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Hydrogen Bubble Evolution and Copper Powder Growth at Cathode

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Abstract

Effects of hydrogen bubble evolution on the production of copper powders at cathode by electrolysis were investigated. The coarsening action of bubbles is discussed mainly. Some factors influeacing the fluctuation of size distribution in yield are also mentioned. The growth of fine dendritic deposits is achieved by a electrolysis of cathode potential lss-nobler than the reversible potential of hydrogen. The evlution of hydrogen bubbles must be avoided to get fine powders.

I. Introduction

The powder produced by electrolysis at cathode is coarsened by the deposits between the individual particles, therefore the fluctuaticns of size distribution in yield are unavoidable if the deposits are not removed frequently from cathode during the electrolysis. To get powders of a desirable size, it is said that any adequate removal of deposited powders from the cathode in regular intervals, or a rapid circulation of the bath is necessary [1] and that the cause of the coarsening deposits between the particles must occur due to a decrease in the current density as the real cathode area increases by the powder deposition.

Some experiments have been made to find the cause of the deposition and to find a method to obtain uniformly fine particles. Therefore in these experiments no additional operation in relation to the deposits was done during the electrolysis. All experiments were carried out concerning the evolution of hydrogen bubbles at the cathode.

II. Size Distribution Study

a. Process of the Powder Sample Production.

The electrolytic cells which were used in these experiments are series-connected containing 5 litres of solution in each and the solution used is copper sulfate and sulfuric acid aqueous solution. The electrolysis were continued for an hour.

After the electrolysis, the deposits were removed from the cathode, washed by

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1) C. G. Goetzel, "Treatise on Powder Metallurgy," Vol. 1, (Intersciense, 1949)

distilled water of 200c.c. per 1 gram of powder, dried in air at 90°C. for two hours, and sieved for ten minutes with a stroke of 4 cm and 4 horizontal reciprocals per second. The sieves used here are 325, 300, 250, 200, 150 and 100 mesh sieves.

The cathode is a copper plate or rod, and for the anode a copper plate is used for high concentration of copper in the solution, or lead plate for low concentration, and the copper concentration changes during the electrolysis, but within 15% of the initial.

b. Size Distribution and Shape of Cathode.

Some typical examples of the size distribution curves are shown in **Fig. 1.** Generally several peakes are recognized in these figures, one at least in the region

