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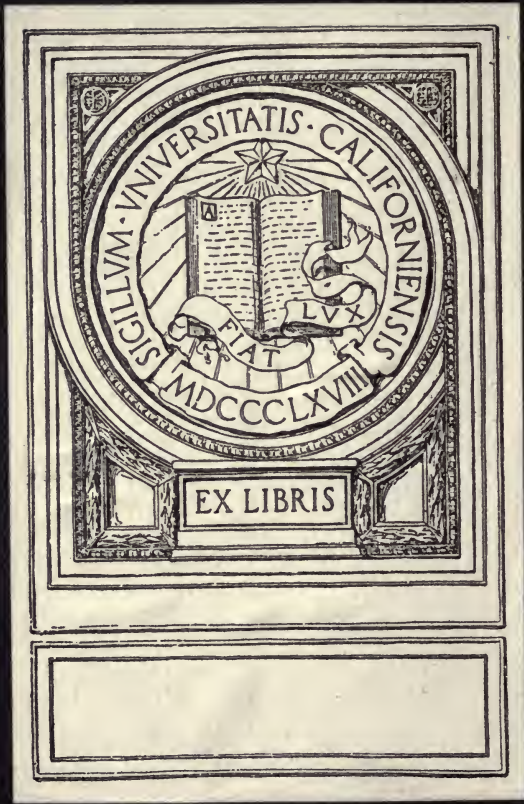
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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

— ON THE —

# ELECTRO-DEPOSITION OF IRON

BY

W. E. HUGHES, B.A. (*Cantab.*)

*Late Chief Research Chemist, Electro-Metallurgical  
Committee, Ministry of Munitions*



LONDON :

PUBLISHED BY HIS MAJESTY'S STATIONERY OFFICE

1922

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WITH AN APPENDIX CONTAINING A  
BIBLIOGRAPHY OF THE SUBJECT

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COMPOSITION OF ROY

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## PREFATORY NOTE

The research, the results of which are embodied in this report, was carried out by Mr. W. E. Hughes, B.A. (Cantab.), with the assistance of grants made by the Department on the recommendation of the Advisory Council for Scientific and Industrial Research.

In view of the extended use of Electro-Deposition of Iron for many industrial purposes and the new applications which it is finding, it was thought advisable, as an exceptional measure, to issue Mr. Hughes' report as a bulletin of the Department. It will be understood that the report is the work of Mr. Hughes, and that the Department must not be taken as endorsing the statements therein contained.

At the Department's request, Mr. Hughes has included, in the Appendix, a bibliography of the subject for which it is believed there will be a general use.

Department of Scientific and Industrial Research,  
16, Old Queen Street, Westminster.  
London, S.W.1.

*March, 1922.*

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# ON THE ELECTRO-DEPOSITION OF IRON

## INTRODUCTION

This report includes, as Division 1, simple descriptions of the structures of a number of samples of iron, electro-deposited from the chloride of iron solution. The purpose is to show how the three factors of deposition, namely, (1) temperature, (2) current density, and (3) movement (of cathode or electrolyte), affect the structure of the iron deposited from the chloride bath. Incidentally, the micrographs disclose variations of structure produced by volume of solution (Figs. 22, 23, and 24), concentration currents (*e.g.*, Figs. 3 to 8), and some other factors.

Although the deposits considered were formed in the chloride of iron solution, there is, it may be said, experimental evidence to show that the conclusions drawn from the structures of deposits built up in that bath may be extended to those formed in other solutions. This point is touched on in Division 2; and, further, some evidence is adduced there to show that extension may be made not only to deposits formed in different solutions (solutions of different salts, that is) of the same metal, but also to deposits of different metals. Indeed, a principal purpose of Division 2 is to show that, in general, this is the rational conclusion of the concentration hypothesis outlined in that Division and based on the assumption that the crystallisation of electro-deposited metal is, essentially, in no way different from crystallisation from rock magmas, molten metals, or salt solutions. In Section III of Division 2 the importance of the study of the structure of deposited metal to electro-deposition in the workshop is briefly pointed out.

It may be mentioned that the author has made a critical survey of such part of the literature upon the electro-deposition of iron as appears to him of use or importance to those about to undertake work on that subject. It has, however, been considered that that review would be published most appropriately elsewhere,\* and it has not, therefore, been included in this report. The papers and researches referred to are, however, detailed (in an Appendix hereto), together with others on the properties of electrolytic iron, in a classification intended to indicate the general subject matter of each, and, thereby, to facilitate the literary labour required to be done by one who undertakes research, for this purpose or that, on electrolytic iron. Patent specifications are, for the most part, excluded; only such as appear to the author to contain subject matter of real value are noted.

The author would be ungrateful if he did not acknowledge the great kindness extended to him by Professor H. C. H. Carpenter, F.R.S., who has exercised a general supervision over the work, and who has been ever ready to afford the author the benefit of his advice and experience. To Professor E. H. Lamb, D.S.C., M.Sc., of the East London College, the author is indebted in many ways, and wishes to tender his sincere thanks. Acknowledgment is also made of the permission of the Council of the Iron and Steel Institute to reproduce the micrographs, marked with an asterisk, that have appeared in the Journal of the Institute.

\* v. Trans. Am. Electroch. Soc., 1921,



## DIVISION 1—DESCRIPTIVE

### GENERAL NOTE ON THE DESCRIPTIONS OF THE DEPOSITS

It has been found by no means easy so to describe the structure of the deposits as to produce even an approximately accurate picture of them, and the variations that occur in them, in the mind of another. The photographs help, of course. But it has to be remembered that the diameter of the visible area of the deposit to be seen is only 2 mm., when using a Zeiss apochromat, 16 mm. objective (N.A. 0.30), to obtain, with the x 8 ocular, a magnification of about 150 diameters. And hence, the photograph represents only a small part of the deposit, which may be, and often is, of varying structure. To reproduce the whole area of a section of each specimen would be an altogether too laborious and expensive task. And, moreover, no photograph, however good it may be, ever conveys to the mind what can be seen by the eye. While, therefore, the photographs have been relied on as aids, the descriptions have been very carefully made. The method adopted, in order to represent the truth as nearly as might be, was as follows:—The structure was described in general outline from direct and immediate observation through and at the microscope. The details were then filled in. The memory was not trusted at all: that is, no appreciable interval of time was allowed to transpire between observation and record. After allowing four or more weeks to pass, another description of the specimen was recorded without any reference being made to the former one. The two descriptions were then compared; and, if necessary, as it sometimes was, the descriptions were checked by renewed examination of the specimen. In this way it was sought (1) to eliminate any bias on the part of the observer—to avoid “seeing” what was not there, and (2) to enable another to gain at least a fairly accurate picture of the structure of the specimen. Further, the descriptions inserted in the following are those finally “settled” and recorded in note-books. No “amendments” have been introduced, except in some very few instances, and then only after reference to the specimens concerned yet once more.

For the purpose of condensing the descriptions, certain terms have been used to denote various types of structure. These terms are, some of them, already employed by the petrologist in descriptions of his rock sections, *e.g.*, columnar, fibrous, and others. Other terms used are names of common objects which are readily pictured in the mind when the eye sees the words by which they are known, *e.g.*, cauliflower, poplar-tree, and so on. The term most frequently, perhaps, made use of is the word “normal.” This will be defined here; but no definition of the other terms used will be given; a list of them is drawn up, and a reference given to one or more photographs showing clearly, in each case, the type of structure to which the term is meant to apply.

Term (or Expression).	Reference.	Term (or Expression).	Reference.
Normal (approx.) ... ..	Figs. 19, 20, &c.	Fibrous* ... ..	Figs. 52, 53, &c.
Columnar ... ..	Fig. 44.	Fan ... ..	Fig. 52.
Mosaic ... ..	Fig. 33.	Cauliflower ... ..	Figs. 34, 38, &c.
Poplar-tree ... ..	Fig. 36.	Fountain ... ..	Fig. 59 especially.

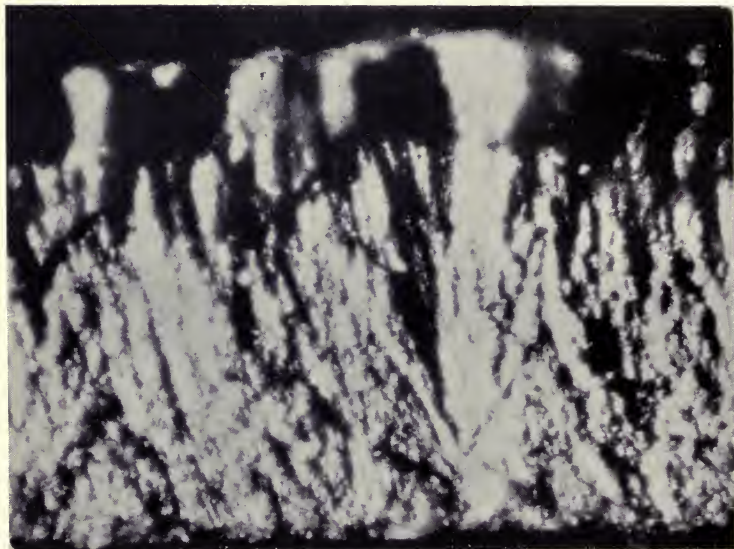
\* This term is employed by C. F. Burgess and O. P. Watts, *Trans. Am. Electroch. Soc.* 1906, vol. 9, at p. 233.





FIG. 1.—Fractured Surface of an Iron Deposit.  $\times 80$ .

(Oblique illumination.)



← Change in structure occurs.

FIG. 2.—Fractured Surface of a Cobalt Deposit.  $\times 140$ .

(Oblique illumination.)

The part of the deposit above the line indicated by the arrow is seen to differ markedly in structure from the part below.



In none of these cases (except that of the term "normal") does any particular (individual) definition seem necessary.

The term **NORMAL** is given to that type of structure which is most frequently of all approached in electro-deposited metal. It is that type in which the grains (whether large or small) have the shape, more or less, of the letter **V**, the angle of the **V** being directed inwards toward the cathode. Such grains are well seen in Fig. 11, and, again, in Fig. 20. As the term is intended to be interpreted, a strictly "normal" type of structure would be wholly composed of grains (of various sizes) having the **V** shape. As a fact, this is never observed in a deposit. The grains are never, all of them, **V**-shaped; nor are the arms of the **V** often straight lines. The ideal "normal" deposit is non-existent; but the "practically" or "more or less" normal deposit is the one that most frequently does occur. The deposits 9, 10a, and 11a, show structures that are more or less nearly "normal": in deposit 11a the normal structure is closely approximated.

Deposits approaching the normal type in structure have been described by several authors. C. F. Burgess and O. P. Watts\* describe and illustrate the cone- or tooth-shaped pieces that they picked out from the fragments of electro-deposited iron when it was broken up by smart hammer blows. It is the longitudinal section of such a cone or tooth-shaped piece that one sees when examining under the microscope a deposit that approaches the normal type in structure. Figs. 1 and 2 show fractured surfaces of electrolytic iron and cobalt, respectively. In both figures the **V**-shaped structure is very evident.

It may be added that this or that type of structure is not confined to any particular metal, and hence the nomenclature here employed is applicable not only to iron but also to other (electro-deposited) metals—copper, nickel, cobalt, and so on. As it is hoped to show, structure does not depend upon the particular metal deposited, but upon conditions of deposition.

## SERIES I

### ON THE EFFECT OF TEMPERATURE

#### A.—DEPOSITION

Constant current density: varying temperature.

**The Conditions of Deposition were—**

<i>C.D.</i>	...	...	...	...	...	120 amp./ft. <sup>2</sup>
<i>Time</i>	...	...	...	...	...	2 hours.

**The cathode** was either copper rod, or steel rod thinly coated with copper in the cyanide bath.

**The cleaning** was as follows (except where stated to be otherwise):—

- (a) *If of copper*, the rod was polished; boiled in potash solution; brushed with Calais sand; swilled in clean running water; treated in an electro-cleaner; swilled in water; dipped in 10 per cent. (by volume) HCl solution; swilled; brushed with Calais sand; and then given a final rinse in running water.
- (b) *If of steel*, the rod was treated as in (a); then given a 10-minute coat of copper in the cyanide bath; swilled; dipped in the dilute HCl; swilled; brushed with Calais sand; swilled again.

\* Op. cit., pp. 233 and 234, and, especially, Figs. 7 and 8,

Expt. No.	Ref. to Micro.	Temp. °C.	Remarks.	Deposit.
A	(No micro.) It would not have been possible to prepare a section of this deposit for examination.	70	Conditions, cathode, and all else, as in Expt. 10 (v. post). <i>N.B.</i> —This expt. was made, at the end of the series, with the object of fixing the minimum temp. employable at the C.D. used (120 amp. per sq. ft.).	<i>Macroscopic.</i> In the middle, the deposit was dark and bright; at the ends, dark and powdery. The character of the deposit became worse and worse, and, after some 20 mins., everywhere split up and became useless.
1	Figs. 3 to 8	90	The electrolysis was conducted in a 500 c.c. glass beaker. Circular anodes. <i>E.M.F.</i> at 1½" rod distance = 0.9 volt. <i>Cathode</i> was copper rod. The solution was filtered just before using.	<i>Macroscopic.</i> Good: smooth and bright. Light grey. Outgrowth (rather cindery) at both ends—more at bottom end. The deposit was split longitudinally from the bottom upwards. <i>On sawing</i> , it was found to be hard and brittle; it broke up and came away from the base metal. <i>Adherence</i> , therefore, poor. <i>Note</i> :—Cathode was not dipped in HCl during cleaning.
9	Figs. 10 & 11.	90	2½ gals. of solution (recently filtered) was used. Swedish iron anodes—6" × 3" × ¼" —2 on each anode rod: 4 in all. <i>E.M.F.</i> 0.9 volt. at 5½". <i>Cathode</i> , copper-ed steel rod.	<i>Macroscopic.</i> Good. Light grey. Crystalline on one side, particularly toward the top end; smooth on the other. <i>On sawing</i> , deposit did not split or break away. <i>Adherence</i> , good.
3	Figs. 12 to 16	100 to 86	Conditions as in 9, except that solution was not filtered before use.	<i>Macroscopic.</i> Very good in colour and smoothness. Thickening, but no outgrowth, at top: rounded outgrowth at bottom end. No spines or attachments. <i>On sawing</i> , no breaking away. <i>Adherence</i> , good.
4	Fig. 21	110	Conditions as in 3, except— <i>E.M.F.</i> 0.8 volt. ( <i>i.e.</i> , rather less than in 3).	<i>Macroscopic.</i> Good, light grey colour. Close and even texture. Matt. Slight thickening at both ends. No outgrowths: no lumps. <i>On sawing</i> , no brittleness shown. <i>Adherence</i> , good.
10	Fig. 18	112	Same solution as used for expt. 9, and same conditions. <i>Cathode</i> , copper-ed steel rod.	<i>Macroscopic.</i> Good colour. Crystalline on one side: matt on the other. Some thickening at bottom end. <i>On sawing</i> , deposit came away from the base metal, but was not brittle. <i>Adherence</i> , bad. ( <i>Note</i> :—Not dipped in HCl during cleaning.)
10a	Figs. 19 & 20.	112	Everything same as in 10, excepting (i) specimen dipped in HCl during the cleaning, and (ii) specimen was suspended vertically in the bath. <i>Cathode</i> , as in 10.	<i>Macroscopic.</i> Good colour, and generally, as cathode of No. 10; but crystalline all over, though rather less coarsely crystalline on the sides facing the anodes. <i>On sawing</i> , no breaking away from the base metal. <i>Adherence</i> , good. ( <i>Note</i> :—Dipped in HCl during cleaning.)
2	Figs. 22 to 24.	116	Electrolysis conducted in solution used in 1, and without filtering. General conditions as in 1, except <i>E.M.F.</i> 0.8 volt. <i>Cathode</i> , as in 1.	<i>Macroscopic.</i> Good colour: bright. Floating particles cause loosely-adherent (sandy) layer on the surface. Some cindery outgrowth at top and bottom; otherwise deposit was similar to that of 1, except (i) it was not split, and (ii) it was more brittle. <i>On sawing</i> , the deposit came away in patches from the base metal. <i>Adherence</i> , bad.



## REMARKS ON THE DEPOSITS OF THE SEVEN FOREGOING EXPERIMENTS

1. **On Adhesion.**—Experiments 10 and 10a show clearly the difference, as regards adhesion, between a cathode that has been dipped in HCl (dil.) solution during the cleaning process and one that has not. Comparison of experiments 1 and 9 shows the same difference. This difference is probably due to the fact that swilling in water is not sufficient in itself to remove alkalis, used in the cleaning process, from the metal—especially from its pores; and, consequently, when the specimen is suspended in the bath for deposition, a reaction occurs between the alkali and the salts of the solution, causing a precipitation on the cathode surface.

2. **On the Volume of Electrolyte.**—Experiments 1 and 9 show the difference made by the volume of solution used for deposition. Where this is small, the deposit is smooth (except for roughness caused by floating matter), bright, and “hard-looking.” Obviously, the texture is very fine-grained. Further, the outgrowths that are formed have a cindery appearance, though their colour remains the same as that of the rest of the deposit. On the other hand, where the volume of solution is large, as in experiment 9, the deposit is not bright but is dull, except where it appears crystalline; it is of a coarser texture. Moreover, instead of outgrowths\* one finds a thickening of the deposit at the ends (due to local increase of current density), and the thickening is smooth and rounded. In this case, too, the deposit is not so hard as it is where the volume of electrolyte is small. It can be hit with a hammer without being broken up. It is, in fact, malleable to some extent.

3. **On Local Differences of Surface.**—Many of the deposits show local differences of macroscopic aspect, denoting differences of structure. These are, no doubt, due to local differences of deposition conditions, especially current density and concentration of electrolyte. As it is these differences in conditions of deposition and their effects upon the structure of deposits that are dealt with in Division 2, especially, of this Report, nothing more will be said here on the matter.

4. **On the Effect of Temperature Variation.**—It may be remarked, in the first place, that this series of experiments, which was conducted quite independently of still another series on the same bath, carried out for other purposes than the present and at an earlier date, confirm the conclusions arrived at before. Macroscopically, the character of the deposit changes in the following way:—Working at a fixed current density (120 amp./ft.<sup>2</sup>), the deposit formed at 70° C. is dark and bright at first, then becomes powdery, and finally splits up. As the temperature is raised, the deposit becomes light in colour and smooth, still remaining bright, till a temperature of (about) 90° C. is reached. As the temperature is still further raised, the deposit becomes more coarse-grained and visually crystalline. In general, then, the effect of rise of temperature upon the macroscopic character of the deposit is, at constant current density, to change the deposit from a fine-grained (*visually*, non-crystalline) one to a coarse-grained and visually crystalline one.

## B.—MICROSCOPIC EXAMINATION

## Deposit of Experiment A

As already stated, no microscopic examination of this deposit was possible.

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\* These outgrowths have nothing in common with what is called, in practical work “burning,” which is due to excessive current density.

## Deposit of Experiment 1

*Description of Structure*, at a magnification = 125 (Obj. 16mm., Oc.  $\times 8$ ).\*

There is a gap in the deposit due to a breaking away under the saw when preparing the section. On one side of this gap the deposit is fibrous in structure, which is uniform throughout the thickness of the deposit—unless, perhaps, the fibres are slightly narrower near the base: the grains are long, narrow, and fibre-like (Fig. 3). On the other side of the gap, the strictly fibrous portion of the breadth of the deposit forms (approximately) one quarter of the whole—from within outwards (Fig. 4). It merges, radially, into an area in which the grains are wider and less perpendicular to the axis of the specimen. They are here shorter, and appear broken, and, further, become distinctly broader as the periphery is approached. The distinction between the inner, fibrous, part and the outer is marked by the more clear and regular appearance of the former, which forms a sort of band. Continuing round the specimen, the same type of dual structure continues for a considerable distance. In this portion of the deposit the variation consists, especially, in the varying widths of the two areas. These vary somewhat irregularly, but, on the whole, the fibrous area decreases while the outer layer increases. Also, in places, the merger of the fibrous into the outer layer is less marked and distinct than elsewhere. And, again in places also, the grains in the outer layer are distinctly wider (Fig. 5). In the portion of the deposit situate at  $90^\circ$  from the gap, the structure merges (circumferentially) into one in which there is nowhere a clear distinction to be seen between the strictly fibrous part and the outer. There is everywhere a gradual merger of the one into the other. Moreover, the inner portion is less pronouncedly fibrous, while the outer consists of considerably larger and wider grains which are still less perpendicular to the axis (Fig. 6). Continuing round the circle, the difference between the two types of structure again becomes more marked, the inner layer merging more quickly into the outer; the fibrous band becomes more and more narrow, while the grains in the outer layer become still broader and broader (Fig. 7). Finally, on the opposite side of the specimen to that where the gap is, the structure has approached the normal type. There is no fibrous area at all (Fig. 8). The segment over which this structure extends subtends an angle of some  $30^\circ$ ; and as the eye travels on round the circle back to the gap a series of changes in structure similar to those described is visible, but the order of the changes is reversed.

Some other features of the deposit are:—

- (i) Very small holes.
- (ii) Oxide inclusions (Figs. 7 and 9).
- (iii) A few cracks. Some of these can be traced from the base metal to (well-nigh) the periphery. They run perpendicularly to the axis of the specimen.

## Deposit of Experiment 9

*Description of Structure*, at a magnification = 125.

This specimen is free from numerous oxide inclusions. The peripheral outline is smooth over about half its length, and undulating over the other half. The undulations of the latter are, however, not extreme. (See

\* In all cases Zeiss lenses were used. For a magnification of 125 diameters, which was that used for most descriptions, the objective used was the 16 mm. apochromat in combination with the  $\times 8$  compensating ocular. The magnifications of the photomicrographs are usually 150 or 200 (obj. = 16 mm., Oc. =  $\times 8$ , plus camera extension).



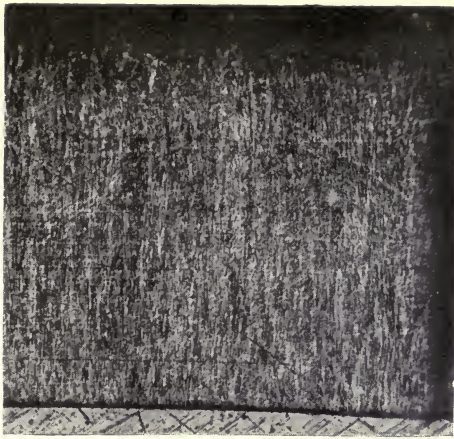


FIG. 3.\*



FIG. 4.\*

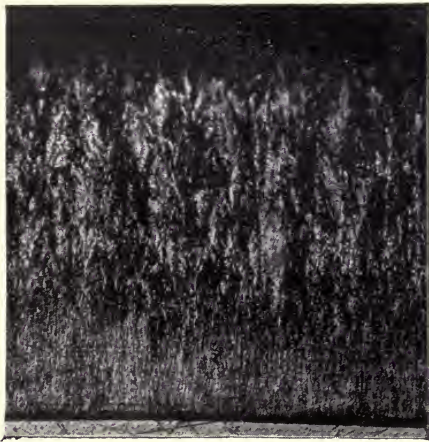


FIG. 5.\*

STRUCTURES OF DEPOSIT 1. (All  $\times 150$ .)

\* Photographs marked with an asterisk were used, in whole or part, to illustrate a paper entitled "Some Defects in Electro-deposited Iron." *Jour. Iron and Steel Inst.*, 1920, Vol. 101, p. 321.

