The tempering of the fourth was done at 620°. Polish-attack gives a coloration nearly homogeneous, on which the old structure can still be distinctly seen.

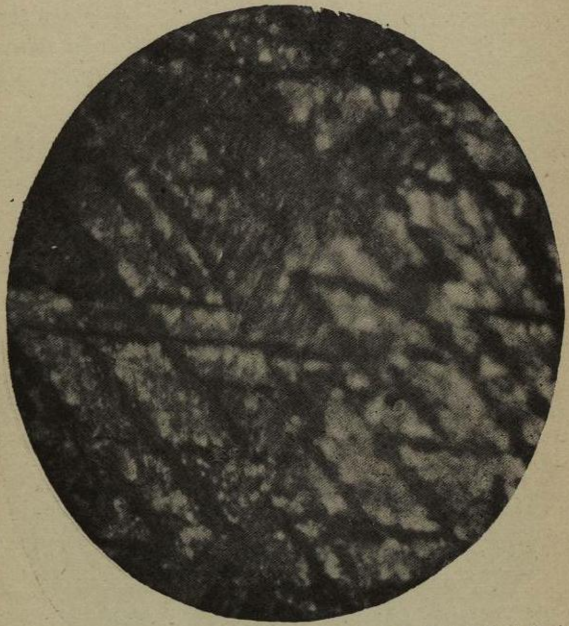

Fig. 171.—Carbon 1·57 per cent. Quenched from 1050° C. in ice water, and reheated to 495° C. Polish-attack. V × 250 diameters.

These results show that tempering progressively transforms hardenite and austenite—the first more quickly than the second—to troosite, and ultimately to sorbite.

CHAPTER VIII.

SEGREGATION IN STEEL AND THE PHENOMENA OF BURNING, OVERHEATING, AND WELDING.

It is only with the aid of the microscope that it is possible accurately to follow the changes which occur during the solidification, overheating, burning, and welding of steel.

When medium and low carbon steels containing small quantities of sulphur and phosphorus pass from the liquid to the solid state, the first portion to fall out of solution is practically pure iron, which crystallises in octahedral skeletons. When the steel cools in a mould these crystallites start to grow on the cool walls and develop inwards at right angles to the sides of the mould. The crystallites growing in this way reject much of the more fusible part of the metal and force it forward. Consequently, the outer layer, or that which freezes first, is always lower in phosphorus and sulphur than the average steel in the ingot. Many erroneous analytical results have been obtained by taking drillings from this outer layer, which frequently contains less than half the sulphur and phosphorus present on the average for the whole ingot. The carbon, no doubt, at first accompanies the phosphorus and sulphur, but much of it diffuses back again. Part of the liquid, rich in metalloids, becomes trapped between the growing branches of the crystallites, and finally solidifies where it has been imprisoned. This is well illustrated in figs. 172 and 173.

Fig. 172.—Photo-micrograph of a cleavage face of iron alloyed with 2 per cent. phosphorus cut from the metal in the cast condition. It was etched with nitric acid, which acted relatively more rapidly on the purer spines, the first to freeze leaving a dark stain. The eutectic of phosphorus and iron containing about 10 per cent. of phosphorus which was the last to freeze is boxed in between the crystallite spines.

Fig. 172 represents an iron rich in phosphorus, and fig. 173 represents an auto-sulphur print from a crystal found in the cavity of a large ingot. In each

there is clearly shown the position where the portion last to freeze has been imprisoned. Although a part of the impure liquid is retained in the crystals, a portion is usually trapped between the crystals as they develop and approach each other. The impurities are generally more concentrated at points where the crystals meet. This is shown in the auto-sulphur print, fig. 173. The dark portion represents the segregation between the crystals. Just at the time when these crystals and intercrystalline segregations are about to freeze, they also carry an excess of carbon as well as an excess of sulphur and phosphorus. During the solidification, and afterwards in steels containing 0·5 per cent. and less carbon, the carbon diffuses outwards and passes into the purer crystallites, which first separate out of solution, so that during the cooling the carbon becomes at one stage equally distributed

