On the Mechanism of the Electrolytic Polishing of Aluminum - Part.2

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	キーワード (Ja):
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	作成者: 西田, 惠三
	メールアドレス:
	所属:
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On the Mechanism of the Electrolytic Polishing
of Aluminum (Part. II)*

Keizo Nishida

Abstract

Continuing from the previous report[1], the author has observed the viscosity and its change with time of each solution, and measured anodic and cathodic single potential on passing current in the solution, then he discussed the results deduced from the above data.

Next, the author has noticed the abnormal phenomena of anode and anolyte on electrolysing, and discussed partly some of their causes.

Lastly, the author has reported the results from the examination by the electron diffraction method on the electrolytic-polished surface of aluminum.

Note : The signs used in this report are about the same as in that of Part I. They are as follows:

Name of Soln.	Vol. of HClO$_4$. (60% aq. soln)	Vol. of $(CH_3CO)_2O$
Soln. (x)	5.0 (c.c.)	95.0 (c.c.)
Soln. (a)	10.	90.
Soln. (b)	20.	80.
Soln. (b—c)	24.	76.
Soln. (c)	30.	70.
Soln. (d)	40.	60.
Soln. (e)	50.	50.
Soln. (f)	60.	40.

These solutions were prepared at 18°C from the previous consideration.

Soln. (b—c) is added to this list noticing that this composition was the critical one.

The testing sample used in these experiments is made from 99.8% Al ingot.

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* Some of this report was lectured at the mass meeting of The Japan Institute of Metals in Sapporo in Sept. 1950.

1) See K. NISHIDA: "On the Mechanism of the Electrolytic Polishing of Al. (Part I)", Mem. Muroran Coll. Tech., Vol. 1, No. 1 (1950), p. 1.

§ 1. On the Aqueous Solution of Acetic Acid.

From the previous report, the author has noticed the electrolyte consisted of much acetic acid, so he examined the aqueous solution of acetic acid by the following method to appreciate the effect of acetic acid on the solution. The concentration of the solution was 20.8%, 41.5%, 62%, 72.85%, and 83.1% by weight respectively.

a) The measurement of electric conductivity.

Using the same apparatus as in Part I, the following results have been obtained (Fig. 1.), where the value for pure water and pure acetic acid respectively was taken from other reference books. The value is very small, acetic acid being weak, as compared with the electrolytic polishing solution.

b) The Measurement of Decomposition Voltage.

Like the previous method, the results gained are indicated in Fig. 2, with ones of Al-electrode together. The true concentration of aqueous solution in the electrolyte correspounds more than 70% from the consideration of the constituents present in each solution. From Fig. 2, the decomposition voltage is between −1.34 volts and −1.65 volts.

§ 2. On the Electric Conductivity of the Solution Again.

The results measured at 25°C is in Fig. 3, with that at 18°C. In this case the tendency is analoguous to the previous one, and that the gap occurred in Soln. (a) to Soln. (b) is larger than the latter. Moreover, in order to see how the gap in electric conductivity occurs after preparing the solution, the change of the property with time was observed. The results are given in Fig. 4, in which the temperature is 25°C. So it is shown that the gap of the curve is instantaneously accomplished after mixing.

§ 3. On the Viscosity of the Solution.

The viscosity was measured at 10°C, 18°C, and 25°C respectively for each solution. Ostwald's viscosimeter was used for it. Because this property is one of the most important factors for electrolytic polishing, as seen from many reports about this property, and that makes it possible to examine the relation between the electric conductivity and the viscosity of each solution. It was summed up in Fig. 5. The above-stated gap is not shown in relation to the viscosity except that there is a maximum value on the composition of Soln. (b—c), and both sides of this composition
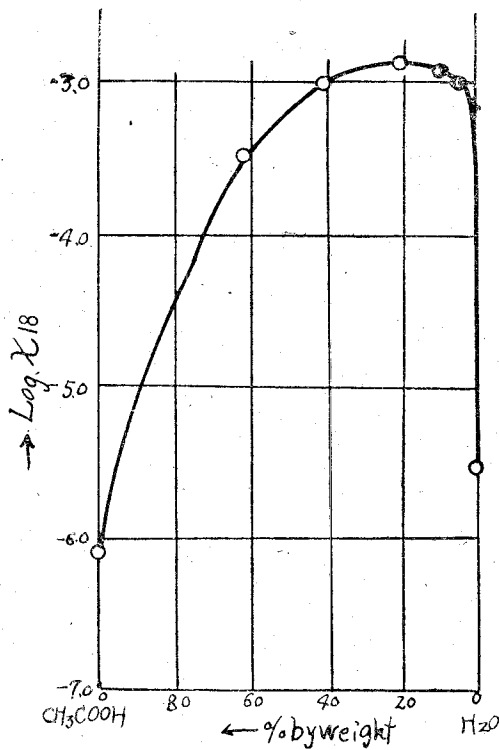
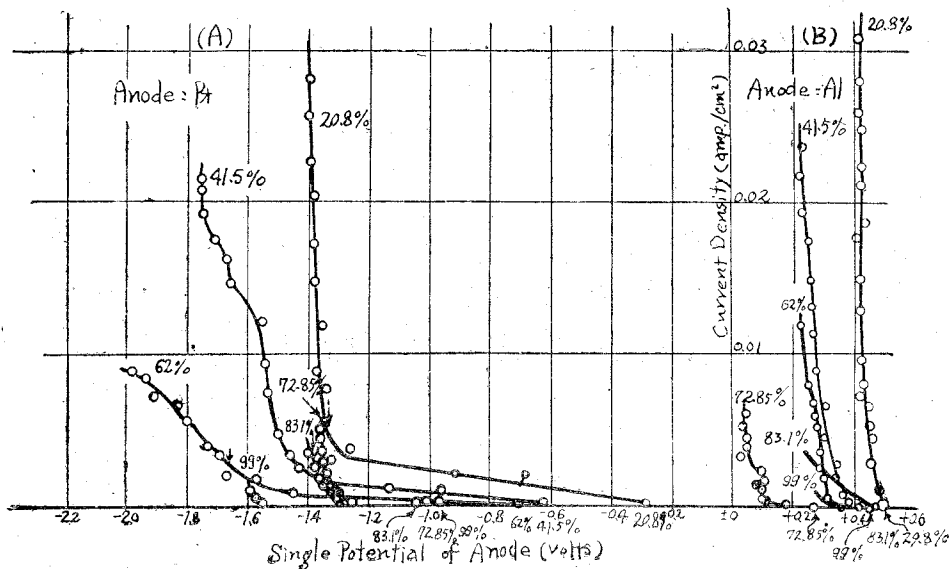Fig. 1. Specific Conductivity of
(CH₃COOH–H₂O) System at 18°C.