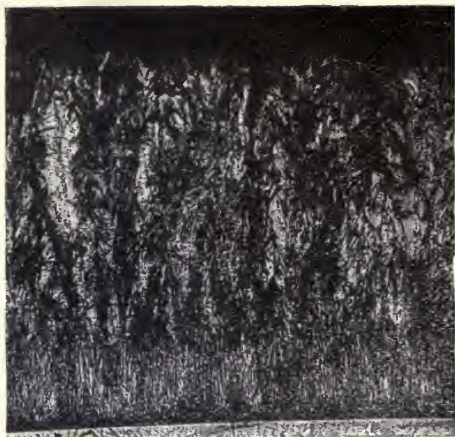


FIG. 6.\*



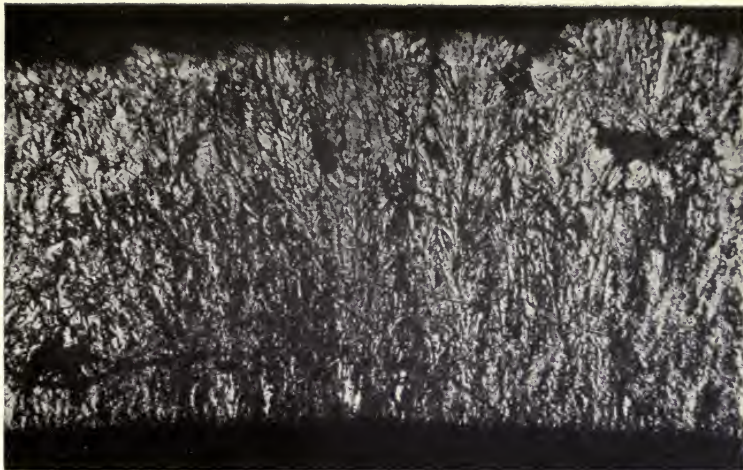
FIG. 7.\*



FIG. 8.\*

STRUCTURES OF DEPOSIT 1. (All  $\times 150$ .)

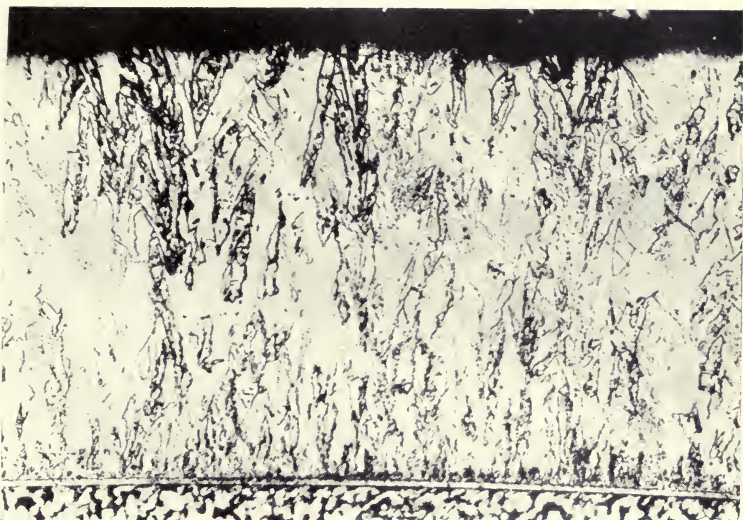




←  
Inclusion of  
Oxide.

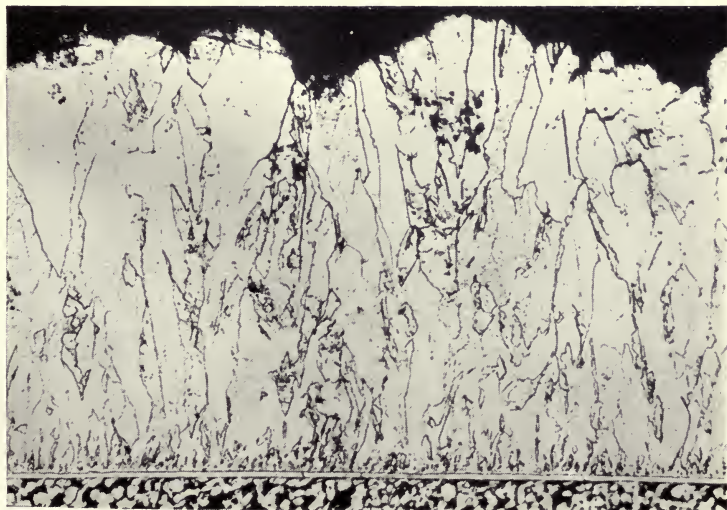
PART OF  
DEPOSIT 1,  
Showing Oxide  
Inclusions.

FIG. 9.  $\times 150$ .



DEPOSIT 9.  
Smooth Periphery.

FIG. 10.  $\times 200$ .



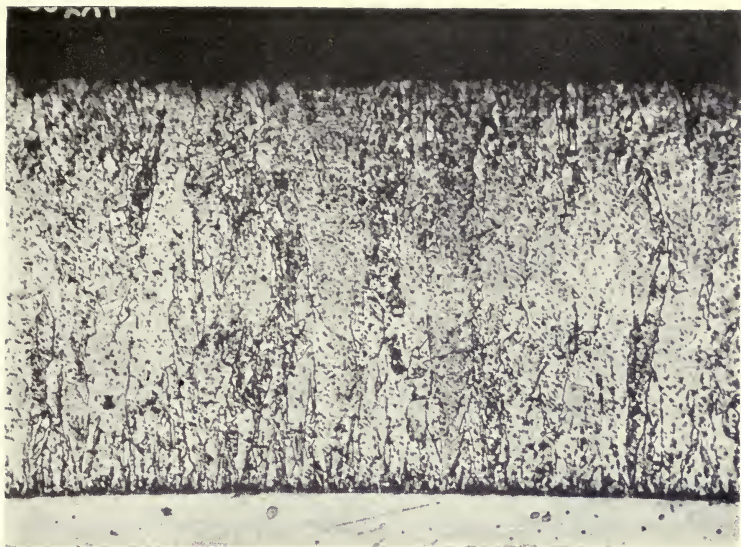
DEPOSIT 9.  
Undulating  
Periphery.

FIG. 11.  $\times 200$ .

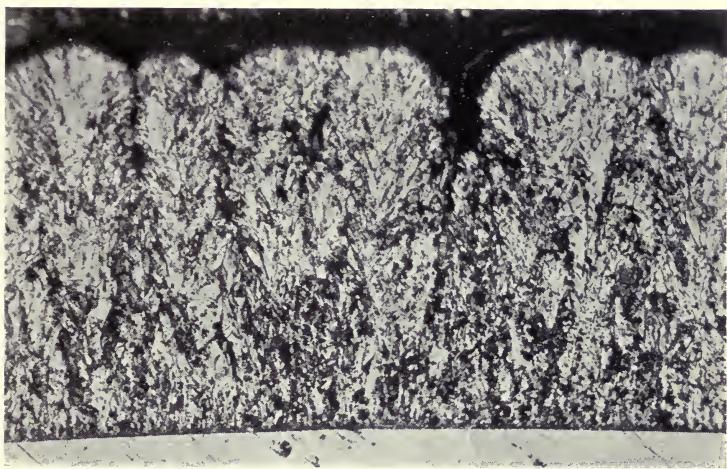
→  
Inclusion of  
Oxide.



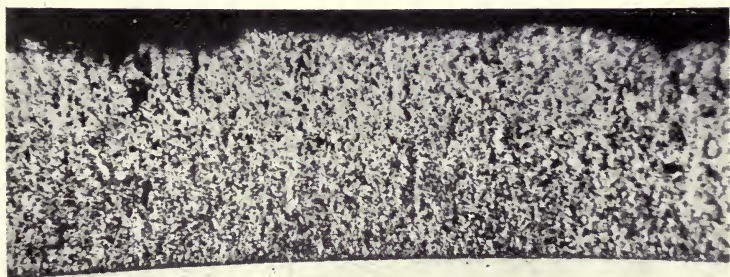




Smooth Periphery. Difficult to etch.  
FIG. 12.  $\times 160$ .



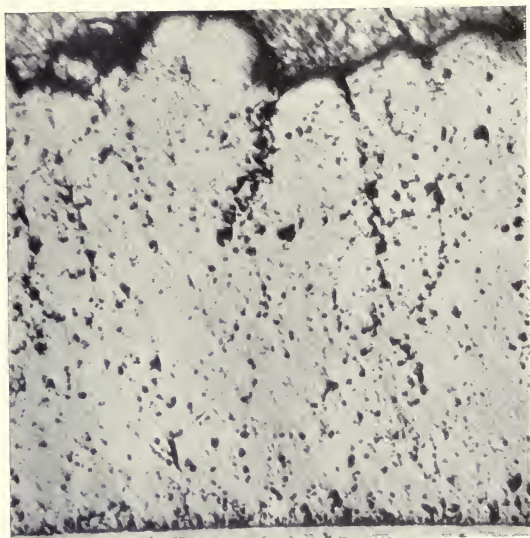
Undulating Periphery. Easy to etch.  
FIG. 13.  $\times 160$ .



Area  $90^\circ$  from those shown in Figs. 12 and 13.  
FIG. 14.  $\times 100$ .

DEPOSIT 3.

*To face p. 7.*



Unetched. Area as Fig. 13.

FIG. 15.  $\times 200$ .



Area near base of deposit.

FIG. 16.  $\times 1,000$ .

DEPOSIT 3.



Fig. 10, and cf. Fig. 11.) The deposit has a dual structure corresponding to the peripheral outline. Where this is undulating, the grains are, comparatively, much larger and more pronouncedly V-shaped; that is, the structure approaches the normal type. Where the peripheral outline is smooth, the structure approaches the normal type much less closely: the grains are more columnar and narrower, and they often appear as though broken up. Owing to the specimen having been cut obliquely to the central axis of the specimen, the approach to the normal structure is not, in many places, so evident as it otherwise would be (Fig. 10). The large grains of the deposit are remarkably clear and free from holes and inclusions. There are two or three radial cracks; and in one place—in the area of smaller grain—the deposit has broken away over a small arc.

### Deposit of Experiment 3

*Description*, at a magnification=125.

The deposit contains numerous small holes and inclusions of solid matter (oxide). This makes it difficult to so etch the specimen that one can see the crystal boundaries well. One side of the specimen was much more difficult to etch\* (satisfactorily) than the other. The side that etched the more satisfactorily is that which consists of the larger grains. The structure appears to approach the normal type over most of the cross-section of the specimen; but the crystal grains are more columnar, that is, less divergent, and also more broken than in the true normal type of deposit.

The structure of this specimen may be considered as twofold: Over one half of the whole annulus (the better-etching half) the grains are much larger (broader and longer) than those in the other half. In the former the crystal boundaries are more easy to see clearly even at 125 magnifications; while, on account of the inclusions and holes, the boundaries of the grains in the latter half are not easy to see at this magnification. Figures 12 and 13 show the difference in structure between the two halves of the annulus more clearly than does Fig. 14, which shows the structure at a lower magnification. The difference in the character of the peripheral outline of the two parts of the deposit is very marked. In brief, it may be said that that part of the deposit which etches the more easily and satisfactorily: (1) consists of larger grains; (2) has an irregular peripheral outline, resulting from the rough surface; and (3) is less full, perhaps, of inclusions and holes.

Fig. 16 shows a portion of the deposit near the base. In this figure the minuteness and number of the small holes (appearing in the photographs as bright spots) can be well seen. In this figure, too, the difference between the holes (bright spots) and the inclusions of oxide (dark irregular patches) is very marked. Fig. 15 shows the surface of the specimen, polished but unetched, at 200 diameters.

### Deposit of Experiment 10

*Description of structure*, at 125 magnifications.†

The deposit extends unbroken over only about two-thirds of the annulus (as in Fig. 17). A central piece (*b*) lies in the gap. The structure is,

\* All the specimens of which photomicrographs are shown in this report were etched with a 2 per cent. solution of pure nitric acid in absolute alcohol.

† No photographs of this specimen—to show the general structure at ordinary magnifications—are inserted, since those of Nos. 9 and 10a show the types of structure that occur in it.

in general, similar to that of the deposit of experiment 9, being of a dual character. The part of the deposit to the right of the dotted line,  $xy$ , corresponds to that part of 9 that has an undulating peripheral outline with large-grained internal structure. The part to the left of  $xy$  corresponds to the portion of 9 that has a smooth periphery. The metal in 10, where the outline is smooth, seems, however, more broken than the corresponding part of 9. It was much more difficult to etch satisfactorily

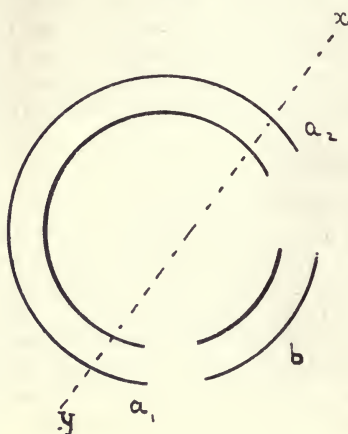


FIG. 17.

than was 9; and it was very much more difficult to etch than that portion of 10 to the right of  $xy$ . In the area  $b$  the grains are very large and clear. They very frequently start at the base of the deposit, and continue throughout the layer. This occurs in the corresponding part of 9, but only exceptionally; the reason is, probably, that the section of 10 is cut more perpendicular to the central axis than is 9.

- At a magnification of 1,000 diameters the metal appears to be over-etched. A curious feature (seen in Fig. 18) is the presence of what look like holes filled with liquid. They are greenish in colour, and more or less rounded in shape; and they are characterised by showing concentric ring markings which follow closely the shapes of the holes. Another matter of note is that these (?) holes are arranged in rows, which frequently run in parallel lines.

### Deposit of Experiment 10a

*Description of Structure, at 125 magnifications.*

The structure is, throughout the section, of a type closely approaching the normal. The two-fold character of deposits 9 and 10 is present in this one also, but it is very much less marked. Where the periphery is most uneven, the grains below are largest and most divergent (V-shaped) from within outwards; and, often, one grain extends over the whole width of the deposit. Where the periphery is more even, the grains are less divergent and narrower; and the structure appears more broken. Nowhere is the periphery of this specimen smooth; it is always more or less uneven. The surfaces of the largest grains appear to contain numbers of small holes, which become bright or dark as one focusses down or up—that is, towards or away from the surface of the specimen. In this deposit a curious dotted appearance of the surface

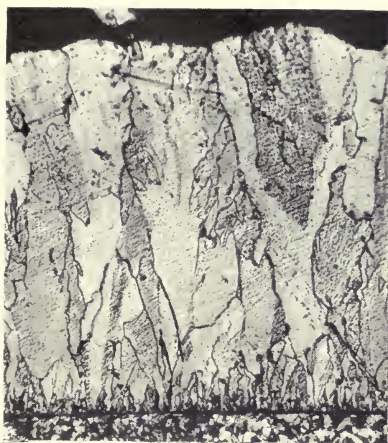




Showing holes filled  
with greenish liquid.  
(Cf. J. C. W. Humfrey,  
Carnegie Mem., 1912,  
vol. 4, p. 82.)

FIG. 18.  $\times 1,000$ .

DEPOSIT 10.



Smooth Periphery.  
The dotted appearance  
of the surface of  
some of the grains is  
notable.

FIG. 19.\*  $\times 150$ .



Undulating  
Periphery.  
(Rough to the  
touch.)

FIG. 20.  $\times 150$ .

DEPOSIT 10A.

*To face p. 9.*

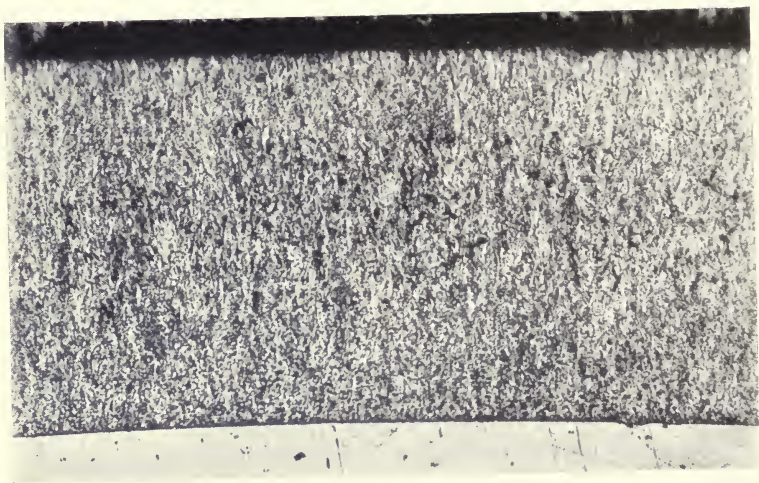


FIG. 21.  $\times 200$

DEPOSIT 4.

of some of the grains is very noticeable (v. especially Fig. 19). The clean division line between the copper and steel on the one hand, and the copper and iron deposit on the other, is to be noted.\* (N.B. This cathode was dipped in HCl, v. p. 4.) The deposit, too, is a clean one—free, that is, from numerous oxide inclusions.

#### Deposit of Experiment 4

*Description of Structure, at 125 magnifications.*

The periphery is smooth over the greater part of the specimen. The structure is columnar, the columns narrowing quickly towards the base metal. It is often possible to trace a grain running through the entire thickness of the deposit from base to circumference, the grain, while mostly of even breadth, widening somewhat as the circumference is approached. The shape of the grains is well seen in Fig. 21. The surfaces of the grains are bespeckled with minute holes or inclusions; but larger patches, such as are found in No. 3, are absent almost entirely. The same bath was used in the two cases. While, however, No. 3 was being deposited there was considerable oxide in suspension; when No. 4 was introduced, all but the finest suspended matter had settled down. The structure of this specimen is more truly representative of the conditions of formation that is No. 3, during the formation of which the temperature varied during the last quarter of the time from 100° C. to 86° C. It is likely, too, that the large amount of floating matter affected the structure of No. 3. The grains of this specimen (No. 4) are considerably smaller than those of Nos. 9, 10, and 10a (cf. the photographs and respective magnifications).

#### Deposit of Experiment 2

*Description of Structure, at 125 diameters.*

No such variation of structure occurs, when passing, in a circular direction, round the annulus, as occurs in the case of the deposit of experiment 1. Other notable differences between the two deposits are:—  
 (i) There is no completely fibrous area, such as is seen in Fig. 3. (ii) There is a distinct thinning of the deposit on one side, forming a, so to say, wide syncline or valley. (iii) Annular wavy rings are seen in the deposit, especially in the half near the base metal. These can be seen to run completely round the circle, but they are more defined in some places than in others. (iv) No radial cracks are to be observed, though (v) the structure is that of a more broken and strained metal. (vi) The deposit is obviously thinner, as can be seen by comparing the photographs of the specimens, which are seen at the same magnification, namely, 150 diameters.

**Traverse of the Annulus.**—Starting observations from a definite place—where, in fact, some small lumps occur on the surface—the deposit approaches the normal type. The grains quickly become considerably wider from within outwards, and continue to widen somewhat as the periphery is approached. The shape of the grains is long and, in general, columnar, or, perhaps, roughly lenticular. Proceeding round the circle, the grains in the outer part of the deposit are seen to be much larger and to, most of them, resemble columns with irregular sides; some of the grains are, relatively,

\* The layer of copper itself is too thin to be seen at most places.



very large and V-shaped (Fig. 22). But the arc of the area in which such large grains are located subtends a central angle of some  $10^\circ$  only. The structure of the next following portion of the deposit varies rather quickly to that first described, and this type of structure then merges, at about  $90^\circ$  from the starting point, into a type in which the grains of the inner portion of the deposit approach the fibrous form, becoming somewhat wider and lenticular outwards as the periphery is approached. This last type extends over about one-quarter of the circle, but, at the same time, the deposit gradually narrows until a minimum width is reached at about  $180^\circ$  from the starting point of observation. The syncline subtends a central angle of some  $30^\circ$ . The structure of the remaining half of the deposit goes through a series of changes similar to those already described, but in a reversed order of sequence.

Minute holes are visible on the surface of some of the grains; and some more or less rounded patches (probably of oxide) are to be seen.

### CORRELATION OF MACROSCOPIC AND MICROSCOPIC FEATURES.

The remarks to be made upon the correlation of features seen in the above-described deposits of Series I will be confined to such features as may be influenced by temperature. For the sake of brevity and clearness, the correlation may, perhaps, best be made in tabular form. Thus:—

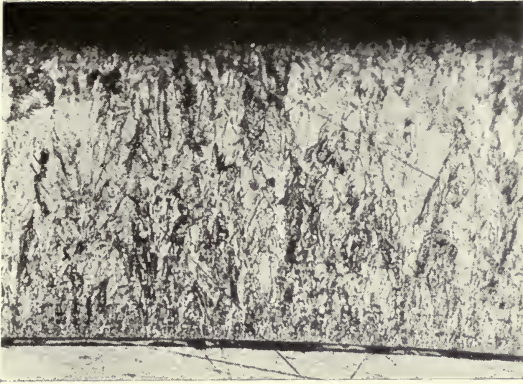
<i>Macroscopic feature</i>	<i>Microscopic aspect</i>
1. Smooth, bright or matt, non-crystalline surface (Nos. 1, 2, 3 and 4).	Fine-grained, fibrous, or only slightly divergent V-shaped grains.
2. Smooth, crystalline surface ( <i>e.g.</i> , No. 10a).	Coarse-grained, non-fibrous, large (roughly) V-shaped grains.
3. Smooth, matt, or finely crystalline on one side (or two opposite sides); coarsely crystalline on the other (or two remaining opposite sides (Nos. 9 and 10)).	As 1, on one side (or on two opposite sides), and as 2, on the other (or remaining two opposite sides). From 2, especially, it seems fair to conclude that the deposit is coarse-grained where it is more coarsely crystalline on the surface.

### CONCLUSIONS—ON THE EFFECT OF TEMPERATURE

It is suggested that one may deduce the general conclusion from the above, that where two deposits are formed under otherwise similar conditions of deposition, that which is formed at the higher temperature will be the coarser-grained in structure.\* It would seem, further, that the coarser the grain, the less brittle and hard the deposit is†, and hence, temperature affects the physical character of a deposit in this respect also. No. 4 does not, at first sight, seem to support this latter conclusion; but it is noticeable that, though even and matt on the surface, and finer-grained (than 9, 10 and 10a), microscopically, they are not so fine-grained as Nos. 1 and 2, and they are not so brittle. The larger (somewhat columnar) structure of Nos. 3 and 4 may possibly be due to the volume of electrolyte used (*v. p.* 4).

\* Cf. W. Blum, *Trans. Am. Electroch. Soc.*, 1919, vol. 36, at p. 221.

† Cf. H. S. Rawdon and E. J. Gil, *Bur. Standards Sci. Paper*, No. 397; *Jour. Franklin Inst.*, 1920, vol. 190, p. 731.



Structure more open in outer half of the deposit.

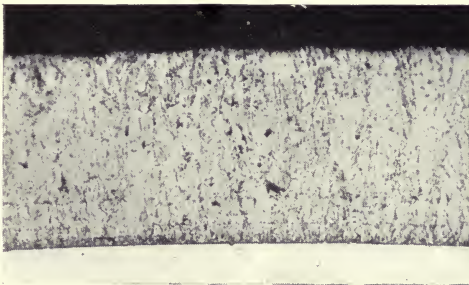
FIG. 22.  $\times 150$ .



Grains narrower in outer half of deposit ; more fibrous in inner half, especially near the base.

← Note : Wavy lines.

FIG. 23.  $\times 150$ .



Wavy lines near base are well seen.

(*v. Jour. Iron and Steel Inst., 1921 (No. 1), vol. 103, p. 355*).

FIG. 24.  $\times 100$ .

DEPOSIT 2.





## SERIES II

### ON THE EFFECT OF CURRENT DENSITY

#### A.—DEPOSITION

Constant temperature: varying current density.

#### The Conditions of Deposition were—

Temperature ... .. 110° C.

Time ... .. This was varied in such a way as to give  
approximately the same thickness of  
deposit in all cases.

The bath used was the 2½ gallon one; and the process of cleaning and the type (shape, &c.) of cathodes were the same as in Series I.