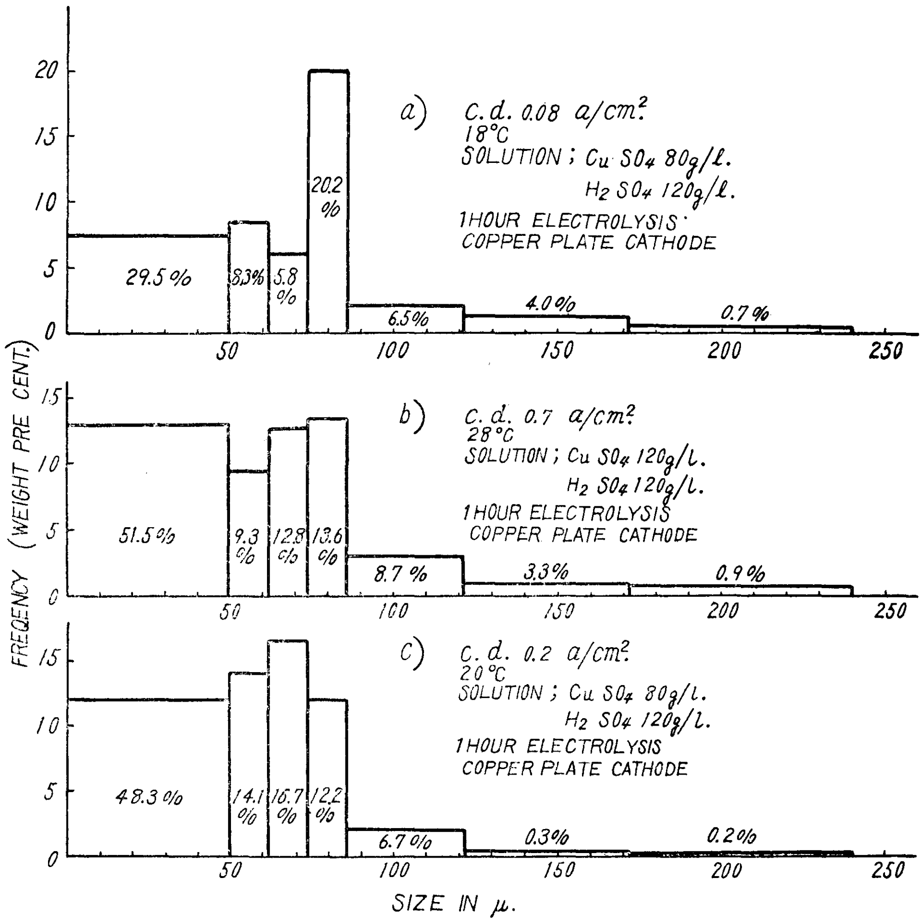


Fig. 1. Size Distribution Histograms. All of the curves represent the peaks at subsieve range. The changes of the position of the peaks for medium size are little : for *a*) at 80μ, for *b*) at 70~80μ, and for *c*) at 70μ.

of subsieve and another in the coarse region. It is noted that changes in current density little affect the position of peaks. As a measure of the characteristics for the curves which indicates the finess and eveness of the powders produced, weight per cent of the subsieve powder were taken. In addition, coarse powder results fluctuations of density for green compact when these powders are used for powder metallurgy,[2] then to increase the subsieve powder is satisfactory for this use. Fig. 2 shows the subsieve powder per cent against the apparent current density relations. Increase in apparent current density increases the subsieve powder but extremely high current density reduces the per cent. Effects of shape of the cathode are as follows.

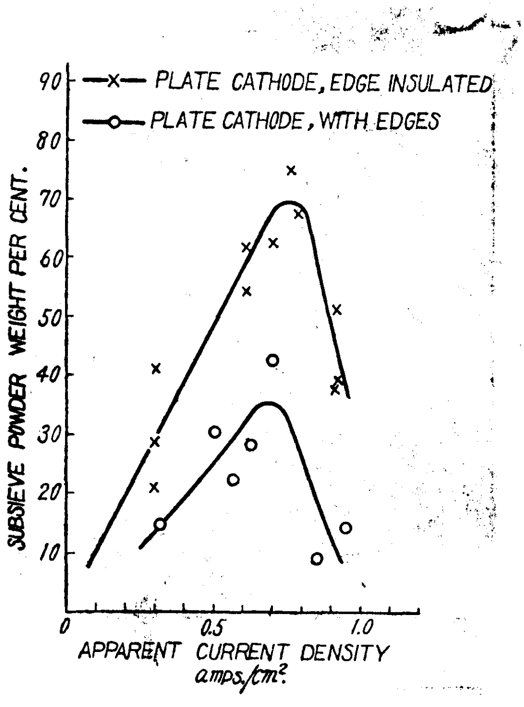


Fig. 2 Subsieve Powder Per Cent for Apparent c.d. Relations. Solution, $CuSO_4$, 50g/l. & H_2SO_4, 150g/l. 1 hour electrolysis.

i) Plate cathode has best characteristics when corners and edges are insulated by coating of wax or enamel. Plate cathode with edges has coarsening characteristics.

ii) Rod cathode has extreme coarsening characteristics but this is not shown in the figure.

iii) Fluctuations of subsieve powder per cent is noticeable in every case.

Accordingly, plate cathode insulated at corners and edges seems to be most satisfactory. But still 60% of the deposits is concentrated near the borders. The reason of this uneven deposits will be discussed later.