Fig. 2. Current Density-Single Potential Curves at 18°C.
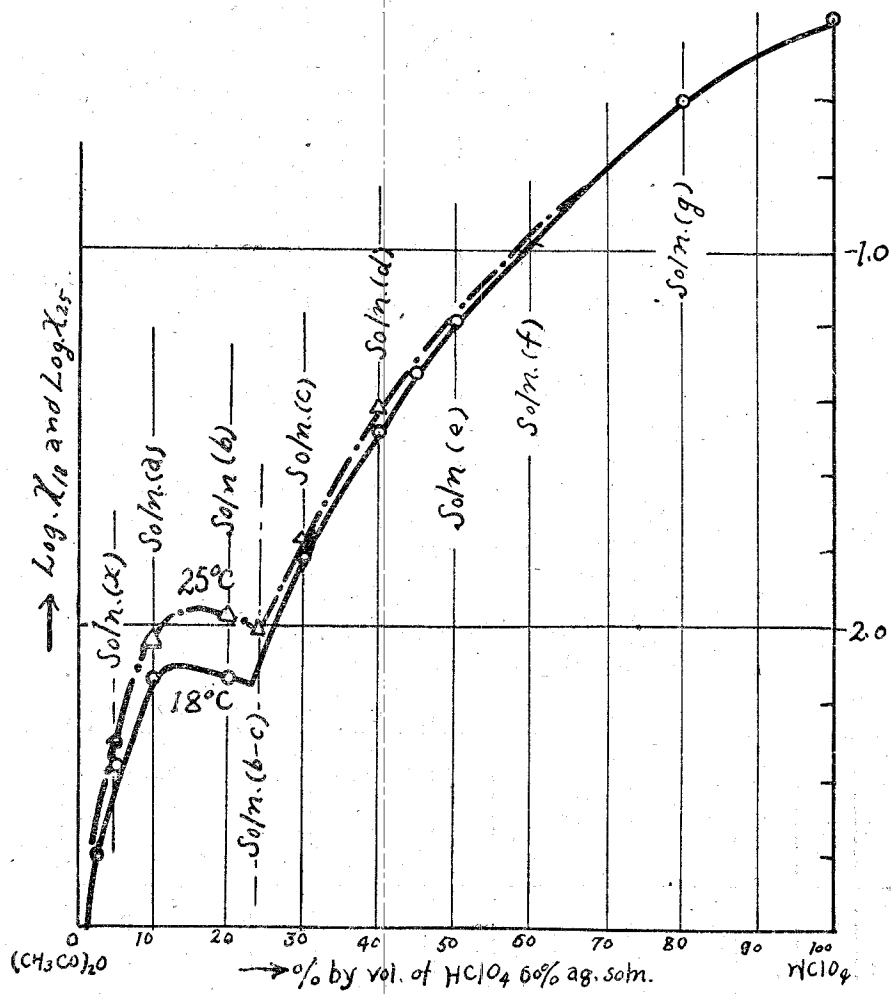Electrolyte: Aqueous Solution of Acetic Acid.

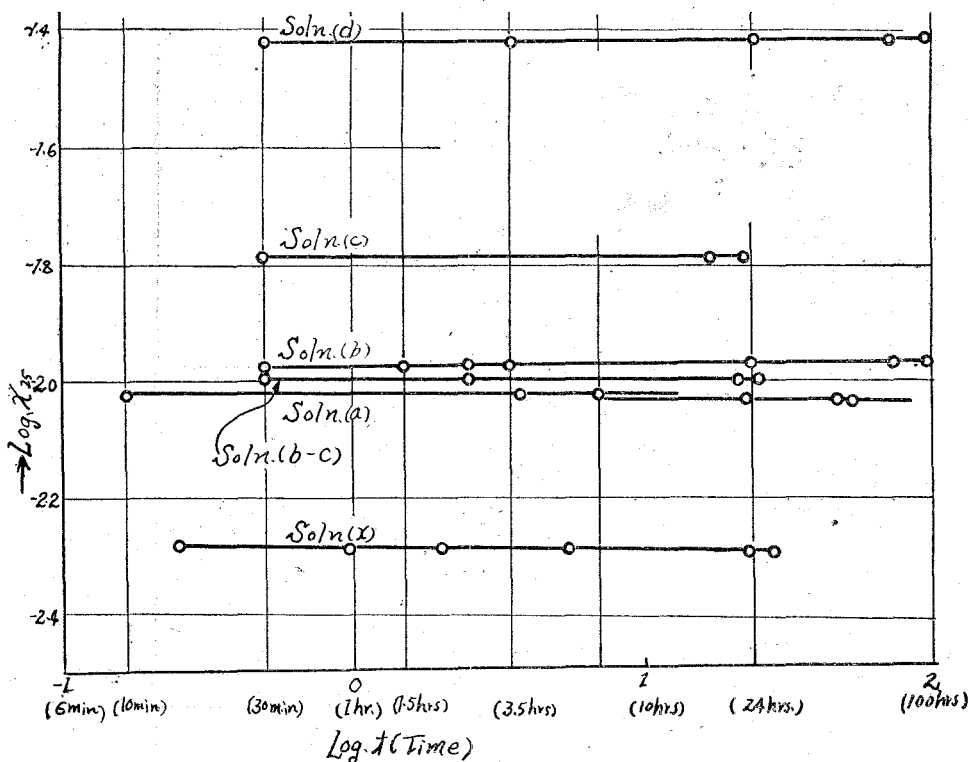Fig. 3.   Specific Conductivity of Each Solution at 18° and 25°C.

