CHAPTER IX.

THE MACRO-STRUCTURE OF STEEL, SULPHUR PRINTING AND HEAT-TINTING.

METHODS of showing the general distribution of the metalloids in steel sections are useful, for by this means local segregations of impurity can be readily and rapidly detected. Etching the complete section in 20 per cent. nitric acid in water produces darker stains on the metal surface wherever higher phosphorus is concentrated. The same result follows the etching by Heyn's reagent, a 10 per cent. solution of cupric ammonium chloride in water, but has the advantage that the stains due to phosphorus are more adherent. In using this reagent it is important to have the metal surface quite clean and perfectly dry, and to immerse the specimen completely in the solution and keep it there for about two minutes; it is then removed and the deposit of copper removed under a stream of water, while gently rubbing the surface with the fingers or a piece of chamois leather. Figs. 183 and 184 represent the structure of rails by Heyn's reagent.

The other method is that described as auto-sulphur etched printing.

AUTO-SULPHUR PRINTING.

Auto-sulphur printing is a method employed for making the portions rich in sulphide in steel and iron indicate their own presence and locality on specially prepared printing paper, or a specially prepared tissue. It was Professor Heyn who first designed a good working method. He impregnated strips of fine silk with mercury chloride and placed them on the polished surfaces of the steel or metal. The upper surfaces of the silk are then moistened with a dilute acid, which, passing through the meshes of the fabric, attacks the sulphides, decomposing them with the liberation of hydrogen sulphide. The hydrogen sulphide, in its turn, attacks the mercury salt. The strips when removed have printed on them stains of mercury sulphide varying in depth of colour and position with the quantity and position of the sulphide in the metal specimens.

The reason for employing the mercury salt, instead of one of silver, is because it is unacted upon by any phosphine or hydrogen phosphide which might be liberated, should the metal contain phosphorus, whereas the silver salts are darkened by phosphine, unless care be exercised in carrying out the operation.

Notwithstanding that Heyn's method is based on more scientific principles, it has been largely superseded in practice by the process of Baumann. In applying this method silver bromide printing paper, after soaking in very dilute sulphuric acid (1 to 3 acid and 99 to 97 per cent. water), is placed on the metal surface and, just as in Heyn's process, the acid attacks the sulphides, and the liberated hydrogen sulphide acts on and darkens the silver bromide.

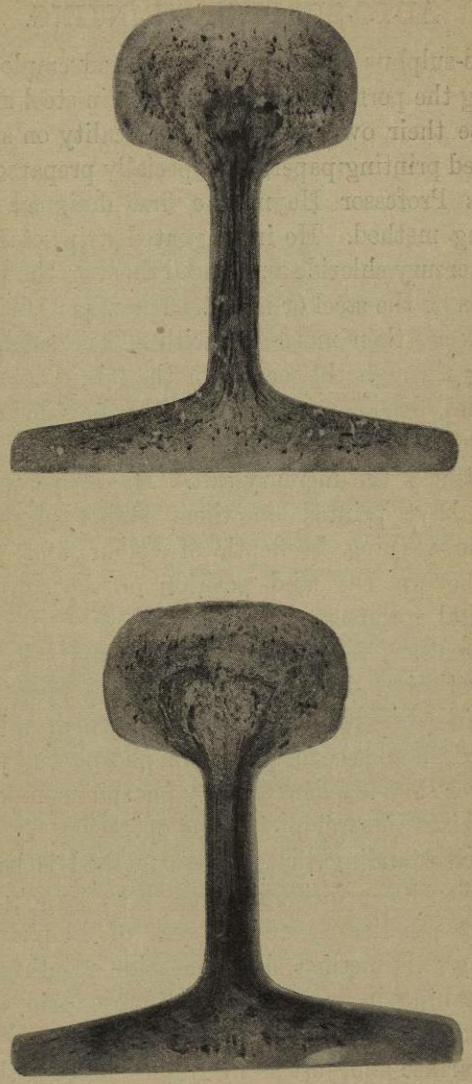

Fig. 189.—Auto-sulphur prints of two rails from different parts of the same ingot. The dark spots represent portions rich in sulphides.

The auto-print is then removed from the metal, washed in water, and the excess bromide is removed by sodium hyposulphite. The print is finally washed in water and dried.

The acidulated printing paper is kept in contact with the specimen for about one minute.

