

# THE FORMS OF ELECTRO-DEPOSITED IRON AND THE EFFECT OF ACID UPON ITS STRUCTURE.

## PART I. DEPOSITS FROM THE CHLORIDE BATH.

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### INTRODUCTION.

During the last three years the author has been able to examine with the microscope a large number of samples of electro-deposited iron. The variety of structure shown by the metal upon such examination was so great that there seemed, at first, but little chance of reducing the chaos to ordered classification of forms. It is, however, known that in the consolidation of deposited metal one has to do with a crystallisation process,<sup>1</sup> and it is also known that the result of that process—the crystal grains—depend for their size and shape upon the conditions under which they are formed. A search was, therefore, made through the literature to ascertain whether anything relating to deposited metal could be found that would be helpful. This search disclosed that there was very little information contained in the literature of electro-metallurgy that threw light upon any association between the structure and conditions of formation of coherent and crystalline deposited metal; but some work published by A. Sieverts and W. Wippelmann,<sup>2</sup> in 1915, upon the structure of electro-deposited copper, as also a paper published by O. Faust<sup>3</sup> upon the structure of the same metal, showed that there is, in the case of copper, a definite relationship between structure and conditions of formation. As a consequence, a series of experiments was carried out with the object of establishing, if possible, the various sets of conditions of deposition that would lead to this or that form of structure of deposited iron. The results obtained were encouraging: they are embodied in a report made upon electro-deposited iron to the Scientific and Industrial Research Department. Examination of still other samples of the deposited metal, formed under known conditions, confirmed these results; and the author was fortunate enough to find among the samples examined during this later work one that contained in itself many, if not, perhaps, all, the different forms of structure that had been previously observed in the individual specimens. This deposit is, therefore, interesting in that it can be looked upon as an epitome of many others; and it is of added interest for the reason that in it is very clearly shown the effect of the presence of acid in the electrolyte upon the structure of the deposited iron—a matter not particularly considered by the author elsewhere. It may be remarked that the deposit was formed in the chloride bath, as is described below: the present communication has reference to the structure of such deposits only.

<sup>1</sup> Cf. F. Foerster, *Elektrochemie wässriger Lösungen*, 1915, p. 328.

<sup>2</sup> *Zeit. anorg. Ch.*, 1915, Vol. 91, p. 1.

<sup>3</sup> *Ibid.*, 1912, Vol. 78, p. 201.

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## DEPOSITION.

The solution employed was composed of ferric chloride and calcium chloride, dissolved in water. Ferric chloride was used as no ferrous salt was available. It was necessary, therefore, to first reduce the ferric iron to the ferrous state, and this was done by adding HCl to the solution and passing a heavy current through the bath between sheet-iron electrodes. The course of the reduction was checked by testing for ferric iron with the usual reagents.

Before describing the formation of the deposit that is, in particular, the subject of this communication, five deposits which were formed under the conditions given in Table I. will be considered. These deposits are referred to here, because they confirm, in several respects, work previously done on the ferrous calcium chloride bath,<sup>1</sup> and, further, they show the effect of the presence of acid in the depositing solution upon the macroscopic appearance of deposited iron.

## A. EXPERIMENTS ON THE EFFECT OF ACIDITY.

The solution consisted, in the first instance, of:—

FeCl<sub>3</sub> solution . . . sp. gr. = 1.375 (56 per cent. FeCl<sub>3</sub>),  
and CaCl<sub>2</sub> anhyd. . . lbs. 5

The volume of the solution was 3 gals., and it was contained in a rectangular wrought-iron tank, lined with asbestos board. The anodes were  $\frac{1}{16}$  in. steel sheet (9 ins. × 6 ins.). The cathode was, in each experiment, a short length ( $1\frac{3}{4}$  in.) of solid copper rod, highly polished and carefully cleaned. The acidity of the solution, after reduction of the ferric iron to the ferrous condition, was such as to turn red Congo paper to a grey-blue colour.<sup>2</sup>

*Conclusions from Experiments 1 to 5.*

1. Very slight acidity results in a deposit that is either matt or very minutely crystalline. The aspect of the deposit usually changes, if the period of deposition is considerable, from dull matt to minutely crystalline.
2. A deposit formed in a *slightly* acid is somewhat malleable (Nos. 1 to 4).
3. Considerable acidity causes the deposit to be bright and, to the eye, non-crystalline (No. 5).
4. Considerable acidity causes the deposit to be hard (*cp.* Nos. 1 to 4 with No. 5).
5. Once the bath is acid, considerable time is necessary to effect neutralisation by means of passage of current (Nos. 1 to 4).

