On the genesis of Widmanstätten structure in meteorites and in iron-nickel and iron-carbon alloys.

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I. Introduction.

In April 1909 a paper on artificial reproduction of meteoric structure in alloys of iron and carbon was read by the author before the Russian Mineralogical Society (Reference 1, see below, p. 183). In that paper special reference was made to the work of Sorby, who, to cite his own words, for ‘more than twenty years . . . commenced to carefully study the microscopical structure of iron and steel in order, if possible, to throw light on the origin of meteoric iron’ (2). A brief survey of the work of Stodart and Faraday, of Osmond, Rinne, and Berwerth was also given and, subsequently, the structure of a carbon-steel containing 0.55% carbon with perfectly developed Widmanstätten figures was described.

This alloy belonged to a series of carbon-steels prepared in 1907 and 1908, at the author’s request, at different Russian steel-works under conditions of extreme slowness of cooling. These researches were undertaken by the author in order to bring into closer harmony the processes of crystallization with the various areas of the equilibrium diagram. The author was deeply impressed by the work of Sorby on meteorites and by that of Anossoff on damascene steel, and, starting under the guidance of his teacher Professor Tschernoff, he ‘directed his early efforts towards obtaining large structures easily discernible with a naked eye’ (3).

Following Anossoff's precepts, the steel alloys were melted in crucibles, over-heated for a certain period of time, and then allowed to cool down slowly in the crucibles together with the furnace. About twenty alloys with carbon-content varying between 0.40% and 2.30% were prepared under conditions of undisturbed and very slow cooling, the interval between 1,500° and 290° C. taking for most of them as much as sixty hours.
Under these conditions all the alloys developed a very fine ‘macroscopic’ crystalline structure and supplied the author with a vast field of research. Particularly beautiful were the crystalline aggregates on the outer crusts of the alloys nos. 1, 2, 5, and 6, and their corresponding macrostructures (4); the real puzzle, however, was offered by the alloy no. 8. The first specimen of that alloy to reach the author was possessed of a characteristic structure of white parallel bands. A first inference to be made was that this structure might be a macroscopic eutectic structure, like that of certain granites and other rocks. As this particular line of research seemed to open vast horizons, a careful study was made of the whole alloy, but, to the author’s disappointment, an entirely new structure was revealed: triangles, equilateral and isosceles, quadrangles, pentagons, and various other configurations, but only exceptionally in sets of parallel lines. Rather reluctantly, this hypothesis of a macroscopic eutectic had to be abandoned and another one substituted; it took the author a considerable time before he realized that in his hands was a perfect example of synthetically reproduced meteoric structure and that the various geometrical markings were, in fact, the famous Widmanstätten figures. As soon as this was realized it became necessary to correlate this structure with reference to the other crystalline structures of the iron-carbon alloys, the network structure and the structure of large crystals. Thus was evolved the hypothesis of the triad of secondary structures, viz. the network structure, the structure of large crystals, and the Widmanstätten structure (5).

In a subsequent paper, presented by the author in the early part of 1914 to the Institute of Metals (6), a further step forward was undertaken and the, so to say, universality of the Widmanstätten structure was shown and its occurrence in various metals and alloys demonstrated. More recently, in a second paper to the same Institute (7), the author returned to the ‘morphological’ aspect of the Widmanstätten structure and the relation of that structure to the inner structure of the crystalline grain.

There remains, still, to follow up, step by step, the genesis of the Widmanstätten structure in alloys of iron and carbon and in those of iron and nickel. Such a study will enable us, it is hoped, to throw some light also on the genesis of Widmanstätten structure in meteorites.

II. The triad of secondary structures in alloys of iron and steel.

Let us consider the equilibrium diagram of iron and carbon alloys (fig. 1). On this diagram temperatures are plotted as ordinates, and the
percentage of carbon as abscissae. The various curves may be interpreted as showing graphically at what temperature a new constituent appears or vanishes in an alloy of a certain concentration. In other words, the equilibrium diagram shows at a glance what changes occur in an alloy and at what temperature they occur.