Expt. No.	Ref. to micro.	C.D. a/ft. <sup>2</sup>	E.M.F. volts at 5½''	Time hrs.	Remarks.	Deposit.
5	Figs. 25 to 27.	60	0·4	4	—	<i>Macroscopic.</i> Good, even: light colour. Very finely crystalline. Slight thickening at lower end. No lumps or outgrowth. <i>On sawing</i> , broke away in one or two places—not badly, however. Rather more brittle than 10 and 10a. <i>Adherence</i> , very fair.
4	Fig. 21	120	0·8	2	—	<i>See Table, Series I.</i>
10 and 10a	Figs. 18 to 20.	120	—	2	—	
6	Figs. 23 to 31.	160	0·8	1½	—	<i>Macroscopic.</i> Light grey: smooth. Finally crystalline. Some thickening—especially at lower end. <i>On sawing</i> , no chipping off. <i>Adherence</i> , very good.
7	Figs. 32, 33 & 34.	200	0·9	1·2	—	<i>Macroscopic.</i> As 6 in colour, &c., but surface somewhat more coarsely crystalline. <i>On sawing</i> , no breaking away. <i>Adherence</i> , very good. The deposit was found to be quite malleable under hammer blows.
8	Figs. 35 & 36.	240	1·2	1	Not dipped in HCl in cleaning.	<i>Macroscopic.</i> Light grey: Rather rough—partly from little hemispherical lumps. More coarsely crystalline than Nos. 6 and 7. No sign of "burning."† <i>On sawing</i> , comes away cleanly from the base metal. Chips under hammer blows and powders. <i>N.B.</i> —HCl dip not used. <i>Adherence</i> , poor.
8a	Figs. 37 to 41.	240	1·2	1	Dipped in HCl.*	<i>Macroscopic.</i> Light grey: smooth. Crystalline. Slight thickening round bottom edge: slightly cindery here. <i>On sawing</i> , no chipping or breaking. <i>Adherence</i> , very good.

\* In experiment 8a a siphon arrangement with a narrow outlet jet was used for introducing water into the bath to replace that lost by evaporation. This prevented stirring up the sludge at the bottom of the tank, which happens when water is introduced in bulk.

† v. note, p. 5.

## REMARKS ON THE FOREGOING DEPOSITS

1. **On Adhesion.**—The same result of not dipping the cathode in dilute HCl, before suspending it in the depositing solution is seen in the cases of Nos. 8 and 8a as was seen in the cases of Nos. 10 and 10a of Series I. The deposit on the dipped cathode, 8a, adhered well, while that on the other, 8, did not.

2. **On Local Differences of Surface.**—This is again noticeable in the deposits of Series II, just as it was in those of Series I.

3. **Effect of Current Density.**—The deposits of Series II show that, at constant temperature, and under otherwise similar conditions, increase of current density causes an increase in the coarseness of the crystalline surface. The variation is from matt at lower current densities, through finely crystalline at intermediate current densities, to coarsely crystalline at the highest intensities employed. It may be conveniently stated here, with respect to the observations made, that although the terms "coarse" and "fine" are relative, and not absolute, in meaning (and hence, the scale of coarseness and fineness may be a different one in the mind of one observer to that present to the mind of another) yet, in the case of the deposits of Series I, II, and III, the author has had the advantage of consulting the note-book of his (one time) assistant,\* who aided him in the deposition. These notes were made *independently*, and are found to agree with the author's in general, and in particular where the terms "coarse" and "fine" are used. It thus appears that increase of temperature at constant current density and increase of current density at constant temperature have much the same effect upon the macroscopic appearance of the deposited iron. But the effect is much less marked in the former case than in the latter.

## B. MICROSCOPIC EXAMINATION

**Deposit of Experiment 5**

*Description of Structure*, at 125 magnifications.

(1) *Before etching.*—The polished surface shows many holes and some irregular patches of oxide. The periphery is, in general, fairly smooth. Several cracks can be seen, some of which extend from periphery to base metal. Four or five of these cracks can be easily seen with a pocket magnifying glass, and at least two with the naked eye.

(2) *After etching* (with a 2 per cent. solution of  $\text{HNO}_3$  in absolute alcohol).

The deposit has a structure which resembles the normal type fairly closely. The grains are moderately large—not so large as those in Nos. 9, 10, and 10a. The structure varies round the circle only in the shape of the grains being more lenticular and irregular in some places: the structure, as a whole, has a more broken look in some places than elsewhere (cf. Figs. 25 and 26). The V-shape of the grains is less apparent in such areas of broken structure. No annular markings are visible at this magnification (125 diameters), but numerous holes are visible, as also are cracks that often run irregularly through the whole thickness of the deposit. It is to be noted that the surfaces of some of the grains have a speckled appearance. The periphery is, in general,

\* Mr. J. W. Gardom.



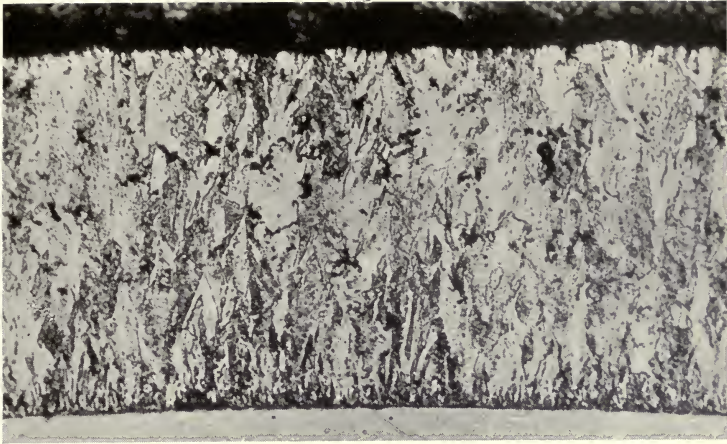


FIG. 25.  $\times 150$ .

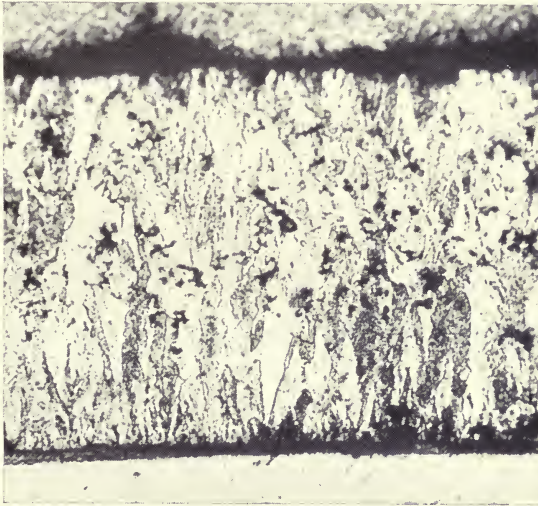
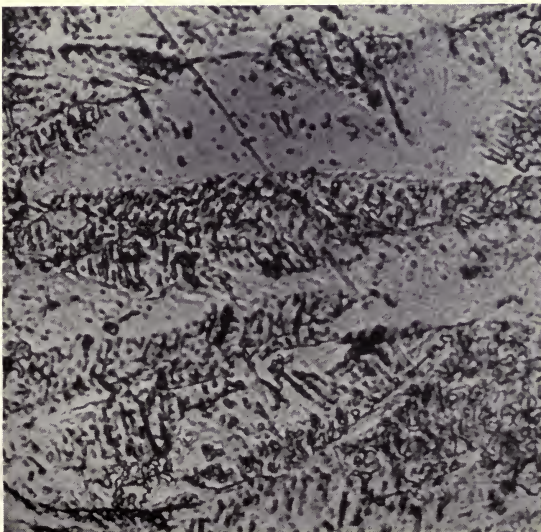


FIG. 26.  $\times 150$ .

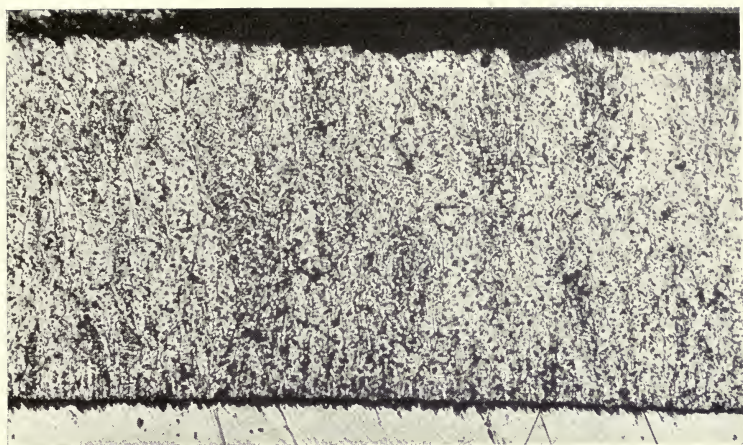


*Cf.* W. Austin's photograph showing effect of oxygen in pure iron.

FIG. 27.  $\times 1,000$ .

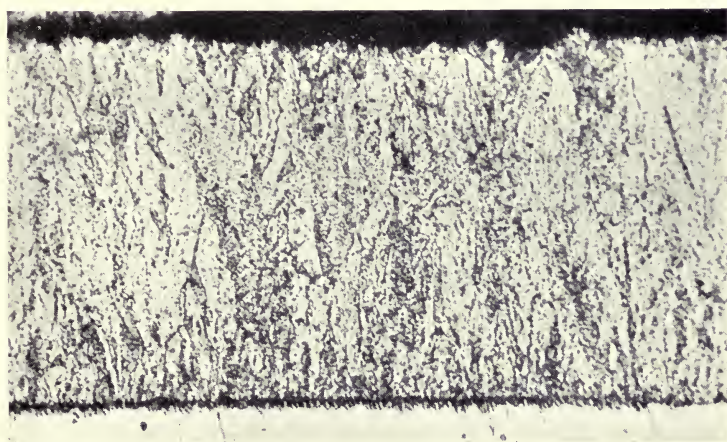






In focus. Numerous holes and inclusions camouflage the structure.

FIG. 28.  $\times 150$ .



Out of focus. Structure better shown.

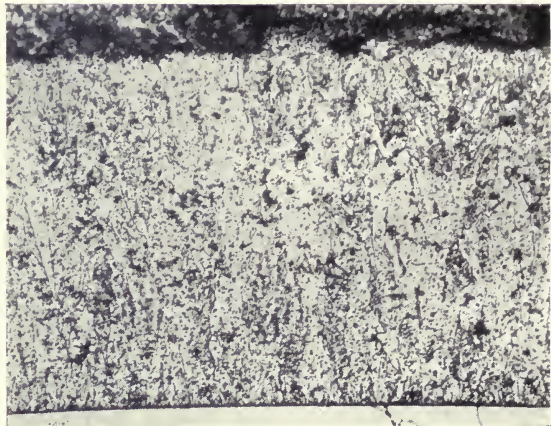
FIG. 29.  $\times 150$ .

DEPOSIT 6.



Structure of area opposite that shown in Fig. 28.

FIG. 30.  $\times 150$ .



Area at  $90^\circ$  from areas of Figs. 28 and 30.

FIG. 31.  $\times 150$ .

DEPOSIT 6.



regular; where a slight lump occurs, the structure is of the cauliflower variety.

At 500 diameters the holes are seen to be irregular in shape, and appear coloured. Other very small holes become apparent, which change from black to slightly grey or colourless (and bright) as one focusses up and down. The speckled surfaces (before alluded to), which are dark (brownish) at low magnification, are seen to have a structure that reminds one of the section of an oxide inclusion illustrated by W. Austin\*, and contained in pure iron to which oxygen has been added. Austin describes this as an eutectic structure. Fig. 27 shows the speckled surface at high magnification.

### Deposit of Experiment 6

*Description of Structure, at 125 diameters.*

In general the structure does not differ very much from that of No. 5; but the holes, which are very small and very numerous, cause it to appear to be of smaller grain than No. 5. A comparison of Figs. 28 and 29 shows, however, that this is not so. Fig. 28 was taken with the specimen in focus: Fig. 29 shows the same area somewhat out of focus. From these it is seen that it is the tiny holes (dark in Fig. 28) that cause the structure to, at first sight, seem of finer grain. Comparing Fig. 25 (specimen 5) with Fig. 29 (specimen 6), it is seen that there is not much difference in grain size, though the grains near the base metal are, in No. 5, more V-shaped than those near the base metal in No. 6. Inclusions of oxide are few only; and no radial cracks that traverse the whole thickness of the deposit are to be found. The structure varies round the circle. It varies between that shown in Figs. 28 and 31 and the structure shown in Fig. 30. In the former the periphery is smooth; in the latter it is lumpy, and the structure is somewhat of the cauliflower type. It was noted that the latter part of the specimen was much more easy to etch satisfactorily than the former. The area shown in Fig. 31 is located between, and at approximately 90° from, those shown in Figs. 28 and 30. It extended over about one-third the circle, and its type of structure gradually merged, on each side, into those shown in Figs. 28 and 30.

### Deposit of Experiment 7

The surface of the polished specimen, as seen before etching, showed numerous holes and inclusions. Where the periphery is undulating,† the locus of inclusions (of oxide) is often, in shape, a curve having a curvature inverse to that of the corresponding undulation of the periphery. In this specimen, the periphery is, for the most part; of an undulating (lumpy) character.

*Description of Structure, at 125 diameters.*

Very light etching (5 seconds) shows the inclusions to often lie along the grain boundaries. In general, the grains are large—much larger than those of Nos. 5 and 6. They resemble (broadly) those of Nos. 9 and 10; but they are, in this specimen, characterised (i) by the boundaries between them being (as before stated) the loci of inclusions, and (ii) by their fan-shaped form, especially towards the periphery (Fig. 32). The

\* Jour. Iron and Steel Inst., 1915 (No. 2), vol. 92, p. 157.

† One has to remember that a periphery which appears lumpy or undulating in a micrograph, at a magnification of 150, will very often appear smooth when examined with the naked eye.



general structure approximates closely to the normal type: the angle of the V is, often, situate among the small grains near the base metal and at or close to this. The surface of the grains is, frequently, much pitted, as though containing very numerous minute inclusions. There seems, in places, to be interlocking or intergrowth between the grains, marked by a difference in the pitting of the surfaces, which is emphasised by the etching, and caused by the comparatively clear surface of one grain, having the V shape, being broken by a pitted area (v. especially, Fig. 33). This is due to the section being cut across the plane parallel to the current lines, with the result that the structure *appears* different in one area than elsewhere. It has a mosaic appearance. Apart from this apparent difference, the structure is uniform over the annulus, except that in places (i) the V-angle of some grains is more acute than in others, and (ii) the individual large grains commence farther from the base metal (cf. Figs. 32 and 34).

### Deposit of Experiment 8

An examination of the polished surface before etching discloses lines that cause the specimen to be full of cracks. The lines often extend throughout the deposit, and, frequently, branch. Usually, they are not radial in direction, but run across the radii. Etching shows most of these lines to be division lines between the grains, the lines being often marked by oxide inclusions (cf. No. 7). To distinguish such lines from true cracks, they have been called "quasi-cracks".\* The periphery of this specimen is undulating or lumpy (cf. No. 7); small holes and inclusions are present, but do not appear numerous on the unetched surface. The thickness varies.

*Description of the Structure*, at 125 diameters.

The structure is fairly uniform all round the annulus. It consists at the base of a layer, of varying width, of small grains, followed by large grains that originate among the small ones at varying distances from the base metal. The outer layer has the cauliflower or "poplar-tree" type of structure, and is similar to part of No. 7. In general, the size of grain is not markedly different from that of No. 7; the grains may, perhaps, be rather narrower. There is some interlocking of grains, but this is nowhere so marked as in No. 7.

The line between the base metal and the deposit is often far from clear, and the grains of the deposit near the base metal are frequently confused. It may be recalled in this connection that the cathode was not, in this instance, dipped in dilute HCl during the final part of the cleaning process.

### Deposit of Experiment 8a

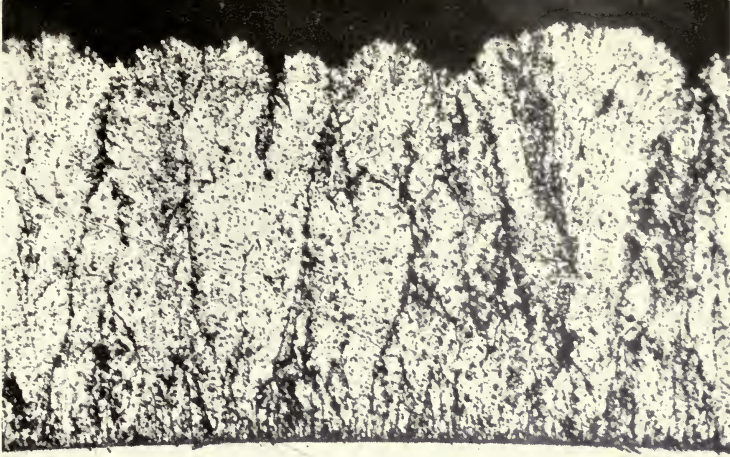
The deposit of this specimen does not vary much in thickness; but it is, in general, thinner than No. 8. The peripheral outline is everywhere undulating; in places it is very irregular. Figs. 37 to 40 show the unetched surfaces and the effects of varying amounts of etching.

*Description of the Structure*, at 125 diameters.

The structure is, in general, similar to the structures of Nos. 7 and 8; it varies between the cauliflower and the poplar-tree types. The lines of inclusions (of oxide), situate on the boundaries between the grains,

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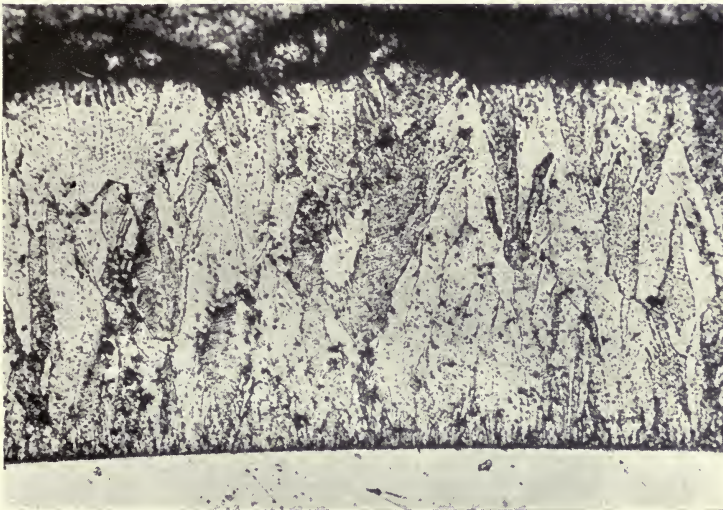
\* See "Some Defects of Electro-deposited Iron" (Jour. Iron and Steel Inst., 1920, vol. 101, p. 321).



← Fan-shape  
grain.

Showing general  
type of  
structure.

FIG. 32.  $\times 150$ .



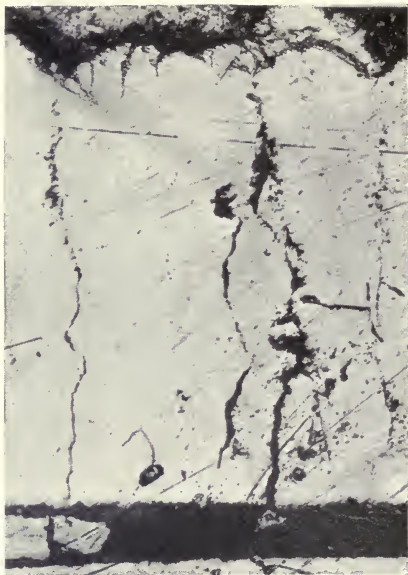
Shows  
inter-locking  
of grains.

FIG. 33.  $\times 150$ .



FIG. 34.  $\times 150$ .

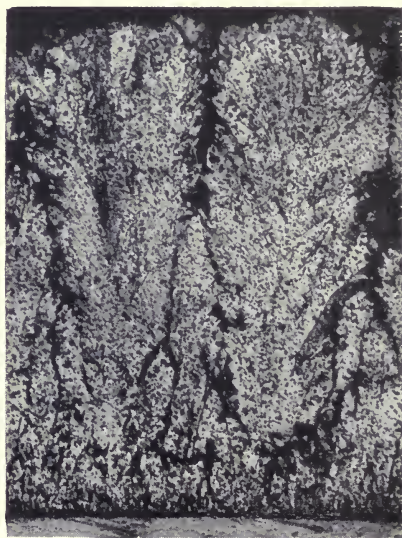




Copper/iron line →  
This specimen was  
not dipped in HCl.

Section unetched, showing "quasi-cracks."

FIG. 35.\* × 150.

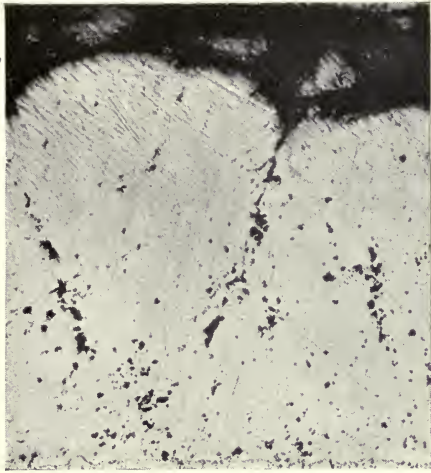


Etched section. "Poplar-tree" structure.

FIG. 36.\* × 150.

DEPOSIT 8.

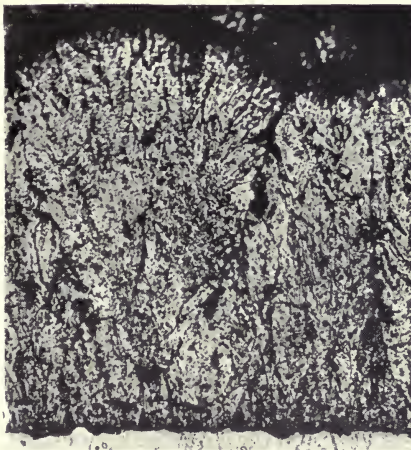




Unetched.

← Clean copper/  
iron line.

FIG. 37.\*  $\times 150$ .



Etched—15 seconds.

FIG. 38.  $\times 150$ .

DEPOSIT 8A.



Etched—  
(15 + 10) secs.

FIG. 39.\* × 150.



Etched—  
(15 + 10 + 10) secs.

FIG. 40. × 150.

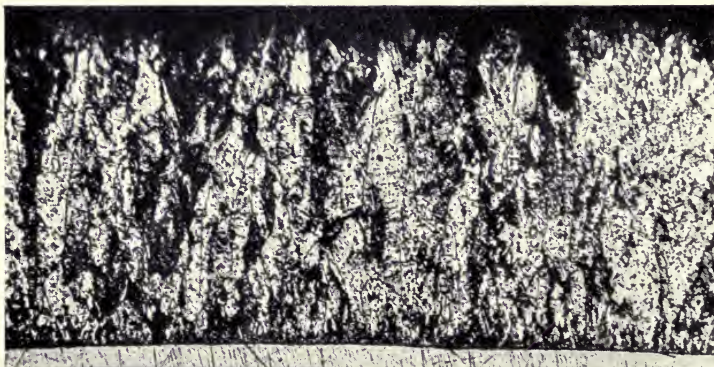


FIG. 41. × 150.

DEPOSIT 8A.

are at places very marked (*see* Figs. 37 and 38). The surfaces of the grains are often very speckled. The mosaic type of structure (Fig. 41) is seen in one part especially; and in this area the surfaces of many of the grains are clearer. The cauliflower (or poplar-tree) and the mosaic types of structure seem sometimes to be confused or combined, the one being, as it were, imposed upon the other.

### CORRELATION OF MACROSCOPIC AND MICROSCOPIC FEATURES

All the deposits of this series (except No. 4) appear crystalline to the naked eye. Observations made and noted at the time of removal of the deposits from the depositing solution were as follows:—

- No. 5 . . . . very minutely crystalline.
- No. 4 . . . . matt.
- No. 10 . . . . crystalline on one side, matt on the other.
- No. 10a . . . crystalline—rather less coarse on the parts facing the anodes.
- No. 6 . . . . minutely crystalline.
- No. 7 . . . . somewhat more coarsely crystalline than No. 6.
- No. 8 . . . . more coarsely crystalline than Nos. 6 and 7.
- No. 8a . . . . crystalline.

An examination of the photomicrographs shows that, in size of grain, the internal structure corresponds quite well with the macroscopic aspect in the case of each of the deposits except No. 4. The more coarsely crystalline the surface is, the coarser (or larger) is the grain of the interior. This fact indicates that observation of the surface of a deposit enables a conclusion to be formed with some certainty as to its internal structure—a fact of considerable importance in the control of deposition. As regards No. 4, all that can be said is that it is an exceptional case for which the only explanation that can be offered is that possibly some change in the deposition conditions occurred just before the removal of the cathode from the bath. Though forming an exception, it was considered proper, nevertheless, to include it.