Fig. 4.　Conductivity-time Curves of Each Solution at 25°C.

have about the same tendency. Next, the change of the viscosity with time was observed on account of the same reason as the electric conductivity, and at this time there was no change of it with time. So, the viscosity must be established as soon as two constituents are mixed.

§4.　The Consideration of the Above-stated Results.

In Part I, supposing that there was some reaction on mixing, and then the chemical species after mixing were somewhat different from what had been before mixing, the calculation led to the conclusion that Soln. (b—c) was the critical composition. And that assumption was verified by the above-stated datum. Moreover, from that datum, the electric conductivity of the solution depends in the so-called non-aqueous composition upon the concentration of ClO_4^- and $CH_3C(OH)_2^-$ ions in acetic acid, and in the aqueous composition that of ClO_4^- ion in water. For the viscosity the quantity of acetic acid seems to play a rôle.

There is no conclusion or verification about the compound which is made from $HClO_4$ and CH_3COOH, except what the author introduced in
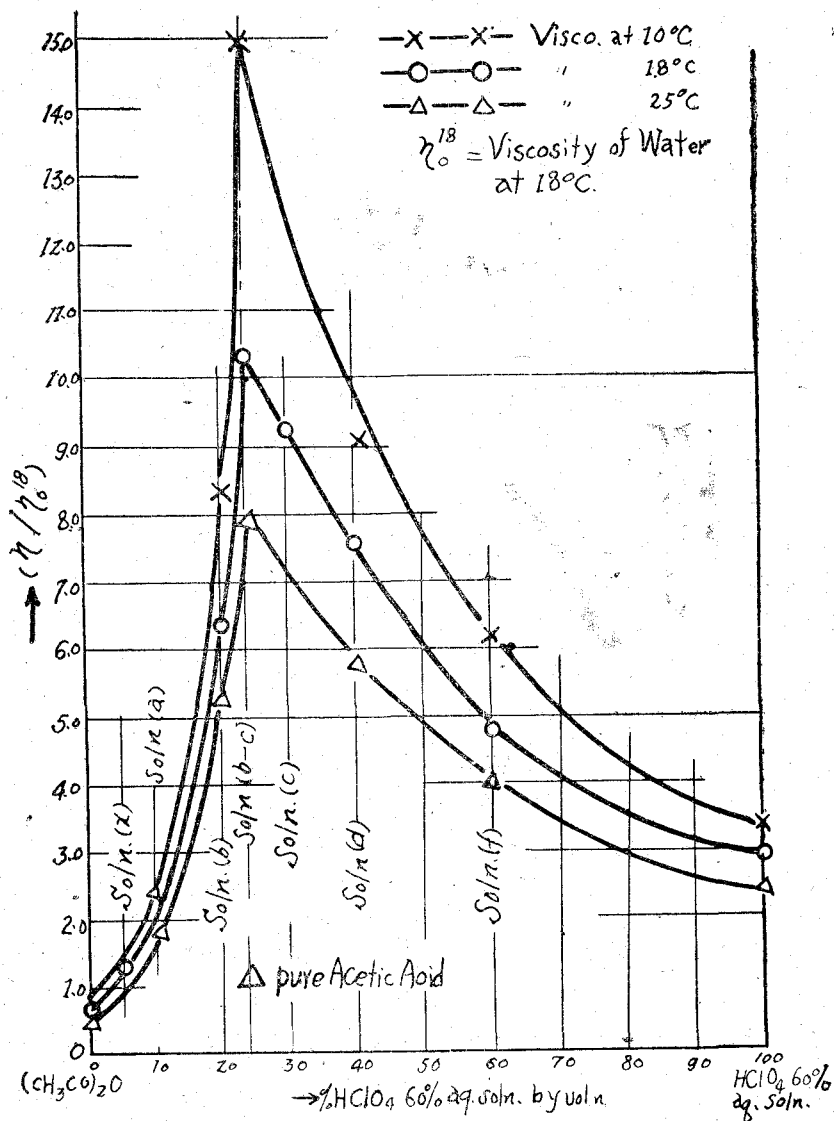
Fig. 5.   Viscosity of Each Solution at 10°, 18°, and 25°C.

Part I.   From the impossibility of the measurement of pH in all solutions[1], there is probably no H^+ ion.

At any rate, it is supposed that the acetic acid in the solution is a sort of reservoir of other ions, as stated in Part I.

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1) The author could not measure the pH of these solutions, and that even of 60% HClO₄ aq. soln., by the antimony, the quinhydron, and the glass electrode. But this HClO₄ aq. soln. has very sigular property and its HClO₄ molecules are all hydrated in the aqueous solution by J. N. PEARCE and A. F. NELSON: J. Am. Chem. Soc., Vol. LV (1933), p. 3075.

§5. The Behaviour of Each Solution for Al Electrode.

a) Natural single electrode.

