Influence of Current Forms on Anodic Oxidation of Aluminum in Sulfuric and Oxalic Acids

Sakaé TAJIMA*, Fujio SATOH*, Nobuyoshi, BABA*
and Toshiro FUKUSHIMA***

Aluminum sheets, 99.99%, 1/2 H were anodically oxidized in sulfuric (15 wt.%) and oxalic (3 wt.%) acid baths at 30° and 0°C by applying currents of various forms (direct current, single phase-half wave, 3-P non-reversed interrupted, imperfectly rectified, superimposed (AC+DC), and alternating currents, as shown in Fig. 1, kept at 1 A/dm² (mean positive current density) for 30 min.

Fig. 1 Various wave forms applied and their circuit diagram.

Table 1 Properties of Sulfuric Acid Films (S₃₀)
H₂SO₄ 15 wt. %, 30°C 1 A/dm² (mean positive current), 30 min

Current Form	Voltage		Coating Ratio	Thickness (μ)	Density	Abrasion Resistance (sec)	Hardness (μ vickers)	Appearance
	DC (V)	AC (V)						
Direct Current (Battery)	13.0	13.0	1.16	8	2.46	455	78	Non-colored transparent
1-P Half wave	13.5	14.5	1.25	8	2.66	435	84	" "
3-P Non-reversed Interrupted	13.0	15.5	1.22	7.5	2.76	640	80	" "
1-P Imperfectly Rectified (2:1)	4.0	10.0	1.10	7	2.32	205	54	Light yellowish-gold, opaque
" " (3:1)	4.5	10.0	1.13	7	2.32	225	46	" "
" " (4:1)	4.5	10.0	1.16	7	2.42	280	64	" "
3-P Imperfectly Rectified (2:1)	5.5	11.5	1.04	6.5	2.38	175	48	" "
" " (3:1)	6.5	11.5	1.08	6.5	2.46	165	47	" "
" " (4:1)	8.0	11.0	1.09	7	2.25	185	47	" "
Superimposed (AC+DC)	10.0	10.0	1.13	7	2.50	370	78	Non-colored transparent
Alternating (AC)	1.6	11.0	1.04	5.5	2.70	155	43	Light yellowish opaque

* ratio of positive (1 A/dm²) and negative current

** specified by Japanese Industrial Standards (JIS-H 8601)

* Laboratory of Electrochemistry, Tokyo City University and Chemistry Division, Metropolitan Industrial Research Institute, Tokyo.

** Metropolitan Industrial Research Institute, Tokyo.

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The properties of the oxide films thus formed were compared and the results were discussed together with the X-ray diffraction patterns and with the oscillographic analysis of the current and voltage (Lissajous' Figure). Results are summarized as follows:

(1) Bath voltage

In both sulfuric and oxalic acid baths, the bath voltage is very much lower when imperfectly rectified currents containing a negative component are applied as compared with the voltages by currents containing a positive component only. But no remarkable difference in effective values are noticed in both types of current.

(2) Appearance

By sulfuric acid (30°C) films, the appearance is not so much different according to the current applied. Usually non-colored transparent films are formed. In spite of this, by the imperfectly rectified currents, the film shows somewhat opaque, light yellowish color.

By oxalic acid films, the colors are yellowish when the current includes a negative component (i.e., in the case of imperfectly rectified and alternating currents) but the color tone is not so much influenced

Fig. 2 Current measuring device

Table 2 Properties of Oxalic Acid Films (X 30)
(COOH)₂·2 H₂O 3wt %, 1 A/dm² (mean positive current), 30 min

Current Form	Voltage		Coating Ratio	Thickness (μ)	Density	Abrasion Resistance (sec)	Hardners (μ Vickers)	Appearance
	DC (V)	AC (V)						
Direct Current (Battery)	42.0	44.0	1.27	8.5	2.6	1330	70	Non-colored, transparent
1-P Half wave	42.0	45.0	1.35	7.5	3.2	865	112	Light yellow, transparent
3-P Non-reversed interrupted	42.0	45.0	1.29	7.0	2.7	980	81	" "
1-P Imperfectly rectified (2:1)*	12.5	34.0	1.22	6.5	2.3	390	40	Yellowish gold
" " (3:1)	14.0	34.0	1.20	6.5	2.5	430	48	" "
" " (4:1)	14.5	36.0	1.23	7.0	2.5	580	49	" "
3-P Imperfectly rectified (2:1)	18.0	33.0	1.20	5.0	2.8	225	49	" "
" " (3:1)	23.0	35.0	1.21	5.5	2.8	580	46	" "
" " (4:1)	24.0	36.0	1.23	6.5	2.6	695	46	" "
Superimposed (AC+DC)	24.0	25.0	1.25	7.0	3.0	670	79	Light yellow
Alternative current (AC)	4.0	40.0	1.14	4.5	2.9	205	48	Yellowish gold

* Ratio of positive (1 A/dm²) and negative current

** Specified by Japanese Industrial Standards (JIS-H 8601)

Table 3 Properties of Sulfuric and Oxalic Acid Films
at 0°C, 1 A/dm² (mean positive current), 30 min.

