Spring 5-15-1957

The Effect of Antimony and Cobalt on the Current Efficiency and the Grain Orientation of Deposits during the Electrolysis of a Zinc Sulfate Solution

Samuel A. Worcester

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A Thesis
Submitted to the Department of Metallurgy
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MONTANA SCHOOL OF MINES
Butte, Montana
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ABSTRACT

Preparation of solutions and apparatus and experimental procedure was described. The effect of antimony and cobalt in a zinc sulfate electrolyte upon current efficiency with increasing time was determined by the hydrogen evolution method. The degree of preferred orientation of grains in the electrodeposits was determined by the reflection method of X-ray diffraction.

INTRODUCTION

In the electrolytic zinc process zinc is obtained by electrodeposition from a purified leaching solution. The current efficiency is dependent upon purity, temperature, and circulation of the electrolyte, current density, and the period of deposition.

When an electrolyte containing a metallic salt and an acid is electrolyzed, either hydrogen will be evolved or the metal will be deposited, depending upon the decomposition voltage of the salt compared with that of the acid. Zinc sulfate has a decomposition voltage of 2.35 v compared with 2.4 v for sulfuric acid on a zinc surface, so zinc is deposited in preference to the evolution of hydrogen during electrolysis. The presence of impurities alters this condition.

One type of impurity has lower hydrogen overvoltage than zinc and a decomposition voltage above that of sulfuric acid. The impurities in this group, in which cobalt is included, lower current efficiency by being alternately deposited on the cathode and redissolved by the acid electrolyte. Antimony is of the type impurity that has a decomposition voltage lower than that of sulfuric acid and a hydrogen overvoltage low enough to cause re-solution of the deposited zinc.[1] Although the effect of various single impurities is easy to predict, several impurities combined may increase or decrease the detrimental effect of any single impurity.

Hard[2] has shown that the presence of cobalt and antimony together in an electrolyte is less detrimental to current efficiency than the presence of either of the impurities singly. He also verified the accuracy of the hydrogen evolution method for the determination of instantaneous current efficiency.

Many of these impurities effect the physical appearance of the deposit. Antimony in quantities as small as one part per million causes a darkening and roughening of the deposit. The relation of this change to the grain orientation of the deposits is investigated in this paper.

The process of cathodic crystal growth is primarily influenced by (a) the concentration of the constituents in, and the temperature and degree of agitation of the electrolyte; (b) the atomic arrangement of the cathode surface; and (c) the current density at certain local parts of the cathode surface.[3] The composition of the electrolyte was the only factor varied to any extent in this work.

Electrolytic deposits generally grow in three stages:[4] (1) a stage with orientation governed by the crystal structure of the initial cathode surface; (2) a transition stage in which orientation is generally random; and (3) a third stage with orientation governed by the composition and temperature of the electrolyte and the amount of hydrogen evolved at the cathode. If a large accumulation of adsorbed hydrogen ions occurs, the final stage tends to become random, whereas evolution of this gas favors preferred orientation. If the amount of hydrogen liberated is small, the most densely packed crystal planes tend to grow parallel to the cathode surface, whereas an increasing amount of hydrogen evolution tends to favor growth of the most densely packed planes by the presence of simple metal ions and low bath temperatures.

Electrolytic zinc deposited from a pure electrolyte containing zinc sulfate and sulfuric acid has been found to be oriented with the (0001) planes parallel to the cathode surface.[5] Deposits with this orientation have been found to have a shinier surface than have deposits with other orientations.

STATEMENT OF THE PROBLEM

The problem is (1) to determine the effect of antimony and cobalt upon current efficiency at various times during the electrolysis of a zinc sulfate electrolyte and (2) to determine the effect of these impurities upon the grain orientation of the zinc deposits.

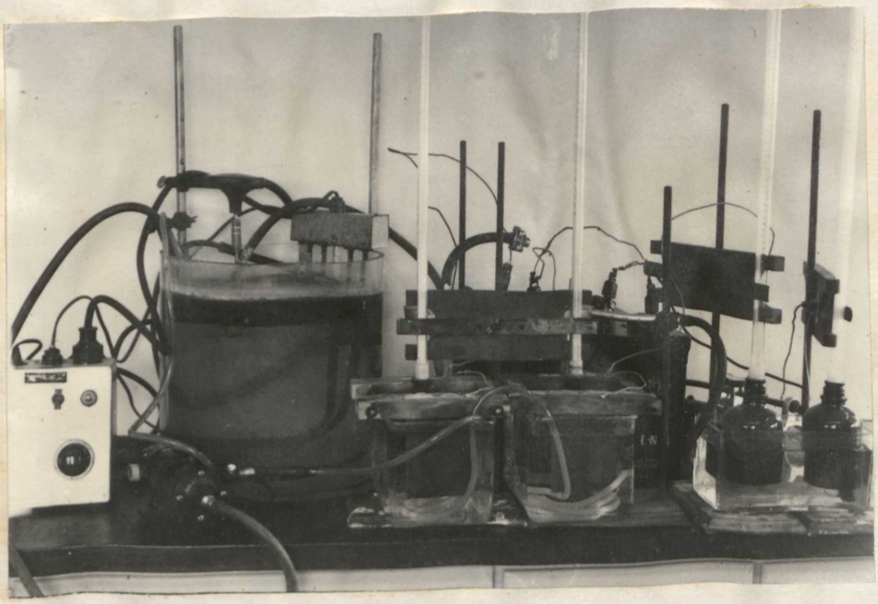
APPARATUS AND MATERIALS

In the following section a discussion of the apparatus used in the electrolytic deposition precedes a description of the apparatus used in the determination of preferred orientation.

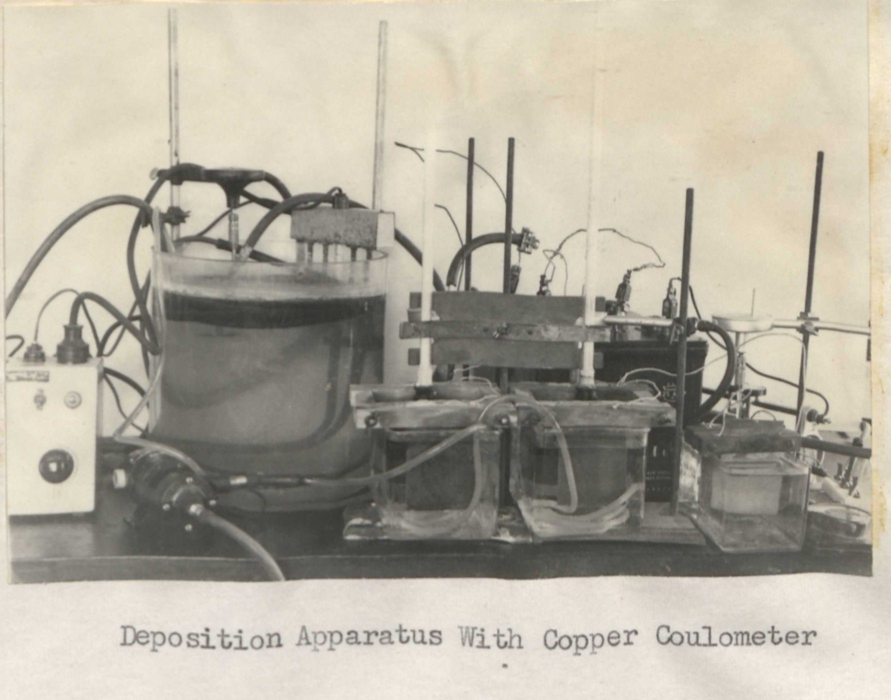
APPARATUS AND MATERIALS USED IN DEPOSITION

The apparatus and materials of importance include the electrolyte, parts of the cells, apparatus for the determination of current efficiency by hydrogen evolution, apparatus for maintaining constant cell temperature, and coulometers. (Fig. 1)

