time (T_d) and a short-circuit duration (T_s).

[13] A power supply for anodizing an aluminum alloy as recited in [9], [10] or [11] above, wherein said pulsed electric power generating section is configured to generate pulsed electric power having a frequency of 8 to 35 KHz.

[14] A power supply for anodizing an aluminum alloy as recited in [9], [10] or [11] above, wherein said pulsed electric power generating section is configured to generate pulsed electric power having a frequency of 10 to 30 KHz.

[15] A power supply for anodizing an aluminum alloy as recited in [12] above, wherein said pulsed electric power generating section is configured to generate pulsed electric power having a frequency of 8 to 35 KHz.

[16] A power supply for anodizing an aluminum alloy as recited in [12] above, wherein said pulsed electric power generating section is configured to generate pulsed electric power having a frequency of 10 to 30 KHz.

[0012] In a method according to the present invention for forming an anodic oxide film on a surface of an aluminum alloy using pulsed electric power, a short-circuit is formed, after application of a positive pulse voltage, between the anode for anodic oxidation and the cathode for anodic oxidation for a very short short-circuit duration during non application of the pulse voltage so that a negative current is controlled to be reduced or eliminated. As a consequence, there can be provided a method for anodizing an aluminum alloy and a power supply for anodizing an aluminum alloy that are capable of increasing the film formation rate and of improving productivity without developing a defect known as "burning of anodic oxide coating". According also to the present invention, there can be provided a method for anodizing an aluminum alloy and a power supply for anodizing an aluminum alloy that are capable of giving an effect that the film formation rate can increase and the productivity can be improved by setting the frequency of the pulse voltage to a value permitting a maximum current to flow when the pulse voltage is applied in addition to the above effect attained by the formation of a short-circuit between the anode for anodic oxidation and the cathode for anodic oxidation.

BRIEF DESCRIPTION OF DRAWINGS

[0013]

FIG. 1 is a graph showing the relationship between the film growth rate and the effective current density in an aluminum alloy anodizing method using pulsed electric power, wherein the effective current density refers to a difference between the positive current density that is achieved when a pulse voltage is applied and the negative current density that flows during non application of the pulse (effective current density = positive current density - negative current density).

FIG. 2 is a view illustrating a structure of a power supply and an electrolytic bath for carrying out the aluminum alloy anodizing method of the present invention.

FIG. 3 is an explanatory view of a pulse setting condition and actual voltage and current waveforms corresponding to the pulse setting condition.

FIG. 4 is an explanatory view of a steady state of film growth during anodizing.

FIG. 5 is an explanatory view of the relationship between the current waveform and frequency of pulsed electric power used in the present invention.

FIG. 6 is a table showing the experiment results in Examples and Comparative Examples of the present invention.

FIG. 7 illustrates the relationship between the short-circuit duration and the negative current in the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Description will be hereinafter made of the present invention in detail.

The present inventors have made a study for the purpose of increasing the film formation rate and found that when a short circuit is formed, after one application of a positive pulse voltage, between an anode for anodic oxidation and a cathode for anodic oxidation to cause a negative current (current which flows in a direction opposite the direction in which a current flows when the pulse is applied) to flow during non application of the pulse voltage, it is possible to reduce the concentration gradients of Al^{3+} and O^{2-} ions in the barrier layer formed during application of the pulse voltage and to discharge the electric double layer at the solid-liquid interface so that a large current can be allowed to flow in the next application of the pulse voltage. However, as described before, the problem is that the magnitude of negative current is large relative to the magnitude of the positive current which flows when a pulse voltage is applied. The present inventors have thus conducted a further study on this issue.

[0015] The present inventors have found that the film growth rate is proportional to the effective current density (FIG. 1), when a short circuit is formed between the anode for anodic oxidation and the cathode for anodic oxidation during non application of a pulse voltage in a method for anodizing an aluminum alloy using pulsed electric power. It has also been found, however, that a problem is caused because when the effective current density is increased, the negative

current also increases.

[0016] The present inventors have investigated a method capable of further improving the film growth rate in order to improve productivity. As a result, the present inventors unexpectedly found that when a short circuit is formed, after one application of a positive pulse voltage, between the anode for anodic oxidation and the cathode for anodic oxidation for a very short period of time during non application of the pulse voltage, the negative current can be reduced or even prevented so that a large current can be allowed to flow without developing a defect known as "burning of anodic oxide coating" when the next positive pulse voltage is applied. The present inventors also found that the film growth rate can be significantly increased when the frequency of the pulse voltage to be applied is set to a value within a specified range. The present invention has been made based on the above findings.

[0017] A method for anodizing an aluminum alloy according to the present invention is characterized in that pulsed electric power is used and that a short circuit is formed, after application of a positive pulse voltage, between the anode for anodic oxidation and the cathode for anodic oxidation for a short-circuit duration of not longer than 15 μ s during non application of the pulse voltage. The short-circuit duration is preferably not shorter than 1 μ s and not longer than 15 μ s, more preferably not shorter than 1 μ s and not longer than 5 μ s, still more preferably not shorter than 1 μ s and not longer than 3 μ s. While the preferred range of the short-circuit duration depends on the type or electrical conductivity of the aluminum alloy to be treated, the negative current can be significantly reduced or even prevented from flowing and a large current can be allowed to flow in the next application of positive pulse voltage when the short-circuit duration is within the above range. Therefore, the film formed is not reduced by a negative current and the film growth rate can be significantly increased without developing a defect known as "burning of anodic oxide coating." It has been considered necessary to remove all the electric charges accumulated in the system by forming a short circuit or applying a negative voltage before the next application of a positive pulse voltage in order both to prevent a defect called "burning of anodic oxide coating" and to increase the film growth rate. However, as a result of a zealous study, the present inventors have found that when only the electric charges at the barrier layer interfaces (Al/Al₂O₃ interface and Al₂O₃/electrolytic solution interface) at which the oxide film is being formed are removed, a substantially reduced electrical resistance state can be realized so that a large current necessary to form a good film is allowed to flow when the next positive pulse voltage is applied. With this method, the film growth rate can be significantly increased since the film formed can be prevented from being melted and reduced by a large negative current.