Reproductions of auto-sulphur prints are given in figs. 115, 173, and 189.

To determine whether the phosphine liberated by very dilute acid stains the paper, a brightly polished specimen was first soaked in the acid itself until all the readily soluble sulphides were removed. The polished face was then rubbed with a clean rag so that the surface of the pure metal was exposed, after which a strip of the acidulated bromide paper was pressed on the surface and allowed to remain there for one minute. On removing the strip of paper the stains were almost imperceptible. Considering the fact that the specimen experimented upon contained 0·5 per cent. of phosphorus, it may be assumed that phosphine liberated during two minutes is practically without effect on the silver paper.

As the Baumann method is so simple in its application, and gives practically the same result as Heyn's method, it is the one almost invariably used.

When it is desired to produce lantern transparencies, bromide-coated glass plates are substituted for the bromide paper. The specimens for this purpose must be perfectly flat and well polished, and the bromide plates must be soaked in a solution one part of acid in two hundred parts of water. The acid-soaked plate is removed from the bath and placed on a flat, smooth surface, with the silvered side uppermost; a layer of acid is now poured on the surface to the depth of about 1 mm. The polished specimen is then rapidly pressed on to the plate, when it instantaneously sinks through the upper film of liquid and comes in contact with the bromide on the plate. A weight is placed on the back of the specimen to bring the metal into close contact with the sensitised surface, care being taken not to cause the specimen to move when applying the weight.

After remaining in contact for two minutes the sensitive plate is removed, washed in water, fixed in hypo, again washed in water and dried. It is sometimes convenient when more than one print on bromide paper is required to use very dilute acid instead of that containing 1 to 3 per cent. If this is done several successive prints can be obtained without re-grinding and re-polishing the metal.

Fortunately, in the preparation of the specimens for auto-sulphur printing, it is not necessary to go beyond No. 1 fine English emery paper in preparing the surface. The printing is quite as effective whether fine scratches are present or absent.

When exploring fractures of ingots with the object of determining whether the gas cavities contain sulphide segregations, it has been found useful to grind up pieces of bromide paper with dilute sulphuric acid so as to make an acidulated pulp. Portions of this are pressed into the blowhole cavities and are then drawn out again with a hooked pin. If there is sulphide segregation, the pulp will be stained almost black.

Dr F. Rogers has developed a method for showing the sulphur distribution on the fractured surfaces of steel without the troublesome necessity of polishing the surfaces. In his method the silver preparation is fixed on a plastic bed. After acidulation the tissue is pressed on to the fractures, and, being plastic, comes in contact with every part of the uneven surfaces.

HEAT-TINTING.

Heat-tinting consists in heating polished specimens of metal until the surfaces become coloured by oxidation films.

Alloys of iron and phosphorus, and commercial steel, contain part of their mass richer in phosphorus than other portions. In fact the iron and the phosphide are seldom intimately mixed in ordinary steel. When polished specimens are placed on the surface of a molten bath of tinman's solder, and the heat gradually raised, the portions of the specimen richest in phosphorus assume oxidation tints earlier than the purer parts; hence it follows that by the time the phosphorus-rich parts have passed through the transition stages of yellow-brown to red and purple, the purer portions will have reached the yellow-brown or red stage, and if at this point the specimen be removed from the source of heat, the phosphorus-rich portions will appear under the microscope as purple or blue on a yellow-brown or red background (see fig. 190). If the heating of the specimen be continued, the phosphorised part will assume a yellowish-white tint, while the purer part will reach the blue stage. Each part will pass through the complete range of colour from yellow to blue and then to nearly white, but not at the same time, because the purer portions always lag behind, the degree of lag depending on the variation in the proportions of phosphorus in the different parts.

Heat-tinting is also useful in intensifying the difference in colour between ferrous sulphide and manganese sulphide when present together in steel. On heating polished metal containing inclusions of each sulphide until it appears to assume a uniform brown tint, the ferrous sulphide, which is naturally pale yellow, will be found under the microscope to have been coloured purple, while the manganese sulphide, naturally a pale dove colour, will have become nearly white. If the heating be continued until the surrounding metal becomes blue, the ferrous sulphide will be blue and the manganese sulphide yellow.