*The Effect of Acidity* upon the macroscopic aspect of the deposit is, therefore, to reduce the size of the grains of which it is composed.<sup>3</sup> The following series of changes of aspect is noted as the solution changes in reaction from acid to neutral:—

Bright, and, apparently, non-crystalline → dull matt, and, apparently, non-crystalline → dull, but minutely crystalline → glittering and crystalline → coarsely crystalline.

<sup>1</sup> Sometimes known as the Fisher and Langbein bath. D.R.P., No. 212,994 (1908); D.R.P., No. 228,893 (1909); D.R.P., No. 230,876 (1910).

<sup>2</sup> It was considered superfluous to use solutions of known strength in acid. For present purposes colour comparisons of Congo paper appear quite sufficient.

<sup>3</sup> Cf. Sieverts and Wippelmann, *op. cit.*; and for the effect of acid in the Bett's lead refining solution, *v. W. D. Bancroft, Trans. Am. Electroch. Soc.*, 1912, Vol. 21, p. 233.

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TABLE I.

No. of Expt.	C.D., Amp./Ft. <sup>2</sup>	E.M.F. Volt.	Temp. °C.	Time, Hr.	Deposit.	Remarks.
1	140	—	95	3	Very good. Light grey. Matt. Malleable.	<i>Acidity.</i> —Congo paper turned grey-blue.
2	140	—	95	3	Good. Light grey. Crystalline—crystals minute. The outgrowth at the bottom end was rounded.	<i>Acidity.</i> —Congo paper changed only very slightly—to a light slate colour. But there was still sufficient acid to act upon the anodes even when no current was passing.
3	140	1.6	97	2½	Good. Light grey. Matt. and plastic in appearance as No. 1. Malleable.	<i>Acidity.</i> —Still sufficient to turn Congo paper to a slate grey colour.
4	140	1.6	95	4	Good. Light grey. Crystalline—crystals minute. Rounded outgrowth at lower end. A little harder, perhaps.	<i>Acidity.</i> —Only sufficient to very faintly affect Congo paper. The acidity was evidently less than in No. 3.
5	140	—	95	4	<i>At first</i> , before acid addition, light grey and crystalline. <i>Then</i> , after acid addition, light grey. Bright and, to the eye, non-crystalline. Very hard.	<i>Acidity.</i> —Sufficient HCl was added, after deposition had proceeded for a while, to turn blue litmus to a bright red and Congo to a dark blue.

## B. CONDITIONS OF FORMATION OF THE PRINCIPAL DEPOSIT.

The bath used for the experiments 1 to 5 was made so acid that Congo paper was turned to a deep blue-black colour. Two new anodes of sheet iron were employed. The deposit itself is compound, each part being formed during a separate period of deposition, and the two parts being joined by a thin layer of copper. The general details of the electrolysis were as follows:—

*1st Period.*

*Cathode* Copper rod (as in Nos. 1 to 5).

*C.D.* 140 amp./ft.<sup>2</sup>.

*E.M.F.* 0.7 (electrode distance = 3½ ins.) at the beginning, but (volt) this increased as the electrolysis proceeded.

*Temp.* 100° C.

*Time* 7 hours.

*2nd Period.*

Conditions same as in 1st period, except—

*Time* 2¼ hours.