### CONCLUSIONS—ON THE EFFECT OF CURRENT DENSITY

Whereas the deposit of experiment 5 is certainly of smaller grain than those of Nos. 10 and 10a, on the one hand, and Nos. 7 to 8a, on the other, it is not easy to decide as to the relative size of grain of Nos. 10 and 10a, on the one hand, and Nos. 7 to 8a, on the other. This seems to depend upon whether each "cauliflower" or "poplar-tree" of Nos. 7, 8, and 8a (Figs. 32 to 41), is to be regarded as one grain or as a conglomerate of small grains. The author's view is that the former view is the correct one. Figs. 33 and 41, in which the (apparent) interlocking of the grains is seen, as well as the starting of the poplar-trees at or near the base metal and their gradual widening outwards, show, it is suggested, that this view is correct. Visual examination of the specimens, which is, of course, much more determinative than photographs, confirms it. If, on the one hand, each "tree" is not one grain but a conglomerate of separately formed grains, then undoubtedly the structure of Nos. 10 and 10a is much larger than those of Nos. 7, 8, and 8a. If, on the other hand, each "tree" forms one grain, then it cannot be said, with any



certainly (either from the micrographs or the specimens themselves), which group of deposits has the larger structure. The deposit of experiment 6 must be considered. This, in grain size, certainly comes between No. 10 (and 10a) and No. 7.

Macroscopic and microscopic observations of the deposits of Series II seem, therefore, to warrant the following conclusions:—

1. As the current density rises from 60 amp./ft.<sup>2</sup> so does the size of grain until—
2. A maximum grain size is reached somewhere in the region of 120 amp./ft.<sup>2</sup>
3. The size of grain then diminishes to a minimum which lies somewhere between 120 and 200 amp./ft.<sup>2</sup>
4. It again becomes larger at the highest current densities used.\*

**Note on the Plane of the Sections.**—It may be conveniently remarked here that it seemed preferable to cut and examine sections that lay in planes parallel to the lines of flow of the current rather than sections at right angles to the current lines. If the latter method is adopted, that is, if sections perpendicular to the current lines are made (as is done by Sieverts and Wippelmann),† the size of the grains, and hence the number of grains per unit area, will depend upon the position of the plane of the section relative to base metal and periphery. For instance, in the case of a deposit of normal structure, the farther the plane of the section is from the base metal, the larger the grains appear, and hence the fewer will be the number of grains appearing in unit area. Hence, unless two deposits, which it is necessary to compare, have the same thickness, and the planes of the sections made of them are at the same distance from the base metal, wrong conclusions as to grain size will, most probably, be drawn.

### SERIES III

#### ON THE EFFECT OF MECHANICAL MOVEMENT

In experiments 12, 12a, and 13, 13a, it was sought to ascertain the effect on structure of mechanical movement. Nos. 11 and 11a were both conducted with moving cathodes, but the cathode was attached to the rotating spindle (used in these cases) in a different way in each case, so that one obtained in each case a different type of movement of the electrolyte against the cathode.

Nos. 11 and 11a can be compared with Nos. 10 and 10a, the deposits of which were formed under similar conditions as were those of Nos. 11 and 11a, except that these were moved while the cathodes of Nos. 10 and 10a were stationary.‡

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\* Similar alternations in grain-size as the C.D. is progressively increased have been observed in the case of copper also. A. Sieverts and W. Wippelmann, *Zeit. f. anorg. Ch.*, 1915, vol. 91 (Zusammenfassung von Teil I). On the other hand, Dr. W. Blum claims that “. . . increase in current density up to a certain point *decreases* the size of the crystals . . .”

† *Op. cit.*, and, sometimes, by Blum.

‡ The difference in the C.D. employed in the two cases (namely, 114 amp./ft.<sup>2</sup> and 120 amp./ft.<sup>2</sup>) is negligible.

## A.—DEPOSITION

## Cleaning.—As in Series I and II.

No. of	Ref. to Micro.	C.D. Amp/ft. <sup>2</sup>	Time hrs.	Temp. °C.	Remarks.	De
11	Figs. 42 & 43.	120	2	—	Dipped in HCl dil. After a few minutes the motor stopped for a minute or two. <i>Cathode</i> was attached with its axis parallel to that of the rotating spindle, so that it did not revolve on its own axis (cf. 11a). Rotation of spindle was very slow—only a few revolutions per minute.*	<i>Macroscopic.</i> Very good. Light blue-grey, almost "metallic" appearance. Very close grain. Very finely crystalline down one side. Very slight thickening round the bottom edge. A few pits caused (probably) by sediment. <i>On sawing</i> , adherence was found very good.
11a	Figs. 44, 45 & 46.	120	2	110	The bath was freed from all but some fine sediment. <i>Cathode</i> dipped in dil. HCl. <i>Cathode</i> was attached to spindle so as to form a continuation of the latter. Hence, it rotated on its own axis. <i>R.P.M.</i> = 100.	<i>Macroscopic.</i> Very similar to No. 11 in appearance. A few pits, elongated in the direction of rotation. Very slightly crystalline on one side. <i>On sawing</i> , deposit broke away from the steel base-metal, carrying the slight coat of copper with it. Poor adherence, probably due, therefore, to defective cleaning.
12a†	Figs. 52, 53 & 54.	120	1½	100–105	<i>Cathode movement</i> , to and fro (suspended from—rod) parallel to anodes. Strokes per minute = 100. After ¾ hour movement stopped for a minute or two. HCl dip was used. One gal. of solution only was used.	<i>Macroscopic.</i> Very fine-grained: smooth. Amorphous appearance. Light grey colour. No outgrowth: very slight thickening at bottom end. <i>On sawing</i> , found that deposit was remarkably hard. <i>Adherence</i> , fair; deposit was inclined to chip.
12	Figs. 47 to 50.	120	1½	100–105	No movement: <i>cathode</i> stationary. 1 gal. of solution only.	<i>Macroscopic.</i> Good colour. Smooth and even. Finely crystalline. Some cindery outgrowth at bottom end. <i>On sawing</i> , deposit was found to be much softer than that of 12a†, and it did not chip off the base-metal at all.
13	Figs. 55 & 56.	144·6	2	98–100	No movement. Copper <i>cathode</i> , cleaning as usual.	<i>Macroscopic.</i> Good light-grey colour. Finely crystalline. Slight (smooth) thickening at bottom end. Some small pits. <i>On sawing</i> , adhered well.
13a	Figs. 57 to 61.	144·6	2	98–100	Movement, as in 12a. No. of strokes was 72 [per minute.	<i>Macroscopic.</i> As No. 13; but could only just (and only in places) discern the crystalline nature of the deposit. <i>On sawing</i> , adherence was found to be good.

\* Unfortunately, through an oversight, the R.P.M. were not counted; but they certainly did not exceed 30.

† Newly made solution, 1 gall. only. (Nos. 11 and 11a were deposited in the 2½-gall. vat).

‡ Both Mr. Gardom and the author make special remark, in their notes, on the hardness of the deposit of 12a as compared with that of 12.

**Remarks on the Foregoing Deposits.**—It is very apparent on actual observation of the specimens themselves that the motion of the *cathode* during deposition causes a distinct effect upon the character of the deposit. Where two deposits are formed under precisely the same conditions, except that one *cathode* is moved mechanically while the other is maintained in a stationary position, the deposit on the moved *cathode* will be of finer

grain than that on the stationary one. This is very apparent, even to the naked eye. The above-described deposits (Nos. 12, 12a, 13, 13a) are typical. Many other samples have been prepared for the purpose of making a comparison between deposits formed under the respective conditions of movement and stationary position\*; the result was always the same. It is, therefore, suggested that—

**The General Effect of Movement** upon the macroscopic character of a deposit of iron is—To diminish the size of grain of the deposit.

It is certain that such an effect is caused by movement in the case of iron deposited from the chloride (neutral) bath.

## B.—MICROSCOPIC EXAMINATION

### Deposit of Experiment 11

*Description of Structure*, at 125 diameters.

The deposit is a clean one, *i.e.*, free from numerous oxide inclusions; it is, too, free from numerous holes. Fig. 42 shows the unetched polished surface. It shows the effect of the stoppage of the rotation that occurred during the formation of the deposit. The whole deposit is divided into two broad layers (an inner and an outer), with a narrow layer between them. This narrow layer was formed during the stoppage of the spindle; it contains numerous inclusions of solid matter (oxide) that settled down upon the deposit during the rest period. The micrograph shows clearly also how the narrow layer forms a source of weakness in the deposit; one part of the outer layer has broken away from the remainder. The thickness of the deposit varies round the circle. This is to be expected, considering the way in which the cathode was attached to the rotating spindle.

Fig. 43 shows the etched surface of the section. In structure the deposit is of the approximately normal type; and it is very much the same at all parts. The structure resembles that of No. 11a at one part of the latter (*see* Fig. 45); and it is not unlike some of the deposits of the two former series, *e.g.*, No. 2 (Fig. 23) and No. 5 (Figs. 25 and 26).

### Deposit of Experiment 11a

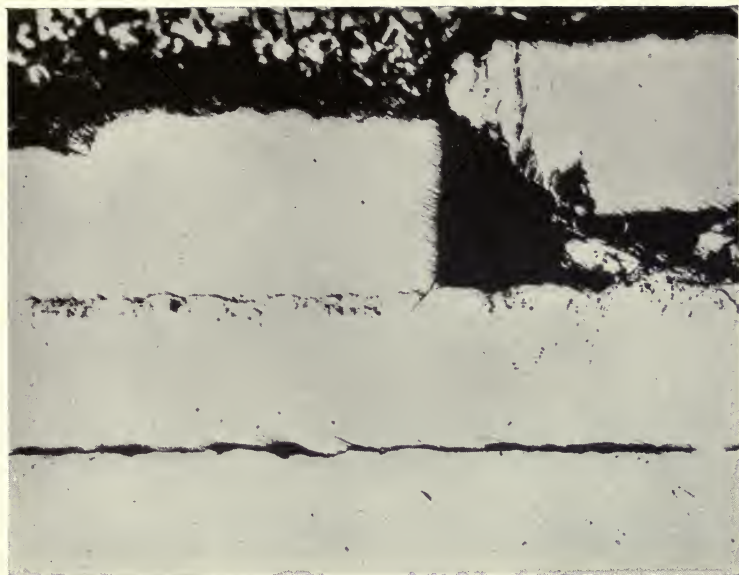
*Description of Structure*, at 125 diameters.

The deposit contains several radial cracks; one is visible with the naked eye. It is "clean," and contains but few holes. It was noticed that the deposit etched differently at different parts.† The part that required longer time to etch extended over an arc subtending a central angle of 45°. Its structure (Fig. 44) was more columnar than that of the remainder of the deposit, which was of the approximately normal type (Fig. 45), and very like that of No. 11. In one part the structure approached very close to the normal (*see* Fig. 46), and resembles that of No. 10a (Fig. 19). The difference, however, between the structure of this deposit at the part seen in Fig. 46 and that of No. 10a, seen in Fig. 19, is that the V-shaped grains of the former are much narrower

\* It is considered unnecessary to insert particulars of all these experiments. Those introduced are typical of all.

† This had frequently been noticed in other specimens, but the difference was particularly marked in this one.

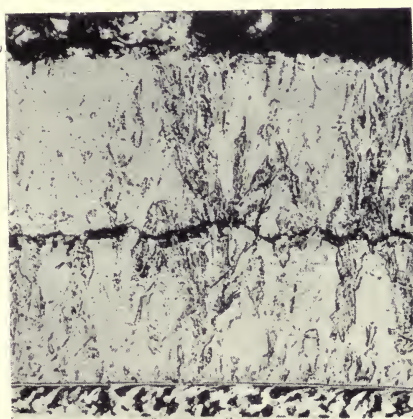




← Part of deposit formed during stoppage of spindle.

Deposit—before etching.

FIG. 42. × 150.



← The clear intermediate layer of copper.  
(Cf. Fig. 35.)

Deposit—after etching.

FIG. 43.\* × 150.

DEPOSIT 11.





FIG. 44.  $\times 150$ .

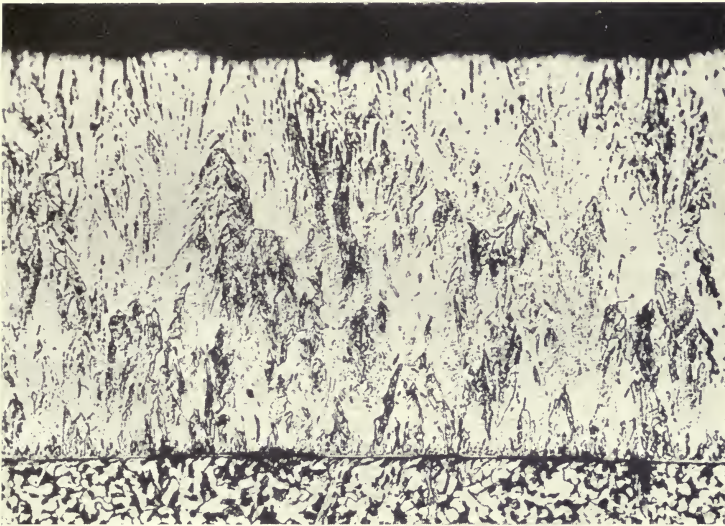


FIG. 45.  
 $\times 150$ .

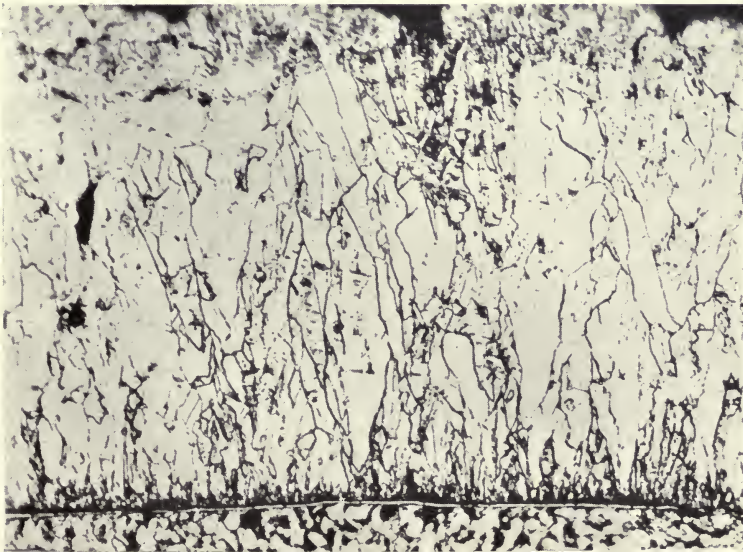
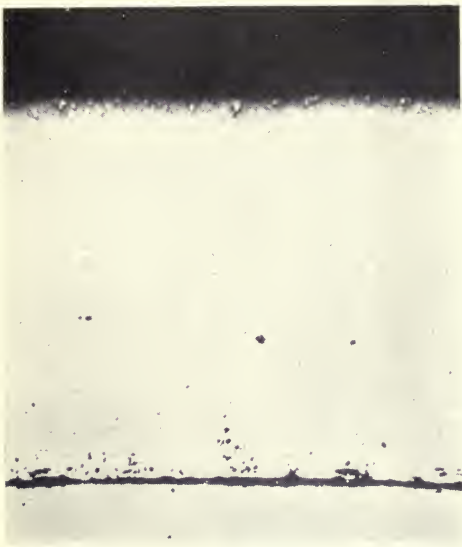


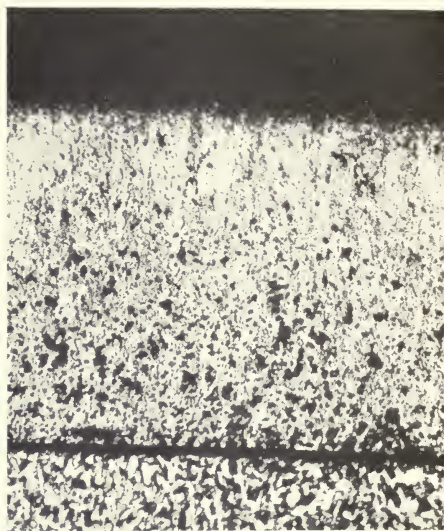
FIG. 46.  
 $\times 200$ .





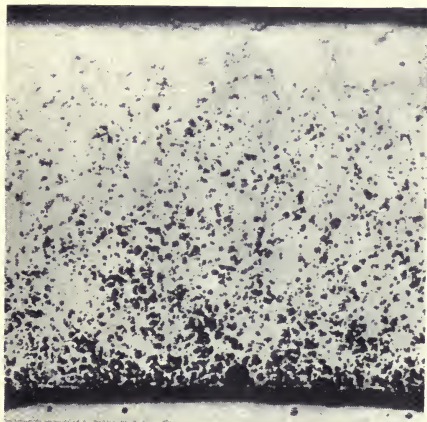
Unetched.

FIG. 47.  $\times 150$ .



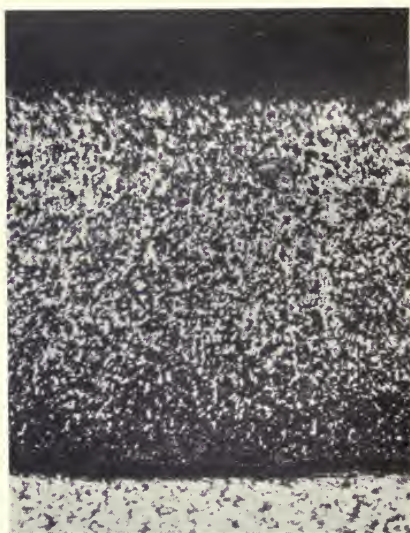
Etched.

FIG. 48.  $\times 150$ .



Unetched.

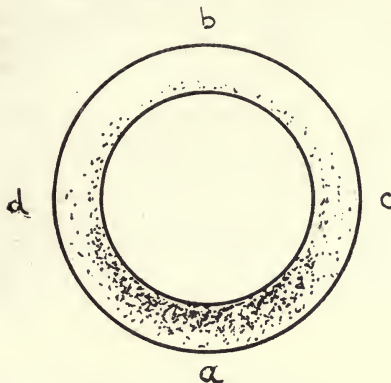
FIG. 49.\*  $\times 150$ .



Etched.

Fig. 50.  $\times 150$ .

than those of No. 10a. This corresponds to a less crystalline appearance macroscopically, or, in other words, to a finer grain.



Polished, unetched section. Enlarged.  
To show how inclusions vary over the  
area of the deposit.

*Diagrammatic.*

FIG. 51.

## Deposit of Experiment 12

*Description of the Structure, at 125 diameters.*

The appearance of the polished and unetched surface of the section of this deposit is seen in Figs. 47 and 49. On one side, *a* (Figs. 51 and 49), the deposit is seen to be crowded with holes or inclusions of oxide; while on the other side, *b* (shown in Fig. 47), there appears a layer of them near the base, but otherwise the deposit seems comparatively clear. Between *a* and *b*, as extremes, there are areas, *c* and *d* (Fig. 51), in which the appearance of the surface is intermediate between that of *a* and that of *b*, as regards the number of holes or inclusions contained in it. There is, in fact, a gradation from *a* to *b* through *c* and *d*.

When the surface of the section is etched there remains the same difference in general appearance. Fig. 50 shows the appearance, when etched, of the surface seen in Fig. 49, and similarly, Figs. 47 and 48, are the unetched and etched surfaces, respectively, of the same part of the specimen—a part situate in area *b*.

The specimen was very difficult to etch at all satisfactorily, and so as to show the grain boundaries. Especially was this the case as regards area *a*. Fig. 48 (area *b*), however, shows the boundaries of the grains with fair distinctness. The structure is fibrous for some distance from the base metal, the fibres then broadening as the periphery is approached; in general, it may be said that the structure, so far as can be seen, varies, radially, from fibrous to columnar. In Fig. 50 the fibrous structure of the deposit can only here and there be seen in the photograph; but it is more obvious on actual visual examination of the specimen.

The periphery is smooth all round; no radial cracks are visible, and the thickness does not vary much.

A principal interest of this deposit is the effect of inclusions upon structure that is disclosed in it. Obviously, what has happened is as

follows:—The solution was not a clean one,\* and the cathode was suspended with the side, a, facing upwards. The suspended matter in the solution has gradually settled down upon the deposit during its formation and become enclosed in it. The upturned face, a, of the deposit received the bulk of the settling matter, c and d much less but more than b.

Another observation made in connection with this specimen is the following:—The section was polished and etched several times before even an approximately satisfactory etching could be obtained. It was noticed when following the extent of the etching under the microscope, that during re-polishing the holes or inclusions gradually became covered with a film, so that finally an appearance was obtained as seen, for example, in Fig. 47, in which the filmed-over holes can be seen in the outside half of the section—especially, close to the periphery. It was much more difficult to arrive at this condition in the case of area, a, than in that of area, b—a consequence, no doubt, of the presence of more holes and inclusions. This is, of course, nothing else than an instance of the effect of polishing first observed and explained by Sir George Beilby.†

### Deposit of Experiment 12a

*Description of the Structure, at 125 diameters.*

The deposit (on steel rod, coppered, as base metal) of this specimen is very brittle. Only a little more than one-third part of the circumference of the base rod is covered with deposit, the remainder having broken away when the sample was sawn. The deposit remaining is piecemeal; one part is separated completely from the rest (the greater piece), and this greater piece is divided up into parts by straight and clean radial cracks (*See* Fig. 53). The deposit is uniform in thickness, and has an even periphery. As compared with No. 12, the number of holes and inclusions is few. Where the deposit has not come away from the base metal on which it was deposited, the copper layer is clear. But in general it *has* come away, and is separated from the base metal by a gap which has become filled up with casting metal‡ that has flowed over into and filled up the gap during the polishing process.

The structure is uniform throughout so much of the deposit as is present. It is of the fibrous type (Figs. 52 and 53): there is no banding, as, for instance, in the deposit of Experiment 1, Series I. There is, indeed, a thin (but very noticeable) central layer between wide inner and outer layers. This is due to the stoppage of mechanical movement that occurred after continuance of the deposition for about three-quarters of an hour. This central layer can be seen in all the micrographs of the specimen; but it is especially well seen in Fig. 54, as also are some circumferential lines.§

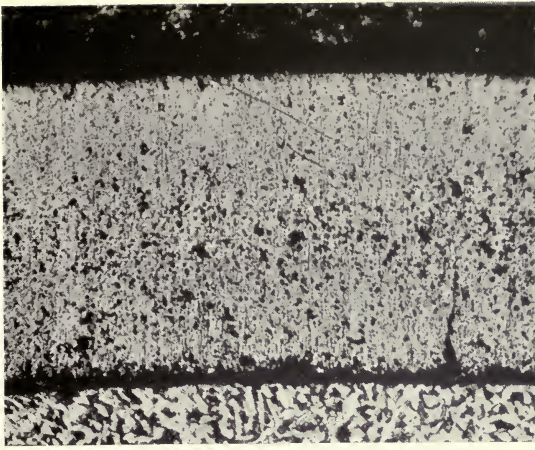
\* The solution used for 12 had previously been used for 12a—the moving cathode, and sufficient time had not been allowed for the oxide formed during the deposition of 12a to settle down. The solution used for 12a was a newly made and clean one; but, being only 1 gal. in bulk, the solution became badly oxidised during the deposition of 12a, and thus was full of suspended matter.

† Brit. Assoc. Rep., 1901, p. 604; Proc. Roy. Soc., 1903–1904, vol. 72a, p. 218; Proc. Roy. Soc., 1913–1914, A., vol. 89, p. 593; Nature, 1914 (Feb. 19), vol. 92. *See also* Nature, 1913, p. 322.

‡ This had not been removed.

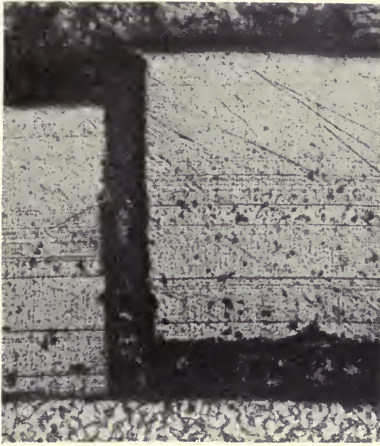
§ The nature and origin of these lines, seen in many other specimens also, has been discussed elsewhere. v. Jour. Iron and Steel Inst., 1921, vol. 103, p. 355.