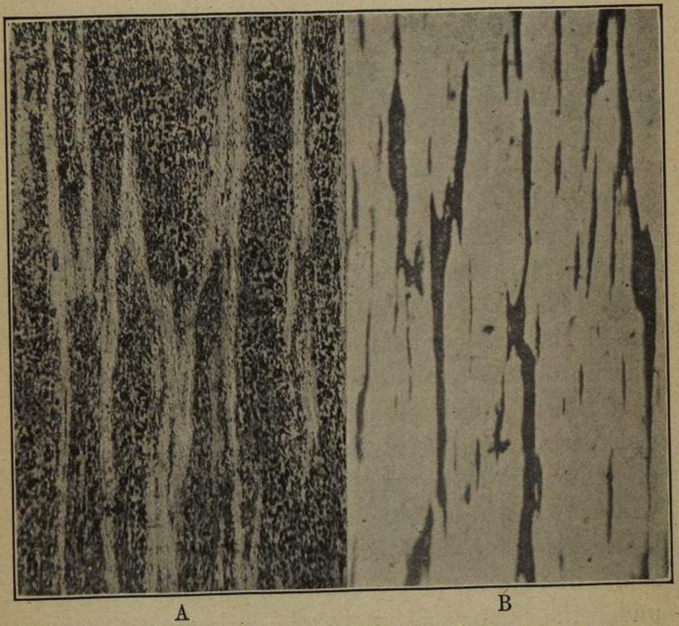

Fig. 190.—Forged steel containing about 0·3 per cent. carbon and 0·3 per cent. phosphorus.
A. Polished and etched in the ordinary way. B. Heat-tinted until the phospho-ferrite bands are oxidised to a brown tint.

To obtain good results by heat tinting, it is absolutely necessary first to apply to the surface a very dilute solution of some acid in alcohol. Picric acid answers admirably, but care must be taken to remove the solution employed before it has time to develop the pearlite or sensibly to etch the metal. After thoroughly washing the specimen in water, it is dried with a perfectly clean rag and heated on a hot plate to about 150° C. It is again rubbed with a warm clean cloth, and is then ready for heating to produce the colour tint.

It is difficult to explain why the preliminary acid treatment is necessary, but that it is so is proved in practice, for if it is omitted, the tinting is always unsatisfactory. It is possible that, during polishing, some of the softer metal becomes spread over the harder part, forming an exceedingly thin layer. This, however, is only a surmise.

CHAPTER X.

CONCLUSIONS.[1]

Theoretical Conclusions.—When the first French edition of this work was published, I was not fully prepared to draw all the conclusions possible. The principal conclusion was that the resemblance of quenched steel to solid solutions was placed beyond all doubt, and most convincing examples of the resemblance of solid solutions to liquid solutions were found.

The progress of physico-chemistry was, however, needed in order to appreciate this conclusion in all its bearings. An article by Le Chatelier,[2] and a discussion on a paper by Sauveur on "The Micro-structure of Steel and the Current Theories of Hardening,"[3] the lecture by myself before the Congress of the International Testing Association held at Stockholm in 1897, the fourth and principally the fifth report of Roberts-Austen to the Alloys Committee of the Mechanical Engineers,[4] several essays of Juptner,[5] and lastly, an important work by Professor Roozeboom,[6] mark the principal stages of subsequent progress.

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[1] This chapter is a revised reprint of the chapter by Mr Osmond in the original edition of this work.

[2] *Revue Générale des Sciences pures et appliqués*, 15th Jan. 1897.

[3] *Trans. Amer. Inst. Min. Eng.*, t. xxvii. p. 584.

[4] *Proc. Inst. Mech. Eng.*, Feb. 1897 and Feb. 1899.

[5] *Stahl und Eisen*, 1898, fasc. 11/2/3/22.

[6] *Bull. Soc. d'Encour.*, Nov. 1900.

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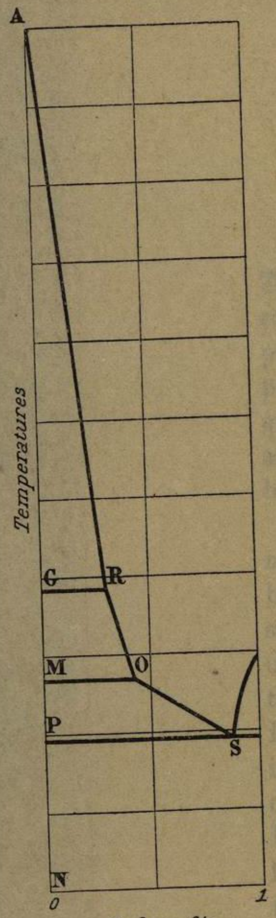

Fig. A.