THE ELECTROLYTE. The original electrolyte contained 50 gm of zinc as the sulfate and 90 gm sulfuric acid per liter. It was made by dissolving Anaconda electrolytic zinc in a known quantity of sulfuric acid. The zinc was allowed to dissolve until the acid had been used up so that the solution would be purified by replacement by zinc in the solution of any impurities more noble than zinc. The resulting solution was diluted to a known volume after filtration, and aliquots were taken and titrated with potassium ferrocyanide to determine the zinc content and with standard sodium carbonate to determine the free acid concentration. The sulfuric acid necessary to give the desired concentration was added and the solution was diluted to a final



Deposition Appartus With.Gas Coulometer



Deposition Apparatus With Copper Coulometer

Figure 1

volume of 6.15 l.

Since it was thought that soluble anodes would tend to maintain a constant zinc concentration in the cells, zinc anodes were employed in the first test, during which the zinc concentration in the electrolyte nearly doubled. In subsequent tests, insoluble lead-silver anodes were used to prevent the excessive increase in zinc concentration. Pure granulated zinc was added to adjust the zinc and the acid concentration after each test.

Weighed quantities of antimony trioxide and metallic cobalt were dissolved in a small amount of 1:1 sulfuric acid before addition to the second cell as impurities.

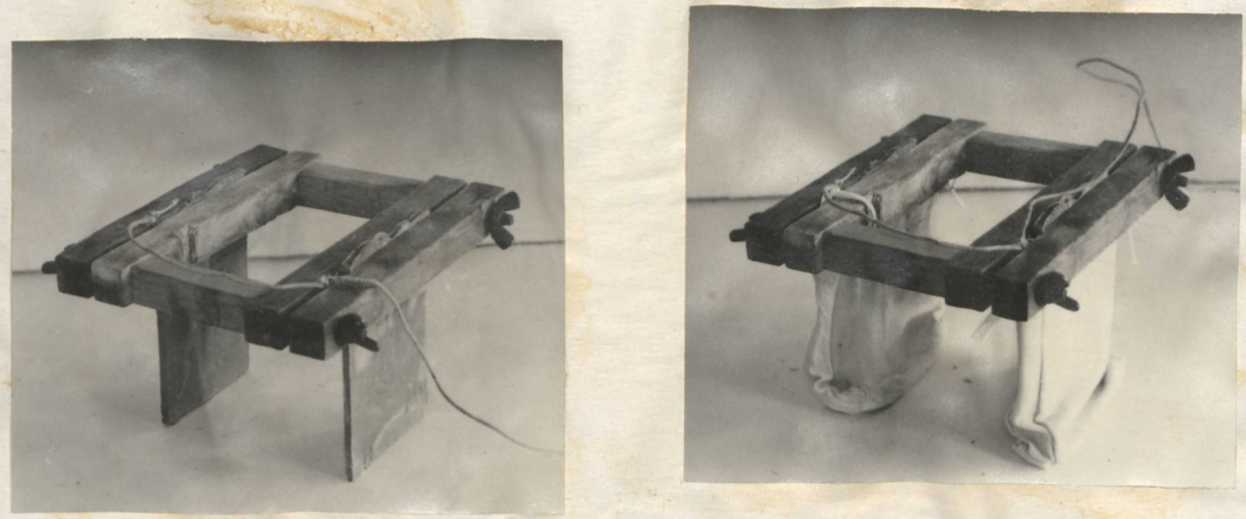
CELLS. The containers for the electrolyte were rectangular in shape and contained 2.2 l of electrolyte when filled to the operating level of the cell.

Anodes. A wooden frame held the anodes in position in the cell as shown in Figure 2a. For the first test the soluble zinc anodes used were covered with canvas bags to prevent contamination of the electrolyte. (Fig. 2b). Both the zinc and the lead-silver anodes used were cast in graphite molds.

Cathodes. The 61S-aluminum-alloy cathodes used in the first test were 3-in. tall and 1.6-in. wide and were suspended on a copper wire covered with Cenco label varnish. Since the Cenco varnish was attacked by the acid in the electrolyte during the 24-hr. period, De Khotinsky cement covered the copper wires during the second test, but it was also attacked by the acid. In the third and fourth tests, the wires were covered by glass tubing sealed over the wire with De Khotinsky cement. This protection for the wire proved satisfactory. After the first test the cathode area was cut in half to allow reducing the current to one amp without changing the current density.

GAS-COLLECTING APPARATUS. Glass hoods were suspended in the electrolyte above the cathodes to collect the hydrogen evolved from the cathode surface. These hoods were made by cutting off the tops of 16-oz. druggist's bottles just below the widest part. Plastic tubing connected the hoods to 50-ml burettes used to measure the volume of gas evolved. The same burette holder that supported the cathodes held the gas-collecting burettes. (Fig. 2c)

TEMPERATURE-CONTROLLING EQUIPMENT. An effort was made to keep the two cells and the coulometer at a constant temperature by circulating water from a constant-temperature bath held at 25° C. through them. It was necessary to provide the water bath with a cooling coil through which tap water was circulated when the room temperature exceeded 25° C. The water from the constant-temperature bath was circulated



(a) Anode Frame

(b) Anodes In Bags

(c) Cathode Assembly

(d) Gas Coulometer Assembly

Figure 2

through plastic tubing in the cells by means of a small electric pump. Stirring for the cells and the water bath was provided by compressed-air stirrers. During the experiments the temperature in the cells varied between 22° C and 23.5° C.

COULOMETERS. A laboratory gas coulometer was tried in series with the cells, but its resistance prevented the passage of the necessary 2-amp current with the voltage available from the two lead storage batteries used. A larger coulometer was made by using lead-silver electrodes and gas collectors similar to those used in the electrolytic cells. The hoods, which were connected to 100-ml burettes, were slightly larger than those used in the cells and extended down over the electrodes to prevent the escape of any of the rapidly evolved gas. The electrodes were cast from a lead-silver alloy in graphite molds, and a copper wire was secured to them during casting. This wire served as both a conductor and a support for the electrodes. Since the Cenco varnish and the De Khotinsky cement used would not protect the support wire for the anode from attack by the sulfuric acid in the electrolyte, use of the gas coulometer was abandoned after the second test.

For the third and fourth tests, a copper coulometer was employed to measure the total charge passed during the tests. The electrolyte was composed of 150 gm of copper sulfate, 50 gm of sulfuric acid, and 50 ml of ethyl alcohol in 1000 ml of water. Copper sheet formed the electrodes. The cathode was weighed before each test, and, immediately after the test, it was removed, washed in water, rinsed in alcohol, dried, and weighed. An ammeter and rheostat in series with the cells and coulometer proved adjustment of the current. (Fig. 3)

POLE FIGURE APPARATUS

Shultz[6] outlined a method for the determination of preferred orientation in cold-rolled sheet by X-ray diffraction using reflection technique. A specimen mount designed to make use of this method on the Norelco goniometer was constructed by Fausner[7] for use at the Montana School of Mines.