III. Microscopic Observation of Powder Shape

The photos under Fig. 3 are dark field photos of powders. The samples were produced by the electrolysis of the following conditions.

c.d.; 0.3 amps / sq.cm. temperature; 20°C.

solution; copper sulfate, 80g/l., sulfuric acid, 120g/l.

a) Subsieve powders, −325 mesh. The size of these powders is represented by I. These powders are agglomeration of finest powders which are about $10\mu\sim1\mu$ in diameter as designated by arrows. When the number of these finest powders in

[2] T. B. Horiuchi, (unpublished work).

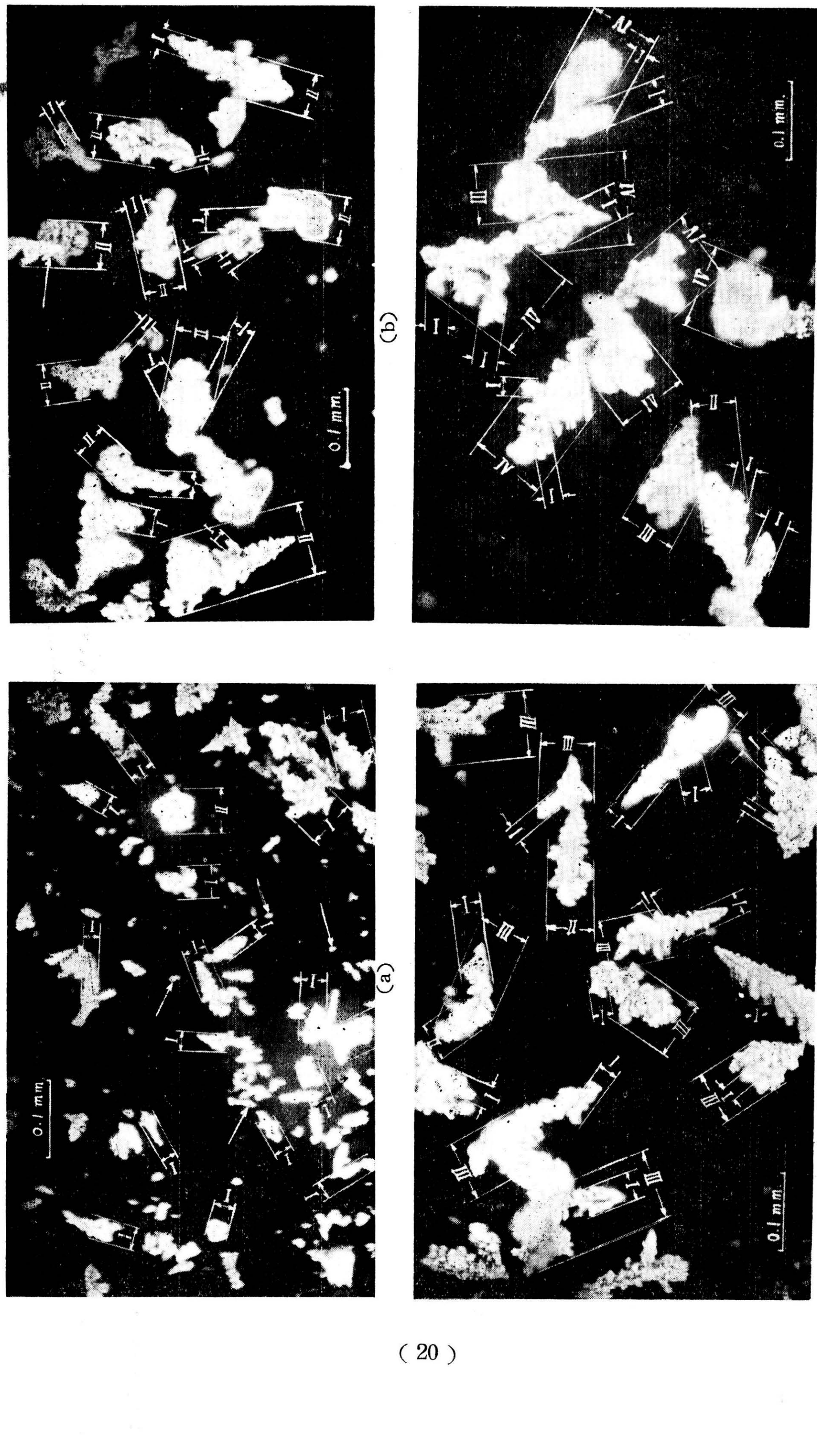


Fig. 3. Micrographs of the Particles

any agglomerated particle increases, the size of the particle increases.

b). +325−300 mesh powders. The size of the particles is represented by II. These particles consist of the particles of size I.

c). +300−250 mesh powders. Average size, III.

d). +250−200 mesh powders. Average size, IV.

From the photos the following facts are noteworthy.

i). The particles are the agglomerations of dendrite.

ii). The finest powders are of single crystalline particles, and as the powders become coarser, the number of the agglomerated paticles becomes greater.

iii). Accordingly, coarse powders will be divided geometrically to fine ones as illustrated in Fig. 3.

Thus, if the coarsening deposits between these particles could be avoided, the powders produced would be ranged in finer sizes.

IV. Hydrogen Bubble Evolution and Modes of Dendritic Growth of Copper