The aluminum testing sample was dipped vertically in the solution. This sample was pre-treated with emery paper (O4), and contained in dryer at 18°C for 24 hrs. Then the value of the single potential of sample was determined from time to time in the solution, using the apparatus of valve
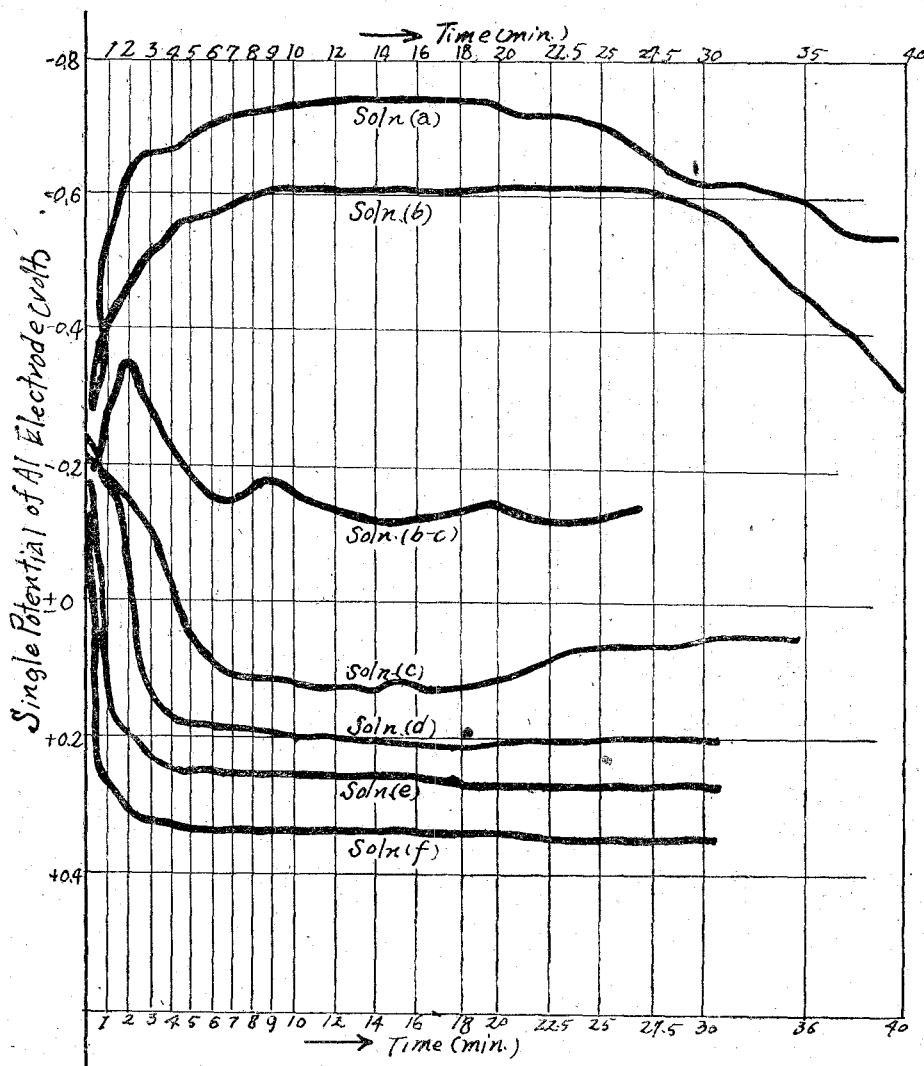

Fig. 6.   Single Potential of Al-Time Curves at 18°C.

potentiometer[1] and with calomel half cell, which connecting circuit was
seen in Part I. In such a measurement, the potential is much affected by
the condition of the surface. But after 5 minutes or more, the tendency
coincides each other, if the other conditions are equal. Therefore, Fig. 6.
is one example of such results. In the figure shifting the potential to
minus sign of ordinate means passivating and to plus sign, means activating
as shown in Part I.

It shows that the aqueous solution like Soln. (c) to Soln. (f) has much
effect of HClO₄ and the non-aqueuos solution like Soln. (b—c) to Soln. (x)
has at first other constituent to effect such as CH_3COOH, but before long
HClO₄ begins to work.

Soln. (b—c) has the very property which lies between two kinds; that
is, at first the potential goes to the passive state, but shortly falls and
reaches the constant value. For the constant potential, there is probably
the product on the pits of surface by the action of HClO₄ and then it will
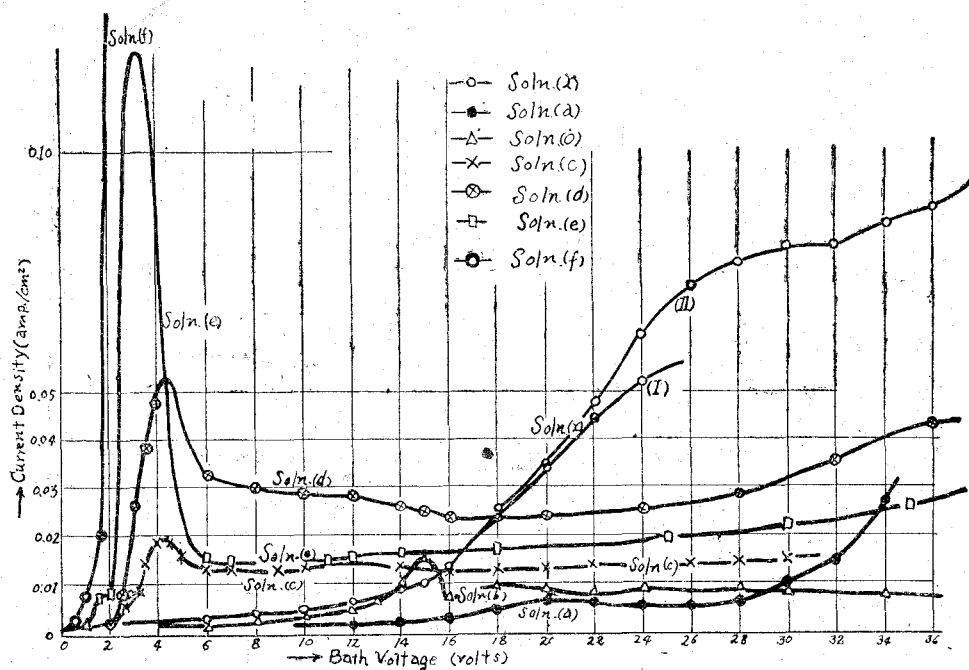decide the potential[2].

Fig. 7.   Bath Voltage-Current Density Curves at 18°C.

1) In order to compare the result from this measurement with the following one, the radio
valve UX12A was used. This valve has the good proportional properties between grid voltage and
plate current.

2) T. Takei : "Experimental Electrochemistry" (1939). Kyōritsu-sya, Tōkyo. Vol. 1, p. 241.

b) The Single Potential of Anode on Passing the Current through the Solution.

At the same time when the so-called " JACQUET curve " was observed, the change of single potential of anode was measured in each solution. Fig. 7. shows JACQUET curve and the corresponding anodic single potential is given in Fig. 8. In this case, as seen in Part I, Soln. (x) to Soln. (b) has the irregularity of current density at higher bath voltage, and Soln. (c) to Soln. (f) has it at lower bath voltage. It is seen in Fig. 8. that the first drop of the single potential occurs before the maximum current density in every solution, especially two drops occurring in Soln. (b—c).