[0018] In the present invention, it is preferred that the pulsed electric power have a waveform having a cycle composed, in the order, of a pulse voltage application duration (T_+), a dead time (T_d), and a short-circuit duration (T_s). In this case, to improve the film formation rate, the pulse voltage application duration (T_+) is preferably approximately 20 to 100 μ s, and the dead time (T_d) is preferably approximately 5 to 10 μ s.

[0019] It is also preferred that the pulsed electric power have a frequency of 8 to 35 KHz, more preferably 10 to 30 KHz. When the frequency is within the above range, a quantity of electricity that can further increase the film growth rate can be supplied to form a film, which, in conjunction with the effect of the short circuit for a very short period of time, further increases the film growth rate.

[0020] FIG. 2 is a view explanatory of the structure of a power supply and an electrolytic bath for use in anodizing an aluminum alloy according to the present invention. A power supply P is constituted of a sequencer 10, a positive side DC power supply 11, a repetition frequency generator 12, a positive side pulse generating circuit 13, a short-circuit side pulse generating circuit 14, a positive side chopper gate amplifier (GA) 25, a short-circuit side chopper gate amplifier (GA) 26, a positive side chopper switch 15, a reverse current prevention diode (D_1) 16, and a short-circuit current control circuit 17, and has output terminals 18 connected respectively to an anode 20 and a cathode 21 in an electrolytic bath 19. Also provided are a positive side output voltmeter (E_1) 22, an electrolytic bath voltmeter (E_B) 23 and an electrolytic bath ammeter (A_B) 24. Designated as 27 is an electrolytic solution.

[0021] The sequencer 10 controls the repetition frequency generator 12, the positive side pulse generating circuit 13, the short-circuit side pulse generating circuit 14 and the positive side DC power supply 11 to transform the waveform of pulsed electric power for use in the present invention into a prescribed shape. The positive side DC power supply 11 generates DC power necessary to apply a positive pulse voltage or positive current pulse set by the sequencer 10. The repetition frequency generator 12 generates a reference repetition frequency necessary for the generation of the pulsed electric power and supplies it to the positive side pulse generating circuit 13 and the short-circuit side pulse generating circuit 14. The positive side pulse generating circuit 13 generates a pulse of duration T_+ , and the short-circuit side pulse generating circuit 14 generates a pulse of duration T_s . A dead time (T_d) is preliminarily set in sequencer 10. The positive side chopper gate amplifier (GA) 25 assumes a role of amplifying the pulse signal from the pulse generating circuit 13 to such a level that the positive side chopper switch 15 can operate reliably according to a pulse width signal determined by the positive side pulse generating circuit 13. The short-circuit side chopper gate amplifier 26 assumes a role of amplifying the pulse signal from the short-circuit side pulse generating circuit 14 to such a level that the short-circuit current control circuit 17 can operate reliably according to a pulse width signal determined by the short-circuit side pulse generating circuit 14. The positive side chopper switch 15 assumes a role of supplying the electric power from the positive side DC power supply 11 to the electrolytic bath in a pulsed manner according to a pulse width signal determined by

the positive side pulse generating circuit 13. The reverse current prevention diode 16 prevents reverse power from flowing to the side of the positive side DC power supply 11. The short-circuit current control circuit 17 forms, after application of a positive pulse voltage, a short circuit between the output terminals 18 of the anode 20 and the cathode 21 for a short-circuit duration T_s during non application of the pulse voltage.

[0022] Anodizing was conducted using the power supply shown in FIG. 2 under the following conditions. As a representative example of materials with high electrical conductivity, a test piece of A1100P was used. The test piece had a size of 50 mm × 50 mm × 1.5 mm (0.53 dm²). As a representative example of materials with low electrical conductivity, a test piece of ADC12 was used. The test piece had a size of 50 mm × 50 mm × 3.0 mm (0.56 dm²). The electrolytic bath contained approximately 200 L of an electrolytic solution, which was stirred by a liquid circulation and micro-aeration system and cooled by a plate type heat exchanger. A lead cathode bar and a carbon cathode plate were used. The bath liquid was free sulfuric acid solution with a concentration of approximately 150 g/L, and the bath liquid temperature was 10°C. The anodizing current density was variously changed up to 20 A/dm². After the anodizing, the test pieces were rinsed with flowing water for approximately two minutes and forcibly dried using hot air.

[0023] FIG. 3 shows a pulse setting condition and actual voltage and current waveforms corresponding to the pulse setting condition. In the drawing, T_+ represents the pulse voltage application duration, T_d represents the dead time necessary to decrease the pulse voltage to zero and to form a short circuit between the electrodes (during which the circuit is open), and T_s represents the short-circuit duration.

The voltage waveform rises according to the setting for T_+ , drops very slightly during T_d , and remains at zero during T_s . The current waveform rises sharply to a local maximum and then drops in an early stage of T_+ . The current waveform remains at zero during T_d . Although a large negative current flows instantaneously at the moment when T_s starts, the current waveform then returns to zero quickly and almost no current flows during T_t . After the elapse of T_t , the negative current increases to a local maximum and then starts decreasing.

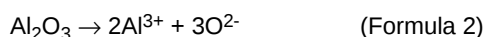
[0024] The above waveforms can be explained as follows. According to a non-patent document (Formation and Dissolution Behavior of Aluminum Anode Oxide Film, NAGAYAMA seiich, TAKAHASHI Hideaki and KODA Mitsuru; Kinzoku Hyomen Gijutsu (Metal Surface Technology) Vol.30, No.9, pp.438 to 456 (1979)), the steady state of anodic oxidation is expressed as shown in FIG. 4 (wherein FIG. 4(a) is an enlarged view of the barrier layer part in the overall structure of an anodic oxide film shown in FIG. 4(c)). That is, an anode aluminum alloy and a cathode carbon are placed in an electrolytic solution. Al is oxidized to Al_2O_3 at the anode, and H^+ ions are reduced to H_2 at the cathode. The growth of the barrier layer is described in the document as follows:

(1) The metal Al in contact with the bottom of the barrier layer is converted into Al^{3+} ions by anodic oxidation (FIG. 4(a), (1)):



(2) A part of Al^{3+} ions generated diffuse in the barrier layer and move into the electrolytic solution (FIG. 4(a), (2)).