The parts of the specimen mount necessary for reflection technique are shown in Figure 4 and are as follows: (1) a base which mounts on the Norelco goniometer unit; (2) a ring which rotates about the axis of the base; (3) the reflection ring containing the sample mount, the top half of which is free to rotate, and (4) a vertical slit which narrows the X-ray beam so that a narrow rectangle on the specimen is irradiated.

There are three important axes about which rotation is made during the determination of a pole figure. Rotation about the goniometer axis determines the Bragg angle. The

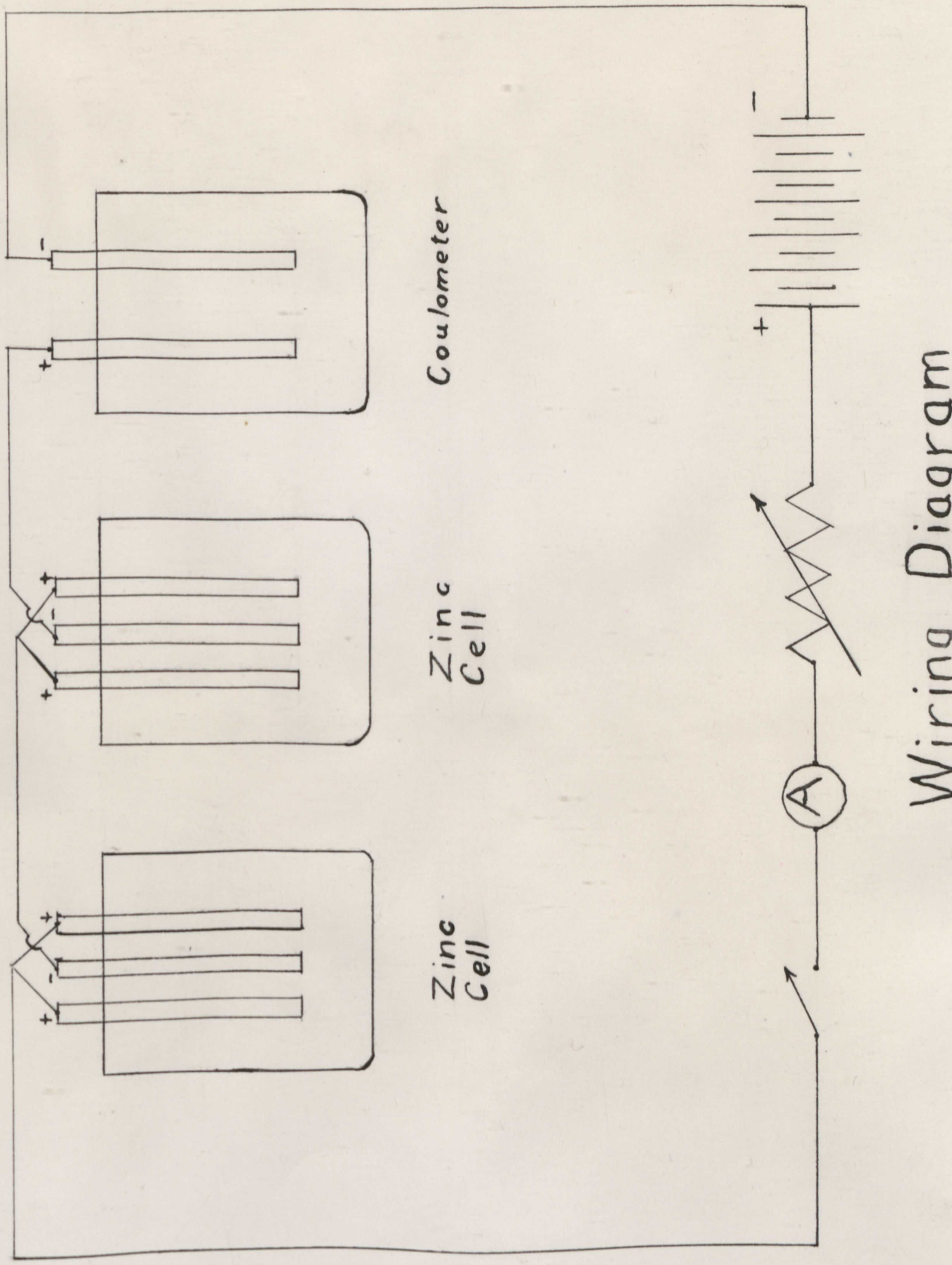


Figure 3

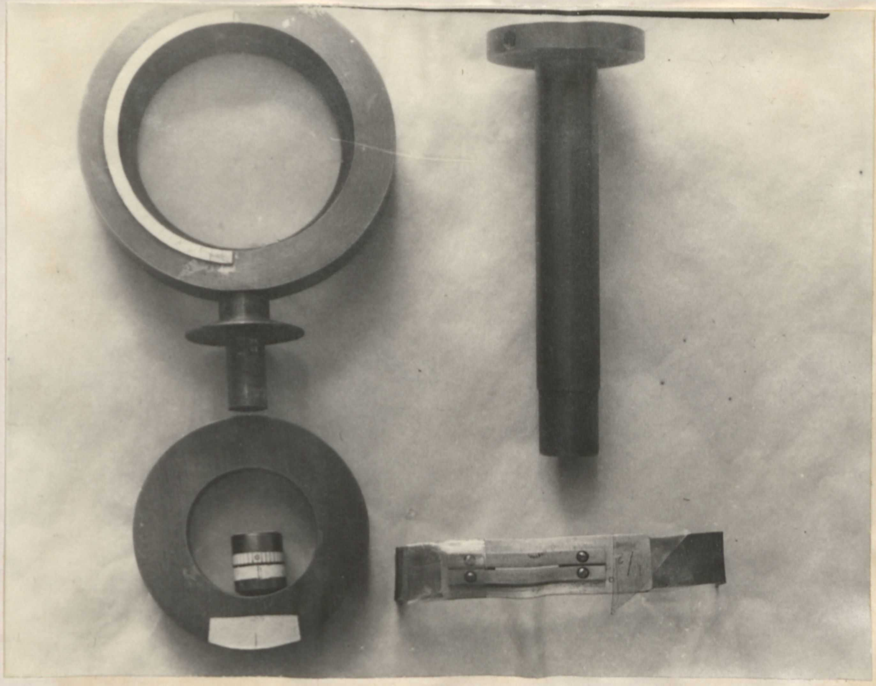
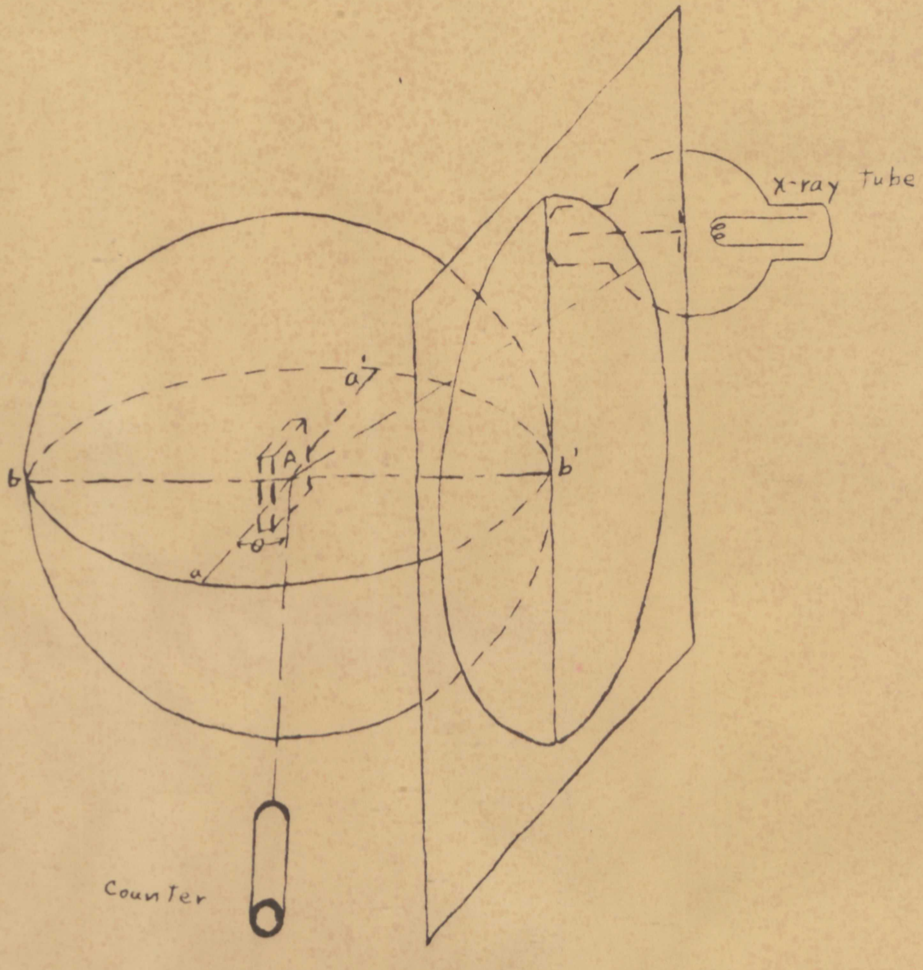