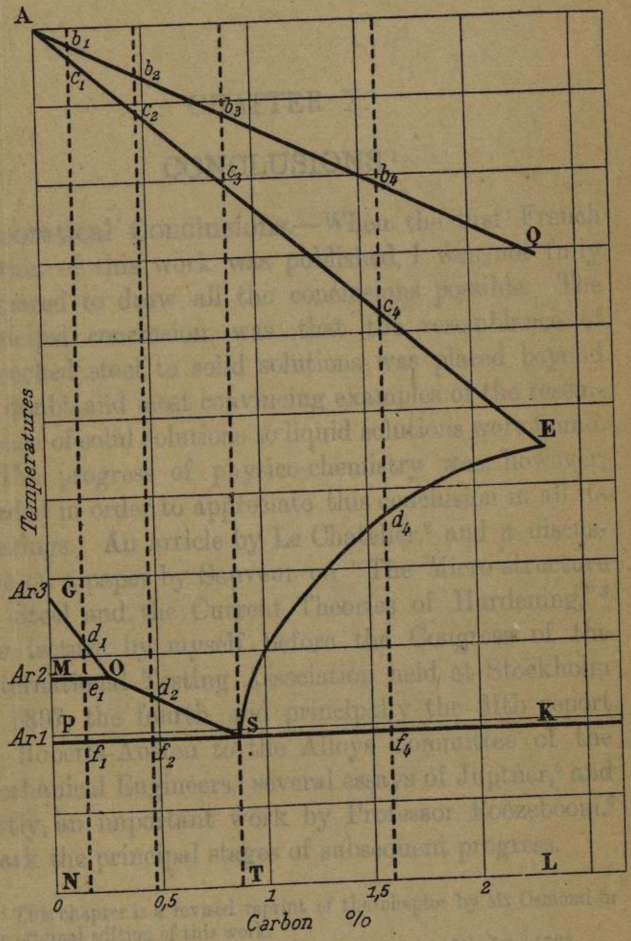

Fig. B.

Even now, although the bearing of certain facts may still be disputed, such modifications as may become necessary will probably be of secondary importance, and the Roozeboom diagram is still the foundation upon which modern theories are built.

Plate III., fig. B, shows diagrammatically the curves of transformation (or equilibrium) of carburised irons between essentially 0 per cent. and 2 per cent. of carbon. The abscissæ are the carbon, and the ordinates the temperature. AQ is the curve of the commencement of solidification, according to the experiments of Roberts-Austen and Stansfield.

The curve AE represents the end of solidification, and has not been determined experimentally: it has been introduced by Professor Roozeboom as a result of a theoretical hypothesis constantly verified in similar cases.

ES shows the commencement of the separation of the cementite. Its existence is proved by the fact that in steels of considerable carbon content the cementite does not appear when quenched below a certain temperature, and has been confirmed by the thermal method in Roberts-Austen's trials.

The branch GO from the point G (Ar_3) shows the transformation of the γ iron to β iron, and the commencement of the separation of ferrite in soft steels.

MO from the point M (Ar_2) is the transformation from β to a, or, more precisely, the beginning of the transformation, which is really progressive.

OS from the point where GO and MO meet gives the transformation from γ to a, and the commencement of the separation of ferrite in steels of ordinary carbon content.

The point S, where OS and SE intersect, is a

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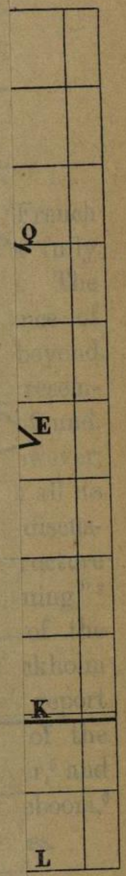

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OS from the point where GO and MO meet gives the transformation from γ to α, and the commencement of the separation of ferrite in steels of ordinary carbon content.

The point S, where OS and SE intersect, is a eutectic point. The horizontal line PSK passing through this point corresponds to the recalescence and simultaneously to a deposit of ferrite and cementite, as pearlite. These four branches GO, MO, OS, and PSK have all been determined by several concordant experiments.