The first change to be taken into consideration is the solidification or, what might be called, primary crystallization. This transformation from the fluid to the solid state is not instantaneous, but gradual and spreads over a certain interval of temperatures. There are, therefore, on the diagram two curves instead of one: $AC$ and $AE$, showing the beginning and the end of solidification. The area between these two curves may be called the area of solidification or of primary crystallization. This crystallization consists in the formation of 'dendrites' of a solid solution of iron and carbon, and all steels after solidification will be built up of juxtaposed and interlocked dendrites mutually limiting each other. Every dendrite is a chemical as well as a crystallographical unit and continues as such, until a new phenomenon of a crystallographical or of a chemical nature takes place.

After solidification every alloy enters the area $AESOG$ (fig. 1), which may be called the granulation area. In this area the crystallographic unity of the dendrites is destroyed by the formation of the new grains or granulae.
of $\gamma$-iron, and the process continues till the whole mass of the alloy is converted into such new grains or granulae, mutually limiting each other.

As the alloys cool down they reach a new critical range where a chemical change—the decomposition of the solid solution—takes place. The process consists first in throwing out of the excess of one of the components and, afterwards, in a 'eutectoid' transformation at a constant temperature of $695^\circ C$, when the remaining saturated solid solution of the composition $0.90\%$ carbon is wholly converted into a minute aggregate of alternating films or lamellae of the two components, ferrite (pure iron) and cementite ($Fe_3C$). This aggregate was called by Sorby the 'pearly constituent', and is now known as 'pearlite'.

The process just described of chemical decomposition of the solid solution may be called secondary crystallization. It occurs in a mass built up of a number of granulae, which are allotriomorphic crystals. Each granula possesses its own crystallographic orientation and is a distinct crystallographic unit. When the process of chemical decomposition starts there is no reason why it should start in any point of the granula in preference to any other. Only where different grains meet is there a kind of neutral zone—a 'no man's land'—where the crystalline matter cannot assume the orientation of either of the grains. This thin layer is, so to say, predestined to facilitate the ejection of the first particles of the crystallizing element. Given sufficient time and other suitable conditions, the whole of the excess element would be ejected to the periphery of the grain, forming a membrane or a shell of a certain thickness. On a plane section such structure would appear as a cellular or network structure.

If the interval of secondary crystallization is covered rather rapidly, a certain amount of the excess element will be forced to crystallize out 'on the spot', that is, not on the boundary, but in the middle of the grain. Such separation will necessarily follow the crystallographic planes of the crystalline matter. As iron and steel in their $\gamma$-state are arranged in a face-centred cubic lattice, these planes will be the four pairs of the octahedral planes. The separation of the excess element will follow in space these planes. On a secant plane such octahedral sections will appear as Widmanstätten figures (7, p. 380). Such figures will bear a distinct character in every grain. The combination of meshes with these figures, as suggested by the author, might be called Widmanstätten structure, as distinct from the Widmanstätten figures themselves.

A third type of structure might be anticipated if, for one reason or other, the granulation process not having taken place, the secondary
deposits were to arrange themselves parallel to the dendritic axes. Such a structure usually occurs in isolated crystals and was called by the author the structure of large crystals.

These three main types of secondary deposits, the network structure, the structure of large crystals, and the Widmanstätten structure, constitute the triad of secondary structures (8). The Widmanstätten structure, the last-named of the triad, has a particular importance to us, being the structure of the class of meteoric irons called octahedrites.

III. Equilibrium diagram of iron-nickel alloys.

The equilibrium diagram of iron-nickel alloys is based, in the first instance, on the Osmond's hypothesis, that with a very slow cooling the transformations resulting in the decomposition of the solid solution would occur at the same temperatures as the reverse process occurs on heating (9). On the basis of thermal curves on heating and, to a still larger degree, on that of the magnetic transformations, Osmond drew up a diagram given on fig. 2. The area covered by this diagram represents, broadly speaking, the processes which in the iron-carbon alloys were designated as 'secondary crystallization'. The complex of the curves $AE, AB, BCD$, and $FCD$ implies that a decomposition of the solid solution takes place within the areas $AEB$ and $BFCDC$. The products of this decomposition would be two nickeliferous ferrites; one to the left of the diagram with about 7% of nickel, and the other in the right-hand side containing up to about 50%. In meteorites such products are actually met with: they are the well-known kamacite and taenite.