To observe the cathode surface during the electrolysis by microscope which is held horizontally, a small electrolytic cell was used. In this case the cathode is a copper wire of 0.8mm. in dia. and held vertically near the wall of the cell.

a. Evolution of Hydrogen Bubbles (Fig. 4)

i). Hydrogen bubbles appear a little after the current is turned on and this retardation decreases as the current density increases and the copper concentration in the solution diminishes. Thus the evolution of bubbles seems to be connected with the lacking of ions near the cathode.[3]

ii). The bubble prefers to grow at the surface cracks or patches produced by the rubbing of emery paper.

iii). At a low current density the bubbles can grow only from the cracks or patches, but at a high current density they grow more uniformly.

iv). As the number of bubbles becomes greater, small bubbles appear being distributed evenly.

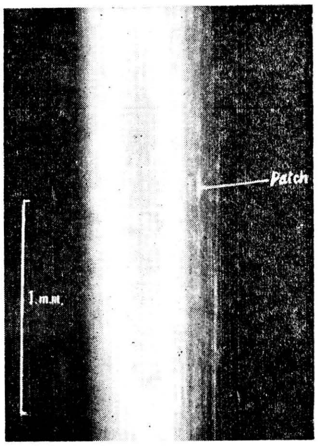
v). The bubbles growing at the successive patches can stay long to be large.

vi). Growing bubbles can move to and fro.

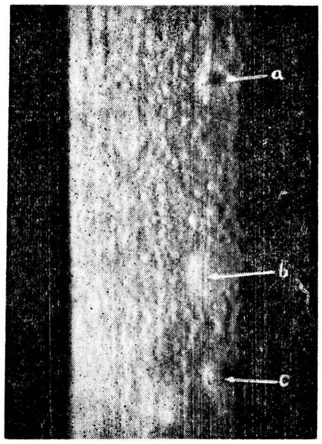
vii). Where the bubbles grow, deposition of copper never occurs and during the electrolysis the places never change.

The size and number of bubbles for current density relations are shown in Fig. 5. As shown in the figure, an extremely high current density only results in the increase of the number of bubbles.

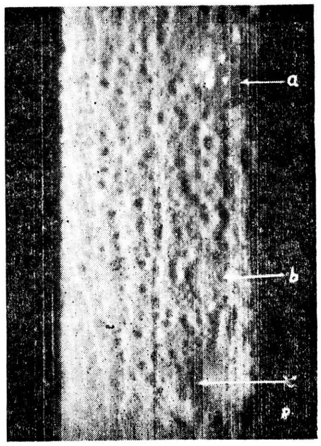
3) O. Kudra, Z. phisik chem., 1935, **175**, 377.
J. N. Agar, Discussions Faraday Soc., 1947, **1**, 26.
B. Levich, ibid., 1947, **1**, 37.