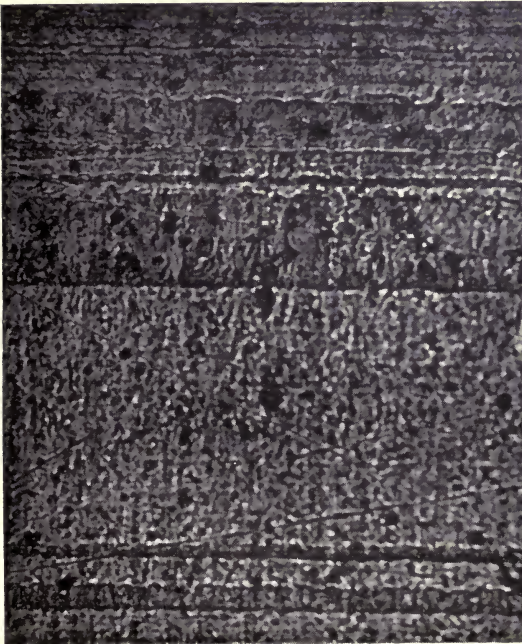
← Radial crack.

FIG. 52. × 150.



← Area formed during stoppage.

FIG. 53.\* × 150.



} Annular rings

} Area formed during stoppage.

FIG. 54. × 750.





Dentate periphery—crystalline macroscopically.

FIG. 55.  $\times 160$ .

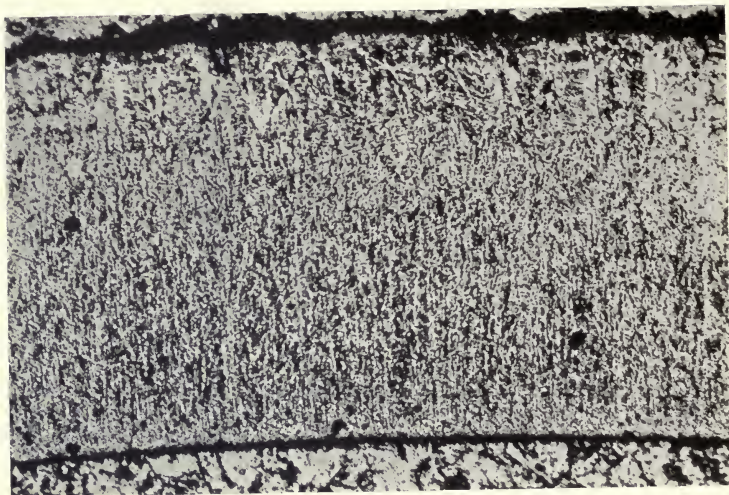


Smooth periphery—matt macroscopically.

FIG. 56.  $\times 160$ .

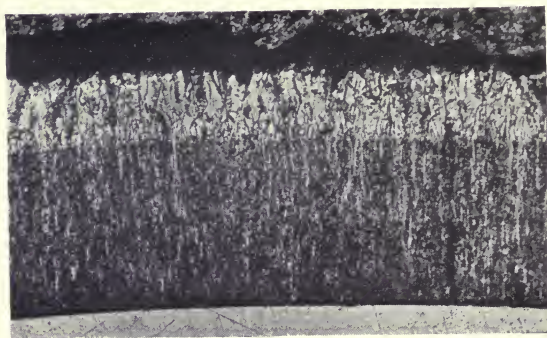
DEPOSIT 13.





Area opposite that of Fig. 59.

FIG. 57.  $\times 160$ .



Banding is shown with particular clearness.

FIG. 58.  $\times 100$ .

DEPOSIT 13A.

A comparison of the structures of Nos. 12 and 12a can be conveniently made thus:—

*Deposit No. 12*

(Cathode—stationary)

1. Full of holes and inclusions.
2. No radial cracks apparent.  
Deposit complete.
3. Fibrous to columnar: fibres broaden towards the periphery.
4. No circumferential lines seen.

*Deposit No. 12a*

(Cathode—moving)

- Few holes and inclusions.  
Many clean radial cracks.  
About two-thirds of deposit absent.  
Fibrous throughout: fibres are narrow and remain of uniform width.  
A large number of lines can be seen running circumferentially round the specimen\*. They continue throughout that part of the deposit which remains.

NOTE.—Attention is particularly drawn to the association of brittleness and clean radial cracks with a deposit of completely fibrous structure. This association is frequently to be observed (*Cf.* Fig. 54, which shows a gap in the fibrous area of the deposit). Reference has before been made to this association†.

### Deposit of Experiment 13

*Description of the Structure, at 125 diameters.*

The general structure of this deposit appears to consist of a mass of allotriomorphic crystals, elongated in a direction more or less perpendicular to the surface of deposition. Figs. 55 and 56 illustrate the two types of structure that exist in the deposit, namely, (1) where the periphery is dentate, a coarser type, consisting of broader, but broken, grains, and (2) where the outline is regular, a finer type of structure, consisting of grains, narrow, almost fibrous, at base, but which very gradually broaden towards the periphery. The structure of this latter type seems to be dual, as if a fibrous structure is imposed upon one of a more or less normal type. A characteristic of this deposit is a herring-bone appearance seen on individual grains at high magnification.

### Deposit of Experiment 13a

*Description of the Structure, at 125 diameters.*

Two distinct types of structure occur in this deposit. On two opposite sides there occurs one type, and on the other two opposite sides (at right angles to the former two) occurs another type of structure. In the one type (illustrated in Fig. 57) the greater portion of the deposit is, from within outwards, strictly fibrous, with the direction of the fibres normal to the surface of deposition, while the remainder—the peripheral portion—consists of fairly large and clear (but narrow) V-shaped grains of often rather irregular outline. Fig. 58 shows the consequent banded arrangement very clearly. The boundary between the two circumferential layers is, however, not always sharp. The fibres of the inner layer can often be seen continuing for some distance into the outer layer. A wave-like

\* The nature and origin of these lines, seen in many other specimens also, has been discussed in *Jour. Iron and Steel Inst.*, 1921, vol. 103, p. 355.

† *e.g.*, in the paper on "Some Defects in Electro-deposited Iron."



appearance can be seen running circumferentially through the crystals of the outer band: this is more clear in some places than in others. In the other type of structure (shown in Fig. 59) there is usually some fibrous layer, which varies in width in different parts but is always narrow. This layer merges radially and gradually into an outer layer which, though it seems essentially fibrous, is composed of, as it were, bundles of fibres that lie at an angle to one another, forming an arch-like appearance, as shown in Fig. 60. This middle area merges in turn into an area where the wavy appearance apparent in the outer layer of the former type of structure



FIG. 60.

can be well seen (Fig. 59). This wave-like appearance proceeds inwards to various depths at different places. It may, perhaps, be described as a "herring-bone" structure: it resembles the lamellar twinning often seen in the orthoclase feldspars of some igneous rocks.\* The outer edge is not so clear and smooth in this type as in the former. The grains in the outermost layer (where the wave-like appearance is most marked) are broader—broadening from within outwards; but the grain boundaries are not definite and clear. The general appearance of these parts of the specimen is somewhat similar to that of a foliated schistose (igneous) rock.†

It may be remarked finally that, in the four regions of the deposit intermediate between the area where the two types of structure above-described are found, the structure is of an intermediate type.

A comparison of the structures of Nos. 13 and 13a may (as for Nos. 12 and 12a) be usefully made thus:—

<i>Deposit No. 13</i>	<i>Deposit No. 13a</i>
(Cathode—stationary)	(Cathode—moving)
1. Larger grain: nowhere of the fibrous type of structure, with the direction of the fibres normal to the surface of deposition.‡	Smaller grain: often fibrous throughout almost the whole of the thickness of the deposit.
2. No circumferential banding.	Banding always present, usually very marked.
3. Some holes and inclusions—more numerous than in No. 13a.	Some holes and inclusions.

#### CONCLUSIONS—ON THE EFFECT OF MECHANICAL MOVEMENT

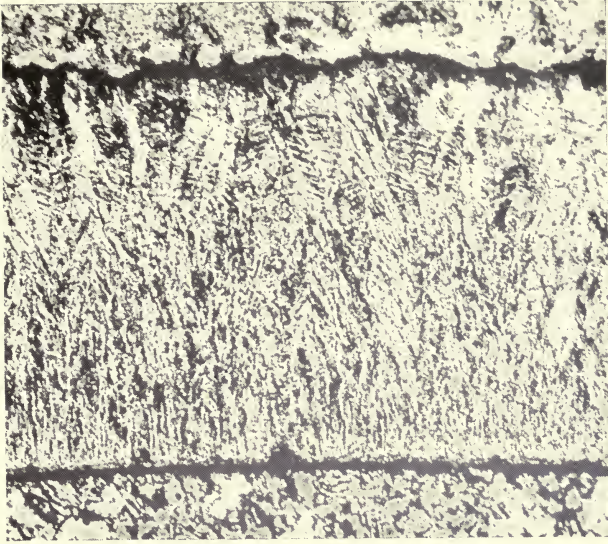
The great and striking difference between two deposits formed in the chloride bath—one in a still vat, the other on a mechanically moved cathode—is that, as was noted in the remarks on the macroscopic examination of the samples, the structure of the deposit formed in the still vat is larger than that of the one formed on a moving cathode. And further,

\* See *Petrology for Students*, by A. Harker, 1895, p. 61 (Fig. 13).

† This expression (schistose) is used to help make clear a type of structure. It is not intended to imply any similarity in mode of origin or development in the two cases.

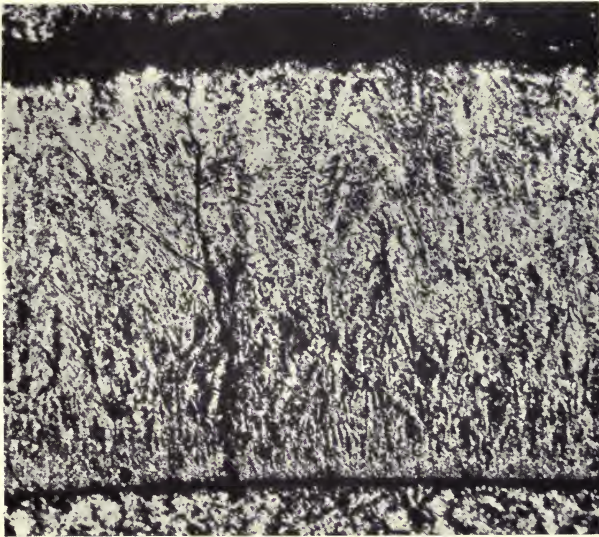
‡ The portion of No. 13, shown in Fig. 56, was found very difficult to etch. It appears to show (even when viewed directly through the microscope) two structures imposed the one upon the other, and the structure is not clear enough to enable deductions to be made.





Area opposite that of Fig. 57.

FIG. 59.  $\times 160$ .



Intermediate area.

FIG. 61.  $\times 160$ .

DEPOSIT 13A.



the predominating type of structure of the latter is the fibrous. This difference is very apparent upon both macroscopic and microscopic examination.

## DIVISION 2—THEORETICAL

### INTRODUCTION

Before attempting to explain the structure of electro-deposited iron, especially as exemplified in the results contained in Division 1, some consideration will be given to the facts and theories that relate to the crystallisation of substances other than electro-deposited metal. This will be done even though it involves a re-statement (which, to some, may appear superfluous) of those facts and theories. An endeavour will then be made to show that the ascertained laws of crystallisation applicable to salts in solution and to fused masses or melts, including rock magmas, are applicable also to electro-deposited metal\*; and that such extended application enables one to understand and interpret what one sees when electro-deposited metal is subjected to microscopic examination. The result of such understanding, from the practical point of view, will then be briefly discussed, namely, that the knowledge acquired can be put to practical application in the workshop, enabling the depositor to more certainly control the operation which is to give him the result he wishes to obtain. Accordingly, the following sub-division of the subject may be made:—

- I. The crystallisation of substances in general.
- II. The application of the theories of crystallisation to electro-deposited metal.
- III. The practical application in the workshop of present-day knowledge of the laws and phenomena of crystallisation.

### I

#### THE CRYSTALLISATION OF SUBSTANCES IN GENERAL

**The Conditions of the Birth and Growth of Crystals.**—A hot, saturated solution of, say, copper sulphate will, if quickly cooled, yield a cloud of very small crystals. It is the same with saturated solutions of numerous other salts. It is common knowledge of the laboratory that:—“In order to obtain as good crystals as possible, the solution is allowed to cool *slowly* without being disturbed. If a substance, on slow cooling, separates out in very coarse crystals, it is expedient, in case a sample of the substance for analysis is desired, to accelerate the crystallisation by artificial cooling, so that smaller crystals will separate out. . . . If a deposit of crystals as abundant as possible is desired, the vessel is put in a cool place—in a cellar or ice-chest, if practicable.”†

With these facts in mind, R. W. Moore‡ has recently produced perfect crystals of potassium sodium tartrate nearly 10 cms. long by cooling, extremely slowly, a saturated solution of the salt. The rate of cooling was regulated to 0°·1 per day for the first day, and then gradually increased to 0°·6 per day as the crystals grew. Sir H. Miers' experiments§

\* O. Lehmann, in 1877, pointed out that many of the phenomena of crystal formation by electrolytic means are comparable with those of ordinary crystal formation (gewöhnliche Krystallbildung). *Zeit. für Krystallog.*, 1877, vol. 1, p. 453. *And see also* O. Lehmann *Zeit. für Krystallog.*, 1890, vol. 17, p. 274.

† Practical Methods of Organic Chemistry, L. Gattermann (Trans. by W. B. Schober), 1905, p. 8, and of, “Crystals,” by A. E. H. Tutton, Chaps. XV. and XVI.

‡ *Jour. Amer. Chem. Soc.*, 1919, Vol. 41, p. 1060.

§ *Proc. Roy. Soc.*, 1907, A, Vol. 79, p. 322; *Jour. Chem. Soc.*, 1906, Vol. 89, p. 413.



have shown that similar rules hold for the production of crystals of salts from the liquid state, by cooling below the melting point, to those applying to crystallisation from solution.

It is the same with the rock magmas of the petrologist. "The distinctive features of these" (the Plutonic) "rocks of deep-seated consolidation are those which point to slow cooling (not necessarily slow consolidation) and great pressure. The rocks are without exception *holocrystalline*. . . . The texture of plutonic rocks may be comparatively coarse, *i.e.*, the individual crystals of the essential minerals may attain considerable dimensions. The typical structure is that known as *hypidiomorphic*, only a minor proportion of the crystals being 'idiomorphic' (*i.e.*, developing their external forms freely), while the majority, owing to mutual interference, are more or less 'allotriomorphic' (taking their shape from their surroundings)."\* In another place Harker says:—"It is evident from the foregoing considerations that slow cooling will cause larger crystals and more rapid cooling smaller crystals."† Professor Iddings'‡ observations with respect to crystallisation in general and to the magmas of igneous rocks in particular are very explicit. "*The size of crystals is dependent on the molecular concentration, or amount of substance in solution, since the rate of separation of solid is proportional to molecular concentration. . . . When crystallisation commences at a certain number of points in a given volume of liquid, the greater the amount of a separating substance in the solution, the greater the amount of material crystallised in a given time. . . . The size of crystals depends also on the degree of supersaturation taken in conjunction with the molecular concentration, for . . . the number of centres of crystallisation varies with the degree of supersaturation for a given concentration of a substance, the fewest occurring when crystallisation starts near the saturation point in the metastable condition, the greatest when it starts in the labile condition. The growth of a few crystals in a given volume of solution must lead to larger individuals than the growth of many crystals in the same volume of liquid. If the degree of supersaturation increases during crystallisation, by reason of the rate of cooling, the number of crystals may increase from time to time, resulting in different sized crystals of the same substance in some cases; the largest being fewest, and the smallest most numerous in most cases.*" And further§:—"The relation between size of crystal and the rate of cooling is seen upon comparing parts of the same body of magma that have cooled at different rates, though it is difficult to eliminate the effects due to viscosity that may have existed in the two cases. It is found that those parts of a magma that have cooled rapidly consist of smaller crystals than parts that have cooled slower. A definite expression of the relation between the two has been attempted by Lane|| and also Queneau."¶

In metallurgy, too, the same general relationship between size of grain or crystal and rate of cooling is recognised. "Whether crystallisation occurs in solidifying from the liquid or during the cooling of an already solid piece, it results in the formation of an aggregate of grains, each one of which is a true crystal. Their size may be large or small. In general, quick cooling means that crystallisation starts from many nuclei, and the resulting grains are consequently small; with very slow cooling, you get

\* A. Harker, *Petrology for Students*, 1895, p. 22.

† *Natural History of Igneous Rocks*, 1909, p. 218.

‡ *Igneous Rocks*, Vol. 1, p. 190.

§ *Op. cit.*, p. 188.

|| A. C. Lane, *Bull. Geol. Soc. Amer.*, 1897, Vol. 8, p. 403; *Rep. Geol. Surv., Mich.*, Vol. 6, part 1; *Ann. Rep. Geol. Soc. Mich.*, 1903 and 1904.

¶ A. L. Queneau, *Sch. of Mines Quart.*, 1902, Vol. 23, p. 181.

a gross structure made up of grains of a much larger size.”\* And again Sauveur, also in regard to metals, says:—“The number of crystalline grains of which a certain mass of metal is composed must depend . . . upon the number of centers or nuclei at which crystallisation begins, and this in turn probably depends upon the metal itself, its rate of cooling, and, according to some, its purity; the slower its solidification and the greater its purity the fewer the nuclei and therefore the larger the crystalline grains.”†

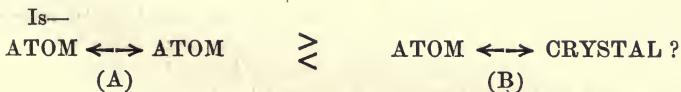
**Conclusions from the above considerations.**—Thus, it is recognised that in the process of crystallisation, whether from solutions or from melts of salts, or from molten rock magmas, or, again, from molten metal:—

- (1) There is a direct relation between rate of cooling and size of grain or crystal;
- (2) Quicker cooling produces a greater number of centres of crystallisation or crystal nuclei, resulting in smaller crystals; and
- (3) Crystals already in being grow where the rate of cooling is slow.

**The Conditions that determine whether Birth or Growth will occur.**

—There is nothing determinate, in the above-cited remarks, upon the answer to the double question: When will a crystal grow? When will a new nucleus be formed? The question may be put into a unified form thus: A number of atoms are, it is supposed, arranged in the regular orientation known as the crystalline, forming a crystal; and the periphery of that crystal is the locus of free metal atoms. Will those free metal atoms join up to the others, and thus form part of a whole, or will they join to one another to form separate entities? In the former case the crystal already formed will grow; in the latter, new nuclei will be formed. In the former case, there will be operative some force or tractation between the atoms of the already formed crystal and the free atoms; in the latter case, the force or tractation that operates acts between the free atoms, the atoms of the crystal being, *pro tanto*, inert.

The matter seems to resolve itself into this:—



The scheme represents that the tractation between free atom and free atom may be greater or less than that between free atom and crystal. If (A) is greater than (B), new nuclei will be formed; if (A) is less than (B), then the already formed crystal will grow.

Though not expressed in the above terms, something of this kind would seem to have been in the minds of the authorities cited above. It can be inferred often from what they say. For instance, Iddings states that: “The number of centers of crystallisation varies with the degree of supersaturation for a given concentration.” When, therefore, the degree of supersaturation is, for a given concentration, exceedingly small, the number of centres of crystallisation is exceedingly small also. But it cannot be intended that the relation holds indefinitely, that is to say until the supersaturation becomes nil and, hence, no nuclei are formed, so that all the while there is any supersaturation, so long will nuclei be formed. If this were so, there would be no growth, but only formation of nuclei. The inference must, therefore, be allowed that there is a

\* J. A. Ewing, *The Molecular Structure of Metals*, Phil. Mag., 1906, Vol. 12, p. 256.

† *The Metallurgy and Heat Treatment of Iron and Steel*, 1916, p. 88.



point—a certain supersaturation in the neighbourhood of a crystal—at which the excess of atoms (or molecules) is insufficient, for some reason or other, to form fresh nuclei. It is only such as to enable addition to be made to an already formed crystal. Or, put otherwise, the supersaturation is not sufficient to enable the inter-atomic (or inter-molecular) attractions to come into play; these are displaced by crystal—free atom (or molecule) attractions.

While one can draw inferences like the above from what the authorities say upon the matter of the general conditions of crystal formation and growth, the fact is that very little is known of the act of crystallisation itself; and this is, no doubt, the reason why so little direct statement about it is to be found in the literature. Even the experimental conditions necessary to effect nucleus formation, on the one hand, or crystal growth, on the other, are not too precisely known. One finds instances given to show that the unexpected may happen—where, in fact, the general and usual effect from a given cause does not result. J. C. Hostetter\* has recently made some interesting observations on this point, in connexion with the formation and growth of crystals from salt solutions. He says:—“The degree of supersaturation in the mother liquor at any time determines the increment of *growth*; consequently, the conditions affecting supersaturation—primarily, temperature and evaporation—must be under definite control” (if, that is, large, well-formed crystals are to be obtained). “Of lesser importance—but, nevertheless, essential—are the direction of concentration currents, and the number of crystals which serve as nuclei for growth. When the variables are controlled, it is not a difficult task to grow very perfect crystals of large size.” But, on p. 93 (op. cit.)—and this is more germane to the matter of immediate discussion—Hostetter says:—“The mere fact that essential conditions are under control in the crystal-growing apparatus described above is not, in itself, a guarantee that any salt can be made to form large crystals under the conditions obtaining therein. Some salts may be readily enough crystallised in large, well-formed crystals—other salts under the same conditions will yield a multitude of small crystals rather than a few large ones. Potassium alum and sodium chlorate were grown successfully in this apparatus; but experiments with ammonium chloride yielded only a mass of fine, fern-like crystals instead of growth on certain crystals which had been introduced as nuclei. In this case the effect was not caused by incorrect adjustment of conditions, for these fine crystals appeared and increased in size in the crystalliser, thus showing that conditions were optimum. On several occasions all crystals except one were carefully removed from the crystallizing chamber and the circulation of the liquid continued, but here again, instead of deposition taking place on the remaining crystal, other nuclei were formed, developing later into the usual feather-like growths.”

Hostetter offers no explanation of the phenomena he describes; but one learns that even though the conditions may be optimum for growth, yet, in some cases, nucleus formation results.

Despite the fact that very little is, in truth, known of the act of crystallisation, the theories of Miers, Wulff, and others, developed of recent years upon the basis of a large number of extraordinarily interesting and beautiful facts, enable one to picture in the mind an image, helpful, although, it may be, untrue, of the mechanism of that act. Miers assumes that the supersaturated liquid in contact with the growing crystal consists

\* “An apparatus for growing crystals under controlled conditions,” Jour. Wash. Acad. Sci., 1919, vol. 9, p. 85.



of molecules of salt uniformly mingled with those of the solvent, and that the *act of crystallisation* consists of the escape of the solvent molecules and solidification of the salt. Where the solution is only feebly supersaturated (where, that is, experiment in general shows growth to be slow), more time is afforded for the escape of the solvent molecules, and for the salt molecules to deposit themselves as directed by the molecular guiding force of crystallisation\*—the “*Richtkraft der Krystallisation*,” of Wulff. On the other hand, where the supersaturation is, at any instant, great, then there may result a labile or metastable shower of crystals, according to the degree of supersaturation, or, in other words, nuclei are formed. As has been already said, a mental picture of the act of crystallisation can be formed from such explanations as that which Miers gives of it, but one derives no help in solving the problem as to why in some cases nuclei are formed, and in others crystals, already in being, grow. Miers leaves one in the position of picturing the escape of the solvent molecules; there is no guidance in forming pictures of the resultant molecules forming nuclei on the one hand, or increasing the size of already present crystals on the other.