Figure 4- Parts of the Specimen Mount

axis of revolution, that axis about which angular changes cause change in the diameter of the concentric circles on the polar net, is normal to the plane of the reflection ring and passes through the center of that ring. The axis of rotation, angular changes about which cause angular changes about any of the concentric circles on the polar net, is normal to the plane of the sample and passes through the center of the sample-mounting pin. The intersection of the axis of revolution and the goniometer axis must lie in the plane of the surface of the sample.

The geometry of the reflection method is shown in Figure 5.[18] As the sample, A, is in the position shown, only those planes parallel to the surface of the specimen and for which the angle set on the goniometer is the Bragg angle are in a position to give reflection which will be counted by the counter. As the specimen is turned through an angle α about the axis of revolution a-a' and through an angle β about the axis of rotation, only those planes which satisfy the Bragg angle and intersect the plane of the sample at an angle α and the axis of revolution at an angle β are in a position for countable reflection. In this work the angle β was made to read zero when the axis of revolution (a-a') was parallel to the sample axis that had been vertical during the electrolysis.



The Geometry of the Reflection Method[8]

Figure 5

According to Schultz[6] no intensity correction is necessary for angles of up to 70°. The only requirement is that the sample be of sufficient thickness to give complete adsorption.

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of two parts, current efficiency tests and pole figure determination.

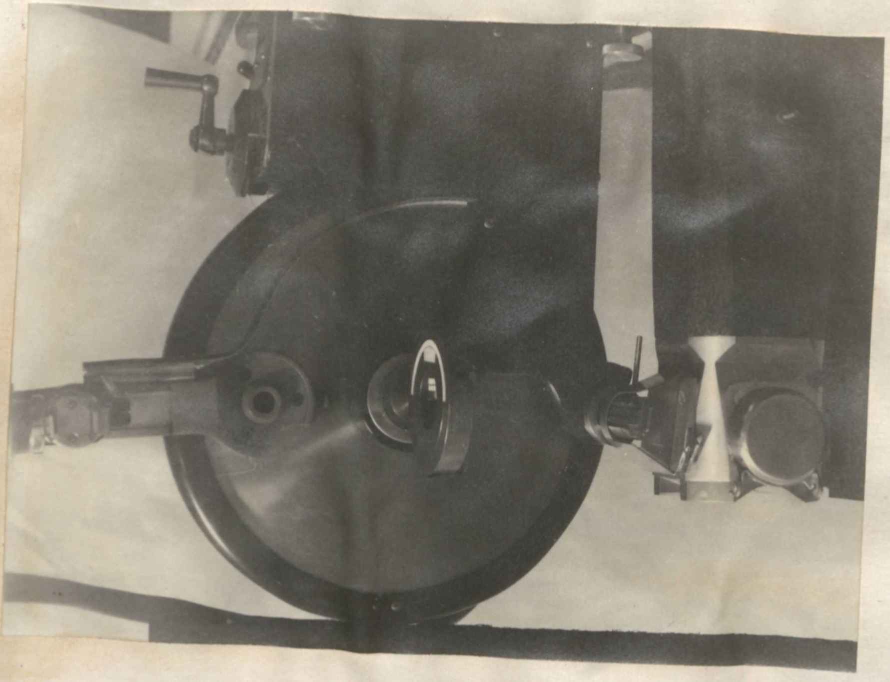
CURRENT EFFICIENCY TESTS

Before any of the current efficiency tests the constant-temperature bath was turned on and the water from the bath was pumped through the tubing in the cells for several hours, giving a cell temperature of between 22.0° C and 23.5° C. In all cases, cell 1 contained pure electrolyte. The cathodes were weighed and fastened to the holder which supported the gas-collection burettes. The cathodes and hoods were lowered into the electrolyte simultaneously, electrolyte was drawn into the burettes with a hose connected to a vacuum pump, readings of the electrolyte level in the burettes were taken, and the circuit was closed. A 2-amp current was used during the first test, but the current was changed to 1 amp for the remaining tests, since the burettes filled too rapidly with the 2-amp current passing through the cells. Cathode size in both cases was adjusted to give a current density of 30 amp/sq. ft. After one of the burettes had filled with the evolved hydrogen, readings were taken, and at certain time intervals the burettes were filled and readings taken again. During the test the barometric pressure and the temperature of the cells were checked periodically. All tests were run for 24 hours, and at the end of each test the cathodes were dried and weighed. For the third and fourth tests, during which the copper coulometer was used, the time between initial and final burette readings was recorded accurately. The current efficiency at various times during the electrolysis was calculated with allowance made for solution vapor pressure and height in the burette, temperature, and atmospheric pressure. The calculation was done in a manner outlined by Hard.[9]