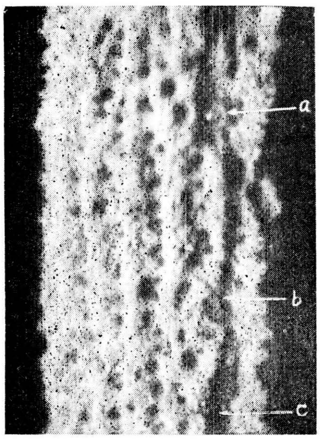
(a)



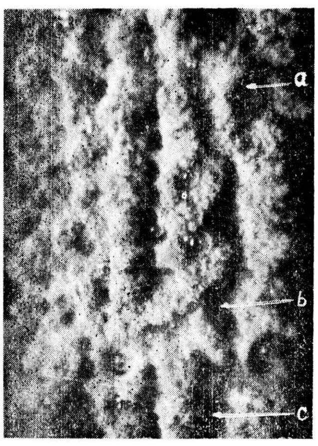
(b)



(c)



(d)



(e)

Fig. 4. Successive Appearances of Cathode Surface. a). Before electrolysis. Several patches are observed. b). 10 sec. electrolysis. At the large patches several bubbles are observed. White spots dispersing over the surface show the points where bubbles have grown. c). 25 sec. electrolysis. The distribution of spots shows that the number of bubbles per unit area have diminished. The places where the bubbles evolve become holes. The size of the holes becomes greater as the size of the bubbles becomes larger. d). 55 sec. electrolysis. Uneveness of the depsits becomes extreme but the position of bubbles never change. e). The trees of copper hang down and resist the bubbles to ascend, thus forming large grooves. 115sec. electrolysis. a,b, and c, represent the coresponding bubbles.

b. Inclination of Cathode

Now it is necessary to ascertain whether the bubbles act to help the powder growth to be large or fine. In this case the inclination of the plate cathode, which is insulated but one surfaces, was changed, because the bubble growing on an up-ward suface will leave the surface before it becomes large. In Fig. 6, the cathode inclination angle against the subsieve powder per cent relations are plotted and this shows that large bubbles coarsen the powders. This agrees with the experimental results of Passer.[4] Therefore the bubble evolution is undesirable for the production of powders but if it be unavoidable, the size of the bubbles must be as small as possible.

c. Surface Treatment for Cathode

It is possible to make the bubbles growing on the surface small by making many patches on the cathode surface, as the bubbles prefer to grow from the patches. Fig.7 shows the subsieve powder per cent for the patch distance relation. The patches were made by rubbing the surface with different grades of emery paper. The figure shows that the smaller the distance between the patches, the greater the subsieve powder per cent and moreover, high polishing rather reduces the per cent. The most interesting is that the plots are on a straight line.

d. Apparent and Real Current Density

Real current density changes from point to point over the deposited surfaces and it is impossible to recognize the real value. But it will be recognized qualitatively that the difference of real current density from the average must increase by the existence

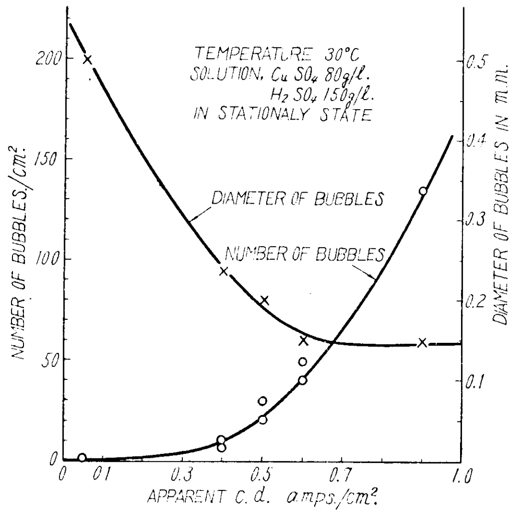


Fig. 5. Bubble Size and Number of Bubbles for Current Density Relations. Vertical copper rod cathode of 0.8mm dia.