The different branches of diagram, fig. B, divide the total area into partial areas, which bear the name "*regions*," and which are defined as follows:—

AESOG is the region in which the iron, in the γ state, contains the carbon, free or otherwise, in solid solution. This solid solution is crystalline. From the study M. Cartaud and I have made, these crystals appear to be fragments of cubes mutually limited and intercepted by numerous lamellæ of twin crystals, or, in a less perfect state, of crystallites of the same type we meet with in martensite, in non-magnetic manganese steels, and certain steels high in nickel. We have proposed, for them, the name of "mixed γ crystals."

The mixed γ crystals are associated with—

1. A liquid residue rich in carbon in the region QAE.
2. The cementite in the region ESK.
3. Free β iron „ „ GOM.
4. „ α „ „ „ MOSP.

Below PSK we have the region of mixed ferrite and cementite, which divides into two sub-regions:—ferrite and pearlite on the left of the vertical ST passing through the eutectic S, and pearlite and cementite on the right of this vertical.

It is now easy to trace the transformations, as much physico-chemical as structural, in a steel of given carbon content. It is sufficient to trace as abscissæ this carbon content, and to follow it in connection with the branches of the diagram.

We will choose as nearly as possible the same steels as those the micro-structure of which we have already studied.

I.—STEEL WITH 0·14 PER CENT. CARBON.

The solidification starts at b_1 and finishes at c_1. From c_1 to d_1 the metal is in the state of mixed γ crystals. Quenching gives pure martensite. At d_1 we have the transformation of γ iron to β iron—that is to say, the β iron separates from a solid solution. The separation is progressive, and the solid solution equally increases in carbon: it contains at the point e_1 a percentage equal to the abscissæ MO. Beginning at e_1, the β iron transforms to α iron, while the solid solution continues to enrich in carbon, the α iron separating out. This continues until the strength of the solution reaches the value PS, practically about 0·85. In f_1 the solid solution transforms to pearlite, on account of the simultaneous separation of the very divided ferrite and cementite.

The examination of the micro-structure is, as we have seen, in accordance with these deductions, and, except on one point, the steel with 0·14 per cent. carbon quenched between c_1 and d_1 ought to be pure martensite, whereas we really have a mixture of martensite with a proportion of ferrite crossing at d_1 towards c_1. If, then, this ferrite is not isolated during the little time the cooling lasts, and if it really existed in the metal at the initial temperature of quenching, we must add to the diagram a line like

AR starting from the point of solidification of pure iron and corresponding to a separation of γ iron from the solid solution (Plate III., fig. A). One can still imagine a similar branch starting from the critical point of Ball and corresponding to a transformation of δ iron to γ iron. This requires elucidation.

II.—STEEL WITH 0·45 PER CENT. CARBON.

The solidification commences at b_2 and ends at c_2. Between c_2 and d_2 the metal remains in the state of mixed γ crystals, and quenching yields pure martensite. At d_2 the iron begins to change to the α state, and the separation continues progressively as far as f_2, the solid solution correspondingly enriching in carbon to 0·85 per cent. At f_2 this solid solution transforms to pearlite, as above.

In this case the diagram is in absolute agreement with the micro-structures.

III.—STEEL WITH 0·85 PER CENT. CARBON.

We have here only a single transformation at S of the mixed crystals to pearlite. We find pure martensite in hardened steel between c_3 and S, and pure pearlite below S, whatever the method of cooling. This is also what occurs practically.

IV.—STEEL WITH 1·57 PER CENT. CARBON.

Solidification begins at b_4 and ends at c_4. Methodical tests have not been made of this region, the existence of which was never suspected before the intervention of Roozeboom. I have two or three sections which were quenched under the necessary conditions, and I notice that the micrographic indications of troostite are visible all along the joints. It would not be impossible for these parts to represent the liquid residue at the moment of immersion. This is, however, hypothetical.