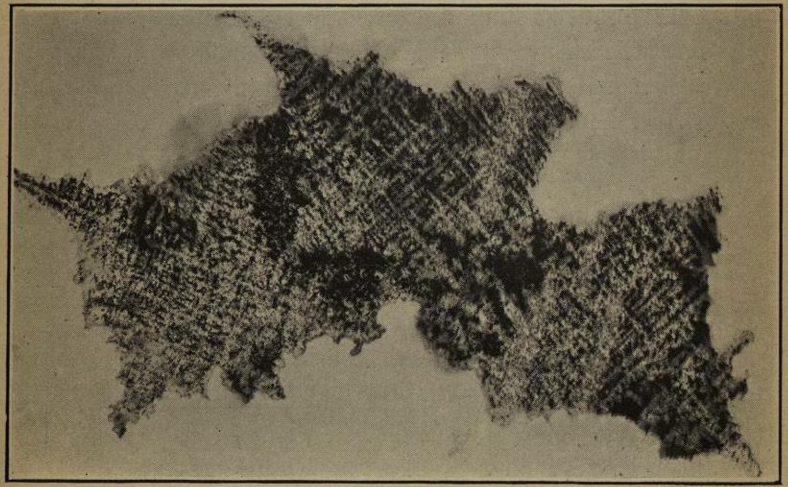

Fig. 173.—Auto-sulphur print from a cavity in a large ingot.

throughout the whole mass of steel. This homogeneity does not, however, long continue, for on further cooling practically the whole of the carbon diffuses outside the enveloping segregate and passes into the purer crystallites, the reason being that, provided there is sufficient free iron in the purer crystallites, it dissolves or attracts the carbon, whilst the phosphorus in the segregate, which diffuses very slowly, has the reverse influence, and expels it. When, however, the cooling is sufficiently protracted, both the carbon and phosphorus diffuse outwards, and nearly perfect homogeneity is effected.

In steels containing very little phosphorus, the segregations in the crystals are so minute and so widely and equally distributed that the phosphorus, as well as the carbon, diffuses into the spines of purer metal during the course of cooling in the ingot. The phosphorus, concentrated between the crystals at their junctions, being in greater quantity, has not time to diffuse in castings and ingots during the limited time they have for cooling, hence in the cold steel these junctions are always free from carbon, although initially they may have contained an excess. Unless the phosphorus is very high, a portion of the carbon diffuses back again into the phosphorus-rich portions on heating the ingot to say 1000° C., and on quenching the steel in cold water it is retained there. If, however, instead of quenching the steel, it is allowed to cool slowly, the carbon diffuses out of those portions rich in phosphorus, leaving them quite free from carbon. If the ingots or castings at 1000° C. are elongated by forging, and are then cooled slowly, the phosphorus-rich portions, which are elongated with the steel, reject the carbon they absorbed on heating up to 1000° C., and appear in longitudinal sections as white ferrite lines. The higher the phosphorus in the steel the thicker and more pronounced are these white carbonless lines in forged steel. Figs. 174–182 illustrate the foregoing statements.

Fig. 174 is a photograph of a steel casting containing about 0·3 per cent. of carbon and 0·05 per cent. of phosphorus.

Fig. 175 is the same heated to 1000° C. and cooled slowly. The white portions represent the parts rich in phosphorus.

Fig. 176 is the same steel forged at 1000° C. to a bar and then cooled slowly. The white streaks represent the elongated portions rich in phosphorus.

Fig. 177 represents steel with 0·50 per cent. phosphorus and 0·3 per cent. carbon.

Fig. 179 shows the same steel after forging.

It is scarcely necessary to advance more evidence than this to account for the white "ghost lines" in steel forgings.

When the steel is very wild in the moulds, and blowholes develop in the freezing crust, the pressure exerted by the cooling gas on the steel above and below the growing blowholes expels a portion of the impure liquid from the spongy solid and liquid mixture. This flows forward in the line of least resistance, and passes into the inside of the freezing walls, and, being lighter than the mass of the unfrozen liquid steel, it ascends and is assisted upwards by the ascending gases towards the upper part of the ingot, where it is finally trapped and imprisoned, and freezes in the upper central axis, constituting what is known as axial segregation (fig. 183). If, however, there is no evolution of gas or formation of blowholes, axial


Fig. 174.