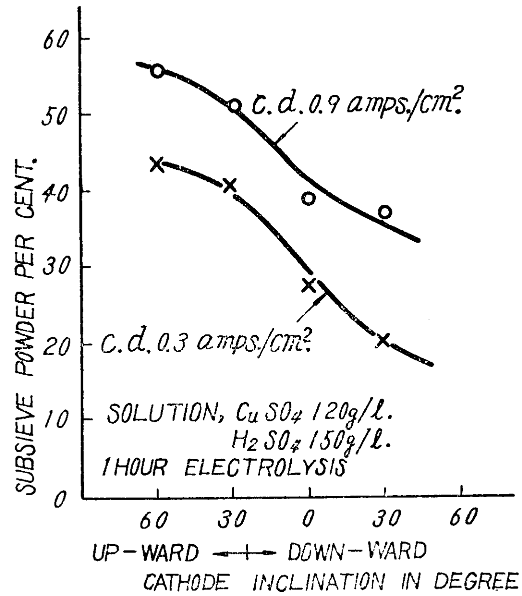


Fig. 6. Cathode Surface Inclination Angle for Subsieve Powder Per Cent Relations. The angles are measured between the cathode surface and plumb.

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[4] M. Passer, Kolloid-Z., 1941, **272**, 97.

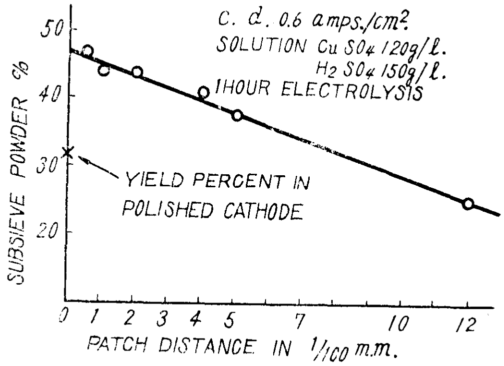

Fig. 7. Patch Distance for Subsieve Powder Per Cent Relation. Patches were made vertically by different grade of emery-paper.

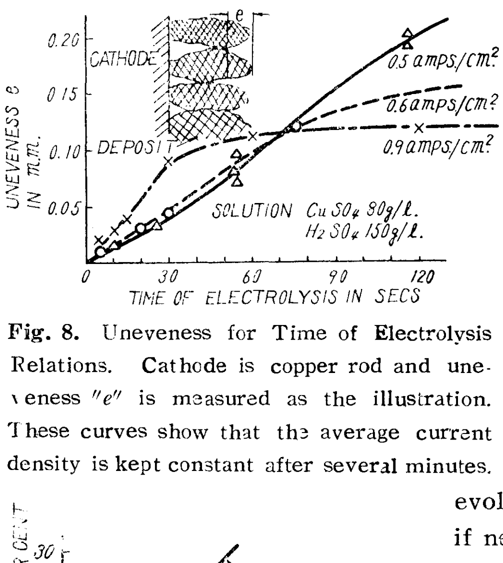

Fig. 8. Uneveness for Time of Electrolysis Relations. Cathode is copper rod and uneveness "e" is measured as the illustration. These curves show that the average current density is kept constant after several minutes.