It is suggested that one can picture the two cases of crystallisation of a salt from its solution somewhat as follows:—

- (1) *If no crystal surface is present.*—The solution, at or near saturation, consists, for the greater part, of salt molecules and solvent (say, water) molecules. The concentration would seem then to be such that the salt molecules are not able to effect any permanent union; that is to say, the inter-molecular tractations are not able to bring about any permanent result. But as soon as the solution becomes supersaturated, as, for instance, by slow evaporation or by a lowering of temperature, then those molecules which come within sufficiently close range of one another effect permanent union. In the case of slow evaporation, the difference between the saturated and supersaturated solutions is one of concentration. There are fewer molecules of solvent per unit volume in the supersaturated solution to separate and keep apart the salt molecules, and one can picture the tractation of these to one another with permanent result. If the supersaturation occurs from sudden lowering of temperature, one can suppose either the kinetic energies of the salt molecules and the solvent molecules to be differently affected, so that the latter are unable to prevent the former effecting permanent union, or that, though the energies of the molecules are equally affected, the energy of the solvent molecules is too small to keep the salt molecules apart, or, again, that some aggregation occurs that allows of the congregation of the salt molecules, so that these can then unite *inter se* permanently. Perhaps there is more than one cause operative. In any case, the determining factor is concentration of the salt molecules, and one can picture their tractations.
- (2) *If a crystal of the salt in solution is present.*—In this case one can imagine that, in a saturated solution, an exchange of molecules occurs as between solution and crystal. Upon very slight supersaturation, water molecules make their escape from

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\* Cf. Tutton, *op. cit.*, pp. 250-252, and the references there given.

the salt molecules (according to Miers' theory), and solidification occurs at the crystal surface. This takes place slowly, producing growth of the crystal. The supersaturation being supposed very feeble, very few salt molecules are available for solidification. Their concentration is very small, consequently—so small that they are not sufficiently numerous or close together to enable inter-molecular tractation to occur, and hence nucleus formation is not possible. Crystal-molecule tractation is dominant under the conditions: "the directive force of crystallisation" is able to operate. If the layer of liquid round the crystal present in the solution suddenly, from one cause or another, became considerably supersaturated, then the available molecules would become more numerous and closer together, and a value of the concentration might be attained at which they would be able to tractate—their tractation *inter se* overcoming that between crystal and molecule.

Molecule  $\longleftrightarrow$  crystal  $>$  molecule  $\longleftrightarrow$  molecule

represents the phenomena at slight supersaturation;

Molecule  $\longleftrightarrow$  crystal  $<$  molecule  $\longleftrightarrow$  molecule

represents them at considerable supersaturation.

The molecular theory and Miers' theory, together, enable one to form a mental picture of the phenomena of crystallisation—a picture of the very act of crystallisation; and it is possible to distinguish between when nuclei will be formed and when growth will occur. The dominant factor is always concentration—number of molecules per unit volume. Ostwald\* puts the matter very clearly for the case of supersaturation from over-cooling. "If, now, the liquid is allowed to cool" (he says), "no crystal being present, the molecules receive no impulse to assume a regular arrangement,† and there is 'over-cooling.' The kinetic energy of the molecules decreases, *they get nearer and nearer together*, and it may happen that amongst the many encounters one may occur so that the molecules will just be in the specially stable regular arrangement that determines the crystal form. The circumstances are then given under which the liquid crystallises spontaneously; the molecules add themselves gradually to the crystalline nucleus, those being retained that approach in a suitable way. . . ." This is said of a super-cooled "melt" or fused mass; but "the spontaneous crystallisation of a supersaturated solution depends on exactly the same circumstances as the solidification of an over-cooled fused mass" (op. cit., p. 152). Indeed, Ostwald generalises in the following words:—"The application of these relations is by no means limited to aqueous solutions; they hold for solutions with other solvents as well as for fusions of all kinds. In particular they play a decisive part—one hitherto far too much neglected‡—in the crystallisation of melted silicates, as in the case of lavas and other eruptive rocks, and form the foundation for the right comprehension of these exceedingly important geological phenomena" (op. cit., p. 152).

\* W. Ostwald, *Outlines of General Chemistry* (trans. J. Walker), 1895, p. 151 and p. 147.

† Because no crystal is present to exert any such influence.

‡ Petrologists, prominent among whom are J. P. Iddings and A. Harker, have done much during the last twenty years to remedy this neglect.



## II

## APPLICATION TO ELECTRO-DEPOSITED METAL

An endeavour will be made in this section to show that the ascertained (general) laws or relations of crystallisation, applicable to other substances hold also in the case of electro-deposited metal.

If the laws governing the phenomena are the same in the two cases, cause and effect may be expected to correspond. That is to say:—

- (1) There will be a direct relation between (not *rate of cooling*, but its equivalent for deposited metal, namely,) *rate of deposition* and size of grain or crystal;
- (2) Quicker deposition will produce a greater number of centres of crystallisation or crystal nuclei, resulting in smaller crystals; and
- (3) Crystals already in being will grow where the rate of deposition is slow.

Again, if the correspondence holds, the dominant factor here also will be concentration: slight concentration will lead to coarse structure, great concentration to fine structure. To show that these relations hold for electro-deposited metal, the coarse and fine crystalline structures (together with lamination and the relation of base metal and deposit), and the conditions under which they are formed, will be considered; and an endeavour will be made to show that these result from differences of concentration. This is, of course, the same as showing that propositions (2) (3) hold good, and, hence, that the direct general relation (1) obtains.

If one may expect to get coarse structures when the concentration is small, and fine structures when it is great, these results should have been obtained in the deposits of the experiments of Series I, II, and III. The effects of temperature, current density, and movement, respectively, upon concentration should be apparent in the structure of the deposits. These will be considered, and it is hoped to show that the effects are, in general, such as might be expected. A few cases of other solutions and one other metal—copper—will be briefly considered.

It is suggested that, in the discussion outlined above, the general relationship between rate of deposition and size of grain will be established. Such correspondence between cause and effect can more easily, perhaps, be shown (for the case of deposited metal) if the nature of the act of deposition has been in the first place, briefly, considered.

A close and detailed examination of a large number of specimens of electro-deposited iron has suggested the conclusion—

*That its crystal structure depends upon the rate at which the ions are discharged and the resultant atoms are able to combine to form crystal grains. Or, one can say—and it amounts to the same—the structure depends upon the concentration of the crystal-forming atoms in the immediate neighbourhood of the cathode.*

If this be true, the type of structure obtained in any given case is the product of two factors, namely:—

- (i) The rate of discharge of the metal ions, and
- (ii) The availability of the resultant atoms for grain formation.

As regards (ii), it has to be remembered that a resultant metal atom may not be able to unite with others to form part of a crystal grain. It may, instead, have to enter into chemical reaction. The alkali and alkaline earth metals are well-known examples. Aluminium and magnesium

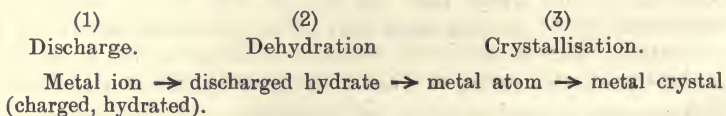


cannot be deposited—alone—from aqueous solutions of their salts.\* Chromium also is difficult to deposit, but it certainly can be deposited. In the cases of all these metals one cannot but suppose that metal ions are discharged; yet, except in the case of chromium, no metal deposits appear on the cathode. Hydrogen, in equivalent amount, appears instead; and the explanation is, that the metal atoms, at the instant following discharge, attack some substance in their neighbourhood, for example, the water, and hydrogen results as the product of the reaction. Nickel, zinc, and iron are, also, more or less difficult to deposit from solutions of their salts containing any considerable amount of free acid.

It is clear, therefore, that the rate of discharge of the metal ions cannot *in et per se* result in the formation of metal deposit: the liberated atoms must be available for the formation of crystal grains. It is the two factors together that determines the concentration of metal-forming atoms present in the cathode neighbourhood at any instant; and it is upon this concentration that, it is suggested, the crystalline structure of the electro-deposited metal depends.

#### TRANSITION:—ION TO CRYSTAL GRAIN

The steps, and their sequence, from ion to crystal have been well set out by H. Freundlich and J. Fischert† in the following way:—



This scheme excludes those cases where, as mentioned above, the liberated atoms enter into secondary reactions with other substances. It assumes the crystalline structure of the solid metal; and this assumption that electro-deposited metal is crystalline is certainly well founded in general.‡ It may be that the presence of colloidal substances in the electrolyte will, in some cases, so far modify the form of the deposited metal that it is no longer crystalline; but the general case is that which is considered here.

Of the three steps of the scheme of Freundlich and Fischer the third is the important one for present purposes, and it will now be discussed at length.

#### TRANSITION:—ATOM TO CRYSTAL

As has been already indicated in Section I, the processes of crystal origin and crystal growth are phenomena of several branches of natural science. Chemists, petrologists, and metallurgists have, all of them, to study these phenomena. The electro-metallurgist does not appear to have concerned himself much with them up to the present; yet the processes of crystallisation do, in fact, closely concern his work. Why is the metal deposited from the acid copper bath sometimes of obviously crystalline character, sometimes plastic in appearance and without visually apparent crystalline

\* It is claimed that magnesium can be deposited together with nickel. Coehn and Siemens, *Zeit. f. Elektroch.*, 1901-1902, vol. 8, p. 249; and H. E. Patten and W. R. Mott state that aluminium can be deposited from acetone solutions. *Trans. Amer. Electroch. Soc.*, 1909, vol. 15, p. 529.

† *Zeit. f. Elektroch.*, 1912, vol. 18, p. 886.

‡ S. Cowper-Coles states that, "the structure of electrolytic iron varies considerably, and in some cases it is found to be amorphous." *Jour. Iron and Steel Inst.*, 1908 (No. 3), p. 147. The former part of this statement is certainly true; but no evidence in support of the latter is produced.

structure?\*. Why is it impossible to deposit some metals from certain of their salts in other than loosely adherent crystal masses, while in the cases of other salts a reguline, adhesive deposit is obtained? These and many other questions of like kind await answers from the electro-metallurgist.

The formation of the crystal embryo or nucleus may or may not be a single, simple process. A nucleus may—it is conceivable—be the end result of a number of operative causes which may be consecutive or may co-exist. In other words, the coming together or tractation of atom to atom to form an embryo may be a resultant process, helped or hindered by others. It is likely that, for many purposes, the possible existence of such operative causes must be considered. But it is suggested that for the purposes of the present study—the crystalline structure of electro-deposited metal in general, and of deposited iron in particular—this is not necessary.

According to modern views on the subject of electrolysis, the ion becomes atom upon discharge. Observation shows that solid metal results, and that that solid metal is crystalline. According to Nernst (and others) metals in the solid state are constituted of atoms. Thus, in some way or other atoms must have come together and arranged themselves in the fixed, regular orientation of the crystal form. Accepting the modern views on electrolysis and also Nernst's view on the constitution of a solid metal, it would seem that, for present purposes, one can leave all else out of account, and consider the atoms at that instant when two or more are on the point of coming together (as the result of whatever causes) to form part of a crystal structure.

The actual transition process (or processes) of the stage—Atom to Crystal—has been, to some extent, considered by other writers. Freundlich and Fischer, in their work on the "Influence of colloids on the electrolytic separation of lead,"† have dealt with the problem that is concerned with the reasons why the presence of colloids in the electrolyte prevents the discharged atoms arranging themselves in the order necessary to crystal form, determining experimentally what minimum amount of this or that colloid will prevent such arrangement. They appear to conclude, from the results of their experiments, that the colloids are adsorbed by the metal, and, in consequence, the velocity of crystallisation is diminished and the denseness and compactness of the metal is favoured. V. Kohlschütter,‡ however, believes that the colloids give rise to colloidal metal (*e.g.*, in the case of silver), and that, therefore, the form of the deposited metal is non-crystalline. The most recent research on the transition stage is that lately published by V. Kohlschütter and E. Vuilleumier.§ They conclude from their experiments that the formation of a deposit from the atoms is not an immediate, single and simple, process, but that there is an intermediate stage, consisting of the formation of compound bodies containing the metal atoms, and that it is after passing through this stage that the atoms come to be available for deposit formation.||

In general, those workers who have dealt with the formation of electro-deposited metal have proceeded with a view to determining what substances will, if present in the solution, prevent the deposition of spongy, loosely-adherent deposits, and conduce to the formation of smooth, reguline,

\* *i.e.*, apart from microscopic observation.

† *Op. cit.* "Über den Einfluss von Kolloiden auf die elektrolytische Abscheidung des Bleis."

‡ *v.* A series of researches, by V. Kohlschütter and collaborators, *Zeit. f. Elektroch.*, 1913, vol 19, p. 161 *et seq.*

§ *Zeit. f. Elektroch.*, 1918, vol. 24, p. 300. *Cf.* also R. Marc, *Zeit. f. Elektroch.*, 1918, vol. 19, p. 431, and H. Stäger, *Helv. Chim. Acta*, 1920, vol. 3, p. 584.

|| *Cf.* J. A. Nussbaum, U.S. Pat., No. 832,024 (1906).



and adherent metal. For the most part the work has been experimental only: causes have remained unconsidered. In other words, the processes of the transition stage—Atom to Crystal—have not been, of themselves, of immediate interest to the majority of workers. Nor can it be claimed that the present research is immediately concerned with them. The position taken as starting point is as follows:—The atoms have been discharged and are ready to form part of crystal grains. The question is—Will they initiate new crystals, or will they aid in the growth of grains already existing? The answer suggested is that—It depends upon the concentration of the atoms, and on that only (that is to say, in the case of deposited metal). That answer is, from our knowledge of the crystallisation of salt solutions, rock magmas, and molten metal, to be expected.

**The birth and growth of crystals of deposited metal.**—Assuming, then, that there are a number of available metal atoms in the neighbourhood of the cathode, will they form new crystal embryos, or will they take their ordered places in grains already formed? The argument is that results show that just the same will happen in the case of the metal atoms as would occur in the case of molecules of a salt. That is to say, whether new crystals are originated or whether growth will occur depends upon the concentration of the available atoms. Metal atoms (derived from ions) and salt molecules give rise to the same effects, namely, crystalline bodies. Like effects suggest like causes. The causes of the formation of crystal bodies from salt molecules have been considered, and the dominant factor seems to be concentration. Does concentration operate as the dominant factor in the formation of crystals of deposited metal? If so, variety of concentration may be expected to produce variety of crystal—large or small, nuclear or growing; and, further, one may expect it to account for a number of features observed in connexion with deposited metal. A number of definite cases will, therefore, be considered, and an endeavour made to ascertain whether these can be explained by means of what one may call “the concentration factor.”

The following definite cases will be discussed:—

- (a) The coarsely crystalline structure;
- (b) The finely crystalline structure;
- (c) Laminated structure; and
- (d) The relation between base metal and deposit.

(a) *The coarsely crystalline structure.*

It is matter of common observation, in the cases of many metals electro-deposited from a solution that is not mechanically agitated, that the surface of the deposit becomes more visibly crystalline as the deposition process goes on. This is so in the cases of zinc, lead, copper, cobalt, cadmium, and other metals; and it is so in the case of iron. The deposit may take longer or shorter time in which to become coarsely crystalline to the naked eye. This, as a fact, depends upon the current density employed and upon the amount of metal salt in solution. The greater the current density is, the more quickly the deposit becomes obviously crystalline; the stronger the solution, the slower it does so. The foregoing statements are statements of experimental facts. It is suggested that the explanation is contained in the following considerations:—

Deposition of metal naturally tends to exhaust the cathode layer of the electrolyte of its metal content. Unless the loss of metal in that layer is made good by input in some way or other, and to the same extent as output (in deposition) proceeds, the content of metal in the cathode layer will become less and less. In a still vat, and at ordinary



temperature, such ingress of metal into the cathode layer must occur through either "concentration currents," liquid diffusion, or ion migration. The second and third means are exceedingly feeble, and certainly would not suffice to maintain constant the content of metal in the cathode layer, except at very small current density. Concentration currents are more effective: they can be seen to cause movement in the cathode neighbourhood. But it is suggested that these cannot suffice to maintain the indicated equilibrium. Consequently, although the current density remains constant, less and less current is carried by *metal* as the electrolysis proceeds—more and more is carried by other cations—fewer and fewer metal ions are discharged, and, consequently, metal atoms available for crystal formation become continually less in number. In short, the concentration of available metal atoms in the cathode neighbourhood becomes continually less as deposition proceeds, until a point is reached at which input does approximately equal output, and the metal content of the cathode layer becomes approximately constant. A very simple experiment visibly illustrates how the electrolyte in the cathode area gradually becomes weaker in metal content, where constancy is not maintained artificially. If copper sulphate (electro-typing) solution be poured into a long glass cylinder, an anode, connected with an insulated conducting wire, placed at the bottom, and a cathode immersed in the liquid at the top, it will be noticed that after electrolysis has proceeded for some while the electrolyte in the cathode area grows pale, and it becomes more and more pale as electrolysis proceeds. Owing to the experimental arrangements the operation of "concentration currents" is obviously almost negated. Hence, little or no mixing, caused by such currents, is effected, and liquid diffusion and migration are far from sufficient to maintain equilibrium of metal content in the cathode area. The result is that the metal content gradually diminishes, the diminution being indicated by the gradual decoloration of the liquid. One has, then, in a still vat (i) the deposit becoming more coarsely crystalline as deposition proceeds, and (ii) at the same time, the catholyte becoming weaker in metal. One knows that the solidification of electro-deposited metal is a crystallisation process,\* and that in a crystallisation process (in general), the slower it proceeds, that is, the less the amount of material available for solidification, the coarser the resulting crystals are. Analogy strongly suggests, therefore, that the increasing coarseness of the electro-deposited metal is the consequence of diminishing availability of metal.

(b) *The finely crystalline structure.*

If small availability of metal gives rise to a coarse structure, then, *per contra*, great availability should cause the structure to be fine. Experimental results show that where a high current density is employed, together with movement of either cathode or solution (or both), the structure of the deposit is small. In this connexion the results obtained by J. G. Zimmerman are of interest.† He found that for copper, "The fineness of the grain is dependent upon the current density, other things being equal, and the fineness increases with the current density until, at a critical value, a powdery deposit will occur. The increase in the number of revolutions per minute increases the critical current density, although whether it is exactly proportional I have been unable to determine. The

\* Cf. F. Foerster, *Elektrochemie wässer. Lösungen*, 1910, pp. 200 and 250, and elsewhere (Knapp, Halle); also M. Schlötter, *Galvanostegie*, Teil. I, p. 36 (Knapp, Halle).

† *Trans. Amer. Electroch. Soc.*, 1903, vol. 3, p. 245. Zimmerman deposited metal on small cylinders of base metal as cathodes. These were rotated on a vertical axis during deposition. See also "The structure of metal electro-deposited upon rotating cathodes," *Jour. Phys. Chem.*, 1921, vol. 25, p. 495.

highest speed which I used was 2,500 revolutions, corresponding to 573 feet per minute, and my observations tend to confirm the statement of Mr. Cowper-Coles that if a peripheral velocity of about 1,000 feet per minute and a current density of about 200 amperes per square foot be used the copper will plate out with a high polish and to any desired thickness." Similar results were obtained with nickel and zinc. The results obtained were certain; but Zimmerman, despite his view as to the connexion between fineness of grain and current density (above cited), seemed to think that the "high polish" was, in a measure, due to some burnishing action of the deposit by the electrolyte through the high speed of revolution. Professor C. F. Burgess, also, seemed to incline to this opinion; but other contributors to the discussion on Zimmerman's paper (including such authorities as Carl Hering and C. J. Reed) differed from it. For instance, C. Hering says:—"I think the explanations given in the paper why the deposit is so much better are not the correct ones. I think that the correct explanation is that with high current densities the molecular layer of liquid next to and in molecular contact with the cathode is exhausted of its metal before fresh liquid can get there, hence hydrogen or other things will be set free, spoiling the deposit, unless, that is, rotation (or other means of agitation) is used." C. J. Reed says:—"I entirely agree with that" (Hering's) "view, that neither the rotation nor the friction have anything to do with the smoothness of the deposit. It is simply the supplying of the ions of the copper in sufficient quantities to transmit the total current. . . . It is the deficiency of the copper and deposition of hydrogen that causes roughness. I do not think that the friction of the liquid has anything to do with it." The present author's view is that the only effect of rotation (or other means of agitation) is renewal of ions at the cathode surface, that rotation replaces quickly those discharged by the high current density, and that the rapid formation of metal atoms results in a deposit of a very fine structure—so fine that, under certain conditions, it may have a burnished appearance.

The connexion between fineness of deposit and current density has been studied and commented upon by Faust,\* Sieverts and Wippelmann,† and others.‡ Faust states that he found that the crystallites were smaller the higher the current density. Sieverts and Wippelmann confirm this up to a point, but they say that their experiments show that the connexion holds only up to a certain current density which in each case depends upon the experimental conditions. At a particular current density, differing as stated, a "minimum of crystal size" is reached.

In the present instance, then, one has (i) a fine-grained deposit, and (ii) at the same time, high current density (plus agitation). High current combined with sufficiently great agitation will effect and maintain a high concentration of metal ions, and, hence, of metal atoms, at the cathode surface. In the crystallisation process (from solutions of salts and from melts) great concentration leads to small crystals or crystal-structure. Here, again, analogy suggests the fineness of grain of electro-deposited metal to be due to great concentration.

#### (c) *Laminated structure.*

By "laminated structure" is meant one, often seen in electro-deposited metal and very often in deposited iron, that causes the deposit to appear to be made up of a number of separate layers. It resembles, broadly, the

\* *Zeit. f. anorg. Ch.*, 1912, vol. 78, p. 201.

† *Zeit. f. anorg. Ch.*, 1915, vol. 91, p. 1, and vol. 93, p. 287.

‡ *e.g.*, the present author, *Jour. Phys. Chem.*, *loc. cit.*



structure often seen in certain argillaceous rocks,\* and particularly in the sand-stones. This type of structure has been noticed in deposited metals by several observers. C. F. Burgess and O. P. Watts refer to what they call "surfaces of cleavages."† As to their origin, these investigators remark: "These surfaces of cleavages seem to be produced when any marked change in or interruption of the deposition process occurs. If the current be interrupted for a time, or if the cathodes are removed from the tank and exposed to the air, a cleavage surface may be produced. It is also believed that a sudden change in the current density may have the same effect." It is the break in the continuity of the deposit, denoted in it by a line of demarcation, and caused by the stopping of the current or the removal of the cathodes from the solution, to which reference is here made. O. W. Storey‡ refers to the lines of lamination here alluded to. He states that he found that the deposit (iron) could be split by a knife along these lines (or planes), and he, again, attributes their formation to momentary stoppage of the current, as occurs when a cathode is temporarily removed from the solution. An instance of such a structure, formed in a deposit prepared by the present author, is shown in photo-micrograph, Fig. 53. In this case, the times of formation of the lines are known to correspond with temporary removal of the cathode from the solution. An extreme case is shown in photo-micrograph, Fig. 42. In this instance, the deposit was formed upon a rotating cathode. When about half the whole period of deposition had elapsed, the rotation was stopped for some minutes, the current flowing the while, and then continued. Two distinct lines of demarcation indicate the stoppage and the re-continuance of the rotation; and they can be definitely said to be due to those causes. The metal shown in Figures 42 and 53 was iron; but the laminated structure here being considered is not confined to that metal. A similar line is seen in photo-micrograph, Fig. 2, which shows the fractured surface of a cobalt deposit. The same structure often occurs in nickel-plating. In this case, one or more of the outer layers will split and peel away from the cathode, leaving the inner (or first formed) deposit intact.

As above indicated, the present author believes the lamina of the structure under consideration are caused by either definite, temporary, but complete, stoppages of the deposition process, such as occur when a cathode is temporarily removed from the solution, or when a definite and marked change in the current conditions (including herein the relation of current density and movement) occurs. A line of demarcation can be seen in most deposits (with the aid of the microscope) to be the locus of difference of structure, the deposit on one side of it having one structure, whilst that on the other side has another. It is considered that an analogy can be found in the crystallisation of other substances. If a saturated solution of (say) copper sulphate is made, saturated at 100°C. or thereabout, the containing vessel be set in water at the same temperature, and the whole be allowed to cool slowly, a layer of crystals of copper sulphate will be slowly formed on the bottom of the vessel. If, when this layer has been formed, the hot water in the outer vessel be removed and substituted by ice-cold water, a shower of minute crystals will be formed which will form

\* Though the lamination in rocks is due to different causes than those that would operate during the electro-deposition of metal. *v.* A. Geikie, Text Book of Geology, 1893, p. 499.