Next, over this region, the potential rises gradually in linear proportion to bath voltage, and that corresponds the range of constant current density.
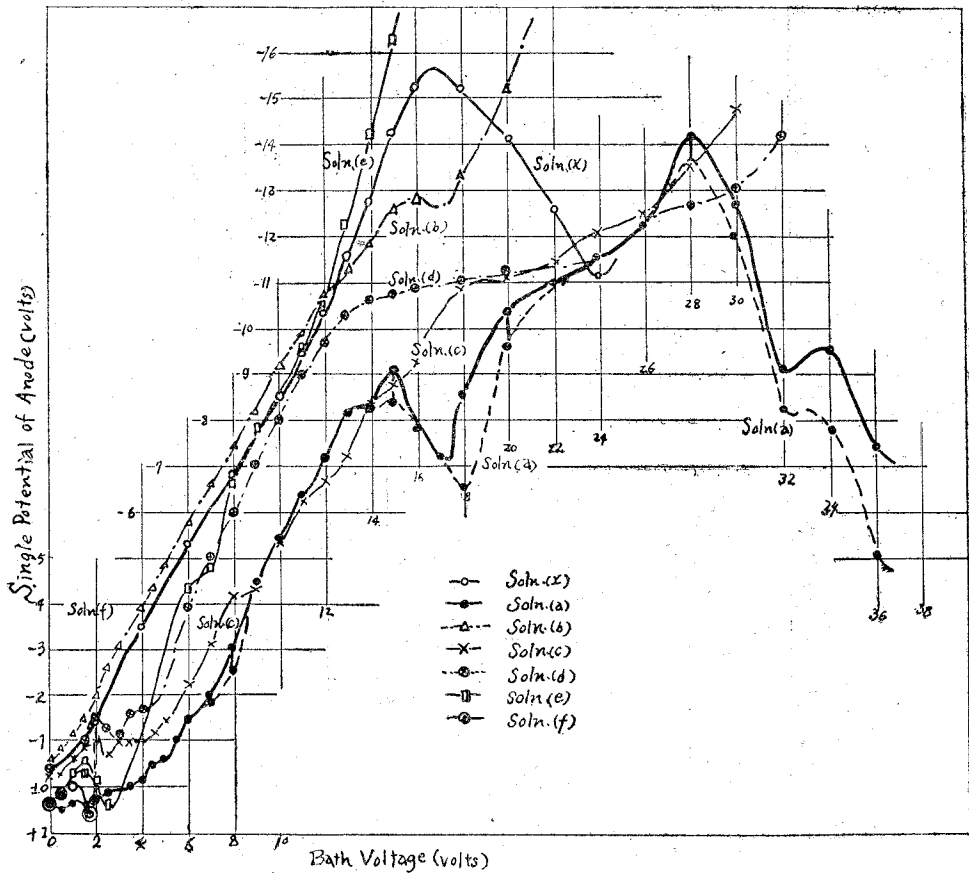

Fig. 8.   Bath Voltage-Single Potential Curves at 18°C.

Lastly, the potential drops once more at the bath voltage where the gas begins to evolve. In this figure the behaviour of Soln. (a) is fully shown, but others are partly because of too high potential. The relation between bath voltage and single potential of anode may be shown as Fig. 9. schematically. From the above datum and the previous report, the following items are deduced.
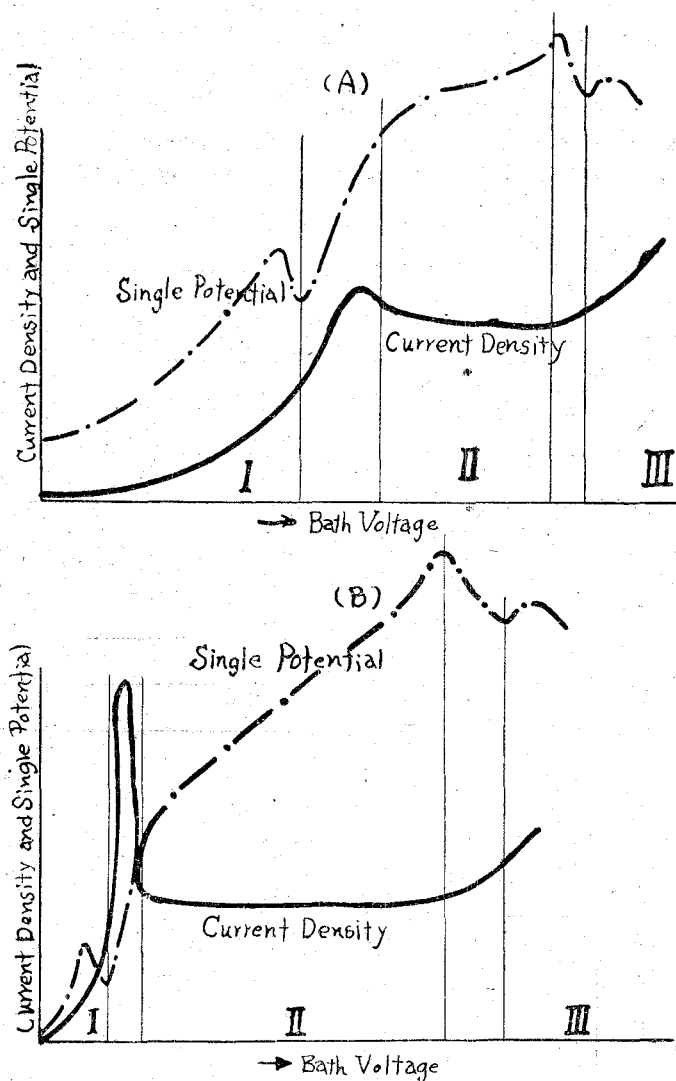

Fig. 9.   The Relation between Current Density and Single Potential of Anode.

In the non-aqueous solution such as Soln. (a) and others, the change of anodic potential at lower bath voltage shows the passivation and that other species rather than ClO_4^- ion may come to the surface of anode, so it shows only the passive state.   When the bath voltage reaches 14 to 18 volts in Soln. (a), the activation of surface by ClO_4^- ion begins, then the preceding relation is broken down.   This may correspond the initial drop of anodic potential on passing the current.

In other solutions in which water is contained, such relation mentioned above will be also presented, but the potential will sooner drop towards the activated state for the sake of many ClO_4^- ions.