*Details of the Course of the Electrolysis During the First Period.*

*Time, 4 hours.*—One effect of the presence of free acid in the bath was a copious evolution of hydrogen at the cathode. A consequence of this is that the observer can note (roughly) the diminution of free acid content from the lessening of the volume of hydrogen evolution. Using this fact as criterion, the acidity was observed to diminish somewhat rapidly during the initial period of deposition, and then more slowly. HCl solution (1 : 10) was added from time to time in quantities (1 to 2 c.c.) just sufficient to maintain the solution acid. It was noticed, here again, that upon each addition of acid the deposit became more hard and metallic in appearance, and closer in grain, and that *as the effect of the acid diminished (i.e. the bath became less and less acid), so the deposit gradually changed from metallic and bright to matt and reguline, and finally became minutely crystalline.*

*Time,  $1\frac{1}{3}$  hour.*—During this period the additions of acid were discontinued. As a consequence the bath had, at the end of 5 hours' deposition, come to contain very little, if any, free acid. This resulted in some oxidation of the solution, marked by the formation of a skin of oxide on its surface.

*Time,  $1\frac{2}{3}$  hour.*—10 c.c. diluted acid (HCl) were added. The deposit—crystalline before the addition—gradually (but rather quickly) attained the hard and metallic appearance again, and its colour changed from light grey to dark and bluish. At the same time, some outgrowth that had formed round the bottom edge of the cathode changed from a cindery to a rounded form.

At the end of the period the deposit had recovered its light grey and matt appearance, but it did not appear crystalline at all to the naked eye.

The cathode was then removed from the bath.

*Details of the Course of the Electrolysis during the Second Period.*

The cathode was removed from the potash solution in which it had been placed in order to prevent it rusting overnight, and the outgrowth round the bottom edge knocked off or flattened down. It was then cleaned in an electric cleaner, suspended in the cyanide of copper tank for two minutes, in order to form a slight coat of copper upon the iron deposit, swilled through water, diluted HCl, and, again, water, and then returned to the depositing (iron) bath. The solution was made just sufficiently acid to react to Congo paper, and the electrolysis was allowed to proceed without interference, except that the cathode was occasionally removed for the purpose of inspecting it. At the end of the period ( $2\frac{1}{4}$  hours) the deposit possessed the following characteristics: Light grey colour; very obviously crystalline—it was lustrous and sparkling after being washed and dried; so malleable that when struck with a hammer the deposit was easily flattened out. The thickness was 1.5 mm. (approximately), and was uniform all round the annulus.

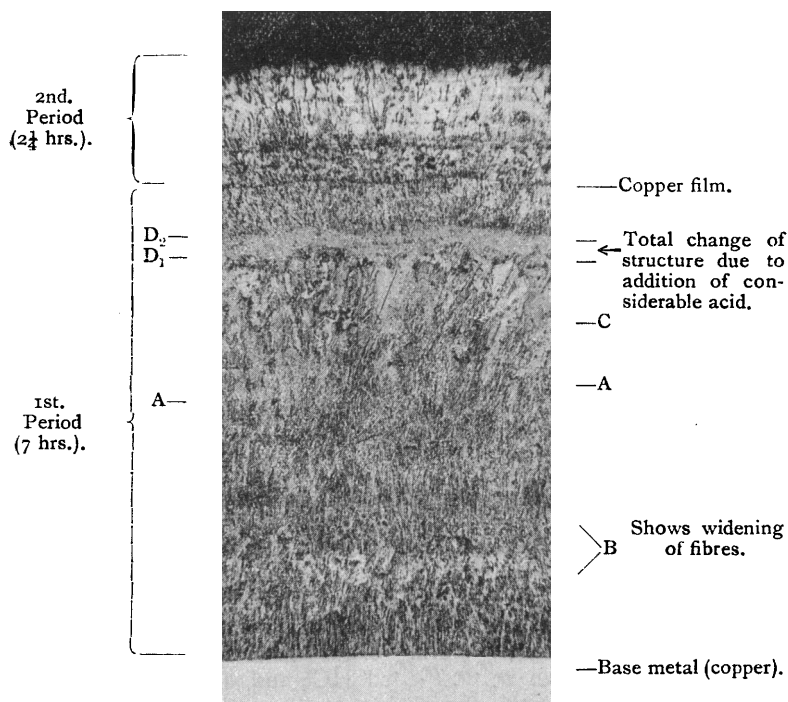
## MICROSTRUCTURE.