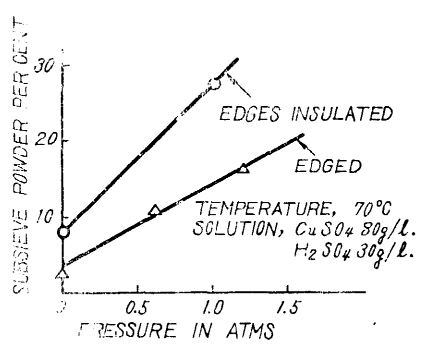

Fig. 9. Pressure of the Solution against Subsieve Powder Per Cent Relations. Increase in the pressure increases the per cent of the subsieve powder.

of bubbles. Uneveness of the cathode deposits against time relations are plotted in Fig.8. Uneveness of the deposition reaches to a saturated value which diminishes with the increase in the current density. This suggests that the real current density at any point does not change with the time lapse.

The cathode insulated by wax or enamel capture large bubbles growing at the boundary on account of the kinks or re-entrant edges formed by the insulater. Thus the insulated part must be leveled to the cathode surface.

V. Bubbles coarsen the Deposited Powders

As described above, bubbles act to decrease the fineness of the powders. But according to Goetzel and others it is said that for the bubbles to co-deposit with the powders is favourable to get fine powders. Thus it is necessary to ascertain whether or not the bubble evolution is necessary to get fine powders; if necessary, why and if unnecessary, how to prevent the evolution. About this problem the following observations will give some answers.

As to the deposition of copper and bubbles, three different parts of cathode surface will be considered.

(A). The place where mainly deposition of copper takes place.

(B). The place where the evolution of hydrogen takes place.

(C). The place where the growth of both copper and bubbles takes place.

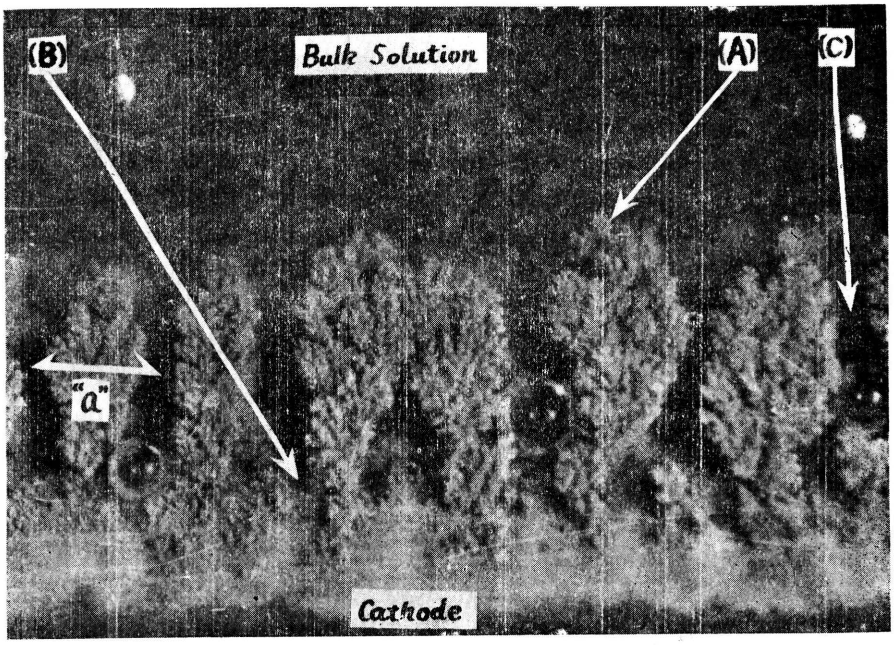

Fig. 10. Two Dimensional Observation of Dendritic Growth at Cathode. The cathode and anode are copper rod of 1 mm dia. which is held between two horizontal glass plates. The solution is injected between them by a pipett. Electrolyzing for a minute, these trees are easily observed. At (A) fine dendritic deposit of copper only takes place. At (B) evolution of bubbles only takes place. Leaving (B), bubbles derange the solution at (C), and at the same time the size of the trees are restricted within "a". Small bubbles become large passing the route (C) and this fact suggest that the deposited hydrogen will be absorbed by these bubbles. (×65)

Looking at Fig.10, one can recognize the first two. These places do not change during the electrolysis as observed in Fig. 4 and will not affect the coarsening of the deposit. Then (C) must be considered.