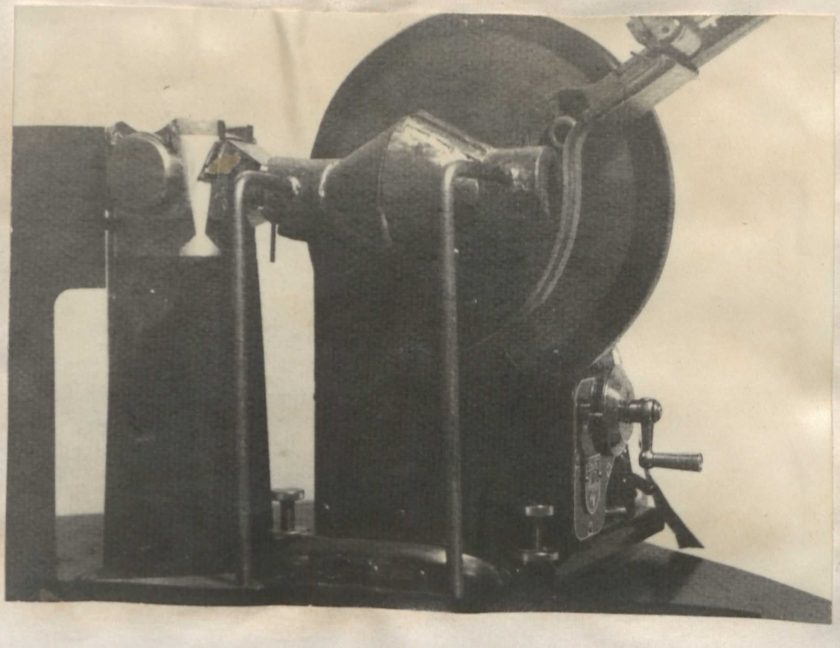
PROCEDURE FOR POLE FIGURE DETERMINATION

Samples for pole figure determination were ground, on the side opposite the face to be studied, to a thickness of .020 in. These were mounted on the specimen holder with the direction that had been vertical in the cell parallel to the axis of revolution when the angle around the axis of rotation read zero. The specimen mount was installed on the Norelco goniometer with the plane of the rings bisecting the angle $(180-2\theta)$.. The goniometer was set to scan a $1\frac{1}{2}^{\circ}$ increment, and a copper X-ray tube with a nickel filter was used. For $(10\bar{1}1)$ and (0002) reflections the goniometer was set to scan through the peaks occurring at angles of $2\theta = 43.23^{\circ}$ and $2\theta = 36.30^{\circ}$ respectively. The angle β was varied in 30° increments while the angle α was varied in 10° increments through 70° for each setting of angle β . Intensity readings were taken at each angle setting, and were plotted on a polar net. Lead shields provided with the specimen mount were used to protect the operator from the X-ray beam. Figure 6a shows the specimen mount mounted on the Norelco unit and Figure 6b shows the unit with the lead shields in place.

A qualitative method for determining the presence of preferred orientation involved mounting the electrodeposited sheets in the standard Norelco specimen mount and obtaining X-ray diffraction patterns of the specimens. A comparison of the intensity of the lines obtained with the intensity of lines from a randomly oriented sample gave an indication of the degree of preferred orientation.



(a)-Specimen Mount On Norelco Goniometer



(b)- Norelco Unit With Lead Shields In Place

Figure 6

RESULTS

RESULTS OF CURRENT EFFICIENCY TESTS

The results of the current efficiency tests are summarized in Figure 7. No deposit was obtained from the contaminated electrolyte from tests 3 and 4, and the deposit from the impure electrolyte from test 2 was thin and dark. The deposit obtained from the impure solution from test 1 was rough and had rod-shaped structures extending in the direction that had been vertical during deposition. Figure 8 shows this deposit along with the deposit obtained from the pure electrolyte during test 1. Deposits obtained from the pure electrolytes during the other tests had similar appearances. The grain size of the deposit obtained from the contaminated solution in test 1 was smaller than that of the deposit from the pure electrolyte, but both deposits had an ASTM grain size of -8. Typical photomicrographs are shown in Figure 9.

RESULTS OF POLE FIGURE DETERMINATIONS

Pole figure determinations were made on the deposit surfaces that had been next to the aluminum sheet, but these indicated a random orientation. Figure 10 illustrates the position of the (0001), $(10\bar{1}1)$ and $(10\bar{1}2)$ planes in the hexagonal lattice. Figure 11 shows ideal pole figures for the $(10\bar{1}1)$ family of planes and the (0001) planes when the