At any rate, it may be understood that by the primary drop of anodic potential the film in all meanings on the surface will be cracked or dissolved roughly, and in the next region of JACQUET curve some of different substances (film or other similar substances) will be produced on the naked surface. From the figure it will be realised, as Mr. MÜLLER says that the increment of single potential in proportion to bath voltage corresponds the consumption of the voltage by the resistance for the passage of current through the film on the surface.

It will be noticed with much attention that the constant current density in JACQUET curve is not true in reality: at first the current density is only apparent, the true area being more than the apparent one, but at higher voltage the area approaches to the true one. Because, it is always observed that even in the measurement of JACQUET curve, the surface of the sample is roughly flattened. So, at first the current density is overestimated, and at higher voltage that value becomes true. From such a consideration so much amount of irregularity of current density curve will not occur in true sense of the word. Naturally such constant current density will be caused owing to the viscous anolyte on the surface, which will be discussed later.

Moreover, the constant current density, and the constant anodic potential which was seen in Part I (Fig. 9.) does not agree for each solution, but by the author for the former the electric conductivity is the main factor determining the value, unless the solution is non-aqueous, and in other cases it depends upon the conductivity of the anodic film. For the latter, the gradient of the potential in Fig. 8. is about equal, so the above stated relation is satisfied.

§ 6. The Single Potential of Cathode on Passing the Current.

For the cathode, by the same procedure as for anode, its single potential was measured.   The result is in Fig. 10, in which the shaded

part means the oscillating value of cathodic potential. But from the result the maximum change of potential is within 2 to 3 volts, so the voltage required for polishing is almost consumed for anodic reaction.
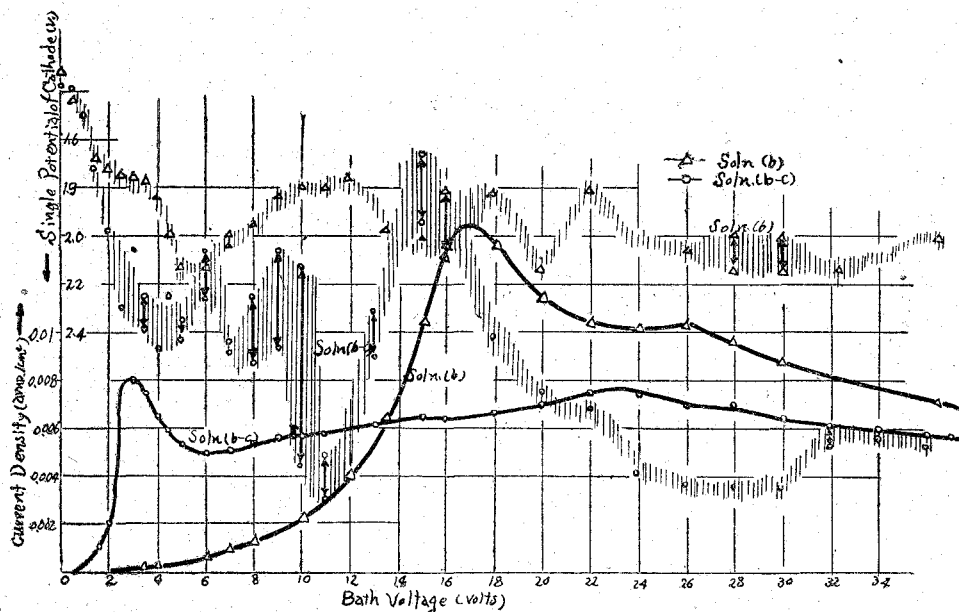

Fig. 10.   Single Potential (Cathode)-Bath Voltage and
Current Density (Anode)-Bath Voltage Curvesat 18°C.

§ 7. The Observation of the Abnormal Phenomena of Anode and Anolyte.

a) On the so-called viscous fluid.

It has been noticed by others that during the electrolysis the viscous material is produced on the surface of anode and that more on the projection and less on the concave, so the polishing action will be accomplished from the difference of electric conductivity of two points. According to the theory of Mr. ELMORE[1], it is concluded that the flattenning proceeds by the diffusion of the viscous material into the solution. However, there is no verification on the property of this substance itself, except some expectations. WEINLAND says that this substance is $[Fe_3(CH_3CO_2)_6(OH)_2]ClO_4 \cdot 4H_2O$ when iron and steel are polished electrolytically in the like solution, but it is not the main factor according to Mr. TAJIMA[2] to polish iron by the process. According to the author it is very difficult to take up this

1) W. C. ELMORE: J. App. Phys., 10 (1939), 742.

2) T. TAJIMA: Metals (Agne-sya).

substance from the anode in pure state, it being very small quantity and that very deliquescent substance, so it will have to be examined how this is analysed chemically. Now the qualitative observations which have been hitherto noticed will be reported.

1) As seen in Part I, this substance begins to produce when the current density is about to fall in JACQUET curve, and then it covers all the surface of anode. Moreover, it flows down before long and then it begins to drop from the end of anode. This phenomenon was caught by Mr. S. SAITO[1] using Schlieren method. The author caught it with micro-scopic photo ($\times 100$), which result is shown in Photo. 1 and Photo. 2. The
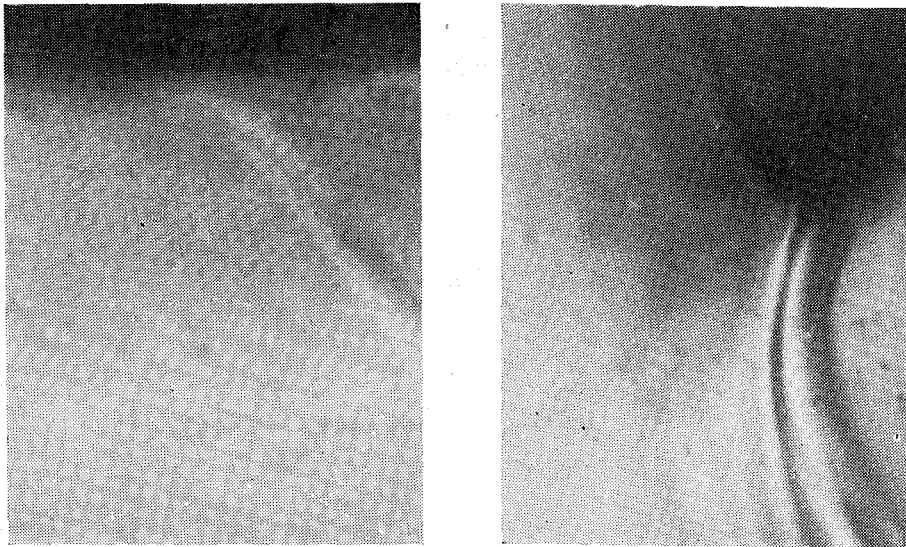

Photo. 1.   Photo. 2.