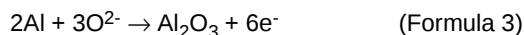
(3) At an interface between an upper part of the barrier layer and the electrolytic solution, the constituent substance Al_2O_3 of the barrier layer is dissociated into Al^{3+} and O^{2-} by the action of a strong electric field (FIG. 4(a), (3)):



(4) The Al^{3+} ions generated as above move into the electrolytic solution (FIG. 4(a), (4)), and

(5) The O^{2-} ions generated as above move in the barrier layer (FIG. 4(a), (5)).

(6) The O^{2-} ions having moved through the barrier layer and reached the barrier layer (Al_2O_3)/Al interface are reacted with metal Al at the boundary to form Al_2O_3 (FIG. 4(a), (6)):



(7) At an interface between an upper part of the barrier layer (Al_2O_3) and the electrolytic solution, H_2O is dissociated into H^+ ions and O^{2-} ions by the action of a strong electric field (FIG. 4(a), (7)):



A part of the O^{2-} ions generated are considered to participate in the generation of Al_2O_3 through the above processes (5) and (6).

The above is the process of growth of the barrier layer, and the anodic oxide film continues growing through the process. Here, it is mentioned that the transport numbers of Al^{3+} and O^{2-} are approximately 40 % and approximately 60 %, respectively.

respectively, when the electric charges move in the barrier layer in the form of Al^{3+} and O^{2-} . It is also mentioned that the transport number of Al^{3+} decreases, that is, the film growth rate increases, as the temperature is lower and as the oxidation current density is higher.

[0025] Here, the potential gradient in the vicinity of the barrier layer is considered as shown in FIG. 4(b).

(1) The Al^{3+} concentration in the barrier layer is higher on the barrier layer/Al interface side and lower on the barrier layer/electrolytic solution interface side (FIG. 4(b), (A)).

(2) The O^{2-} concentration in the barrier layer is lower on the barrier layer/Al interface side and higher on the barrier layer/electrolytic solution interface side (FIG. 4(b), (B)).

(3) Since there is a limit to the diffusion speed of Al^{3+} in Al_2O_3 , Al^{3+} ions are accumulated at the Al/ Al_2O_3 interface with the progress of electrolysis. Thus, the Al^{3+} concentration at the interface further increases (FIG. 4(b), (C)).

(4) Similarly, there is a limit to the diffusion speed of O^{2-} in Al_2O_3 , O^{2-} ions are accumulated at the Al_2O_3 /electrolytic solution interface with the progress of electrolysis. Thus, the O^{2-} concentration at the interface increases (FIG. 4(b), (D)).

[0026] From the above understanding, the voltage waveform and the current waveform in FIG. 3 can be explained as follows.

(1) It is considered that the voltage waveform slightly drops during T_d (FIG. 3, (1)) because Al^{3+} ions at the Al/ Al_2O_3 interface and O^{2-} ions at the Al_2O_3 /electrolytic solution interface diffuse to the Al side and the electrolytic solution side, respectively.

(2) The current waveform rises sharply in an early stage of T_+ (FIG. 3, (2)) because the reactions of Formulas (1), (2) and (3) proceed quickly with an increase in voltage.

(3) The current waveform then reaches a local maximum value (FIG. 3, (3)) and then drops because the concentration gradient (potential barrier) in the barrier layer including both the interfaces increases with the progress of electrolysis as shown in FIG. 4(b).

(4) When the current value decreases, the applied voltage and the potential barrier are soon balanced and the current reaches a constant value (FIG. 3, (4)).

(5) Because the applied voltage is zero (the circuit is in an open state) during T_d , the current is also zero (FIG. 3, (5)).

(6) A current flows for a very short period of time during T_s (FIG. 3, (6)) because the electrostatic charges in the form of Al^{3+} (or holes) at the Al/ Al_2O_3 interface and O^{2-} (or electrons) at the Al_2O_3 /electrolytic solution interface are released and discharged all at once at the moment when a short circuit is formed between the electrodes at the beginning of T_s .

(7) Then, almost no current flows during T_t (FIG. 3, (7)). After the elapse of T_t , the negative current increases to a local maximum and then starts decreasing (FIG. 3, (8)). The negative current is considered to be derived from reverse reactions of Formulas (1), (2) and (3). It is also considered that T_t is a time constant necessary for the reverse reactions to start and is determined by the type of the aluminum alloy or the composition of the electrolytic solution.

[0027] From above, when the short-circuit duration T_s is shorter than T_t , almost no negative current flows. It was experimentally confirmed that when A1100P, which has high electrical conductivity, is used as the Al alloy, almost no negative current flows when the short-circuit duration T_s is approximately 2 μs . It was also confirmed that when ADC12, which has low electrical conductivity, is used as the Al alloy, almost no negative current flows when the short-circuit duration T_s is approximately 15 μs . Therefore, it is estimated that T_t is approximately 2 μs in the case of A1100P and approximately 15 μs in the case of ADC12. In the case of A1100P, a very small, if any, negative current, flowed as long as T_t was 5 μs or less, and no negative current was observed when T_t was 2 μs or less. In the case of ADC12, on the other hand, a large negative current suddenly flowed when T_t exceeded 15 μs . As described above, a preferred short-circuit duration depends on the quality of material of the Al alloy.

[0028] From above, when the electric charges at the Al/ Al_2O_3 interface and the Al_2O_3 /electrolytic solution interface in the potential barrier are removed, a large current can be allowed to flow when the next pulse voltage is applied.

As described above, when the short-circuit duration is approximately 5 μs or less, preferably 1 to 5 μs , more preferably 1 to 3 μs , in the case of A1100P, the film growth rate can be improved since the film generated is not reduced by a negative current. In the case of ADC12, when the short-circuit duration is 15 μs or less, preferably 1 to 15 μs , more preferably 1 to 10 μs , the film growth rate can be improved.