† *Trans. Amer. Electroch. Soc.*, 1906, vol. 9, at p. 233; and *see op. cit.*, figs. 5, 6, and 7, p. 231. *Cf.*, also C. F. Burgess and C. Hambuechen, *Jour. Phys. Chem.*, 1903, vol. 7, p. 409.

‡ *Trans. Amer. Electroch. Soc.*, 1914, vol. 25, p. 489.



a very marked and distinct layer upon the layer of larger crystals first formed. The line of demarcation between the layers corresponds to a line between two lamina of a deposit. Further, the lines of division are, in the author's opinion, due to the same cause in the two cases, namely, to change in supersaturation, in the one case of salt molecules, and in the other of metal atoms, though, of course, this change is brought about by different means in the two cases. It is suggested, too, that such a line of demarcation between two layers of one and the same deposit is due to the same cause as the clear line of demarcation which, so far as the microscope discloses, always exists between base metal and deposit. Reference will now be made to this.

(d) *Relation between base metal and deposit.*

Despite the use of the highest powers of the microscope there always appears to be a line of demarcation between base metal and deposit.\* This line is more or less clear according as the surface of the base metal was clean or not clean at the time when the cathode was put into the depositing solution.† It may possibly be that the metal first deposited forms an alloy with the base metal, and that at the junction or, rather, forming a junction between base metal and deposit, is a thin (ultra-microscopic or irresolvable) layer of alloy which appears, under the microscope, as a very thin line. There are authorities to support the view that such an alloy is formed‡; but it would lead to too long a digression to discuss the subject in detail here. Reference to the micrographs enables one to see that, in every case, the deposit adjacent the base metal is small in structure. It either remains small and approximately uniform throughout the width of the deposit, or it gradually becomes coarser from within outwards, according to whether the deposit was formed in an agitated or still solution.§ One may call this the microscopic equivalent of the macroscopic observation before referred to. If a piece of metal be taken, say, copper, that has an obviously crystalline structure, and deposits of the same metal, copper, be formed upon it, the crystals of the base metal do not grow. No instance of such growth has ever been observed.|| The deposit is *always* of the finely crystalline type at first, and then, in a still vat, becomes coarser and coarser, from within outwards, as deposition proceeds. If, after deposition has proceeded for some time—an hour or two, the process is interrupted and then continued after a short interval, the second deposit will be finely crystalline to commence with, becoming coarser as the second period of deposition proceeds; and the point of interruption of the deposition is marked by a line, so that the two deposits form laminae. The explanation suggested is that the concentration of available atoms at the cathode surface is greater at the commencement of each period of deposition than at any time afterwards during each period as a consequence of the gradual exhaustion of the metal in the cathode layer of solution as deposition goes on, and that it is this variation of concentration that effects the variation in the structure of the deposit.

\* Cf. O. Faust, *op. cit.*

† A base metal that is liable to chemical attack by the electrolyte may cause the line to be confused in appearance, instead of definite and clear.

‡ *E.g.*, M. Schlötter, *Chem. Ztg.*, 1914, vol. 38, p. 289, and C. H. Desch, *Brit. Assoc. Rep.*, 1912 (sect. 3); also see G. Gore, *Electro-metallurgy* (Longmans).

§ This statement refers to deposits formed in *neutral* solutions only. In acid solutions, the deposit frequently shows the small and uniform structure, whether agitation is used or not. This, however, is not always so.

|| Cf. O. Faust, *op. cit.*

A CONSIDERATION OF THE RESULTS OF THE EXPERIMENTS  
OF THE SERIES I, II, and III

Attention may now be redirected to the experiments on the effect of temperature, current density, and movement, respectively, upon the structure of iron deposited from the (neutral) chloride bath, with a view to considering how far the explanation advanced in regard to the structure of electro-deposited metal in the foregoing pages is justified by the results of those experiments.

(i) **Effect of Temperature.**—It is stated on p. 10 and elsewhere that the results of both macroscopic and microscopic investigations show that, *ceteris paribus*, increase of temperature causes increased coarseness of deposit. In an earlier series of experiments made on the Fischer-Langbein bath, it was found that a series of changes occurs in the physical character of the deposit as the temperature is gradually raised from (about) 45° C. (a temperature considerably below the working temperature of the bath), while the current density is maintained constant. Below and at 45° C. the deposit is dark and metallic, extremely hard and brittle; it may even be cindery and friable. There is, too, considerable gas evolution (hydrogen). As the temperature rises the deposit becomes lighter in colour: it becomes at first light grey and bright-metallic in appearance, and still hard and brittle; but as the temperature continues to rise the deposit becomes successively dull, matt, and finally crystalline. The temperature is then 90° to 100° C. In the same series of experiments, it was noted that two effects of hydrogen in the cathode neighbourhood were (1) that the deposit was bright and metallic in appearance, and hard and brittle, and (2) that there was considerable gas evolution. It may also be added that, as a fact, a bright, hard metallic deposit connotes a finely crystalline internal structure. There is one other experimental fact about the ferrous calcium chloride bath that may be conveniently mentioned here. When the solution cools after use a pale green salt crystallises out. The same salt separates after a solution, that has been made (but not used for deposition purposes), has stood idle for some while. Analysis of this salt showed\* that it contained chlorine and iron in approximately the percentages that would be contained in a double (or complex) chloride having the formula,  $\text{CaFe}(\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ . The actual figures were:—

	Fe	Cl
	(found)	(found)
Analysis 1 ... ..	26.4 %	35.45 %
Analysis 2 ... ..	27.05 %	35.45 %

The percentages contained in  $\text{CaFe}(\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ , supposing it to exist,† would be:—

Fe ... ..	27.5 %
Cl ... ..	35.0 %

It is, therefore, suggested that this salt is largely present in the solution at lower temperatures, and that when the solution is electrolysed at low temperature calcium ions carry the greatest portion of the current and are discharged at the cathode. Upon discharge the calcium reacts with the water of the solution, giving rise to hydrogen evolution, and the calcium hydrate formed at the same time causes the catholyte to be

\* The analyses were carried out for the author by Mr. J. W. Gardom.

† Salts of the same type known to exist are:  $2\text{KCl} \cdot \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $2\text{NH}_4\text{Cl} \cdot \text{FeCl}_2$ ,  $2\text{CdCl}_2 \cdot \text{FeCl}_2 \cdot 12\text{H}_2\text{O}$ , and  $\text{HgCl}_2 \cdot \text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . See Dammer's Handbuch, 1893, vol. 3, p. 309, and Gmelin-Kraut Handbuch, 1875, vol. 3.



alkaline. It is believed that the result on the deposit is to cause it to contain compounds (perhaps oxides), and that the dark colour is the result. At the lowest temperatures (ordinary and temperatures not much above this), another result of the basic condition of the solution around the cathode is that the deposit, after a short time of deposition, is not reguline, bright, and metallic, but dark, powdery, and loosely adherent. But it is suggested that according as the temperature rises the double salt becomes destroyed, and the resulting ferrous chloride supplies more and more ions to act as carriers of the current. In the result, with increasing temperature the discharge of ferrous ions increases, while the discharge of calcium ions decreases, and the deposit contains a continually increasing percentage of iron, until, finally, at a temperature of (about) 90° C., normal deposition of iron occurs. It must be further remarked that as the discharge of calcium ions decreases so will the evolution of hydrogen. The known effect of hydrogen upon the structure of deposited metal is to cause it to be very small in size of grain and often bright in appearance. The experiments of Sieverts and Wippelmann with copper\* have shown that acidity causes smallness of grain, and the present author's experiments with iron show it to be so in the case of this metal; while it is the author's experience with many metals—iron, nickel, zinc, and others—that acidity causes the deposit to be bright. It is, therefore, considered that it is the hydrogen which causes the deposit of iron, in the case under consideration, to be bright and metallic, at first dark on account of the admixed iron compounds, and then light. No explanation is here offered as to how the hydrogen produces its effect. Pfanhauser has, indeed, given an explanation, but this is dissented from by Sieverts and Wippelmann. In fact, the cause has not been experimentally determined, and one has, therefore, only conjecture to rely upon.†

The matter that it is wished to make clear is that as the temperature approaches the working temperature less and less hydrogen will be evolved (in consequence of diminishing discharge of calcium ions), and the deposit becomes more normal; and, further, that the reason why a deposit formed at a higher working temperature is more coarse in structure than one formed at a lower one is because at the higher temperature the catholyte (or the cathode layer of it, at least) becomes the weaker in metal at a greater rate, and this diminution of concentration more quickly makes itself apparent. The author is perfectly well aware that the foregoing explanation involves some assumptions which (although not unreasonable yet) require to be justified by experiment. At the same time it is suggested that, if the assumptions were justified by experiment, the explanation would afford an understanding of the phenomena on the most rational basis, namely, that the structure of a deposit is dependent upon concentration of the ions of the metal deposited.‡

(ii) **The Effect of Current Density.**—The observations made upon the effect of current density on the size of grain of a deposit are summarised on page 16. The size of grain appears to alternate. As the current density increases, the size of grain at first increases also, then diminishes, and then seems to increase again. The explanation is as follows: The cathode

\* *Op. cit.*

† The remarkable change that acid may cause in the structure of a deposit (v. W. E. Hughes, *Trans. Faraday Soc.*, 1921) has not, it is suggested, been sufficiently closely considered by W. Blum in his work on "Factors Governing the Structure of Electro-deposited Metals." *Trans. Am. Electroch. Soc.*, 1919, vol. 36, p. 213.

‡ Compare W. Blum's suggestions as to the cause of increased coarseness of grain in deposits formed at higher current density. *Trans. Am. Electroch. Soc.*, 1919, vol. 36, p. 221.



layer of solution is diminished in metal content by deposition. This will occur more quickly, the greater the current density employed; and since the lower the concentration, the greater the grain size, it follows that the greater the current density is, the greater the size of grain will be. It is suggested that the change from larger to smaller grain when a certain region of current density is reached (which will depend on the temperature) is due to increased discharge of hydrogen ions. The effect of acid (*i.e.*, hydrogen ions) is, as has been already said, to diminish the size of grain of the deposit. The uncertainty of the possible further change from smaller to larger grain as the current density goes on increasing is such as to render discussion unprofitable. If it occurs, it would be difficult to explain; but, it is suggested, the conditions at (about) 200 amperes per square foot and a temperature of 110° to 120° C. are such that any change in size of grain may be due to quite other causes than increase of current density in and by itself.\* For instance, at 120° C. (approx.) the boiling point of the solution is either nearly or quite reached (this depending upon the concentration of the solution), and the mechanical disturbances produced might well of themselves be sufficient to vitiate conclusions on the effect of current density.

(iii) **The Effect of Mechanical Movement.**—The effect of movement of the cathode upon the structure of the deposits from the chloride of iron bath is certain. The effect is that movement causes diminution of grain size; microscopic examination confirms visual observation. This is what is to be expected. Movement of the cathode helps to maintain constant the concentration of metal in the cathode area and the supply of ions at the cathode. The diminution in metal content of the cathode layer is, if not entirely, largely prevented. Hence conditions favourable to growth of large crystals do not exist;† and either crystals must grow out from the large number of nuclei formed on the cathode surface at the commencement of deposition, or fresh nuclei be formed. Very probably both events occur; but the fibrous structure of the deposits formed on the moving cathodes points to the former occurring to, at least, a very considerable extent.

#### SOME REMARKS ON DEPOSITS:—(1) FROM OTHER IRON SOLUTIONS, AND (2) OF OTHER METALS

The deposits particularly considered in the foregoing discussion were formed in the chloride of iron bath—neutral, in regard to the presence of free acid. General conclusions cannot, of course, be drawn from what happens in the case of one metal deposited from one type of solution only. But there is evidence to show that, in general, the same relations between structure of deposit and conditions of deposition hold good.

(1) **Deposits from Other Iron Solutions.**—In order to obtain some information as to the above-mentioned relation in the case of another and quite different type of iron solution, some deposits were formed in the Klein-Maximowitsch iron bath.‡ This is a solution of an entirely different constitution to that of the ferrous calcium chloride bath. It is comparatively dilute, and is worked either at the ordinary temperature, or at tem-

\* Compare similar suggestions respecting the marked effect by a factor not under study on any change produced by one that is being considered. W. Blum (*op. cit.*, p. 219.)

† Cf. Sieverts and Wippelmann, *op. cit.*, and M. von Schwarz, *Internat. Zeit. f. Metallographie*, 1915, vol. 7, p. 124.

‡ *v. Zeit. für Elektroch.*, 1905, vol. 11, pp. 52 and 91.

peratures not much above the ordinary. It is, too, a solution that can be operated at a very low current density only (0.3 to 0.5 amp./dcm.<sup>2</sup>)\*

The solution from which the deposits were formed contained:—

1½ lbs.	...	...	...	FeSO <sub>4</sub> ·7H <sub>2</sub> O.
4 ozs.	...	...	...	MgSO <sub>4</sub> aq.

dissolved in one gallon of water.

It was treated with bicarbonate of soda in the way described by Maximowitsch.\* The solution was shown to be saturated with respect to the iron salt by the fact that, upon cooling to ordinary temperature from that of deposition (v. inf.), some of the iron salt separated out.

The conditions of deposition were as follows:—

Current density...	...	4.6 amp./ft. <sup>2</sup> (0.5 amp./dcm. <sup>2</sup> approx.).
Temperature ...	...	34° C.
Time of deposition ...	...	24 hours.

The Deposit was of a beautiful silver-grey colour, lustrous and glittering. It was obviously crystalline. A photograph of the cathode with the deposit upon it is shown in Fig 62 at three-quarters actual size. In Fig. 63 is seen the internal structure of the deposit. The result in this case is just what would be expected, and, indeed, is what was anticipated. Low-current density, stationary cathode, and neutral solution should give a structure of the "normal" type and large grain. It is seen that this is the structure that was obtained. The experiment was repeated several times, using cathodes of different sizes and composition (copper, steel, and iron) with, in all cases, a like result.

## (2) Deposits of Other Metals

(a) *Copper*.—Reference has already several times been made to the work of Faust† and of Sieverts and Wippelmann.‡ Their results seem to be in general harmony with those obtained by the author, they working with copper and the author with iron. Reference has also been made to Zimmerman's results,§ which were obtained by depositing copper on rotating cathodes, and which support some results obtained by Cowper-Coles.|| Further, the work of M. von Schwarz¶ on idiomorphs of electro-deposited copper, and, later, that of the present author\*\* on the same subject, show that a similar relation between structure and conditions of deposition holds for copper as obtains for iron, and one and the same explanation appears applicable in the two cases.

Mention must also be made of some recently published work by W. Blum, H. D. Holler, and H. S. Rawdon,†† which, so far as it goes, appears to support the general conclusions formed and the observations made by the present author. The conclusions of Blum and his co-workers (which they illustrate by photo-micrographs) are:—That "with low current density, especially at higher temperatures, the copper possesses a relatively coarse structure except at the surface where the initial deposit is made. By increasing the current density, particularly at lower temperatures, the structure assumes a columnar appearance, the crystals being long and finger-like. With still further increase in

\* *Op. cit.*

† *Zeit. f. anorg. Ch.*, 1912, vol. 78, p. 201.

‡ *Ibid.*, 1915, vol. 91, p. 1, and vol. 93, p. 287.

§ *Trans. Amer. Electrochem. Soc.*, 1903, vol. 3, p. 245.

|| *Trans. Far. Soc.*, 1905, vol. 1, p. 215.

¶ *Internat. Zeit. f. Metallog.*, 1915, vol. 7, p. 124.

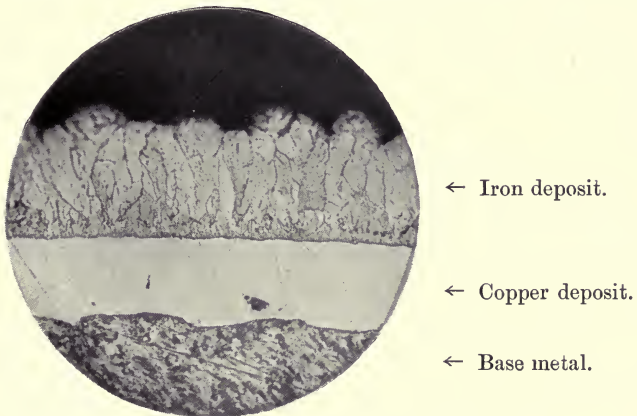
\*\* *Jour. Inst. Metals*, 1920, vol. 23, p. 525.

†† *Trans. Am. Electroch. Soc.*, 1916, Vol. 30, p. 159.



Cathode with deposit from Klein's bath.

FIG. 62.  $\times \frac{3}{4}$ .†



Section (etched) of deposit shown in Fig. 62.

FIG. 63.  $\times 150$ .

† This photograph was taken for the author by Dr. G. D. West, D.Sc. (Lond.), lately of the Physics Department, East London College.





the current density, the structure is much broken up, and numerous evidences of twinning are found. In every case the direction of growth of the crystals is perpendicular to the surface of deposition." It is to be noted that agitation was used in the experiments of these investigators.\*

(b) *Other Metals*.—So far as the author can ascertain, little or no systematic and sufficiently thorough work appears to have been done in connection with the crystalline structure of other metals than copper and iron.† Some few photo-micrographs of electro-deposited zinc are, indeed, to be found in the literature, and, in those cases where the conditions of deposition are given at the same time, these certainly seem to show that the relation between structure and conditions of deposition which, it is suggested, obtains for iron and copper, holds also for zinc, and that, therefore, the concentration hypothesis is valid for that metal. But, as indicated, a sufficient amount of work (*ad hoc*) has not been done—or, at any rate, published—to enable one to form a positive opinion in regard to zinc.

### GENERAL CONCLUSIONS

It is suggested that sufficient evidence has been adduced in the foregoing pages to show:—

1. That the general theories entertained in regard to the crystallisation of other substances hold also for the case of deposited metal.
2. That the dominant factor governing the structure of the crystallised substances is, in all cases, concentration—of molecules or atoms.
3. That, in the case of electro-deposited iron and copper (and, perhaps, other metals), concentration of available metal atoms at the cathode surface is the dominant factor, other factors of deposition, such as temperature, current density, and so on, being contributors;‡ and that, consequently, there is a direct relation between conditions of deposition and structure of deposited metal.
4. That, specifically, great concentration (plus agitation) leads to small grain-size, and, conversely, small concentration (with or without agitation) leads to large grain-size.
5. That recognition of the relation stated in 3—the deduction from the concentration hypothesis—will enable one to explain the history of an electro-deposit.

\* Blum's work (*op. cit. supra*) leads him to different conclusions on several points from those reached by the present author, who, however, reserves criticism of Blum's work to another occasion.

† Dr. Blum frankly admits the incompleteness (to date) of his experiments and observations. *Op. cit.*, p. 214.

‡ It has been recently suggested anew by authors whose views are entitled to respectful consideration that the cathode potential exercises an important influence on the form and structure of deposited metal. (H. Stäger, *op. cit.*, A. H. W. Aten et M. Boerlage, *Rec. des Travaux Chim. des Pays-Bas*, 1920, vol. 89 p. 720). Prof. W. D. Bancroft appears to have expressed a similar view, thus:—"Increasing the current density, increasing the potential difference at the cathode . . . . decreases the size of the crystals" (*v. Trans. Am. Electroch. Soc.*, 1904, vol. 6, p. 27; *Journ. Phys. Chem.*, 1905, vol. 9, p. 277, and *Trans. Am. Electroch. Soc.*, 1913, vol. 23, p. 266. And *cf.* also W. Blum, *Trans. Am. Electroch. Soc.*, 1919, vol. 36, at p. 223. The present author has considered this view. He has, however, come to the conclusion that cathode potential takes its place with current density, temperature, and the other factors of deposition, which, as he suggests, operate only in that and in so far as they affect concentration, which is the dominant *causa causans*.

The converse of the statement contained in 5 will now be very shortly considered, that is to say, that one can, by the aid of the concentration hypothesis, build up a deposit of this or that structure. It enables one to adopt those conditions of deposition which will lead to the formation of a deposit having the desired structure. In other words, the hypothesis becomes of practical utility in the workshop.

### III

#### WORKSHOP APPLICATION

The application of laboratory results to works practice must always be cautiously made. This is true in general: it is true in particular of investigations carried out on the structure of electro-deposited metals. Nevertheless, laboratory results, applied with due caution, can often be used, either to the betterment of the products of the workshop or to effect some improvement in the general control of the processes of production. The practice of the electro-deposition of metals has been long established; but workshop practice has not, for the most part, been based on scientific knowledge, which has been conspicuous chiefly from its absence. Freundlich and Fischer state the position, as it existed in 1912, quite truly in the following words\* :—"The form in which the metal is separated during electrolysis is, in the majority of electrolytic processes of decisive importance. Yet, regarding the conditions which favour the formation of a coarse or a finely crystalline form, or, again, an adherent or loose deposit, there is still, at the present time, very little known. It is known that metals are separated in an adherent and finely crystalline form when deposited from solutions in which the metals are contained in complex ions; it is, further, known that the addition of quite small amounts of foreign substances will often influence the form of the deposited metal to an extraordinary degree. But it is found that the statements concerning the most advantageous composition of solutions for electro-plating . . . and other objects have, for the most part, the character of purely empirical recipes." Since 1912, however, the results of several investigations relating to the effect of the various factors of deposition upon the structure of deposited metals, have been published. The papers containing these results have been frequently referred to in either the text or notes of this Report. It appears clear from them, as well as from the results contained in Division 1, that current density, concentration of metal, temperature, and other factors influence, often in a very marked manner, the structure of the deposited metal. But the work so far done has had relation to individual cases, and the results cannot be said to have much general application. It is, indeed, still too early to generalise with any great confidence: much must be done before the general influence of this or that factor can be said to be known. Hence, it is necessary to use with caution such information as has been obtained in regard to any one metal. What has been found to be true for one metal may not hold for another, and thus, any attempt to apply in the workshop the information gained as to the former may lead to trouble if that knowledge be applied to another different metal. Then again, factors such as the presence of free acid or of some colloid, may cause usual results to be modified in a greater or less degree. For instance, the acid copper bath contains a considerable percentage of free sulphuric acid; yet, as Blum, Holler, and Rawdon have shown, the deposits obtained at low current densities have a typical coarse

\* Zeit. f. Elektroch., 1912, Vol. 18, p. 885.



structure.\* In the case of iron, however, there are indications that free acid causes the structure to be fine-grained,† even when the acid is present in small quantity only and a low current density is used. Some of the general conclusions that have been stated in Division 2 (e.g., Nos. 3 and 4, p. 41 *ante*) appear to hold as well for copper (deposited from the acid copper bath), iron (from the sulphate bath), and, probably for zinc, as for iron deposited from the chloride solution, in the absence of such factors as, for instance, the presence of colloids. But there is, at present, no certainty about this. It can, however, be said that, as a consequence of work on individual metals, results obtained in the case of a metal that has been thoroughly investigated can be put to good use in the workshop; one has only to take care that these results are not hastily applied in connection with the deposition of another metal. One important fact is becoming more and more clear, namely, that one can, with the necessary knowledge of the relation between structure and conditions of deposition, build up a deposit having any desired structure, and hence, possessing certain desired physical properties.

It will be useful to illustrate the present position by an example or two.

(1) The author has several times been asked how a deposit of iron that will not be hard and brittle can be obtained. Electrolytic iron is commonly believed to be both hard and brittle, and it often is. The answer to the question just stated is contained in the following remarks. Experience shows that iron can be deposited (from the chloride bath, at any rate) with structures that vary with and depend upon the conditions of deposition. If acid be present in the solution, the structure will be fibrous;‡ it will, again, be fibrous, if agitation of the electrolyte or movement of the cathode be employed during the deposition.§ Experience also shows that a deposit from the chloride bath possessing a fibrous structure is hard and brittle. On the other hand, if no free acid is present in the solution, and if "still vat" conditions are maintained, then a deposit from the chloride bath will possess a *normal* structure,|| and experience has shown the author that a deposit from the chloride bath possessing that structure is soft and malleable—so much so that the iron can be flattened out under hammer blows.