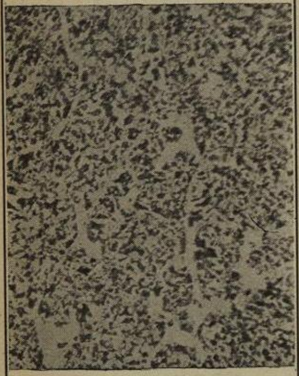
Fig. 175.

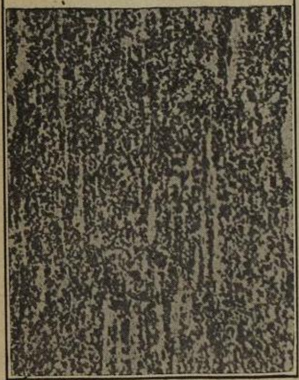
Fig. 176.

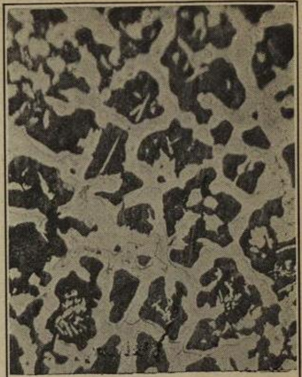
Fig. 177.


Fig. 178.

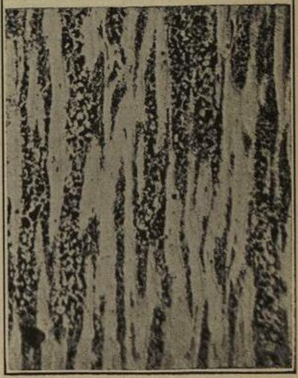
Fig. 179.


Fig. 180.

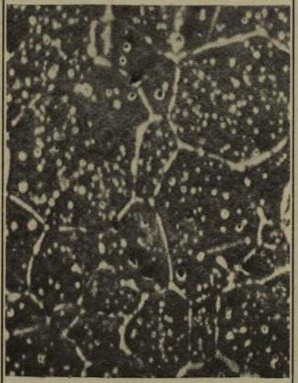
Fig. 181.

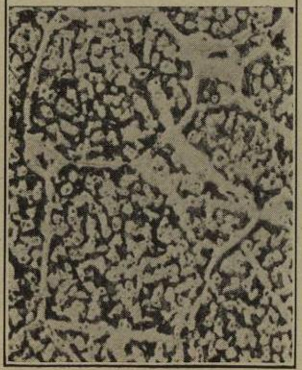
Fig. 182.

