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Author	Horiuchi, Toshio
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Growth of Parallel Grooves on Soluble Anodes by Electrolysis

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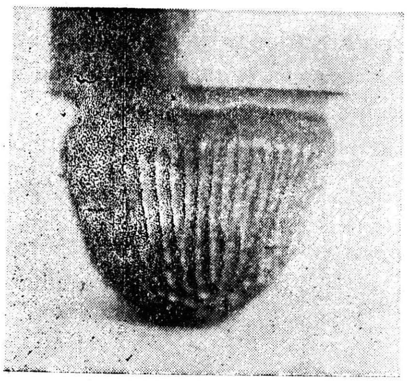
Toshio HORIUCHI

Abstract

Some qualitative experiments on the growth of grooves and similar phenomena which are found on the surface of soluble metal anodes subjected to oxygen bubbles during electroysis; influence of the bubbles on the phenomena are described.

I. Introduction

On the surface of the soluble metal anodes such as copper, brass and iron, pallel grooves and hollows and constricitions are made during high current electorolysis as shown in Fig.1.



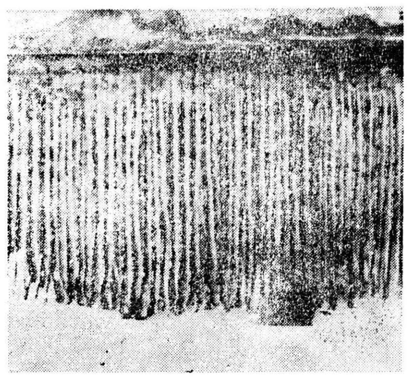


Fig 1. (a) Brass rod anode × 2 (b) brass plate anode × 1.5

When the anode is a cylindrical rod the number of the grooves has a certain relation with the diameter of the rod as shown in Fig.2, and it is found that the intervals of the grooves are nearly equal. Some qualitative experiments on this phenomena are described here.

The present experiments were chiefly performed with brass rods and plates as the anode, but the same results are obtained with other soluble metal anodes.

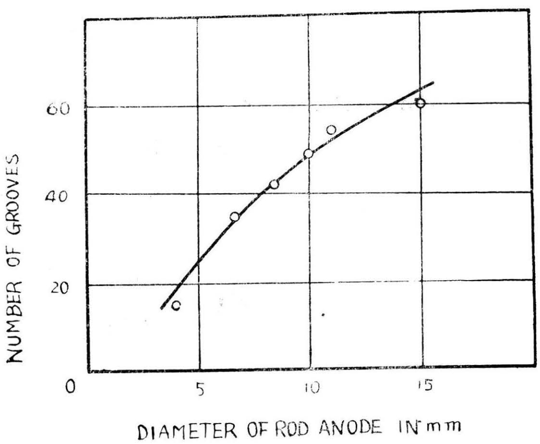


Fig.2. The relation between the number of grooves and the diameter of rod anode

* Asistant of Faculty of Eng., Keiō Univ.

II. Experimental Apparatus

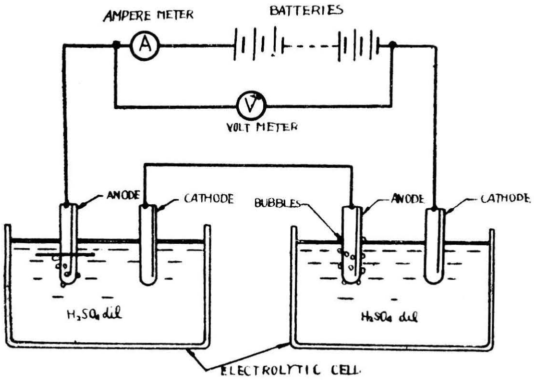


Fig.3. Experimental apparatus. Anode of the left cell is attached with a bakelite plate

The experimental apparatus is shown in Fig. 3. A pair of series connected electrolytic-cells were used to compare the effects of the treatment on the anode; for example, the effects of different shapes of anodes. The electrolytic solution is IN. H_2SO_4 aq. and the power supply are the batteries.

III. Action of oxygen bubbles

At first, it was considered that the grooves appeared due to the inhomogenuity of the material. For example, it is possible that a strain was caused within the material by the machining and the strain pattern became visible in the electrolysis. To test this, an annealed brass anode was electrolyted but the same phenomena were observed on the surface of the anode. Moreover, as shown in Fig. 4, the grooves formed verticaly on the surface of the curved rod. So, the growth of the grooves are not connected with the material itself; there should be some difference in the condition of dissolution between the edges and the bottoms of grooves. As a clue to this problem, the following facts were observed.