[0029] As shown in FIG. 1, the film growth rate is proportional to the effective current density. It was found that a decrease in effective current caused by a negative current which flows when a short circuit is formed can be reduced and consequently the film growth rate can be improved significantly by significantly shortening the short-circuit duration. In addition, according to the present invention, the film growth rate can be further improved by optimizing the pulse

frequency.

[0030] FIG. 5 shows the current waveform shown in FIG. 3 in more detail, in which FIG. 5(a) shows a case where the frequency is low (T_+ is long), and FIG. 5(b) shows a case where the frequency is high (T_+ is short). In the case of FIG. 5(b), T_s is set to 2 μ s so that almost no negative current can flow.

The frequency f of the pulse is calculated as follows:

$$f_{(i)} = 1/(T_{+(i)} + T_d + T_s) \quad (\text{Formula 5})$$

Here, i refers to an i -th frequency of a plurality of frequencies which are tested for optimization.

The quantity of electricity Q used for the anodizing is the integral $S_{(i)}$ of the current waveform in FIG. 5. When the frequency at this time is $f_{(i)}$, Q is obtained as follows;

$$Q_{(i)} = S_{(i)} \cdot f_{(i)} \quad (\text{Formula 6})$$

The larger $Q_{(i)}$ is, the higher the film growth rate will be. It is possible to consider that the range of $T_{+(i)}$ which gives a large $Q_{(i)}$ is between $T_{+(m)}$ at which the current value reaches a local maximum and $T_{+(e)}$ which makes Area (a) = Area (b) in FIG. 5.

[0031] From a current waveform obtained in the experiment,

$$T_{+(m)} \approx 25 \mu\text{s}$$

$$T_{+(e)} \approx 90 \mu\text{s}.$$

When T_d and T_s are set to the above preferred values, that is, $T_d = 5 \mu$ s and $T_s = 2 \mu$ s in the case of A1100P or $T_s = 15 \mu$ s in the case of ADC12 as shown in FIG. 5(b), the frequencies corresponding to them are:

$$f_{\max} \approx 1/(25 + 5 + 2) = 31.3 \text{ KHz}$$

$$f_{\min} \approx 1/(90 + 5 + 15) = 9.1 \text{ KHz}.$$

In reality, it was confirmed experimentally that anodizing can be carried out without any problems in a frequency range of 8 to 35 KHz, preferably 10 to 30 KHz.

[Examples]

[0032] The following Examples will further illustrate the present invention. It should be understood, however, that the present invention is not intended to be limited to the Examples.

Example 1 and Comparative Example 1

[0033] Using the power supply shown in FIG. 2, anodizing was carried out under the following conditions. As a representative example of materials with high electrical conductivity, a test piece of A1100P was used. The test piece had a size of 50 mm $\times$ 50 mm $\times$ 1.5 mm (0.53 dm²). The electrolytic bath contained approximately 200 L of an electrolytic solution, which was stirred by a liquid circulation and micro-aeration system and cooled by a plate type heat exchanger. A lead cathode bar and a carbon cathode plate were used. The bath liquid was a free sulfuric acid solution with a concentration of approximately 150 g/L, and the bath liquid temperature was 10°C. The anodizing current density was variously changed up to 20 A/dm². After the anodizing, the test piece was rinsed with flowing water for approximately two minutes and forcibly dried using hot air.

The positive current supply duration T_+ was 80 μ s, and the dead time (circuit open period) T_d was 5 μ s. Although the positive current density I_+ to be achieved upon application of a pulse voltage was changed variously, the positive current density I_+ was fixed at 20A/dm² since anodizing was able to be carried out stably when $I_+ = 20$ A/dm². The negative

current was measured at short-circuit duration T_s of 2, 3, 4, 5, 10, 20 and 40 μs . The results were summarized in a table of FIG. 6 and in FIG. 7.

Almost no negative current flowed when $T_s = 2 \mu\text{s}$. When $T_s < 5 \mu\text{s}$, a very small, if any, negative current flowed. Although the rate of increase of negative current increased when T_s exceeded 5 μs , the negative current was still in an allowable range when T_s was not longer than approximately 15 μs . When T_s exceeded 20 μs , the negative current significantly increased.

That is, when the short-circuit duration T_s is equal to or less than approximately 15 μs , the negative current can be sufficiently reduced or suppressed to almost zero so that the film growth rate can be improved.

Example 2 and Comparative Example 2

[0034] An experiment was conducted under the same conditions as those in Example 1 except that the positive current supply duration T_+ was 40 μs , and that the negative current was measured at short-circuit durations T_s of 2, 5, 10, 20 and 40 μs . The results were summarized in a table of FIG. 6 and in FIG. 7.

Although almost no negative current flowed when the short-circuit duration was 2 μs , the negative current increased rapidly as the short-circuit duration T_s increased to 10, 20 and 40 μs . The negative current was in an allowable range when T_s was not longer than approximately 10 μs . When T_s exceeded 20 μs , the negative current significantly increased.

Example 3

[0035] An experiment was conducted under the same conditions as those in Example 1 except that a test piece (size: 50 mm $\times$ 50 mm $\times$ 3.0 mm (0.56 dm²)) of ADC12, having lower electrical conductivity, was used and that changes in negative current were observed with T_+ , T_d and I_+ fixed as follows: $T_+ = 80 \mu\text{s}$, $T_d = 5 \mu\text{s}$, $I_+ = 10 \text{ A/dm}^2$. As a result, almost no negative current flowed when T_s was shorter than 15 μs but a large negative current flowed when T_s was equal to or longer than 15 μs .