Attempts to produce such duplex structures in artificial alloys were for a very long time without result (10). In 1910, however, Dr. Carl Benedicks succeeded in bringing out the duplex meteoritic structure in an alloy containing 11.7% of nickel (10 i). For a while the conclusiveness of these experiments was contested by Fraenkel and Tammann (10 h), but it was subsequently strengthened in Dr. Benedicks's later paper (11), and further proved in D. and H. Hanson's paper (10 j). The Hanson diagram slightly differs from that of Osmond in that the $FF'$ or taenite line is placed, not at about 50%, but at about 32% of nickel. In all essentials, however, both diagrams are quite similar (cf. figs. 2 and 4).

The Osmond's diagram was adopted for meteorites by F. Rinne in 1905 (12). He even suggested that the classification of meteoric irons might be based on such a scheme, and he introduced the three groups of 'lacunites', 'sublacunites', and 'superlacunites'; the first group roughly
comprising the hexahedrites, the second the octahedrites, and the third
the nickel-rich ataxites. He also suggested the word 'eutropic' for the
transformations in the solid state which in technical alloys are called
'eutectoid' transformations; thus Rinne brought forward again the
analogy between the eutectoid pearlite and the plessite of meteoric irons.
He further added to the Osmond's diagram the then hypothetical lines
of primary crystallization, and thus made the two diagrams as similar as
possible. Afterwards these curves were experimentally determined by
Guertler and Tammann (13), and quite recently confirmed and subst-
tantiated by D. Hanson and J. R. Freeman (14). The latter's diagram
is reproduced in fig. 4. The analogy of the left parts of the diagrams of
fig. 1 (iron-carbon alloys) and of fig. 4 (iron-nickel alloys) is very remark-
able: in both diagrams there are the lines of primary crystallization and
the curves of transformations in the solid state—the secondary crystalliza-
tion. In each case these two areas are separated by areas of solid solu-
tions—the granulation zones. The analogy is further strengthened by
the important fact that both the iron-carbon and iron-nickel alloys
crystallize in the regular system; it is to be noted more particularly
that in both kinds of alloys the solid $\gamma$-solutions of the granulation zone
crystallize in the face-centred cubic lattice.

Therefore, in both kinds of alloys we must expect the occurrence of
similar structures under similar circumstances, and, more particularly,
the appearance, under suitable conditions, of the Widmanstätten struc-
ture. In steels, as previously shown, this structure regularly appears
under favourable treatment, whilst in meteoric irons it has long been
recognized as a characteristic feature.

IV. Granulation hypothesis and $\delta$-iron.

Let us now consider more closely the morphology of the Widmanstätten
structure. This structure is characterized by a combination of a network
and of Widmanstätten figures, both the figures and the network being
secondary deposits of an excess element in a solid crystalline medium.
As the Widmanstätten figures are octahedral sections, the first funda-
mental condition for their appearance will be the octahedral crystalliza-
tion of the solid solution (6, p. 48); in other words, the solid crystalline
matrix where the secondary constituents are deposited must be arranged
in space in the face-centred cubic lattice (7, p. 398).

The second self-evident fundamental condition will be the occurrence
of the secondary crystallization, as it is the secondary deposits which
bring forward the octahedral character of the crystalline matrix. This
second condition implies, therefore, the presence in the equilibrium diagram of the complex of curves of secondary crystallization. But, as shown above in section II, the secondary deposits may lodge themselves not only as Widmanstätten figures inside the granulae, but might segregate completely round the granulae as envelopes; in the absence of granulation they might even lodge themselves parallel to the axes of primary dendrites, as in the structure of large crystals. Only in the first instance will the Widmanstätten structure appear; therefore a third condition is to be added to the two first fundamental ones—namely, the occurrence of granulation and such velocity of transformation as to lead to the separation, of a part at least, of the secondary deposit inside the granulae.