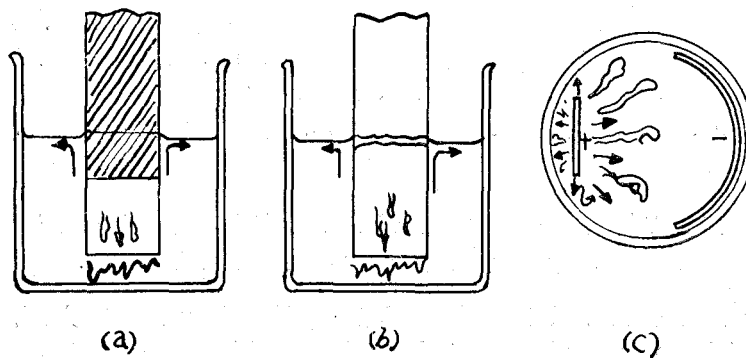(a)   (b)   (c)

Fig. 11.   The Phenomenon of Anolyte during Electro-Polishing :
(a) with Coating, (b) and (c) without Coating.

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1) S. SAITO : Magazine of Electric Society of Japan, Vol. 69, No. 4.

viscous fluid is flowing down and the outside solution is flowing upword.

2) When the testing sample is not covered with something such as wax or tar at the contact line of it with the solution, many abnormal phenomena are to be seen. In Fig. 11 (a), with the cover such a phenomenon is not found. Otherwise, as shown in (b) of Fig. 11, the viscous substance is shooting out from the surface into the solution, and scattered around the electrode. Nevertheless it does not reach the cathode and on the mid way of the bath it sinks down gradually. In such a case, the temperature of the solution around the surface of electrode rises and the contact part is deeply etched, but it appears polished.

And in the solution, the surface of electrode is not so much flattened as the contact point, although the total current density become too high. Of course the viscous fluid is seen even in this case. It will be the chance of the resolution of the mechanism of electrolytic polishing to peep into how it will be happened.

b) The Relation between Pit-making and Gas-evolution.

The evolution of gas was discussed in Part I, and there is another problem of the growth of pits in relation to this. Pits on the surface of electrode are very apt to grow, and one of the most undesirable defects. The form of pit is about semi-sphere and it has two or three small holes in the bottom. Moreover, from the above-stated inspection by the microscope, when the gas-evolution diminishes, it remains to evolve the gas at a certain point, and when the current density begins to rise at higher bath voltage the babble creats on the surface like a pearl and does not leave the surface unless it grows bigger. From the above observations, the growth of pit may be much affected by the irregular surface: when the small babble is produced at the certain point of the surface, it does not leave that place soon, so gas, liquid, and solid are co-existed, then the solution of metal will be fast, so the babble grows, and so on. In the end the pit grows like a semi-sphere, and becomes big. Therefore, the surface of the sample to be polished must be flat mechanically as well as possible. For example the once polished surface is very easy to re-polish.

§8. The Examination of the Polished Surface of Anode by the Electron Diffraction Method.

The author observed the electrolytic polished surface of Al, and then the one which was secondly treated, with the aid of the electron diffraction method. The polished surface was washed with water and then with alcohol, and dried out in air. The sample was preserved in pure ether not to change the surface before the use of the examination. The solution

which was used was Soln. (b) to Soln. (d), other solutions having many difficulties. Their results are summed in Table I, where the standard wave length of electron was determined by the check of pure Al (99.99%).

TABLE. I.

Name of Sample & Solution	State of Sample and Condition of Treatment	Examination with E. D. Method	Consideration or results
B–I Soln. (b)	Newly annealed sample was polished electrolytically with stationary current density.	There were only two halos which were not clear. They corresponded to d = 1.26 and 2.00 Å.	These halos were seen later, but it looks like what the rings of γ' alumina[1] were diffused.
B–II Soln. (b)	Old annealed sample was treated with 27 v. and 0.05 amp/cm² at 40°C. It has bigger grains than newly treated sample.	There were almost only halos except other two rings, but both were not clear.	They would occur with high temperature. The surface of sample was amorphous state. There may be some intermediate phase between γ and γ' alumina.
B–III Soln. (b)	The sample of single crystal was treated with 30 v. and 0.03 amp/cm². The surface was flattened on the microscopic scale (×444).	With two obscure halos, there were only three spots, which flowed up and down. Moreover, there was seen KIKUCHI's line.	The flow of spots means the flatness of the surface. From the presence of halos and spots, it is concluded that there may be amorphous film on the surface and it is too thin for the electron diffraction measurement.
B–C I Soln. (b–c)	Newly annealed sample was treated first with stationary current density untill it had mirror-like surface, then etched anodically with low voltage and maximum current density for short time. It had bigger grain.	With the big grain the rings consisted of many spots. So, it was very difficult to decide the position of the ring. There was no halo.	These rings consisted of that from γ and γ' alumina. This figure may be resulted from the secondary treatment.
B–C II Soln. (b–c)	Old annealed sample was treated with stationary current density, then dried out at 100°C with the viscous substance on the sample, washed in water. It had mirror-like surface under microscope.	The rings corresponded almost to that of γ alumina but they were not shown clearly. The position of halos was about d = 1.245 and 2.31 Å.	Owing to the heating, γ' would change to γ alumina. With the diffused rings, the surface may be amorphous. This γ alumina is probably produced by the secondary treatment.
B–C III Soln. (b–c)	The sample was treated with the same condition as that of B–C II, then it was dried out at 80°C in air, then washed by water.	The rings were the same as that of B–C II, but they were rather obscure.	There were seen the transformation of γ to γ' alumina, but rather strong halos.
C–I Soln. (c)	Old annealed sample was treated with 16 v. and 0.015 amp/cm², and yet it was repeated.	Only halos were seen, and there was no diffraction ring. And the position of this halos were like that of B–C II.	Whatever the surface may be covered with, it means that the structure of the surface is amorphous.