Claims

1. A method for anodizing an aluminum alloy to form an anodic oxide film on a surface of said aluminum alloy using pulsed electric power, **characterized in that**, after application of a positive pulse voltage, a short circuit is formed between an anode for anodic oxidation and a cathode for anodic oxidation for a short-circuit duration of not longer than 15 μs during non application of the pulse voltage.
2. A method for anodizing an aluminum alloy as recited in claim 1, wherein said short-circuit duration is not shorter than 1 μs and not longer than 15 μs .
3. A method for anodizing an aluminum alloy as recited in claim 1, wherein said short-circuit duration is not shorter than 1 μs and not longer than 5 μs .
4. A method for anodizing an aluminum alloy as recited in claim 1, 2 or 3, wherein said pulsed electric power has a waveform having a cycle composed, in the order, of a pulse voltage application duration (T_+), a dead time (T_d) and a short-circuit duration (T_s).
5. A method for anodizing an aluminum alloy as recited in any one of claims 1 to 4, wherein said pulsed electric power has a frequency of 8 to 35 KHz.
6. A method for anodizing an aluminum alloy as recited in any one of claims 1 to 4, wherein said pulsed electric power has a frequency of 10 to 30 KHz.
7. A power supply for anodizing an aluminum alloy for use in a method for anodizing an aluminum alloy to form an anodic oxide film on a surface of said aluminum alloy using pulsed electric power, comprising a pulsed electric power generating section configured to generate such pulsed electric power that, after application of a positive pulse voltage, a short circuit is formed between a terminal connected to an anode for anodic oxidation and a terminal connected to a cathode for anodic oxidation for a short-circuit duration of not longer than 15 μs during non application of the pulse voltage.
8. A power supply for anodizing an aluminum alloy as recited in Claim 7, wherein said pulsed electric power generating

section is configured to generate pulsed electric power which provides a short-circuit duration of not shorter than 1 μ s and not longer than 15 μ s.

5 **9.** A power supply for anodizing an aluminum alloy as recited in Claim 7, wherein said pulsed electric power generating section is configured to generate pulsed electric power in which the short-circuit duration is not shorter than 1 μ s and not longer than 5 μ s.

10 **10.** A power supply for anodizing an aluminum alloy as recited in any one fo Claims 7 to 9, wherein said pulsed electric power generating section is configured to generate pulsed electric power having a waveform composed, in the order, of a pulse voltage application duration (T_+), a dead time (T_d) and a short-circuit duration (T_s).

11. A power supply for anodizing an aluminum alloy as recited in any one of Claims 7 to 10, wherein said pulsed electric power generating section is configured to generate pulsed electric power having a frequency of 8 to 35 KHz.

15 **12.** A power supply for anodizing an aluminum alloy as recited in any one of Claims 7 to 10, wherein said pulsed electric power generating section generates pulsed electric power having a frequency of 10 to 30 KHz.

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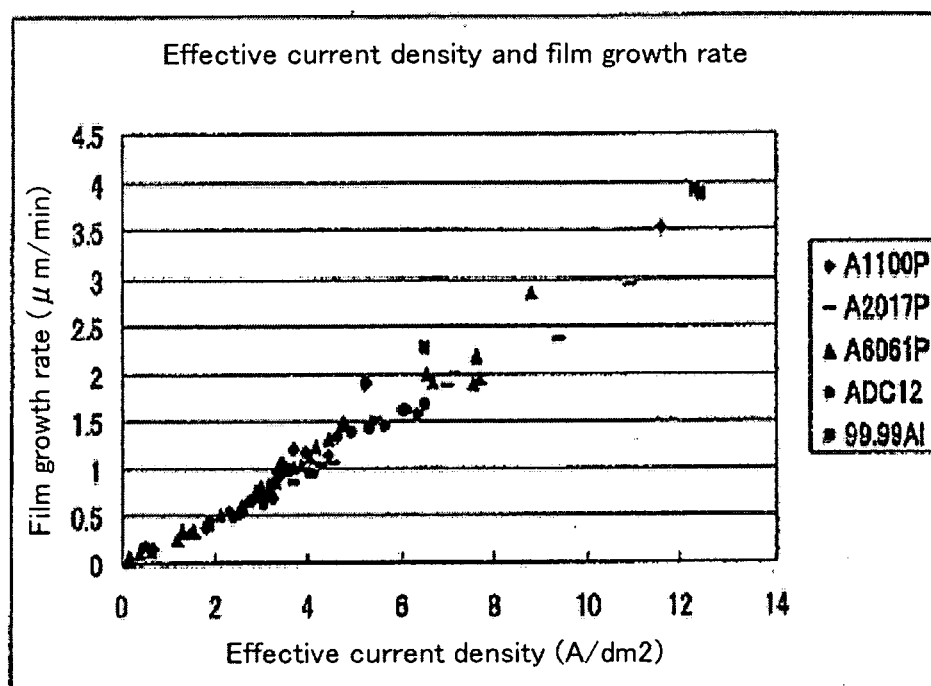
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FIG. 1