Fig. 1 shows a polished and etched cross-section of the deposit. In the first place, it will be noted that the two periods of deposition are separated by a black line—the locus in the specimen of the thin film of

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copper formed upon the iron deposit of the first period. It is very noticeable that the copper cathode on which the deposit was formed has not etched at all. A like remark applies to the thin layer of copper deposited upon the iron deposit of the first period and seen at high magnification in Fig. 2. The copper (rod) base will serve as a starting place for description.

The structure of the iron deposit near the cathode (copper) is clearly of a fibrous type: it continues to be so as far as A (Fig. 1). In this section the only noticeable variation of the structure is the widening of the fibres in places, as, for instance and especially, at B. In the section C there is a continuous broadening of the fibres from within outwards so

FIG. 1.  $\times 60$ .

that the grains lose entirely their fibrous form, and the deposit becomes of the normal type. At D<sub>1</sub> a complete change of structure occurs. The deposit between D<sub>1</sub> and D<sub>2</sub> can scarcely be seen (at the magnification of the photograph) to have a structure at all, except towards the outer edge of the band where the apparently structureless deposit merges into metal possessing a distinctly fibrous structure. From D<sub>2</sub> to the thin copper (the dark line in the photograph) the structure remains fibrous, though as the copper layer is approached the fibres broaden somewhat.

The section of the deposit above the copper layer is the part formed during the second period of deposition. It is obviously fibrous within and gradually becomes coarser and more open as the periphery is approached. Some circumferential lines are noticeable in this section. It

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may be said at once that most, at any rate, are due to removal of the cathode from the bath for inspection purposes: the lines indicate, therefore, breaks in the continuity of the deposition.

## CORRELATION OF CONDITIONS OF DEPOSITION AND STRUCTURE.

If the observations made upon the changes in the appearance of the deposit during its formation be borne in mind when studying the structure of the deposit as shown in Fig. 1, it becomes clear that a number of definite conclusions can be drawn with respect to (1) the relation between macroscopic and microscopic features, and (2) the effect of the conditions of deposition of the metal upon its structure—in the particular instance the effect of acidity.



—Copper film.

Shows the thin un-etched copper film.

FIG. 2  $\times 3000$ .

(1) *Relation Between Macroscopic and Microscopic Features.*

Briefly, it can be said that the connection between these features is so close that an operator can form an opinion as to the internal structure of a deposit as a result of his periodical inspection of the exterior. For instance:—

(a) A very close-grained, matt, and, so far as the unaided eye can see, non-crystalline exterior connotes a fibrous interior; while

(b) A crystalline external appearance is the mark of a coarse grained internal structure—one that approaches more or less closely to the normal type.

(c) A bright metallic appearance indicates that the internal structure is of such fine grain that it is visible at higher magnification only.

A knowledge of these relations between macroscopic and microscopic features is of great importance in connection with the proper control of the deposition of iron in the workshop.



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(2) *The Effect of Conditions of Deposition (Acidity) on Structure.*

This can best be seen if the conditions obtaining during the formation of the deposit be set side by side with its structure. The periods into which the whole time of deposition is divided clearly correspond with the formation of the different types of structure seen in sequence in Fig. 1.

TABLE II.

Time (Hours).	Conditions.	Structure.
1st period 4	Periodical small additions.	Fibrous to lenticular.
1½	No further addition of acid, nor other interference with the deposition process.	Gradual change from fibrous to normal.
after 5	Considerable addition of acid.	Complete change of structure—normal to extremely fine-grained (structureless at low magnification).
1½	No further addition of acid.	Change in structure from extremely fine-grained to fibrous.
2nd period 2¼	Solution acid at the start. No change in the conditions except such as are caused by the electrolysis itself.	Gradual change from fibrous to coarse-grained.

The conclusions which, it is suggested, can be drawn from the observations contained in Table II. are:—

1. Acidity causes the deposit to possess a fibrous structure: excess of acid causes the structure to be of extremely fine grain.
2. As the acid diminishes in concentration the structure of the deposit change from fibrous to the normal type.
3. Undisturbed deposition results in a structure that becomes coarser and coarser in grain size as the deposition continues. It may be added that this increasing coarseness is marked, macroscopically, by increase in the size of the crystals on the surface of the deposit.