At (A), replenishment of copper ions are enough for copper to deposit, but at (B), as the supply of copper ions is very poor because almost all of the ions are spent at (A), only the evolution of bubbles takes place. These bubbles continue to grow till they leave the cathode surface. Leaving the cathode bubbles agitate the solution at (C) and lacking ions are supplied by the influx of copper rich bulk solution. This again causes the deposition of copper at (C), but the deposit may in some cases not be dendritic because the current density at (C) will be very low and the solution is very rich in copper ions. This process was found by observing the convection current rising from the cathode surface. In this case the processes that occur at (C) are intermittent and cause the coarsening of former dendrites. Accordingly, after several minutes, each tree which can at first be separated into fine powders easily, become coarse dendrites.

Besides the facts mentioned above, consideration of the distance between these bubbles which are illustrated in Fig.10, derive another action of bubbles. When large bubbles grow at the cathode, the distance *"a"* is large. The size of trees is restricted within *"a"*, for the trees can stretch to a size *"a"* at the greatest. Then the value *"a"* determines the largest size of the powders and the modes of bubble evolution affect the distribution of the powder size. If the solution is very poor in copper concentration, this coarsening power of bubbles will be poor, and consequently trees will still be separable after a long electrolysis. Accordingly, in addition to the conclusion by passer that the bubbles have a coarsening power that is mechanical, the author concludes that the bubbles have a pulverizing power. Namely, when the bubble size is controlled by changing the cathode inclination, for example, the distribution of the size of powders changes in a wide range.

The mechanical action of bubbles, thus, will be prevented by using a solution of low copper content and high acid content. The geometrical action will be controlled by making fine patches on the cathode surface as mentioned in 4.c). But the most important thing will be to prevent the evolution of hydrogen bubbles. This is quite opposit to the current knowledge. It is necessary to ascertain how fine dendritic or spongy deposits occur.

VI. Mechanism of Fine Dendritic Deposition at Cathode

In general, it is said that increasing current density increases the nucleation rate at cathode forming fine powders. This mechanism only explains how fine grained deposits occur by increasing current density and never explains how isolated crystalline particles do not deposit. Any obstacle which prevents the deposition between the particles must be considered.[5] According to my recent experiments, the evolution of hydrogen bubbles is not necessary to get fine powders. The most important thing is to deposit hydrogen with copper.[6] Thus as shown in Fig.10, the powder growth at (A) is maintained by the codeposition of copper and hydrogen. The concept that the evolution of bubbles is necessary to the deposition of metal powder is not correct. The conditions which are most suitable for producing powders of copper and some other metals will be stated elsewhere in detail.

VII. Conclusion

From the results obtained by these experiments, some factors which affect the growth of powdery deposit at the cathode are found. especially concering the evolution of hydrogen bubbles.

i). The evolution of bubbles is not necessary for powders to deposit at cathode.

5) G. I. Finch, H. Wilman and Yang, Discussions Faraday Soc., 1947, 1, 144.

6) To be published elsewhere

ii). The evolution of bubbles coarsens the deposited powders: the bubbles agitate the solution resulting the coarsening deposits between the isolated particles.

iii). Fluctuations of the powder size distribution can be controlled by changing the size and distribution of evolving hydrogen bubbles.

Producing the metal powders such as iron and nickel powders by electrolysis, the evolution of hydrogen bubbles may be unavoidable and in these cases the considerations mentioned here may suggest some methods to obtain uniformly fine powders.

VIII. Acknowledgements

The author wishes to thank Dr. M. Masima who has attentively guided him, Mr. T. Nagai who has so freely given him the benefit of his expert knowledge, and all his colleagues for their kind collaborations.