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1) E. J. W. WERWEY: Z. Kristallogr., 91 (1935), 65; 317.

Name of Sample & Solution	State of Sample and Condition of Treatment	Examination with E. D. Method	Consideration or results
C–II Soln. (c)	Old annealed sample was treated with 16 v. and 0.015 amp/cm², and then etched with anodically 2 v. and 0.009 amp/cm² for 1 min.	Many spots corresponded to that of Al, but the rings in that figure (not clear) were seen later.	These rings, which is not clear, may be that of the intermediate phase of γ and γ' alumina. Then there may be naked Al and alumina simultaneously.
D–I Soln. (d)	Old sample was treated with 17 v. and 0.628 amp/cm², then it was etched at once with 2 v. and 0.02 amp/cm² for 1 min. The voltage was once dropped to zero from 17 v. and then raised to 2 v.	Almost two halos, with two obscure rings were seen, but they were part of what seen in C–II.	This surface is shown in Photo. 3. Such a etching does not wipe out the halos.
D–II Soln. (d)	The sample was treated like that stated in D–I. But, at this time, the sample was once picked up and dried out, then etched once more with 2 v. and 0.02 amp/cm² for 3 min.	There were halos with three rings which were not clear.	In the end, it will be the intermediate phase between γ and γ' alumina. The structure of the surface is shown in Photo. 4.
D–III Soln. (d)	This sample was treated as in D–II, then etched with 2 v. and 0.02 amp/cm² for 3 min.	There were many spots upwards, and they corresponded to that of Al. The rings were seemed to be of $Al_2O_3 \cdot 2H_2O$, which was hitherto not seen[1].	The surface of this sample is shown in Photo. 5.

From the above data, and results, the following items are deduced.
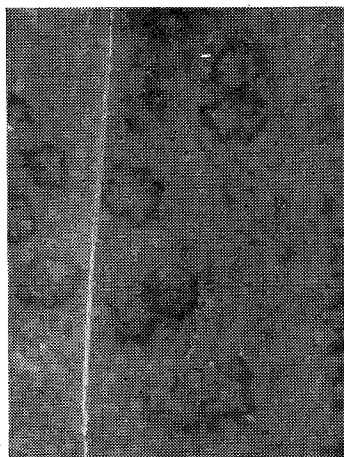

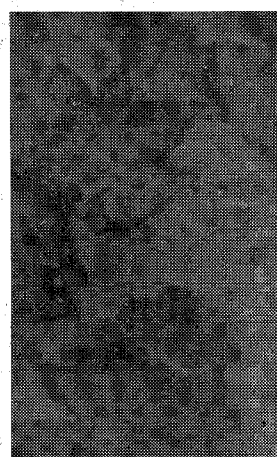Photo. 3.   Photo. 4.   Photo. 5.

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1) This sample was reserved in alcohol after the treatment, so it was resulted.

1) Finishing the polishing anodically, there will be certainly seen some halos, so whatever the substance which covers the surface may be, it will be amorphous and that, from the diffusion of the diffraction rings, the surface will be flat under the scale of electron diffraction method.

2) Concerning the substance covering the surface, there is no suggestion or other verification to decide the composition from the electron diffraction figures, because the diffused rings become merely more clearly as the polishing proceeds.

However, from the above data, there may be so thin amorphous film that the electron beam could pass through, and even if there may be some oxide, it is not of the perfect one, but it lacks oxygen very much. So it is the type of γ' alumina or of the preliminary type, and such a substance will be changed to γ' and then to γ alumina by heating or other secondary influence.

3) Moreover, it has been much noticed that the electrolytic-polished surface of aluminum has better corrosion resistance than otherwise treated one[1]. By the author, it will be attributed to the compact film of alumina over the surface undoubtedly, and still more it will be affected first by the flatness of the surface.

On the mechanism by which the amorphous film is produced, Mr. TAKAHASHI[2] concluded that in case of brass in H_3PO_4 electrolyte, Cu_2O was produced by the selective solution of Zn and the displacement of Cu in the semi-liquid state. But it did not reach the experimental conclusion. Mr. SAITO[3] reported in his paper that the dissolving velocity of each point is not equal at projection and concave, so the flatness of surface was resulted. But he did not touch the structure of the surface.

By the author, there may be any change of anodic surface suddenly, when it is picked up from the solution, and that will be closely bound up with the production of amorphous film. If this film is the inevitable product during the process, high potential energy will be required to produce such a state, not to pass the current through the viscous fluid. If there may be the case, it is even reasonable that such a process will occur in all anodic solutions of metals.

In recent years, many reports have been presented about the electrolytic polishing with the alternating current, and others said that there were abnormal decrease of the valency of Al in that process[4]. So, the

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1) S. TAJIMA : ibidem.

2) N. TAKAHASHI : App. Phy. Japan, 17, 212 (1948).

3) S. SAITO : Electrochem. Japan. Vol. 18, No. 6 ; No. 7 ; No. 8 (1950).

4) From the generalisation of the post-war electrochem. of surface of metals by S. TAJIMA, but not in detail.

production of aluminum oxide itself is not a decisive factor, but is probably the accompanying phenomenon. And in other meanings, the anode would dissolve with block under microscopic scale. For the subject, the author will discuss in detail with experiments in future.

Summary

1) The results in Part I were recognised again by the measurement of the viscosity of each solution.

2) It was found that the curve for single anodic potential of Al on passing the current corresponded to JACQUET curve, and yet that the first drop of the potential curve occured before the voltage at which maximum current density was seen.

3) For the case of Al, the whole bath voltage is used by anode, not by cathode.

4) The so-called 24 hrs.-aging of electrolyte does not find its meaning in such a solution.

5) The polished surface is flat under the scale of electron diffraction method and that is covered with amorphous film wich composition is not determined, but the film is very thin to be able to pass the electron through.