## TYPES OF STRUCTURE OF ELECTRO-DEPOSITED IRON.

As the result of the examination of a very large number of specimens, the author has come to the conclusion that, as regards iron deposited from chloride baths, the great variety of structure seen in the metal, upon examination of it with a microscope, is misleading. One is apt to suppose that the types of structure characteristic of the metal is very great: it is suggested here that, really and truly, the varieties seen are variations of two characteristic types. These two characteristic types are they which have been several times referred to in the foregoing as—

- (1) the *normal*, and
- (2) the *fibrous*.

Of these, the former does not actually occur; it is the standard or model to which the structures of deposits formed under given sets of conditions are referred—which they more or less closely approximate.

*The "Normal" Type of Structure.*

A deposit of true normal structure would, in section, appear as though it consisted of grains that, all of them, possessed the shape of the longitudinal section of a cone, the boundaries of each grain forming the letter V. The size of grain and the magnitude of the angle of the V vary from grain to grain. It is as if the deposit were composed of a multitude of cones of various dimensions, all situated with their solid angles towards the base metal on which the deposit is formed. This is the type of structure to which approximation is more or less close where the deposit is formed under one set of conditions, which is characterised by absence of motion—whether of electrolyte or electrode—and neutral reaction. A deposit formed in a "still" vat and neutral solution will approximate more or less closely to the normal type of structure. The closeness to which the normal structure is approached depends, in each case, upon the particular set of conditions that has obtained during the formation of the deposit. Temperature, current density, concentration, absence or presence of floating matter (oxide or other) suspended in the solution, and other factors—all and each—influence or affect the degree of proximity to the normal. But such factors do not, any one or all of them together, cause a change to a completely different type of structure: the varieties of structure produced by the operation of such factors are varieties of the normal type. It is suggested that a general survey of the forty or so micrographs contained in the report on electrolytic iron before referred to shows that this last statement is true—at least in regard to differences produced by temperature and current density changes. The differences effected by these factors result, in fact, from concentration changes—alterations in the concentration of metal ions in the immediate neighbourhood of the cathode. And hence, concentration may be added to temperature and current density as a factor that affects the variety of the normal type of structure that a deposit will have: like these it does not change the type.

*The "Fibrous" Type of Structure.*

This, the alternative, type of structure seen in iron deposits formed in the chloride baths is, in longitudinal section, characterised by an appearance suggesting that the deposit is composed of a mass of threads or fibres situated at right angles to the cathode surface. The fibres may (and do) vary in thickness from sample to sample, but the form of the grains has nothing in common with that of those of the normal type of structure. This type of structure is quite characteristic of deposits formed in (i) a well-agitated solution, or (ii) a bath that contains free acid. If two baths be made up that differ only in that the one contains free acid while the other is neutral in reaction, the deposits formed in them, as "still" baths, under like conditions of deposition, will differ in that the deposit formed in the acid bath will possess the fibrous structure, while that laid down in the neutral bath will possess a structure of the normal type. This is shown by the alteration of *type* of structure, caused by acid addition, in the deposit that has been considered above. It is true that, for the formation of this deposit, one bath only was used; but addition of acid to the neutral solution in effect resulted in the constitution of an acid bath in all respects similar to the neutral bath, except for the presence of free acid. The change in type of structure, resulting from the addition of acid, was always one from normal to fibrous, marked by a change in



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the macroscopic appearance of the deposit from coarsely crystalline to bright, metallic, and, to the eye, non-crystalline. It will be shown elsewhere that this change may be brought about so suddenly that the form of the surface deposit existent at the moment when the acid is added can be fixed, so to say (*v. Fig. 2*); and this fact may be put to an interesting purpose.