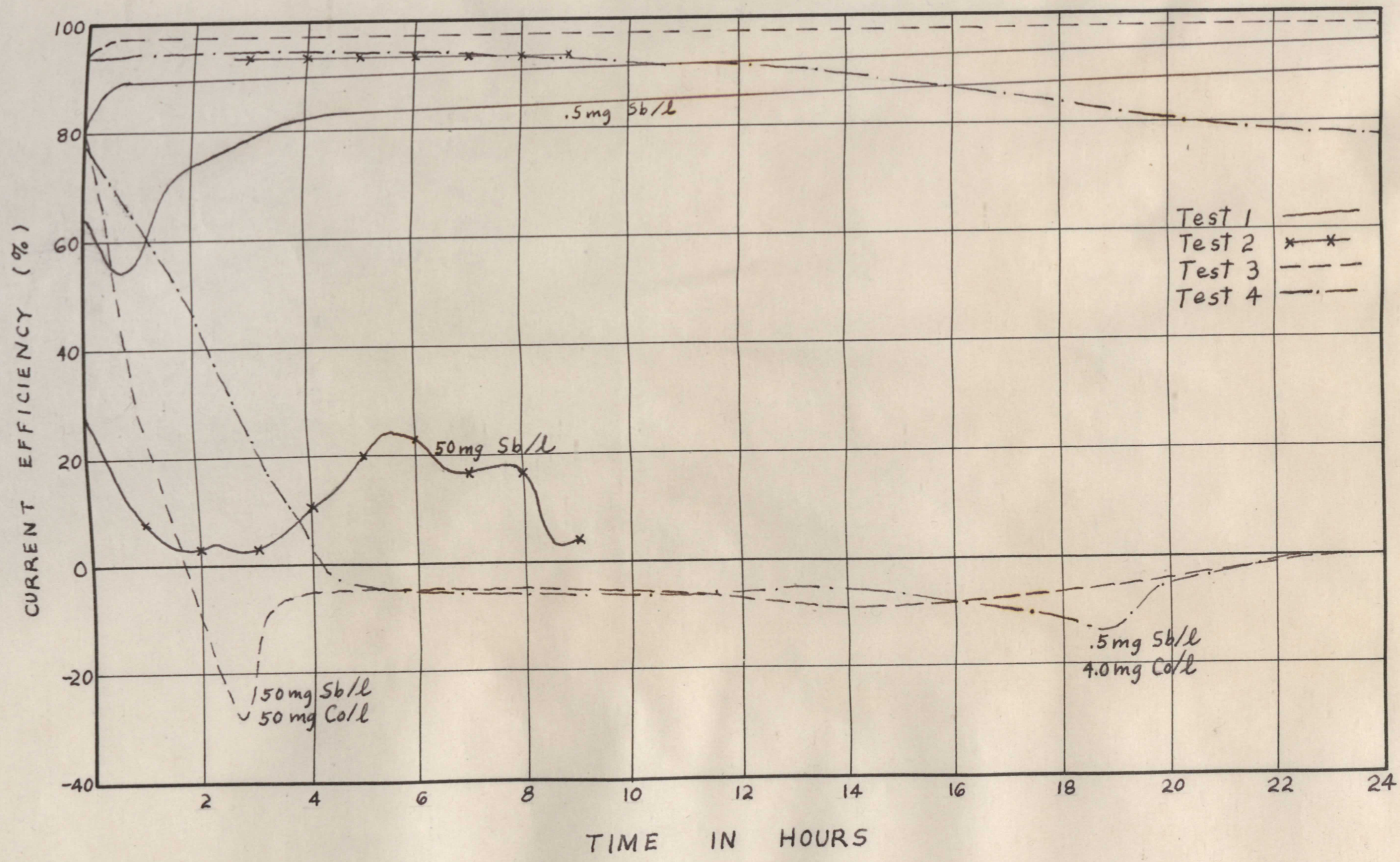


Fig. 7 — PLOT OF CURRENT EFFICIENCY vs. TIME

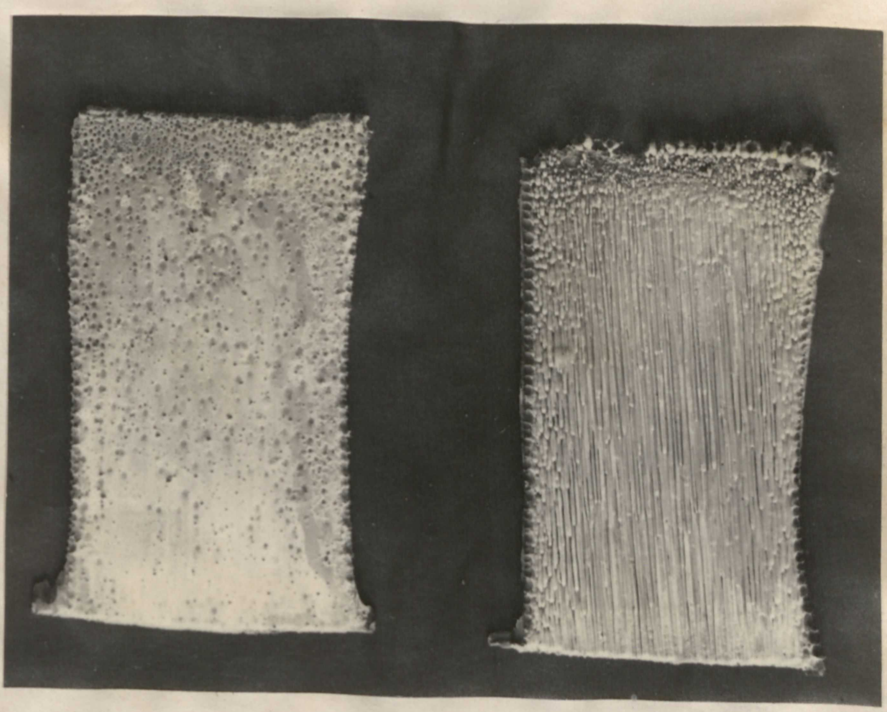
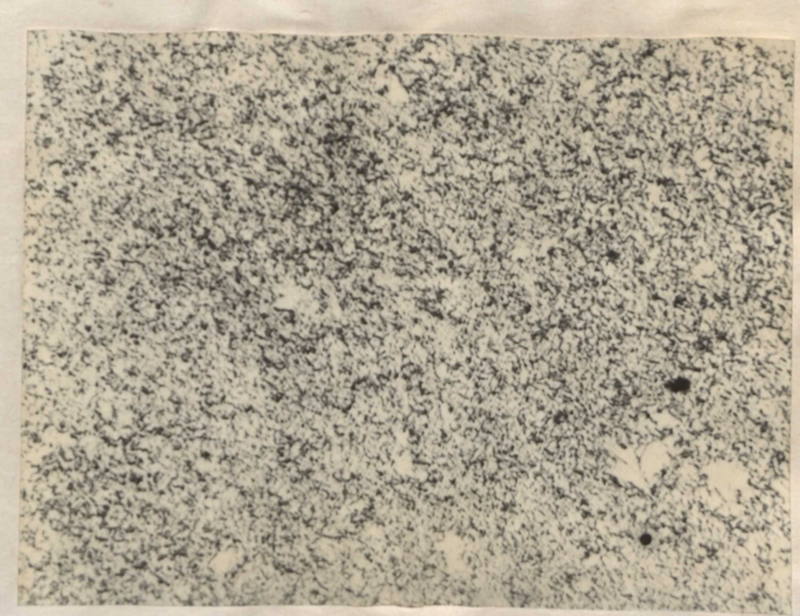


Figure 8 - Zinc Deposits,
Left - From Pure Solution
Right - From Solution Containing 0.5 mg/l Sb