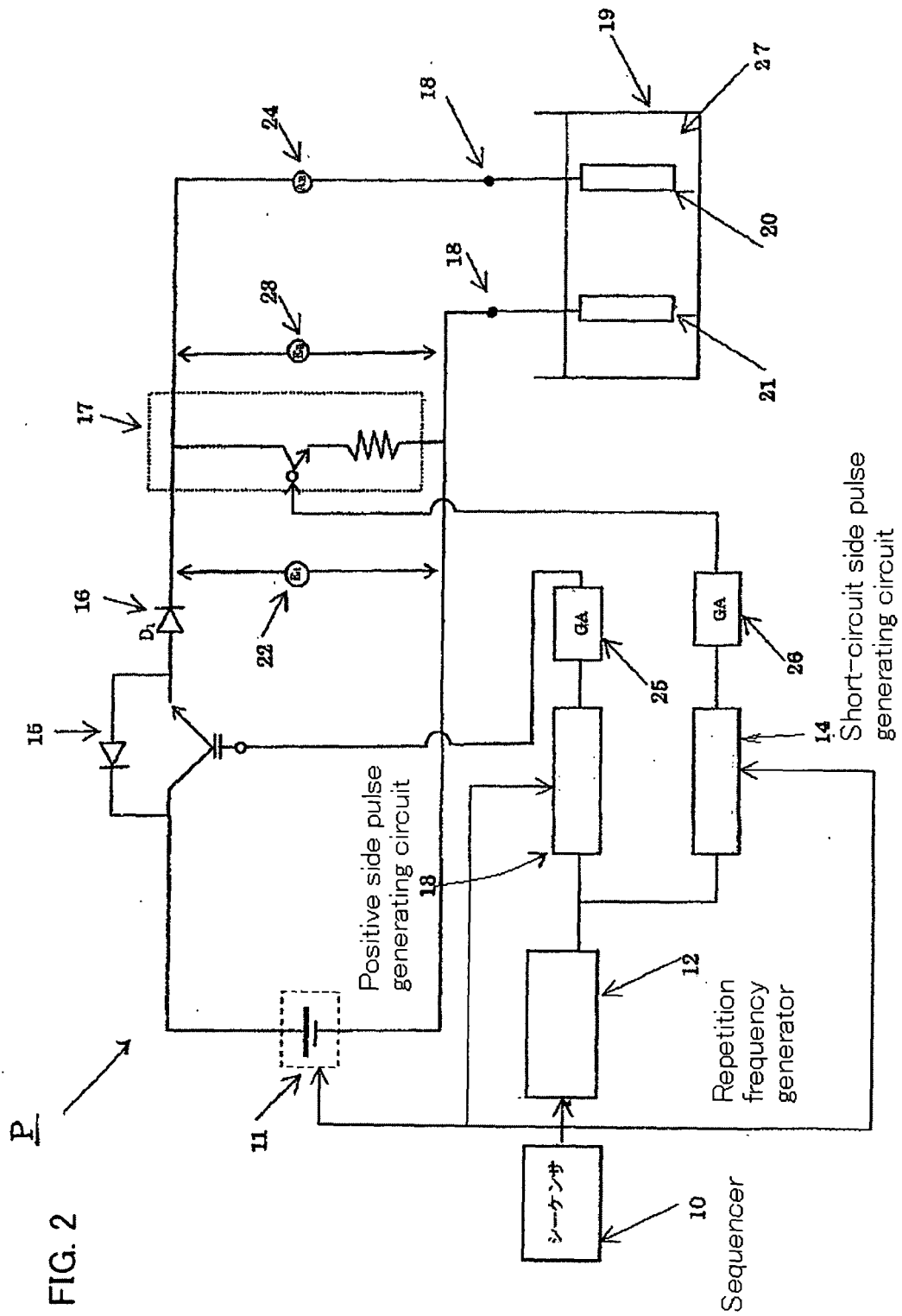


FIG. 3

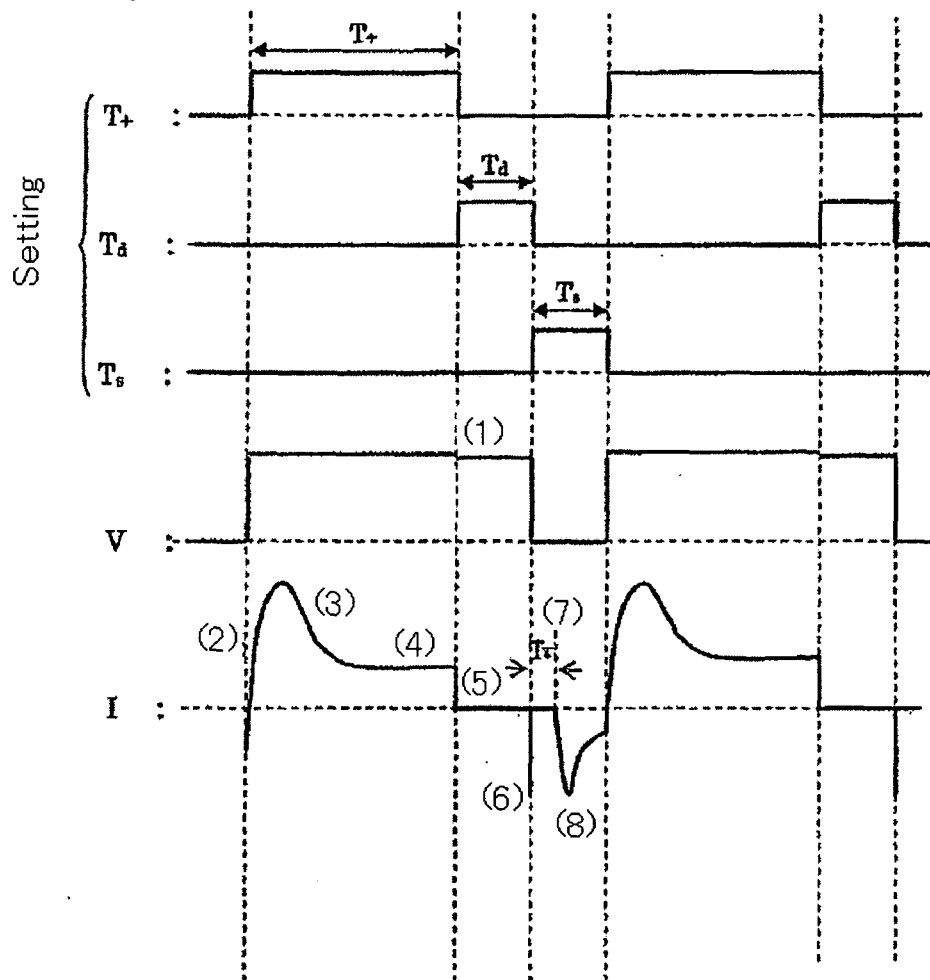


FIG. 4(a)