The granulation process occurs after the solidification had been accomplished, i.e. in a solid state. It is governed by Tammann's laws of spontaneous crystallization and of the linear velocity of crystallization. As suggested by the author in a previous paper (4, 1920, p. 16; 5, p. 379), this process might be linked up and even caused by the allotropic change in iron, i.e. by the appearance of a new phase.

As the granulation area is the true γ-zone, there must exist in the solidification range another allotropic modification. This is given by the δ-iron, which has been brought into evidence in the iron-carbon series.
by Ruer and Klesper (15). In iron-nickel alloys the same $\delta$-transformation has been quite recently established by Hanson and Freeman (14). Their diagram is reproduced in fig. 4, where, in the left-hand top corner, the $\delta-\gamma$ transformation is clearly shown. In fig. 3 is reproduced one of the latest iron-carbon diagrams, that of Honda, which also shows $\delta$-iron lines (16). The comparison of these two diagrams brings out very clearly the similarity of the processes in steels and in nickel-irons. In both cases there is a granulation zone, and in both cases too there is the $\delta-\gamma$ transformation.

As previously mentioned, the author suggested the necessity of admitting such a transformation in the iron-carbon alloys. He always felt, however, that until a similar transformation was detected in the iron-nickel alloys, the granulation theory in its application to the Widmanstätten figures of meteorites would not be on a sure basis. He takes, therefore, this opportunity of drawing attention to Dr. Hanson's paper.

Let us consider now the influence of the rate of cooling on the occurrence of the Widmanstätten structure. Let us suppose that the fundamental conditions, already enumerated, are complied with, i.e. that the alloys in question:

1. crystallize in the face-centred cubic lattice;
2. they are subject to transformation in a solid state, i.e. to secondary crystallization;
3. this secondary crystallization occurs in an already 'granulated' alloy.

Then, as previously mentioned, two causes would be open to the secondary deposits: either to segregate at the boundaries, or to separate inside the grains as well. If the whole of the secondary deposit has time to segregate round the granulæ, then a pure network structure would ensue. If, on the other hand, the process were to proceed at a more accelerated pace, a certain proportion of the deposit would be forced to crystallize out 'on the spot', i.e. not at the boundaries, but in the middle of the grains. The acceleration of the rate at which the secondary phases are being deposited usually results from a certain increase in the velocity of cooling; therefore, contrary to what was previously thought (10f), the rate of cooling through the area of secondary crystallization need not be exceedingly slow.

Acting on the previous hypothesis of very slow cooling, the author subjected the first series of his alloys to as long a cooling as was practically possible. In every case the structure was remarkably well developed, but, whilst the hyper-eutectoid alloy with 1.80% of carbon...
had the structure of large crystals, the other one with 0.60 % carbon exhibited a macroscopic network structure with very large meshes, but with only faint signs of ill-defined Widmanstätten figures. On the other hand, the alloys of the second series, and particularly the alloy 'no. 8' with 0.55 % carbon, showed a remarkably developed Widmanstätten structure (fig. 5).

Chemical composition and the size of the granulae of the two last-named alloys ('nos. 5 and 8') are the same; therefore we may infer that the conditions of cooling through the granulation zone were the same. On the other hand, the alloys of the second series were taken out of the furnace earlier than those of the first series, presumably before the secondary crystallization had started. That difference in the conditions of cooling might account for the difference in the separation of the deposits and for the occurrence of the Widmanstätten structure.

In the experiments of Dr. Carl Benedicks (10 i) a procedure was adopted to avoid the dendritic crystallization and thus, so to say, to 'prepare the
ground for a possible Widmanstätten structure. The cooling through the area of secondary crystallization was relatively very slow. On the other hand, Dr. Benedicks was led by his experiments to suggest that in the same area meteorites were cooled relatively rapidly, which is in entire agreement with the author's theory.

There remains still one more important consideration, and that is with reference to the size of the granulæ. The larger the size of these, the more difficult will it be, at a given velocity of transformation, for the whole of the secondary deposit to segregate at the boundary and, therefore, the greater the probability of obtaining a Widmanstätten structure (3, p. 66). Therefore, a rate of cooling which would cause the largest possible granulation and, afterwards, the quickest separation of the constituents are the conditions most favourable for the production of the Widmanstätten structure. Such or like conditions are, apparently, realized in meteoric irons: a very high temperature of the mass below the temperature of fusion, a resulting large granulation (17), and, then, a relatively rapid cooling, resulting in a quick separation of the kamacite and taenite, thus leading to the appearance of the beautiful meteoric Widmanstätten figures.