Deposit From Pure Solution
150 X- Palmerton's Etch



Deposit From Solution Containing
.5 mg/l Sb
150 X- Palmerton's Etch

Figure 9-Microstructures

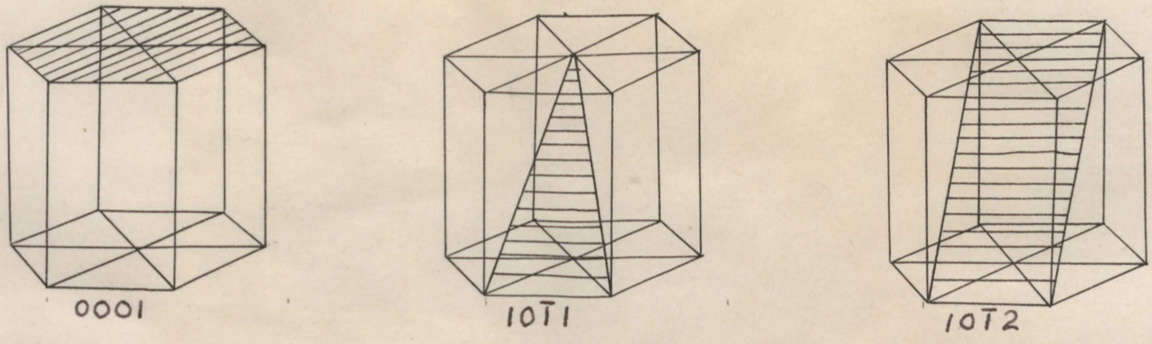


Figure 10--Planes in the Hexagonal Lattice

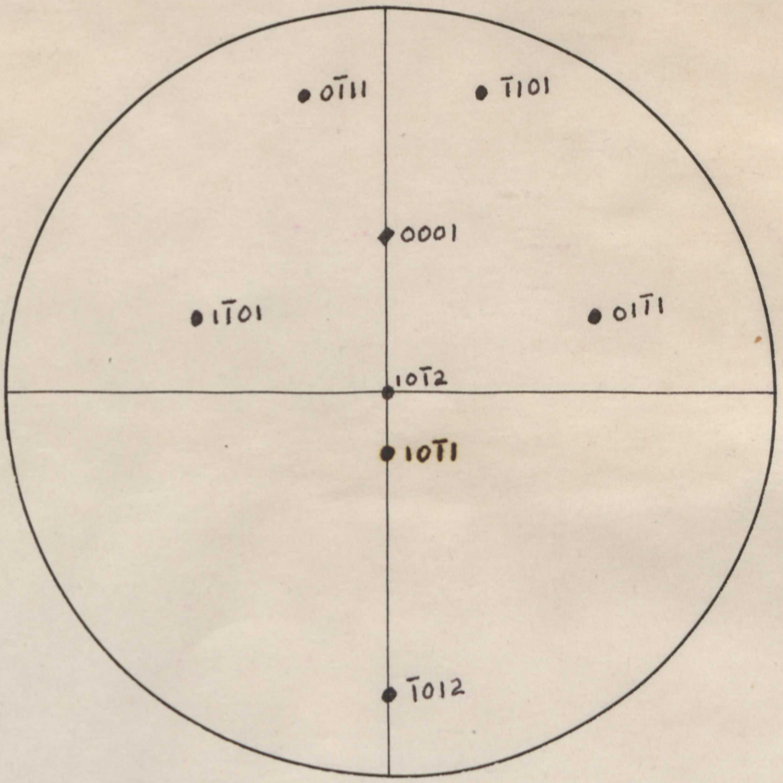
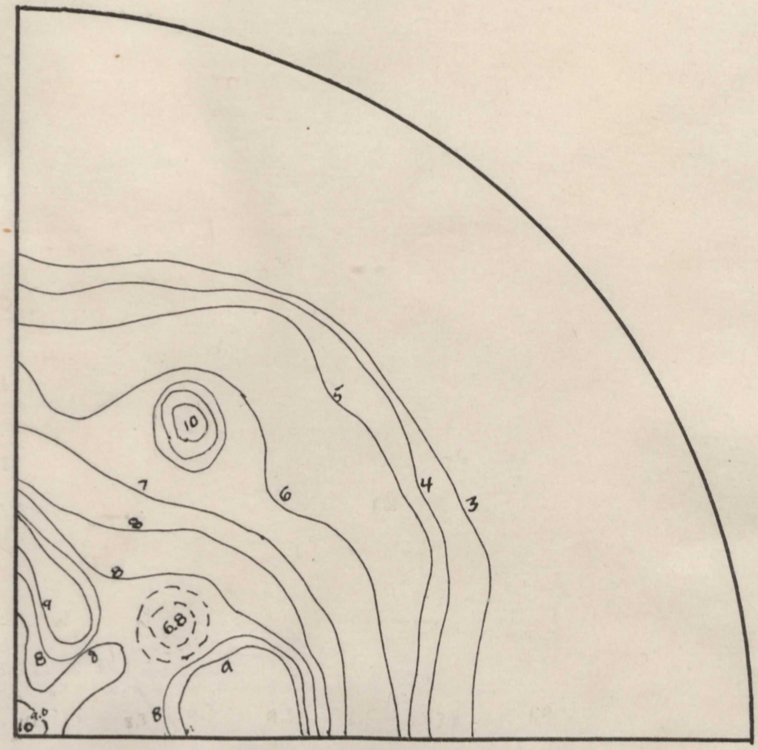


Figure 11--10$\bar{1}$2 Projection for Zinc

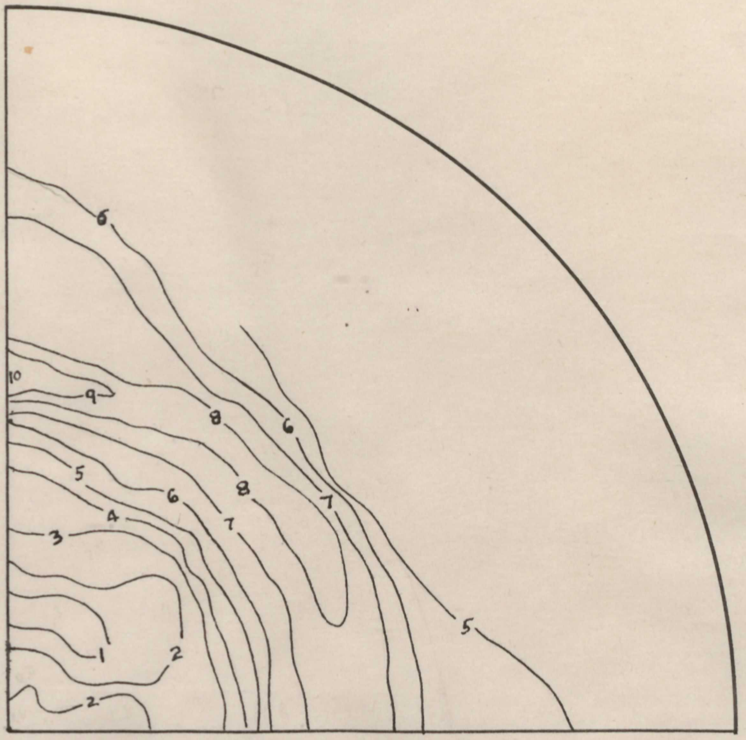
($10\bar{1}2$) plane is parallel to the projection plane. Preferred orientation is indicated by the pole figures of the pure zinc deposit from test 4 and the deposit from the impure electrolyte from test 1. (Fig. 12 and 13)



Zinc from Pure Electrolyte

Zinc from .5 mg/l Sb Electrolyte

Figure 12--(10$\bar{1}$1) Pole Figures



Zinc from Pure Electrolyte

Zinc from .5 mg/l Sb Electrolyte

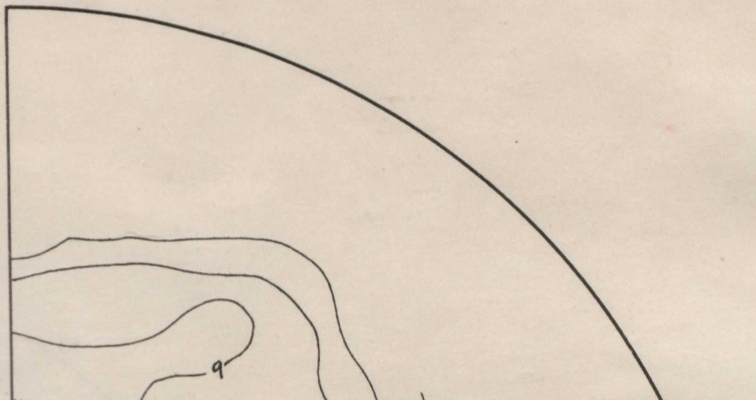


Figure 13--(0001) Pole Figures

DISCUSSION OF RESULTS

DISCUSSION OF CURRENT EFFICIENCY TESTS

The current efficiency tests showed that antimony in small amounts (0.5 mg/l) in a zinc sulfate electrolyte decreases the current efficiency. Since no additional antimony was added after the electrolysis was begun, the rise in current efficiency after the first hour indicates that the antimony in the solution becomes depleted and that some of the deposited antimony is plated over by zinc. The columnar structure of the deposit indicates the presence of local cells which cause rapid evolution of hydrogen from certain cathode areas.

The negative current efficiencies obtained in tests 3 and 4 indicate rapid re-solution of the deposited zinc. Since cobalt alternately deposits and dissolves, it may prevent the formation of a coherent deposit and may prevent the zinc from plating over the antimony. During tests 3 and 4 the cathode deposit continually broke off and dissolved in the electrolyte.

The detrimental effect of antimony and cobalt together as in test 4 is in conflict with the results obtained by Hard.[9] This may be due partly to the 24-hr deposition period.