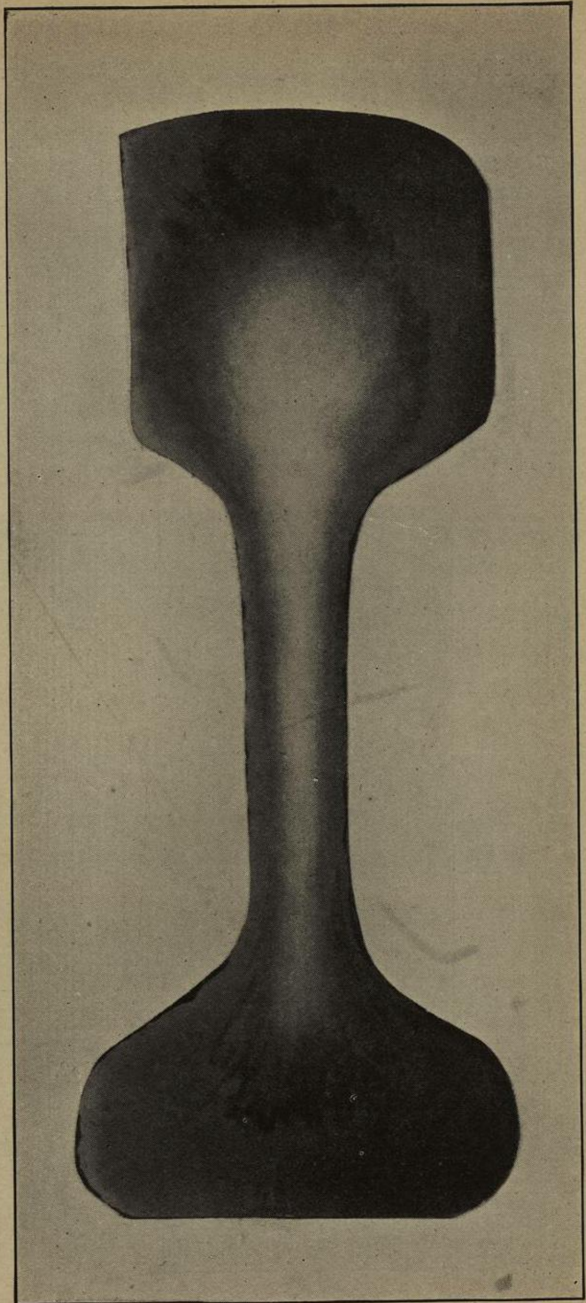

Fig. 183.—Steel rail with a central portion of nearly pure iron.

segregation is reduced to a minimum, and the place where the segregation is usually found is occupied by a large pipe or cavity. Steel that is wild in the moulds circulates more freely than that which is quiet. The circulation of the wild steel in the mould causes the whole mass to cool gradually down to the freezing-point, and the solidification of the metal at the top and sides of the mould is retarded. When the steel is quiet and "dead" in the moulds the central part of the ingot takes longer to solidify, whilst the outer layers solidify more quickly; hence it is that quiet steel always appears to set more quickly than the frothy and gaseous material.

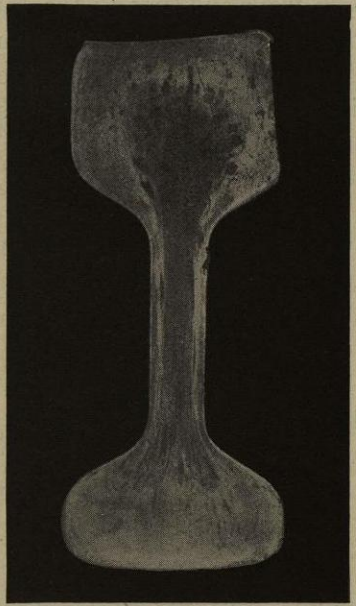

Fig. 184.—Segregated rail broken on the road. The core was unsound and may have been defective before placing on the track. The dark curved line on the right represents a crack.

When the ingots are very large, and are placed vertically in a soaking pit or furnace, the cooling of the liquid steel in the centre is checked. During this cooling, whilst the crystallites of purer iron grow from the internal sides of the solid shells of steel, there is much evidence to show that some of them fall away from the walls and sink to the bottom of the still liquid column, or pure crystallites may form in the liquid and fall to the bottom and be concentrated there. If this hypothesis be correct, it accounts for the lower central axis of ingots so often being purer than the average of the whole ingot. Incidentally with the replacing of the liquid below, it is probable that the portions last to freeze ascend, and tend to become trapped higher up. If the ingot be partially rolled when the central part has become a spongy mass of pure iron crystallites, and of impure residual liquid, the liquid may be forced upwards to the narrow part of the ingot and fill the pipe cavity, leaving a lower central axis of almost pure iron. An example of this is given in fig. 184, and the analyses below show the composition of the inner and outer portions:—

	Outside. Zone 1.	Ragged Fringe. Zone 2.	Under the Fringe. Zone 3.	Central Axis. Zone 4.
	Per cent.	Per cent.	Per cent.	Per cent.
Carbon . .	0·340	0·395	0·200	0·125
Manganese . .	1·196	1·205	1·094	1·077
Silicon . .	0·084	0·084	0·075	0·103
Sulphur . .	0·071	0·093	0·043	0·019
Phosphorus .	0·062	0·086	0·035	0·021

Recent researches by B. Talbot have shown that when steel ingots are passed once or twice through the rolls whilst the central column of steel is in a pasty condition, the more liquid portion—the last to freeze — is forced into fissures formed along the internal walls of the ingot, which portions, being easily broken up, do not extend with the solid thick envelope, with the result that the more impure portion of the steel becomes concentrated at the places where it is likely to be least objectionable. The central axis, when the process is conducted properly, then contains about 25 per cent. less carbon, sulphur, and phosphorus than the thick outside envelope.