	Form	Coating Ratio	Thickness (μ)	Density	Hardness* (μ Vickers)	Appearance
S ₀	Direct Current (Battery)	1.65	7.0	3.8	80~90	Glassy gray cracked
	1-P Half wave	1.72	7.5	4.4 (?)	70~100	"
	1-P Imperfectly rectified (2:1)**	1.55	8.0	8.0	80~90	Gray, Foams are included
X ₀	Direct current	1.59	8.0	3.5	80~90	Light yellow, Smooth
	1-P Half wave	1.63	8.0	3.5	70~90	Yellowish gold, Smooth
	1-P Imperfectly rectified (2:1)	1.20	8.0	1.8	70~90	Deep yellowish gold-brown Foams are included

* Not correct values, because the films are thin

** Ratio of positive (1 A/dm²) and negative currents

by the quantity a of negative component.

When the temperature is low (0°C), both films show various deep colors in the case of the imperfectly rectified currents.

(3) Coating ratio

A maximum value was obtained by the single-phase half-wave current and the value becomes smaller in the order of 3-P non-reversed interrupted current, DC, AC+DC, imperfectly rectified current and AC (the smallest). In the imperfectly rectified current, the value is larger by single phase than by 3 phase current and decreases with increase of the negative component.

(4) Apparent Density

Apparent density of the film is higher by the interrupted currents (single phase-half wave and 3-phase non-reversed interrupted) than by any other of forms current.

(5) Thickness and Microhardness

Here also, the values are highest by the interrupted currents when the mean positive current is the same. But the real hardness can not measured because the films are too thin. The films thicker than

Sulfuric acid (15 wt %), 30°C , DC 1 A/dm²

Oxalic acid (3 wt %), 30°C , DC 1 A/dm²

Sulfuric acid (15 wt %) 30°C , 1 P half wave, 1 A/dm²

Oxalic acid (3 wt %) 30°C , 1 P half wave 1 A/dm²

Condition of X-ray diffraction (C. M. Bulb)

Target	Cu	Scanning Speed	$4^{\circ}/\text{min}$
Filter	Ni	Divergency	1°
Voltage	30 kVP	Chart Speed	2 cm/min
Current	15 mA	Receiving Slit	0.2 mm
Count Full Scale	500 c/s	Soller Slit	2.5°
Scale Factor	8	Glancing Angle	5°
Time Constant	1 sec	Date	1958. 2. 5
Multiplier	0.8		

Fig. 3 Results of X-ray diffraction

Fig. 4 Oscillograms of various currents

Fig. 5 Voltage-current Lissajous' figure.

30 μ formed at 0°C showed nearly correct hardness, viz, 300~400 μ Vickers.

(6) Abrasion resistance after steam-sealing

The coatings by 3-P non-reversed interrupted current and DC show the highest abrasion resistance and those by single phase-half wave and AC+DC gave a slightly inferior resistance. The coatings by imperfectly rectified and alternating current gave fairer lower values.

From these observations and from the oscillographic analysis of the voltage and current relations (Fig. 4 and 5), the following considerations were made:-

By the alternate currents, the discharge of hydrogen ion occurs in addition to the usual anodic oxidation, which destroys mechanically the oxide structure in the micropores or promotes the chemical dissolution of the film in the electrolytes, so the properties of films are rather inferior. But the X-ray patterns give similar amorphous oxide structure regardless of the currents applied.

An electrostatic capacitance existing on the electrode surface reduces an anodic (Faradaic) portion of the total current, thus decreasing the current efficiency of the oxide formation.

By the interrupted current such as single phase-half wave, and 3-P non-reversed interrupted currents, a current larger than the mean value indicated by ammeter passes promptly in a short time, followed by a pause (Fig. 4). Therefore, a good quality film is produced just as in the case of anodizing under a higher current density. Diffusion and cooling of the electrolyte by current interruption also favor preventing the dissolution of the oxide films, thus improving coating ratio etc.

In conclusion, anodizing by interrupted current give, in general, oxide films of the best quality as compared with other possible wave forms including direct current when the positive current density and the total current are the same.

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