DISCUSSION OF POLE FIGURE DETERMINATIONS

The more severe intensity gradients in the first pole figure of Figure 13 as compared with the second pole figure indicate a greater degree of preferred orientation in the zinc deposition from the pure solution. There is no indication of any tendency for one crystallographic axis to have a preferred direction in the plane of the sample. For example, no axis tends to be parallel to the axis of the deposit that had been vertical during deposition. This randomness is shown by the concentric arcs of similar intensity in the pole figures instead of specific points like those shown in the ideal pole figure. The position of greatest intensity in the (0001) pole figures exclude the possibility of preferred orientation with the (0001) planes parallel to the surface, since the greatest intensity would have been in the center of the (0001) pole figure if that orientation had existed. The author believes that the zinc deposited from the pure electrolyte has its $(10\bar{1}2)$ planes parallel to the cathode surface in preferred orientation, because the position of maximum intensity for the (0001) plane is around 50 degrees. The zinc from the impure electrolyte may have preferred orientation with its $(10\bar{1}1)$ planes parallel to the surface, but this is less positive, since the maximum intensity for the (0001) planes ranges from 40° to 60°. This leaves the possibility of either the $(10\bar{1}1)$ or $(10\bar{1}2)$ planes being parallel to the cathode surface. The $(10\bar{1}1)$ pole figures give no indication as to which of the two above planes are parallel to the surface except that the broadness of the $(10\bar{1}1)$ intensity might indicate a preference for the $(10\bar{1}2)$ planes parallel to the surface.

CONCLUSIONS

(1) Antimony lowers the current efficiency in the electrolysis of a pure zinc sulfate solution, but its effect diminishes with time if no additions of antimony are made.

(2) Although the presence of cobalt in the solution with the antimony raises the current efficiency during the start of the electrolysis, its effect is much more detrimental during the later stages of the electrolysis.

(3) The presence of antimony in the electrolyte altered the physical appearance of the deposit obtained, while cobalt in solution with the antimony prevented any deposition after a 24-hr period.

(4) The detrimental effect of cobalt after about 4-hr is probably due to the depletion of antimony in the solution.

(5) Deposits from the solution containing antimony had smaller grain size than those deposited from the pure electrolyte.

(6) A deposit obtained from the pure electrolyte developed a preferred grain orientation with the $(10\bar{1}2)$ planes parallel to the cathode surface. The orientation of grains in the deposit obtained from the electrolyte containing antimony developed a preferred orientation similar to that obtained in the pure deposit but with a lower degree of

preferred orientation.

(7) The pole figures indicated no tendency for a preferred orientation with respect to the vertical axis of the cathode during deposition.

APPENDIX

CURRENT EFFICIENCY TEST 1

Conditions of Test: Initial zinc concentration 50 gm/l, sulfuric acid concentration 90 gm/l, current density 30 amp/sq ft, soluble zinc anodes; .5 mg/l antimony added to cell 2 at start of test.

DATA:

Time in Hours	Per Cent Current Efficiency	
	Cell 1	Cell 2
0	80.2	64.4
0.7	89.0	54.0
1.7	89.1	72.4
2.7	89.2	78.2
3.7	90.1	81.3
4.7	87.1	77.8
8.2	91.6	86.2
24.0	95.6	89.6

CURRENT EFFICIENCY TEST 2

Conditions of Test: Initial zinc concentration 66 gm/l, sulfuric acid concentration 53 gm/l, current density 30 amp/sq ft, insoluble anodes; 50 mg/l antimony added to cell 2 at start of test.

DATA

Time in Hours	Per Cent Current Efficiency Cell 1	Cell 2
0		38.8
0.25		22.7
0.75		10.5
1.50		2.7
2.25		4.8
2.75	93.0	2.0
3.50	93.1	7.8
4.50	93.2	14.2
5.50	93.2	24.1
6.50	92.5	18.2
7.50	93.8	18.6
8.50	94.1	13.0
8.83	92.7	13.9

Gas coulometer failed during the night and opened the circuit

CURRENT EFFICIENCY TEST 3

Conditions of Test: Initial zinc concentration 66 gm/l, sulfuric acid concentration 53 gm/l, current density 30 amp/sq ft, insoluble anodes; 50 mg/l antimony and 50 mg/l cobalt added to cell 2 at start of test.

DATA:

Time in Hours	Per Cent Current Efficiency Cell 1	 Cell 2
0	95.3	80.1
0.33		51.9
0.58	97.4	24.7
1.33	97.6	46.8
1.68		38.6
2.13	98.1	-8.6
2.25		-21.7
2.58		-29.3
2.92		6.1
3.05	97.7	- 6.9
11.28	98.1	- 7.2
12.17		-10.0
13.23	98.0	-10.0
14.85	97.8	- 6.6
22.63	98.6	- 1.2
24.00	97.6	- 0.2

CURRENT EFFICIENCY TEST 4

Conditions of Test: Initial zinc concentration 80 gm/l, sulfuric acid concentration 70 gm/l, current density 30 amp/sq ft, insoluble anodes; 0.5 mg/l antimony and 4.0 mg/l cobalt added to cell 2 at start of test.

DATA:

Time in Hours	Per Cent Current Efficiency	
	Cell 1	Cell 2
0	94.9	77.9
0.75	95.3	66.8
1.30		60.5
1.75		51.4
2.25	95.5	38.7
2.75		28.5
3.25	95.4	16.7
13.32	90.0	- 5.0
18.62		-16.0
19.13	80.0	- 3.2
21.13		- 3.8
24.00	78.8	0.0

POLE FIGURE DATA FOR OUTSIDE SURFACE OF ZINC DEPOSITED FROM PURE ELECTROLYTE DURING TEST 4

$(10\bar{1}1)$ Data:

	Relative Intensities			
α	$\beta = 0$	$\beta = 30$	$\beta = 60$	$\beta = 90$
0	10.0	10.0	8.1	--
10	8.1	7.8	8.4	8.0
20	8.0	9.1	8.1	8.3
30	9.1	8.2	6.8	9.3
40	7.8	7.0	8.2	9.3
50	5.6	10.0	6.5	6.5
60	4.8	5.4	5.6	3.8
70	1.7	2.3	2.6	1.9

(0002) Data:

0	1.4	1.7	1.1	1.5
10	2.2	2.0	3.2	1.9
20	0.5	0.3	1.0	1.8
30	3.0	2.9	1.9	2.5
40	4.1	2.1	6.0	6.8
50	10.0	8.3	8.4	7.7
60	7.7	5.9	1.5	5.2
70	6.8	2.3	1.7	5.2

POLE FIGURE DATE FOR OUTSIDE SURFACE OF ZINC DEPOSITED FROM IMPURE ELECTROLYTE DURING TEST 1

$(10\bar{1}1)$ Data: Relative Intensities

α	$\beta = 0$	$\beta = 30$	$\beta = 60$	$\beta = 90$
0	7.9	8.2	9.1	8.4
10	8.3	7.4	8.4	8.2
20	8.0	8.4	7.8	8.6
30	7.8	9.2	8.6	10.0
40	8.7	8.1	8.1	8.8
50	6.5	7.1	7.0	7.6
60	4.6	5.5	5.0	5.1
70	2.4	3.2	3.5	2.5

(0002) Data:

0	4.8	4.9	4.5	4.1
10	5.2	4.6	4.5	5.0
20	3.8	5.3	5.5	5.5
30	6.1	6.1	6.5	6.2
40	8.2	9.4	7.5	7.9
50	9.8	8.7	8.2	8.7
60	8.1	10.0	8.1	9.3
70	3.3	7.8	5.3	6.2

ACKNOWLEDGEMENT

The author wishes to express his appreciation for the help and guidance given him by Dr. F. A. Hames, Dr. S. T. Shih, and Mr. R. I. Smith, Professors of Metallurgy.

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