Blowhole Segregation.—When steel ingots evolve gases during solidification, the gas continues to pass out of the steel, even when the metal is partially solid, with the result that gas bubbles or "blowholes" remain, as such, in the solid ingot.

Howe and others have noticed that some of the deep-seated blowholes contain material very rich in sulphur, and Stead has found that the sulphides are always associated with phosphorus. When ingots, showing blowhole segregation, are rolled into bars, the corresponding positions of these segregations are readily located in polished and etched longitudinal sections of the metals by the so-called "ghost lines" or lines of ferrite, in which are embedded lenticular particles of the drawn-out sulphide inclusions. After much careful research it was proved by Stead that these blowhole segregations rarely exist in the blowholes in the upper outer envelopes of ingots, although the blowholes are usually most pronounced in that position. They begin to appear lower down, and are usually strongly in evidence in the envelope of the bottom half of the ingot. The explanation of this peculiarity is that after the blowholes have formed, and the upper portion of the ingot is sealed up with a solid cap of frozen steel, gases still continue to be generated, and exert considerable pressure on the liquid in the inside of the ingot. The inner ends of the radial, deep-seated blowholes terminate in a spongy mass consisting of pure iron crystallites and an impure liquid, and when internal pressure develops, some of this impure liquid is forced into the small cavities and solidifies, and it is this that constitutes a "blowhole segregation." The reason why the blowholes in the lower part of the ingot are partially filled and not those above, is explained by the fact that the internal pressure is greater below than it is higher up the ingot, by reason of the pressure exerted by the column of liquid steel itself. Blowhole segregations are never found in blowholes near the outer skin, the reason being that their inner terminations become completely sealed by solidified steel before the internal pressure is developed. In a large ingot of soft steel, broken specially to make a search for blowhole segregations at about 2 inches from the external skin of the ingot, a blowhole partially filled with segregate was found. Fig. 185 clearly shows the appearance of a cross-section. It indicates that the hole was originally nearly three times the size of the remaining cavity, and that about two-thirds of its volume is occupied by a segregate rich in phosphorus and sulphur which had been forced into it by the internal pressure, which probably was equivalent to three atmospheres. On heat tinting, the metallic portion of this segregate rapidly assumed a blue tint at the stage when the external steel became brown,

an indication of a large amount of phosphorus, estimated to be at least 0·50 per cent. The tinting of the inclusion was, however, variable, indicating that the phosphorus was not evenly distributed. The non-metallic sulphide inclusions were estimated to occupy at least 10 per cent. of the total mass, probably representing a sulphur content of about 4 per cent. in the segregate. The sulphides consisted in greatest part of pale yellow iron sulphide, associated with dove-coloured globules of what appeared to be manganese sulphide. Fig. 185A clearly shows these two constituents associated.

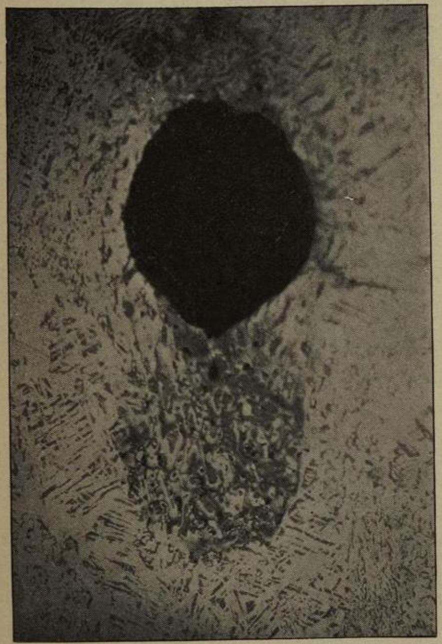

Fig. 185.—Cross-section of blowhole heat-tinted and showing the phosphorus segregate.

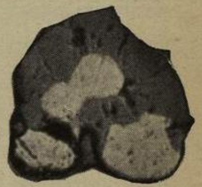

Fig. 185A. — Sulphide constituents in segregated portion shown in fig. 185.