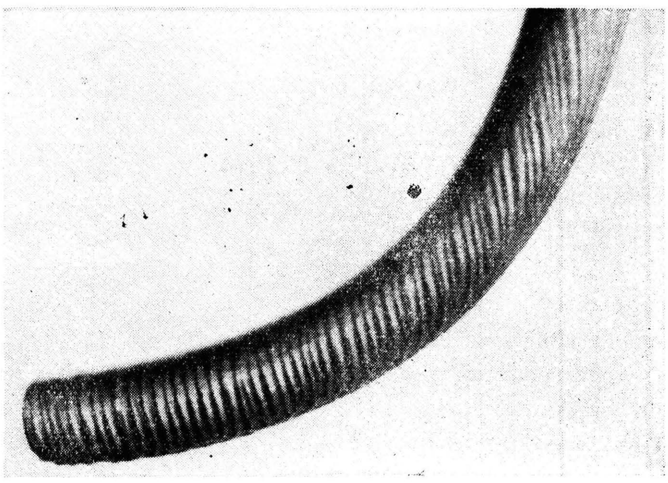


Fig.4 Grooves of curved rod anode × 2

a) The grooves do not grow in the electrolysis of a low voltage in which no oxygen bubbles apper, and they grow only in case where oxygen bubbles appear.

b) The bubbles ascend along the bottoms only and never along the edges.

c) Slight grooves begin to be found several minutes after the current is turned on and become conspicuous with the time lapse. When the conspicuously grooved anode was electrolyted under condition in which oxygen bubbles do not grow, the grooves become slight with the time lapse.

From the facts mentioned above, it is clear that the action of the oxygen bubbles are very important to the phenomena. About the action of the bubbles, following experiments were performed.

d) To ascertain whether the oxygen bubbles dissolve the anode directly, the anode with oxygen bubbles attached on its surface was electrolyted under the condition in which no new oxygen bubbles appeared. Then, it became clear that the oxygen bubbles have no direct activity against the anode but act rather as an insulator.

e) A rod anode with a bakelite plate at its middle part to prevent the bubbles from ascending along the surface of the anode beyond it was tried. Then the grooves grew on the surface beneath the plate only. On the contrary, when plate with holes which allowed the bubbles to ascend along the surface of the anode in various places was used, the grooves extended to the upper part of the anode only where the bubbles could ascend through the holes, as shown in Fig. 5.

Fig.5. Comparison of two anodes, both are attached with bakelite plate, but the plate of the left anode has holes × 2

Accordingly, it is clear that the action of the bubbles causes the growth of the gooves.

f) When the anode is conical, the depth of the grooves grow uniformly but when the anode is shaped semispherical, the grooves do not grow in uniform depth as shown in the Fig. 6.

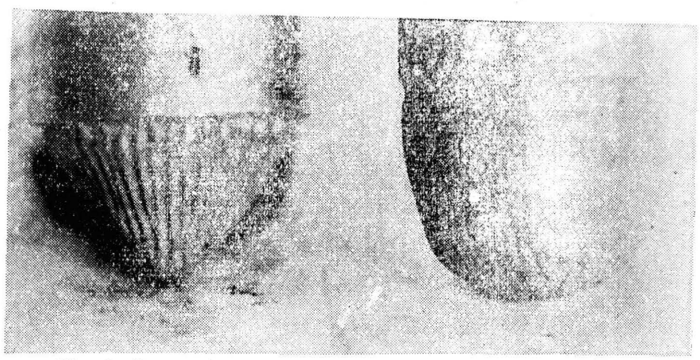


Fig. 6. Comparison of grooves of conical and semispherical anode × 2

Accordingly, it is clear that the grooves are formed by the action of ascending bubbles which impose pressure on the surface of the anode.

IV. Observation of ink flow

To explain the effects of the bubbles which ascend on the surface of the anode imosing a pressure, following experiment were performed: A glass plate is inked on one surface, dried, and some small oil balls are placed on the inked surface. When this plate is dipped in water, the ink begins to melt and flow down along the glass surface. The effect of the oil balls on the flow is observed. As shown in Fig. 7, the concentration of the ink is lighter just under the oil balls.