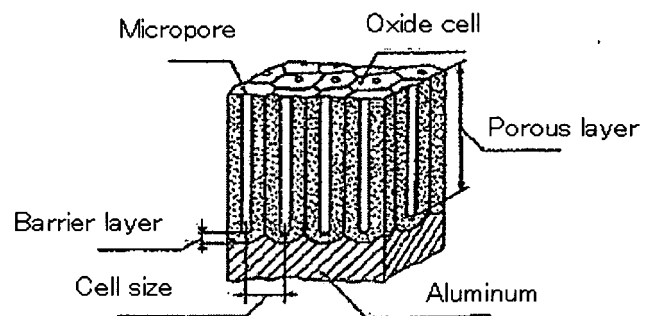
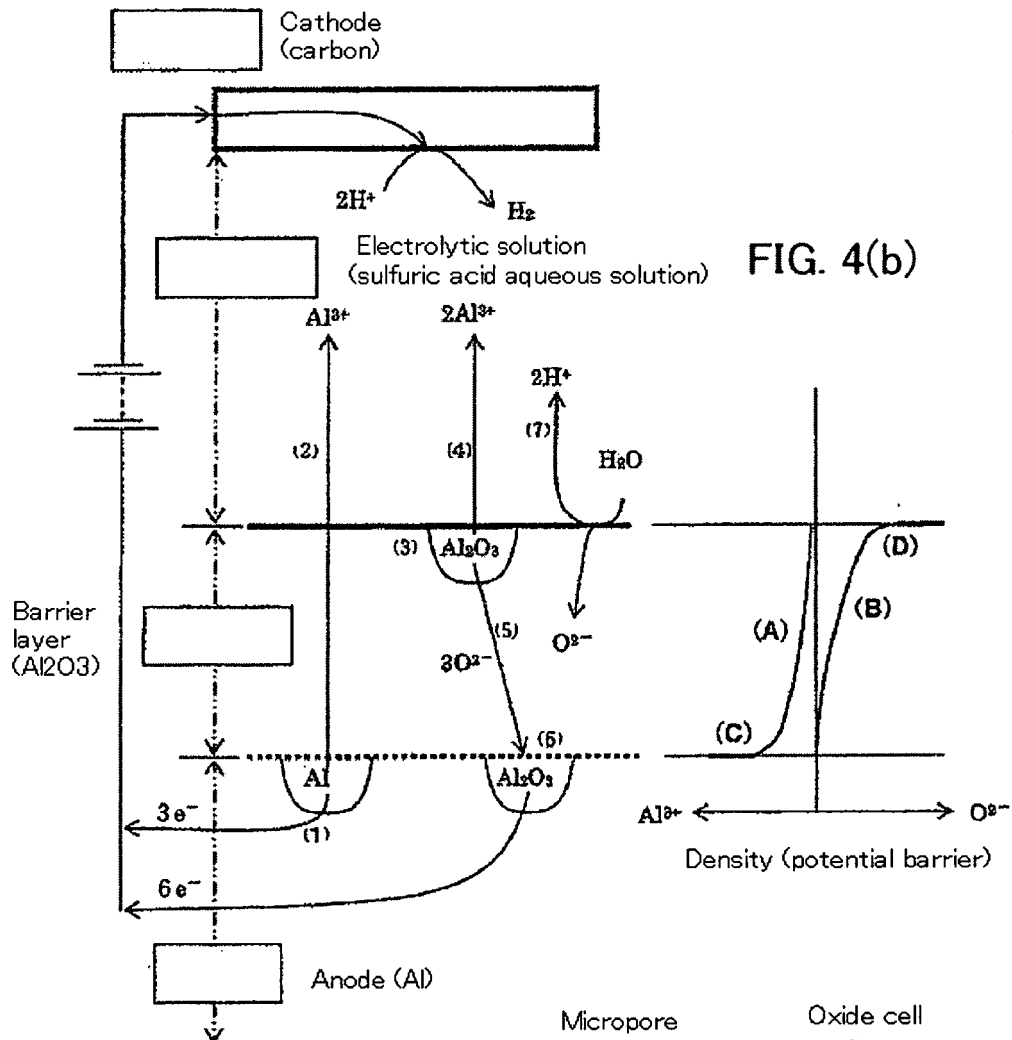


FIG. 4(c)