Between c_4 and d_4 we know that the quickest quenching, or that which keeps them best *in statu quo*, gives a mixture of austenite and hardenite. Nothing in the diagram indicates the presence of a new constituent. Professor Roozeboom has investigated this matter, and has proposed very ingenious explanations. Another explanation may be given without the formation of a new phase. It must be noticed that the martensite cannot represent the *intact* mixed γ crystals: they keep their crystalline forms well, but, since it is magnetic, part of the iron must return to the α state. Austenite, on the contrary, which there is reason to consider non-magnetic, can represent *intact* mixed γ crystals. That granted, we see that the greatest proportion of carbon which can be in solid solution in iron is 1·80 to about 2 per cent.—a quantity insufficient by itself to maintain, on account of the osmotic pressure involved, the whole of the iron in the γ state, so rapid is the cooling. The transformations then will commence, but they will not commence at random. They begin with cleavage planes of mixed crystals, and continue until the increase of volume, resulting from a partial transformation from γ iron to β iron, would have added to the osmotic pressure of the dissolved carbon a mechanical pressure sufficient to arrest the transformation of the γ iron throughout the remainder of the mass. The hardenite, the edges of which can correspond, and in reality do correspond, to the cleavages, represents the quantity of iron which the partial transformation has necessitated to suppress the transformation of the surplus—that is to say, of the austenite. And that proportion of the hardenite would be as much greater as the amount of total carbon is less, in forming the sole constituent, when the osmotic and mechanical pressure are together insufficient to maintain entirely in the γ state an aliquot fraction of the mass.

Between d_4 and S_4 cementite separates progressively: the amount of dissolved carbon diminishes correspondingly. Quenching between these two points will give mixtures of cementite and hardenite, with eventually a quantity of intervening austenite.

At last, below f_4 there only remains a mixture of pearlite and cementite.

In the above conclusions we have not found a place for troostite or sorbite, nor is this necessary if these constituents are transition forms. The existence of such forms is inevitable, since the transformations require a certain length of time, and they are of great practical importance on account of the mechanical properties which they confer on steel; but the diagram which shows the definite states of equilibrium does not show them.

However, if we remember that troostite does not usually mix with martensite, and if we consider the conditions of its genesis, we may assume that it corresponds to some transitory association between β iron and carbon. This is a question which requires investigation.

In conclusion, we have just seen that, except for a few remaining difficulties which require further research, the results of the study of the micro-structure of steel are in perfect accord with the deductions to be drawn from the diagram of equilibrium curves. Taken alone, this diagram could be constructed in its main lines, as quenching fixes the initial state and suppresses the ulterior transformation, at least in part. On the other hand, the diagram of equilibrium curves could have been constructed independently of micrography by the thermal method. In fact, it has been by the co-operation of the two methods that it has been controlled and, in certain circumstances, completed.

Practical Conclusions.—Setting aside all theoretical speculation, we have seen that—

1. The temperature of heating,
2. The temperature of quenching,
3. The rapidity of cooling,

that is to say, the principal circumstances of the heat treatment of steels, reveal themselves, in the variations of structure, with a precision which the mere inspection of fractures is certainly far from furnishing. But to get any industrial results from these facts, it would be necessary to have the different aspects of the structure correlated with the corresponding mechanical properties.

The practical application of metallography to Metallurgists and Engineers requires, then, for each metal, a preparatory study. But, when this study is made, it will be easy to determine with sufficient exactness the heat treatment undergone by a finished article or piece of metal, to see if this treatment, which is of first importance, has conformed or not to given specified rules, to rectify it if needful, and to take the responsibility in case of rejection. Professor Sauveur, when engineer to the Illinois Steel Company, devised a regular system of micrographic analysis.[1]

For industrial applications the complete method which has been described in this paper will not, as a rule, be necessary. Like the general rules of chemical analysis, this method allows, according to circumstances, simplifications suggested by experience. It is a method of investigation which may be laborious in the case of original research, but which will, eventually, be much simplified.

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[1] *Trans. Amer. Soc. of Min. Eng.*, t. xxii. p. 546.

APPENDIX I.

PURE ELECTRO-DEPOSITED FERRITE.

In a recent research by Stead on Pure Electro-Deposited Iron manufactured by the Langbein-Pfannhauser - Werke, Leipzig - Sellerhausen, some remarkable observations were made.

The analyses according to "Röhl" and "Pattinson & Stead" were as follows:—

	Röhl.	Pattinson & Stead.
	Per cent.	Per cent.
Iron by difference . . .	99·991	99·967
Carbon	Nil	0·008
Manganese	Nil	0·009
Silicon	0·003	0·014
Sulphur	0·006	Trace
Phosphorus	Trace	0·002
	100·000	100·000

The strips of iron when received were exceedingly ductile, and could be cold rolled to eight times their length without breaking up. The iron had evidently been annealed after it had left the electrolytic tank. The crystalline structure was identical with that of the purest commercial ferrite, but the size of the