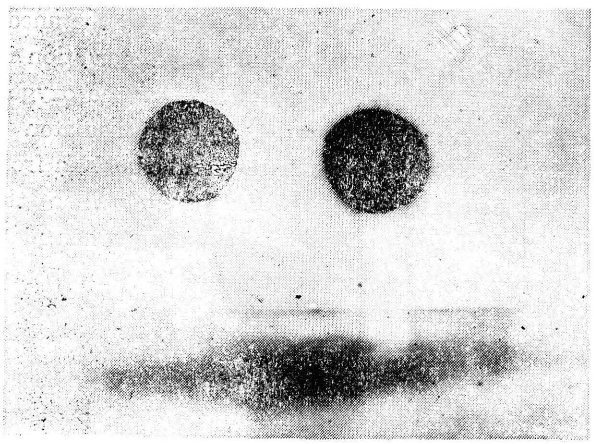
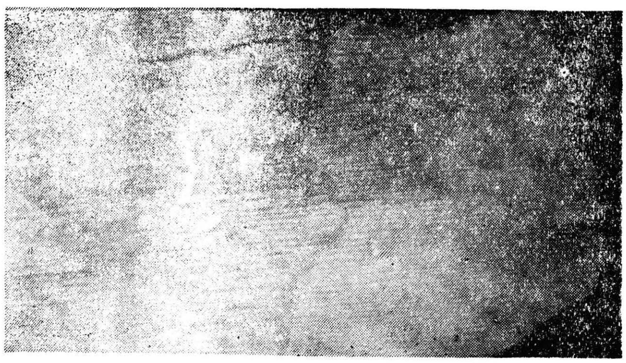


Fig. 7. Flow of ink over a glass plate surface. Two black spheres are oil balls × 2

Similarly, it is reasonable to think that concentration of the metal ion in the solution is lighter along the locus of the oxygen bubbles.

In consequence, along the locus where bubbles has ascended, the concentration gradient of metal ions is greater than other parts so that the metal is dissolved extremely there and the grooves are formed along the locus. After the growth of slight grooves, the bubbles ascend along them and make them deaper, and at the same time, the growth of oxygen bubbles are greater along them.

By the results of the former investigation, it is sure that the growth of the grooves depends upon the "gutter-cleaning" action of the oxygen bubbles. The phenomena, then are not only concerned with dissolution of the metal by the electrolysis but with the dissolution of any material which generate the bubbles. To verify this investigation, a marble block was dipped in HCL aq. and the same parallel grooves were found to grow on the surface as shown in Fig. 8.



Fgi. 8. Grooves formed on a flat surface of marble block × 2

V. Bubbles in order

The above should be sufficient explanation for the growth of the gooves, but another important problem still remains; how the slight grooves grow first which become conspicuous later, and moreover with almost equal distance from each other. The growth of oxygen bubbles should be at random and they can ascend haphazardly. They would not ascend with a purpose to make the parallel and equal inteval grooves later.

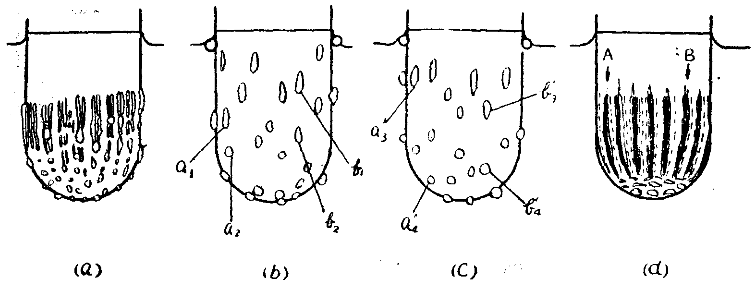


Fig. 9. (a) Ascending bubbles at a instant when the current is turned on. The small bubbles ascend in regular order; (b), (c) Ascending bubbles at arbitrary instants. They ascend along the lines which become the grooves later as shown in (d)

To examine this problem, the ascending bubbles, on the surface of the anode where no groove has yet grown were observed. Fig. 9 contains schematized illustration made from the photographs taken at arbitraly instants before the growth of grooves. From the observation of the illustrations, it is recognized that the bubbles ascend along the lines which become the bottom of the grooves later, and the lines are almost in equal intervals.