Again, if two baths be made up that are in composition alike, and deposits formed in them under otherwise the same conditions, except that, in the one case, there is no mechanical agitation, while, in the other, either the solution is well agitated or the cathode is moved (fixed on the end of a rotating spindle, say), then the deposit formed in the "still" vat will possess the normal structure, while that formed in the other will be fibrous. The difference of type of structure brought about by the difference—absence or presence of mechanical agitation (or movement)—occurs every time. It is not a chance effect. It is not suggested that *any* degree of agitation is sufficient to effect the change. Concentration or convection currents will not, it seems, produce it; nor will liquid diffusion or the movement due to gas evolution at the cathode do so. The requisites for the formation of the fibrous structure seem to be either (*a*) constancy of concentration of metal ions in the cathode layer of electrolyte, or (*b*) presence of free acid; and the effect of mechanical agitation is, *ceteris paribus*, to maintain constant the necessary concentration of metal ions in the cathode area.

*The Connection Between the Normal and the Fibrous Types of Structure.*

It has been seen that a gradual change of structure occurs—from fibrous to normal—as an acid solution changes gradually to neutral. It has also been shown that a change occurs in the reverse direction when acid is added to a neutral, but that the change is more or less (sometimes, quite) sudden. Similarly, in the case of an agitated solution, when this is neutral in reaction, stoppage of the agitation results in a change of structure from fibrous to normal. A change from one type to the other may, then, occur, and the change may be gradual—at any rate in one direction, namely, fibrous to normal. Nevertheless, it is suggested that the two types of structure are separate and distinct, each type resulting from definite and known conditions which it is known beforehand will produce that type. Varieties of each type may and do occur; but so far as the author's experience goes, these varieties of type are as distinct as the types themselves. For instance, variation of a condition of deposition when the essential requisites to the formation of the fibrous structure obtain will cause a variation of the fibrous type: the variety will not be one of the normal type.

*On the Effect of the Composition of the Electrolyte on the Structure.*

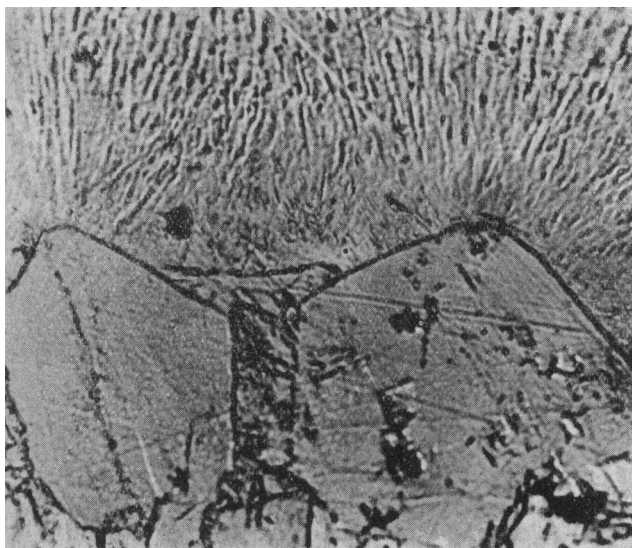
The foregoing considerations are concerned with deposits from the chloride bath: the deposit of which the structure has been particularly described was formed in such an one. The question now arises: Are the same two types of structure, the normal and the fibrous, to be found in deposits formed in baths of other composition than chloride?

Solutions may differ from the chloride (1) in that they contain other acid radicals, or (2) because they contain some substance of the kind often

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referred to as an "addition agent," by which is usually meant an organic substance, such as a gum, oil, gelatin, a sugar, and many others. The question really becomes: What is the effect the acid radical or an "addition agent" upon the structure of an iron deposit? This matter is at present under investigation.

$D_1D_2$ —  
of  
Fig. 1.



Shows how addition of acid may cause such complete change of structure as to fix a surface.

FIG. 3  $\times 1500$ .

## SUMMARY.

It is suggested that it is shown in the foregoing that:—

1. The effect of acid upon the structure of an iron deposit formed in the chloride bath is to prevent the usual (normal) structure being obtained, and that the structure of a deposit laid down in an acid bath will be fibrous.
2. Structures found in iron deposits formed in chloride baths are varieties of two general and distinct types, namely, the normal and the fibrous; and that the type which is obtained depends upon the particular set of conditions that prevail during the deposition, the fibrous type being characteristic of deposits formed in (a) acid, and (b) agitated solutions.
3. Macroscopic features correspond to definite microscopic structure—a fact which enables the depositor to control the process more effectively.