Summary.

(1) The Widmanstätten structure belongs to a triad of secondary structures, the other two being the structure of large crystals and the network structure.

(2) The fundamental conditions for the occurrence of Widmanstätten structure which an alloy has to comply with are:

(a) to crystallize in the face-centred cubic lattice;

(b) to be subject to secondary crystallization;

(c) the transformation resulting by this secondary crystallization to occur in an already 'granulated' alloy;

(d) the rate of cooling through the area of secondary crystallization to be such as to favour the deposition of the excess element, not at the boundaries only, but also inside the granulæ.

It follows that a large, well-developed granulation will be favourable to the occurrence of Widmanstätten structure. It also follows that one and the same speed of cooling may, or may not, produce the Widmanstätten structure, since the speed has to be in a certain ratio to the mean diameter of the granulæ.

(3) The analogy between the equilibrium diagrams of the iron-carbon and iron-nickel alloys is very striking. Not only in both cases exist the
areas of primary and secondary crystallization, and of granulation, but
the latest researches have shown that the $\delta$-transformation also occurs in
both cases.

(4) From the character of the equilibrium diagram of the iron-carbon
and iron-nickel alloys it is to be presumed that under suitable conditions
the Widmanstätten structure may occur in both instances. As it happens,
the Widmanstätten structure is of usual occurrence in iron-carbon alloys,
and the Widmanstätten figures are a characteristic feature of meteoric
irons.

(5) As a rate of cooling which would cause the largest possible granula-
tion and, afterwards, the quickest separation of constituents, will be also
the more favourable to obtain the Widmanstätten structure, it may be
inferred that such or like conditions were, apparently, realized in meteoric
irons; viz. a very high temperature of the mass below the temperature
of fusion, a resulting large granulation, and, then, a relatively rapid
cooling, resulting in a quick separation of the kamacite and taenite.

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(7) N. T. Belaiiew, The inner structure of the crystal grain as revealed by meteorites

(8) See Ref. (4) and (5), and more particularly (8), pp. 64-71.

(9) F. Osmond and G. Cartaud, Sur les fers méloïques. Revue de Métallurgie,
1904, vol. 1, p. 69.

(10) For early efforts to reproduce and imitate the meteoric structures in
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(c) H. C. Sorby, On the microscopical structure of meteorites and meteoric iron. Proc. R. Soc. London, 1865, vol. 18, p. 333; and On the microscopical structure of iron and steel. See Ref. (2), particularly the paragraph on p. 286, under the title Imitation of meteoric iron.

(d) A. Daubreè, Expériences synthétiques relatives aux météorites. Paris (Dunod Ed.), 1868.


(j) D. Hanson and Hilda E. Hanson, The constitution of the nickel-iron alloys. Journ. Iron and Steel Inst., 1920, no. 2, vol. 102, pp. 39–60. At the end of this paper a bibliography of papers dealing with the constitution of the iron-nickel alloys is appended. See also E. Cohen, Meteoritenkunde, Stuttgart, 1905, pp. 78–85; and L. Fletcher, An introduction to the study of meteorites, 1914, pp. 35–42.

As to the reproduction of Widmanstätten structure in iron-carbon alloys, see:


(m) N. T. Belaiew, Thesis, 1909 (Ref. 4); and Sur la reproduction artificielle de la structure de Widmanstätten dans l'acier au carbone. Revue de Métallurgie, 1910, vol. 7, p. 510; and Ref. (1).


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(17) The meteoric irons are usually 'unigran', but it is not uncommon to find meteorites with several granules. See for instance: A. Himmelbauer, Orientierung von Schnittflächen an Meteoris. Tschermaks Min. Petr. Mitt., 1909, vol. 28, pp. 153–169. (Reference is there made to the meteorites of Laurens County, of Mukerop, and of Bethany.)