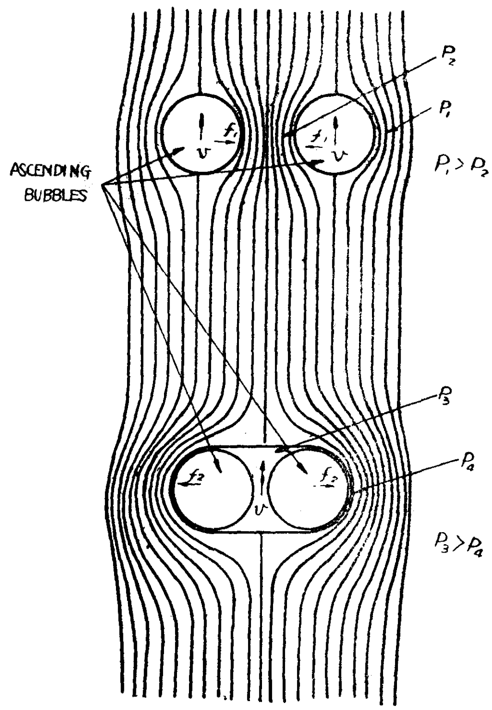


Fig. 10. Interaction of two bubbles moving at a velocity v. f_1 gnd f_2 are attractive and repulsive forces respectively

About this arrangement of the bubbles, König's theory on the pattern of the powder in the Kundt's tube is available[1]. As shown in Fig. 10, a pair of bubbles ascending at short distance from

1) Load Layleigh, Theory of Sound Vol. II. (MacMillan and Co, London, 1929)

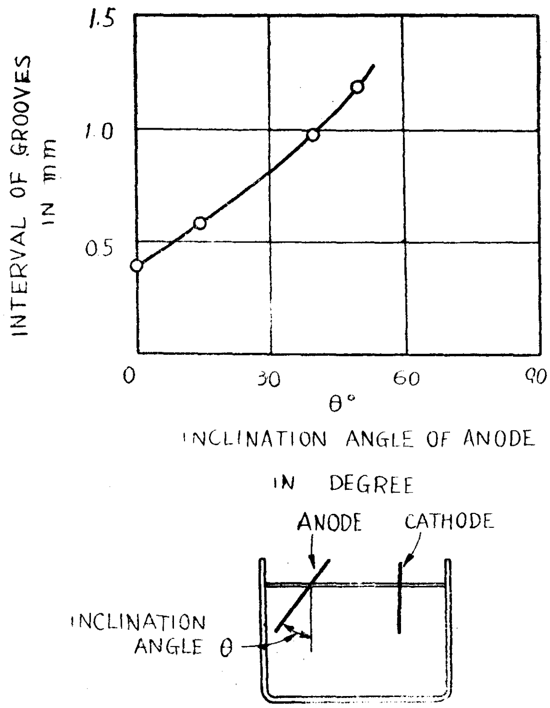


Fig. 11. The reaction between the interval of grooves and the angle of anode inclination

each other pull each other but when they are brought too close together, the repulsive force arises between them and are separated. Therefore the bubbles grown at random can not ascend haphazardly but must perform the "march past" with constant interval. The interval of the bubbles acending in regular order is determind by the size and ascending velocity of the bubbles, viscosity of the solution, etc.

According to my observation, the diameter of the bubbles are almost always the same so that they keep regular order, or the same intrveal. This line up of the interval is kept all the time by the reason described in IV and the grooves become visible after several minutes. The bubbles can be in regular order only when there is no disturbance by external forces.

So the rotation of rod anode arround its axis prevents the growth of the grooves.

To verify further my former investigation about arrangement of the bubbles, a plate anode was inclined at various angles and the intervales of the grooves which should be influenced by the size of the bubbles were measured.

As in Fig. 11, the interval of the grooves increases in accordance with the increasing inclination angles as measured in the figure, and no grooves grow when the inclination angle is larger than about 60°. In this range of angles, the grooves are substituted by hollows.

VI. Film of bubbles

The growth of the hollows and the constrictions are rather connected with the motion of thin films such as that of the soap bubbles. The bubbles in liquid are somewhat similar to that in vapour; the bubbles in liquid are also surrounded by thin films which move in a complicated manner. For example, the films are always in motion even when the bubbles stagnate, which is observed by the motion of the dust on the film. It is considered that by the action of the film, the bubbles in halt exert the same effects against the anode as the moving bubbles but further investigations and experiments will be necessary.

VII. Conclusions

The conclusion is as follows: The grooves are formed first by the bubbles of the same size which grow at the lower part of the anode and large enough to begin ascending by themselves and sweep away the smaller bubbles on upper part of anode. They ascend in the order of the 'march past'. Then the grooves become conspicuous by the 'gutter-cleaning' action of the oxygen bubbles. The constrictions and the hollows are both formed by the movement of the films of the solution between the anode and the bubbles. The growth of the grooves and other phenomena disappears in a dissolution not accompanied by the bubbles, or when the solution is confused by a mixer.

VIII. Acknowledgments

Finally the author wishes to express his deep gratitude to Professor M. Masima and colleagues to whom he has turned for advice and discussions.

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