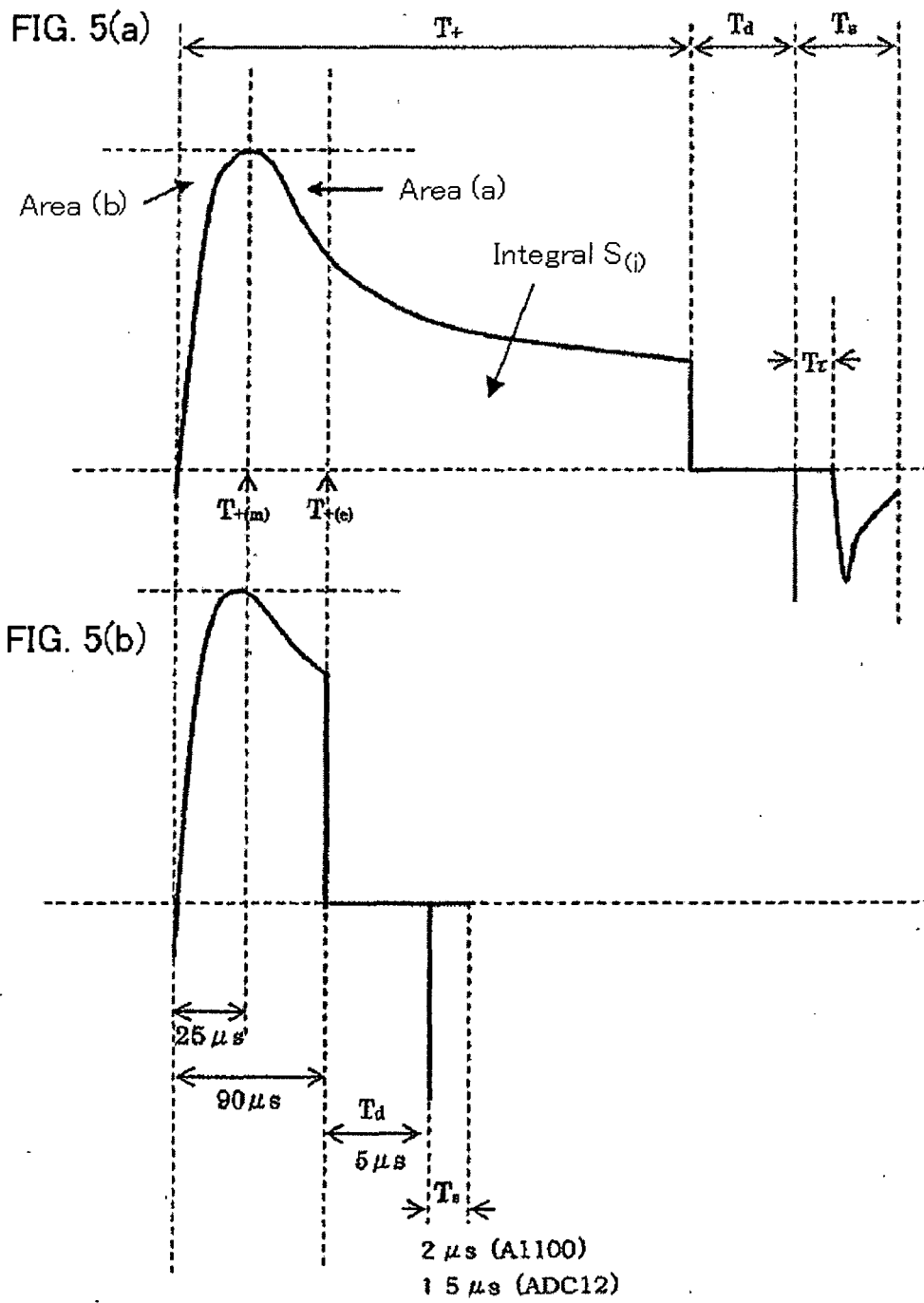


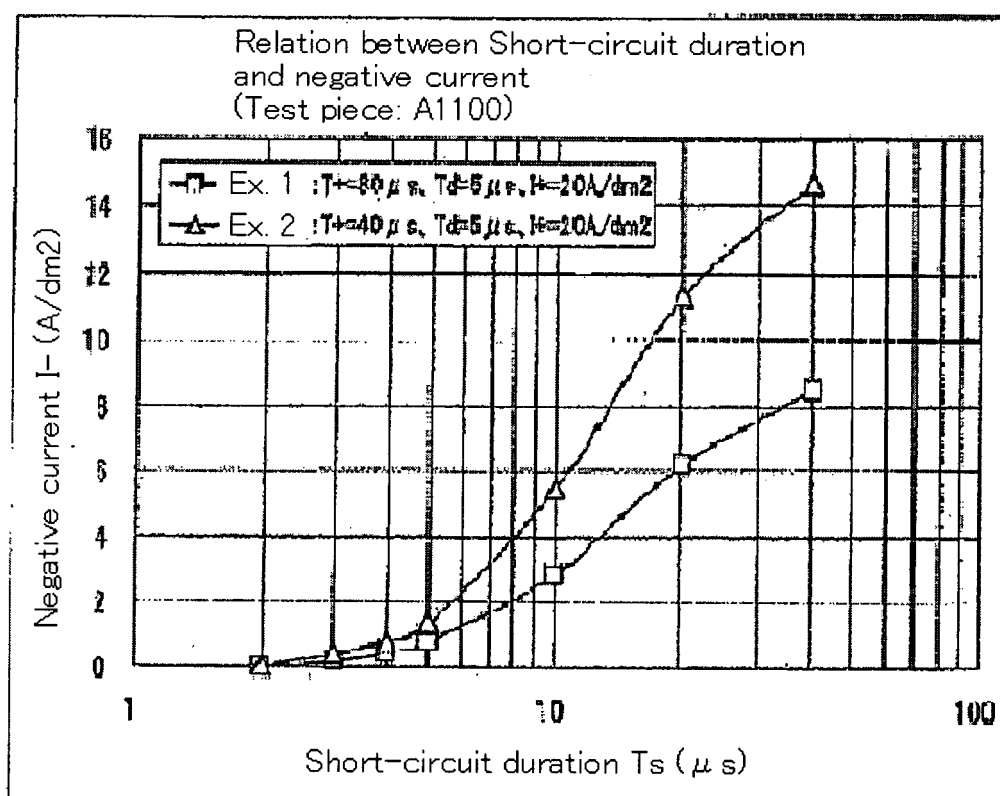
FIG. 6

Experiment results

 T_{+0} : Positive current supply duration (μs) T_d : Dead time (circuit open period) (μs) T_s : Short-circuit duration (μs) I_+ : Positive current density achieved upon application of pulse voltage (A/dm^2) I_- : Negative current density observed when short circuit was formed (A/dm^2)

	T_+	T_d	T_s	I_+	I_-
Example 1-1	80	5	2	20	0.0
Example 1-2	80	5	3	20	0.2
Example 1-3	80	5	4	20	0.4
Example 1-4	80	5	5	20	0.8
Example 1-5	80	5	10	20	2.8
Comparative Example 1-1	80	5	20	20	6.2
Comparative Example 1-2	80	5	40	20	7.5
Example 2-1	40	5	2	20	0.0
Example 2-2	40	5	5	20	1.3
Example 2-3	40	5	10	20	5.5
Comparative Example 2-1	40	5	20	20	11.3
Comparative Example 2-2	40	5	40	20	14.7

FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/063501

A. CLASSIFICATION OF SUBJECT MATTER

C25D11/04 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D11/00-C25D11/38

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI (C25D_011_04/ic)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2006-083467 A (Suzuki Motor Corp.), 30 March, 2006 (30.03.06), Claim 6; Par. Nos. [0017], [0043] & US 2006/0037866 A1	1-12

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search
21 September, 2007 (21.09.07)Date of mailing of the international search report
09 October, 2007 (09.10.07)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

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REFERENCES CITED IN THE DESCRIPTION

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- **NAGAYAMA SEIICHI ; TAKAHASHI HIDEAKI ; KODA MITSURU.** Formation and Dissolution Behavior of Aluminum Anode Oxide Film. *Kinzoku Hyomen Gijutsu*, 1979, vol. 30 (9), 438-456 [0024]