(2) Let it be assumed that a thick, smooth deposit of iron is required. Experience has shown that where the deposit is of fine and fibrous grain within, the surface is smooth; but that if the structure be of the normal type, the surface is irregular. In other words, there is a correlation between internal structure and surface features; these can be observed continuously as deposition proceeds, and hence, control of the structure of a deposit maintained. To obtain a fine and fibrous structure, one must employ a solution that contains free acid, or one must agitate the electrolyte or move the cathode during deposition. To secure a *thick* and smooth deposit, it is necessary, in addition, to maintain approximately constant the concentration of metal in the solution; for concentration is always an important—the author believes it to be the dominant factor determining the structure of a deposit, the other factors affecting the structure, if not, perhaps, wholly, then, at any rate, especially, in consequence of their effect upon the concentration. To

\* "Preliminary Studies in the Deposition of Copper in Electro-typing Baths," Trans. Am. Electroch. Soc., 1916, Vol. 30, p. 159.

† Cf. Trans. Faraday Soc., 1921.

‡ Cf. "The Forms of Electro-Deposited Iron, and the Effect of Acid upon its Structure," Trans. Faraday Soc., 1921.

§ v. Figs. 52 *et alia*, Division 1.

|| v. especially, Figs. 11, 19, & 20, which are typical of the "normal" structure.

obtain a thick, smooth, deposit of iron, one must therefore use a bath containing free acid or must agitate the electrolyte or move the cathode during the deposition, and one must, in addition, see to it that the metal concentration of the bath does not become appreciably diminished.

The author does not, of course, pretend to be either the first or the only student of the structure of electro-deposited metal to point out the value of such studies to works practice. Among workers in this field of research, Dr. W. Blum is, perhaps, the most prominent. He and his collaborators, working at the Bureau of Standards, Washington, U.S.A., have carried out much research in connection with the structure of electro-deposited metal, and much of the work has been specially directed to the practical application of their observations. In regard to this matter, Dr. Blum writes as follows\* :—" From the point of view of the plater we may usually define a 'good deposit' as one which is fine grained, since fineness of grain is in general accompanied by a high lustre, relative freedom from porosity, and comparative hardness†. *In electro-typing, the structure of the metal may be even more important since it largely determines the physical properties upon which the durability of the product depends. It is therefore highly desirable to define, if possible, conditions of operation which will produce a fine structure (or which in some cases will permit any change in structure required to produce the desired finish), which conditions should be susceptible of control and should permit favourable operation over a considerable range.*"

## APPENDIX

### BIBLIOGRAPHY ‡ COMPRISING REFERENCES TO PUBLICATIONS ON—

- I. The Electro-deposition of Iron and Phenomena connected therewith.
- II. The Properties of Electrolytic Iron.
- III. Works of Reference relating to Electro-deposition of Iron.

#### I. IRON DEPOSITION

The publications contained in Sections 1 and 2 are less concerned with the deposition of iron generally, than with its deposition from particular types of solution—the sulphate or the chloride. In several instances, *e.g.*, those of Pfaff's work and the Langbein-Pfanhauser patents, the optimum conditions for working such solutions are worked out or given. This enables a comparison as to the relative merits of the two types to be made, and it renders the easier the choosing of this or that solution for a particular practical purpose.

##### 1. Sulphate Solutions

C. HOEPFNER and KLIE. v. a paper by K. Arndt, *Zeit. für Electroch.*, 1912, vol. 18, p. 233, entitled :—" Zur Geschichte des Elektrolyteisens."

E. KLEIN.—Klein worked with a mixed, chloride-sulphate, bath also; but the solution usually associated with his name is the sulphate bath, developed and improved by Maximowitsch (*q.v.*, *infra*). See the following :—

*Eng. Pat.* 1869, No. 2456.

\* *Trans. Am. Electroch. Soc.*, 1919, Vol. 36, at p. 215.

† The present author can, as the result of independent work and work on a metal (iron) that Dr. Blum has not especially examined, confirm this general statement.

‡ This bibliography is not exhaustive; but it is believed to contain all the most important literature.



*M. H. von Jacobi.*—Bull. de l'Acad. Imper. des Sci. de St. Petersburg, 1869, vol. 13, p. 40.

“Note sur la production des dépôts de fer.”

(This contains an account of some of his work by Klein himself.)

*M. H. von Jacobi.*—Brit. Assoc. Rep., 1869, p. 67.

“On the electro-deposition of iron.”

*W. Roberts-Austen.*—Jour. Iron and Steel Inst., 1887 (No. 1), p. 71.

“The electro-deposition of iron.”

The following papers contain information concerning Klein's solution:—

*F. Haber.*—Zeit. für Elektroch., 1898, vol. 4, at p. 413.

“Über galvanisch gefälltes Eisen.”

*S. Maximowitsch.*—Zeit. für Elektroch., 1905, vol. 11, p. 52.

“Ein neues Verfahren zur Herstellung des Elektrolyteisens.”

*A. Russ and A. Bogomolny.*—Zeit. für Elektroch., 1906, vol. 12, pp. 701 and 702.

“Studien über die elektrolytische Abscheidung des Eisens aus wässerigen Lösungen seines Chlorürs und Sulfats.”

*C. F. Burgess and C. Hambuechen.*—Trans. Am. Electroch. Soc., 1904, vol. 5, p. 201; Electro-chem. Ind., 1904, vol. 2, p. 184.

“Electrolytic Iron.”

The following papers contain considerations of the work of Burgess and Hambuechen:—

*A. Neuburger.*—Elektroch. Zeits., 1904-1905, vol. 11, p. 77.

“Einige Bemerkungen zu dem Vortrag von Burgess und Hambuechen, über elektrolytisches Eisen.”

*R. Amberg.*—Zeit. für Elektroch., 1908, vol. 4, p. 326, and *Ib.*, 1910, vol. 16, p. 125.

“Notiz zur Darstellung von Elektrolyteisen.”

*H. Lee.*—Abhandl. der deutsch. Bunsengesellschaft, No. 2, 1909.

“Das Elektrolyteisen.”

*A. Müller.*—Metallurgie, 1909, vol. 6, p. 145.

“Über die Darstellung des Elektrolyteisens, dessen Zusammensetzung und thermische Eigenschaften.”

*A. Pfaff.*—Zeit. für Elektroch., 1910, vol. 16, p. 220.

“Über die elektrolytische Abscheidung von Eisen.”

*A. Russ and A. Bogomolny.*—Op. cit. supra.

*R. Amberg.*—Op. cit. sup.

*H. Lee.*—Op. cit. sup.

*A. Müller.*—Op. cit. sup.

*A. Pfaff.*—Op. cit. sup.

*W. A. Macfadyen.*—Trans. Far. Soc., 1920, vol. 15, p. 98.

“An Aspect of Electrolytic Iron Deposition.”

*M. Schlötter.*—D.R.P., 309271.

## 2. Chloride Solutions

*W. M. Hicks and L. T. O'Shea.*—The Electrician, 1895, vol. 35, p. 843; Brit. Assoc. Rep., 1895, p. 634.

“Some Points connected with the Preparation of Pure Iron by Electrolysis.”

*E. Merck.*—D.R.P., No. 126839, 1900. Pfaff has studied and commented upon Merck's method for iron deposition. (Op. cit.)



THE LANGBEIN-PFANHAUSER PATENTS.—The most important are:—

D.R.P., No. 212994 (1908, issued 4th Sept., 1909). “Verfahren zur Herstellung von geschmiedigem Elektrolyteisen.”

D.R.P., No. 228893 (1909, issued 24th Nov., 1910). Same title.

D.R.P., No. 230876 (1909, issued 7th Feb., 1911). “Gewinnung von reinem Eisen aus gewöhnlichem Eisen auf elektrolytischem Wege.”

Eng. Pat., No. 24841 (1909). Corresponds to D.R.P., No. 212994.

Eng. Pat., No. 25092 (1910), sub. nom. E. C. R. MARKS. “Improvements in the Manufacture of detachable Electrolytic Iron Deposits.”

Eng. Pat., No. 25969 (1910). Corresponds to D.R.P., No. 228893.

The author has tested the workshop efficiency of the ferrous calcium chloride bath patented by the Langbein-Pfanhauser A.-G. It may be stated that much of the work done in elaborating the solution was carried out by A. Fischer. Consequently, the bath has come to be known as the Fischer-Langbein solution: the product is sometimes referred to as “Fischer’s iron.”

The following are some papers containing information respecting the properties of iron deposited from this bath:—

*Anon.* Zeit. für Elektroch., 1909, vol. 15, p. 595.

*W. Pfanhauser, Junr.*, Galvanotechnik, 1910, p. 750.

*C. Duisberg.* Internat. Cong. App. Chem., 1912, vol. 28, p. 60.

*J. ESCARD.*—Le Génie Civil, 1919, vol. 75, Nos. 8, 9, and 10, pp. 165, 199, and 225; v. also Stahl und Eisen, 1919, at p. 805. Abstracted in The Electrical Review, 1920, vol. 86, p. 490.

“Fabrication, propriétés, et utilisation industrielle du fer électrolytique.”

RUSS and BOGOMOLNY, and MÜLLER, also give the results obtained by them when working with chloride baths. Müller’s paper contains an excellent comparison of the results he obtained from chloride and sulphate solutions.

### 3. Sulphate-Chloride Solutions

The work that has been done on baths containing both ferrous sulphate and ferrous chloride, as original components, is small. It is, too, unimportant, except for one notable exception, namely, that of O. P. Watts and L.H.Li (v. inf. Sub-sect. 4). The work of these investigators was, however, directed to determining the effect of the presence of “addition agents” in solutions intended for iron deposition. Ammonium chloride has been sometimes used in sulphate solutions: in these the ammonia salt is, usually, intended to act as a “conducting salt.” No advantage has been claimed as resulting from the use of such mixed baths: on the other hand, many complications and difficulties in matters of control are introduced. References to them are, therefore, omitted, since the author wishes this bibliography to be of practical use, and not merely an indiscriminate collection of miscellaneous references.

*F. VARRENTAPP.* Ding. Polytech. Jour., 1868, vol. 187, p. 152.

“Galvanische Fällung von Eisen in cohärenter Form.”

This paper is given as being of historical interest.

### 4. General Researches on Iron Deposition

In this sub-section there are included references to researches of a more general character on the electro-deposition of iron, while Sub-section 5. contains references to publications of a more purely scientific kind.

A. WATT.—The Electrician, 1887, Nov. 11 and 25, Dec. 16 and 30; *Ib.*, 1888, Jan. 13.

“Electrolysis of iron salts.”

A. RUSS and A. BOGOMOLNY. (*Op. cit.*, sup.)

E. F. KERN.—*Trans. Am. Electroch. Soc.*, 1908, vol. 13, p. 103.

“Electrolytic refining of iron.”

S. COWPER COLES.—*Jour. Iron & Steel Inst.*, 1908 (No. 3), p. 134.

“The Production of finished Iron Sheets & Tubes in one operation.”

The following references containing criticisms of Cowper Coles' work will be useful:—

W. PALMAER and J. A. BRINELL.—*Met. & Chem. Eng.*, 1913, vol. 11, p. 197.

W. PALMAER.—*Chem. Zeitg.*, 1913, vol. 37, p. 393.

L. GUILLET.—*Jour. Iron & Steel Inst.*, 1914, vol. 90, at p. 67. (*v. sub. Applications.*)

A. MÜLLER.—*Metallurgie*, 1909, vol. 6, p. 145. (*v. sup.*)

S. A. TUCKER and E. SCHRAMM.—*Jour. Ind. & Eng. Chem.*, 1910, vol. 2, p. 236.

“A Comparison of the Methods for depositing Iron electrolytically.”

O. P. WATTS and L.H.Li.—*Trans. Am. Electroch. Soc.*, 1914, vol. 25, p. 529.

“The Effect of Addition Agents in the Electro-deposition of Iron.”

E. H. ARCHIBALD and L. A. PIGUET.—*Trans. Roy. Soc., Canada*, 1917-1918, vol. 11 (series III), p. 107.

“The Electro-deposition of Iron from Organic Solvents.”

R. KREMANN and his collaborators.—The work of Kremann and his co-workers relates more to the electro-deposition of alloys of iron with nickel and magnesium than to the deposition of iron alone. The following papers contain interesting results:—

R. KREMANN, C. TH. SUCHY, and R. MAAS.—*Monatsh. für Chem.*, 1913, vol. 34, p. 1757.

“Die bei gewöhnlicher Temperatur abgeschiedenen Nickel-eisen-legierungen.”

R. KREMANN and J. LORBER.—*Ibid.*, 1914, vol. 35, p. 603.

“Über versuche zur Abscheidung von Eisen-magnesiumlegierungen aus wässrigen Lösungen.”

R. KREMANN and R. MAAS.—*Ibid.*, 1914, vol. 35, p. 731.

“Die bei höherer Temperatur aus Sulfatbädern abgeschiedenen Nickeleisenlegierungen.”

R. KREMANN and H. BREYMESSER.—*Ibid.*, 1917, vol. 38, p. 359.

“Über die bei gewöhnlicher Temperatur unter höheren Wasserstoffdrücken erhaltenen kathodischen Abscheidungen von Eisen und Eisen-nickellegierungen.”

##### 5. *Phenomena Connected with Iron Deposition, together with the Preparation of Pure Iron*

\*F. VARRENTTRAPP. *Op. cit.* (Sub-sect. 3).

\*J. THIELE.—*Lieb. Annal.*, 1891, vol. 265, at p. 58.

“Zum Nachweis des Arsens.”

\*W. M. HICKS and L. T. O'SHEA. *Op. cit.* (Sub-sect. 2).

\*R. AMBERG. *Op. cit.* (Sub-sect. 1).

An asterisk denotes publications containing work on the preparation of pure iron.

F. FOERSTER.—*Abhandl. der deutsch. Bunsengesellschaft*, No. 2, 1909.

This symposium contains the following:—

- F. Foerster* and *V. Harold*.—"Das elektromotorische Verfahren des Eisens."
- O. Mustad*.—(Diss. Dres., 1909): "Die Abscheidungspotentiale des Eisens aus Ferrosulfat- und Ferrochloridlösungen."
- H. Lee*.—(Diss. Dres., 1906): "Das Elektrolyteisen."
- R. KREMANN** and **J. LORBER**.—*Monatsh. für Chem.*, 1914, vol. 35, p. 1387.  
"Über die kathodischen, funkenden Abscheidungen aus gemischtem Eisensulfat-magnesiumchlorid, glycerinhaltigen Bädern."
- \***J. R. KAIN**, **E. SCHRAMM**, and **H. E. CLEAVES**.—*Bur. of Stand., Sci. paper*, No 266, 1916, vol. 13, No. 1, p. 1.  
"Preparation of pure iron and iron-carbon alloys."  
(This monograph contains a bibliography on the preparation of electrolytic iron.)
- R. KREMANN**, **R. SCHADINGER**, and **R. KROPSCH**.—*Monatsh. für Chem.*, 1917, vol., 38, p. 91.  
"Versuche zur Darstellung kathodischer, funkender Abscheidungen aus glycerinhaltigen Eisensalzlösungen bei Zusatz anderer Salze, im besondern von Cerchlorid."
- W. A. NOYES**, *Junr.*—*Compt. rend.*, 1919, vol. 164, p. 971.  
"Sur le potentiel nécessaire pour électrolyser les solutions de fer."
- N. R. DHAR** and **G. URBAIN**.—*Compt. rend.*, 1919, vol. 164, p. 1395.  
"Tensions de polarisation du fer dans les solutions de ses sels complexes. Relations entre ces tensions et la dissimulation des caractères analytiques des ions ferriques."

## II. ELECTROLYTIC IRON

### 1. Composition and General Properties

- M. H. VON JACOBI**.—*Bull. de l'Acad. Imp. de St. Petersburg*, 1868-1869, vol. 14, p. 252.  
"Notiz über die Wasserstoffabsorption des galvanischen Eisens."
- R. LENZ**.—*Jour. für prakt. Chem.*, 1869, vol. 108, p. 438; *Pogg. Annal.*, 1871, p. 242. (5th *Ergänzungsband*.)  
"Über einige Eigenschaften des auf galvanischem Wege niedergeschlagenen Eisens."
- L. CAILLETET**.—*Compt. rend.*, 1875, vol. 80, p. 309.  
"Sur le fer hydrogéné."
- F. WINTELER**.—*Zeit. für Electroch.*, 1897, vol. 4, p. 338.  
"Einiges über Metallniederschläge."
- F. HABER**.—*Zeit. für Electroch.*, 1898, vol. 4, p. 410.  
"Über galvanisch gefälltes Eisen."
- R. ABEGG**.—*Stahl u. Eisen*, 1901, p. 736.  
"Über die Electrochemie des Eisens."
- A. SKRABAL**.—*Zeit. für Electroch.*, 1904, vol. 10, p. 749.  
"Über das Elektrolyteisen."
- H. LEE**.—*Diss. Dres.*, 1906 (v. *F. Foerster*, I, 5, sup.).  
"Über den Wasserstoffgehalt des Elektrolyteisens."
- ANON.**—*Zeit. für Electroch.*, 1909, vol. 15, p. 595.  
(Properties of Fischer-Langbein Iron.)
- A. PFAFF**.—*Zeit. für Electroch.*, 1909, vol. 15, p. 703.  
"Über den Schwefelgehalt des Elektrolyteisens."
- C. F. BURGESS**.—*Trans. Am. Electroch. Soc.*, 1911, vol. 19, p. 181.  
"Electrolytic refining as a step in the production of steel."



L. GUILLET and A. PORTEVIN. *Compt. rend.*, 1913, vol. 156, p. 702.

“Sur quelques propriétés d'un fer électrolytique industriel.”

J. ESCARD.—*Le Génie Civil. Loc. cit.*

This author's articles in *Le Génie Civil* contain an excellent exposition of the properties of electro-deposited iron.

## 2. Individual Properties

The number of publications in which information is to be found on some property of electrolytic iron is very great. Those cited below are such as will, it is hoped, facilitate research into the literature, since the researches referred to are, mostly, by eminent authorities and the papers containing them provide, often, numerous references to work connected with the subject matter dealt with by them in each case.

### (a) Crystallising Properties.

J. E. STEAD and H. C. H. CARPENTER.—*Jour. Iron & Steel Inst.*, 1913, vol. 88, p. 119.

“The Crystallising Properties of Electro-deposited Iron.”

### (b) Mechanical Properties.

B. NEUMANN. (V. *Infra.*)

A. MÜLLER. *Op. cit.*

L. GUILLET. *Op. cit.*

J. ESCARD. *Op. cit.*

### (c) Thermal Properties.

A. MÜLLER. *Op. cit.*

L. GUILLET and A. PORTEVIN. *Op. cit.*

W. BRONIEWSKI. *Compt. rend.*, 1913, vol. 156, p. 699.

“Sur les points critiques du fer.”

L. GUILLET. *Op. cit.*

C. BENEDICTS.—*Jour. Iron & Steel Inst.*, 1914, vol. 89, p. 407.

“Experiments on the Allotropy of Iron: Behaviour of Ferromagnetic Mixtures: Dilatation of pure Iron.”

O. W. STOREY.—*Trans. Am. Electroch. Soc.*, 1914, vol. 25, p. 489.

“A Microscopic Study of Electrolytic Iron.”

J. COURNOT.—*Compt. rend.*, 1920, vol. 171, p. 170.

“Sur le recuit du fer électrolytique.”

(For other references, v *Sub-sect. e.*)

### (d) Electrical and Magnetic Properties.

C. F. BURGESS and A. H. TAYLOR.—*Trans. Am. Inst. Electrical Eng.*, 1906, vol. 25, p. 459; *Electroch. and Met. Ind.*, 1906, vol. 4, p. 208.

“The Magnetic Properties of Electrolytic Iron.”

B. NEUMANN.—*Stahl u. Eisen*, 1914, vol. 34, p. 1637.

“Magnetische und mechanische Eigenschaften reinsten Elektrolyteisens.”

G. K. BURGESS and I. N. KELOBERG.—*Jour. Wash. Acad.*, 1914, vol. 4, p. 436.

“Electrical Resistance and Transformation Points of Pure Iron.”

E. GÜMLICH.—*Stahl u. Eisen*, 1921, vol. 41, p. 1249.

“Die magnetische Eigenschaften von Elektrolyteisen.”

### (e) Thermo-Electric Properties.

C. BENEDICTS.—*Jour. Iron and Steel Inst.*, 1916, vol. 93, p. 211.

“A New Thermo-electric Method of Studying Allotropic Changes in Iron and other Metals.”

G. K. BURGESS and H. SCOTT.—*Jour. Iron and Steel Inst.*, 1916, vol. 94, p. 258.

“The Thermo-electric Measurement of the Critical Ranges of Pure Iron.”

## 3. Structure

C. F. BURGESS and O. P. WATTS.—Trans. Am. Electroch. Soc., 1906, vol. 9, p. 229.

“A Microscopic Study of Electro-deposits.”

O. W. STOREY.—Trans. Am. Electroch. Soc., 1914, vol. 25, p. 489.

“A Microscopic Study of Electrolytic Iron.”

W. E. HUGHES.—Jour. Iron and Steel Inst., 1920, vol. 101, p. 321.

“Some Defects in Electro-deposited Iron.”

W. E. HUGHES.—Trans. Far. Soc., 1921.

“The Forms of Electro-deposited Iron and the Effect of Acid upon its Structure.”

W. E. HUGHES.—Jour. Iron and Steel Inst., 1921, vol. 103, p. 355.

“Slip-lines and Twinning in Electro-deposited Iron.”

Cowper Coles, J. Escard, and J. R. Cain and his co-workers show micrographs of electrolytic iron, but the structure of the deposited iron is not made the subject of study.

## 4. Applications

S. COWPER COLES.—Op. cit. (v. I. 4, sup.).

C. F. BURGESS.—Trans. Am. Electroch. Soc., 1911, vol. 19, p. 181.

“Electrolytic Refining as a Step in the Production of Steel.”

L. GUILLET.—Jour. Iron and Steel Inst., 1914, vol. 90, p. 66.

“Electrolytic Iron, its Manufacture, Properties, and Uses.”

J. ESCARD.—Op. cit. (v. I, 2, sup.).

W. E. HUGHES.—The Engineer, 1920, vol. 130, p. 350.

“Electro-deposited Iron: Its Value for Engineering Purposes.”

W. E. HUGHES.—The Electrician, 1920, vol. 85, p. 530.

“The Industrial Future of Electro-deposited Iron.”

C. P. PERIN and D. BELCHER.—Mining and Metallurgy, 1921 (Dec.), p. 17. “Commercial Production of Electrolytic Iron.”

The publications of von Jacobi, R. Lenz, and W. Roberts-Austen, all cited above, should be consulted. The deposition of iron for repair work is described in Machinery, 1920, vol. 27, p. 381.

## III. WORKS OF REFERENCE

The following works of reference contain useful general information on the electro-deposition of iron. It is unfortunately the case, however, that they are, most of them, out of date.

E. JORDIS.

“Die Elektrolyse wässriger Metallsalzlösungen,” pp. 63 to 66. (1901, Knapp-Halle).

A. WATT (Ed. A. PHILIP).

“Electro-plating and Electro-refining of Metals,” p. 348 et sq. (1902, Crosby, Lockwood & Son.)

B. BLOUNT.

“Practical Electro-chemistry,” pp. 281 to 283. (1906, Constable.)

M. SCHLÖTTER.

“Galvanostegie, 1. Teil. Über elektrolytische Metallniederschläge,” pp. 81 to 101. (1910, Knapp-Halle.)

W. G. McMILLAN (Ed. W. R. COOPER).

“A Treatise on Electro-metallurgy,” pp. 230 to 236, and p. 289. (1910, Griffins.)

A. J. ALLMAND.

“The Principles of Applied Electrochemistry,” pp. 121, 229 et sq., and 316. (1912, Arnold.)

F. FOERSTER.

“Elektrochemie wässriger Lösungen.” (1915, Barth-Leipsic.)

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