The researches of Rohl have demonstrated beyond doubt that ferrous and manganese sulphides crystallise together in the proportions of 60 per cent. FeS and 40 per cent. $MnS = Fe_3Mn_2S_5$; and in mixtures containing increasing quantities of manganese sulphide up to 100 per cent., forming homogeneous isomorphous compounds of $Fe_3Mn_3S_5 + MnS$, all of which under the microscope have the same appearance. Levy and Law, however, state that the homogeneous substance which contains the most FeS is lighter in colour than that containing less.

When the FeS exceeds 60 per cent. in the mixture, a eutectic consisting of 7 per cent. MnS and 93 per cent. FeS appears, having a freezing-point of 1181° C.

When iron in excess is present in addition to an excess of FeS over the mixture $Fe_2Mn_2S_5$, a ternary eutectic is formed freezing at 980° C. Rohl found the freezing-point of pure MnS to be 1620° C., or about 120° C. higher than that of pure iron, and the freezing-point of the compound $Fe_3Mn_2S_5$, 1365° C.

Judging from these most valuable researches, it may be accepted beyond any doubt that when iron sulphide, and what appears to be manganese sulphide, are found associated together in the same sulphide inclusion what looks like MnS is not that compound but is $Fe_3Mn_2S_5$.

As the sulphides in the blowhole segregation referred to above were associated with FeS, it may be concluded that what appeared to be the dove-coloured manganese sulphide was really the isomorphous mixture, $3FeS + 2MnS$, or Rohl's $Fe_3Mn_2S_5$.

It may also be concluded that the last portion to freeze in this blowhole segregation was the ternary eutectic of Rohl, which solidified at about 980° C.

The sulphide inclusions in the steel surrounding the blowhole were all more or less globular and of the dove-coloured type, and exceedingly minute. Pure iron sulphide inclusions were entirely absent, but at wide intervals some of the globular dove-coloured inclusions contained specks, in the centre of the globules, of a different substance, probably iron sulphide.

It is well known that sulphur is always present in the portions of steel which are last to solidify; also, that some of these portions taken from the central axis of steel ingots do not contain sufficient manganese to combine with all the sulphur to form the compound MnS, and it is generally admitted that manganese does not segregate.

There is reason to believe that when the steel is liquid the sulphur is not entirely associated with the manganese, even when more than sufficient is present to combine with the sulphur, but is combined with the iron and manganese in the proportion present in the liquid steel, usually about 98 of iron to 1 per cent. or less of the manganese, and in consequence of this, the last portion of the steel that solidifies has its freezing-point materially reduced by the preponderating proportion of iron sulphide.

It is also concluded that the iron sulphide during the solidification range reacts upon the manganese of the metal, and changes more or less completely into MnS, according to the proportion of manganese in the metal $FeS + Mn = MnS + Fe$.
Assuming that the metal pressed into the blowhole contained the same amount of manganese as in the average steel, an assumption which is justified by the fact that usually manganese in segregates is about the same as it is in the steel from which the segregate

came, and as this was about 0·35 per cent., the segregate would not contain more. Now if the whole of this manganese passed out of the metal as sulphide of manganese, it would only account for about 0·20 per cent. of sulphur of what is computed as about 4 per cent. This indicates that at least 99·5 per cent. of the sulphides present must exist as iron sulphide. This conclusion justifies the long-held hypothesis above enunciated. The presence of minute inclusions of what appears to be iron sulphide in the dove-coloured globules of the external steel also tends to support that view, for initially, if this hypothesis be correct, these globules must originally have contained an excess of iron sulphide, and that the reaction between this and the manganese in the metal external to them, starting from their exterior boundaries, had not been complete, hence the presence of the internal residue of iron sulphide. After the steel had just become solid it is probable the two sulphides existed as a fusible eutectic, and this, during the very slow cooling, had been resolved into its parts or constituents.

THE BURNING AND OVERHEATING OF STEEL.

The careful researches of Stead, quite recently published,[1] have proved almost beyond dispute the correctness of the hypotheses of Dr A. Stansfield, who, in 1903, presented the results of a most classical research to the Iron and Steel Institute. His definitions were practically as follows, viz.:—

---

[1] "The practical use of the Iron-Carbon equilibrium diagram, with special reference to the critical points A 1, 2, 3; and the Burning of Steel," North-East Coast Institution of Engineers and Shipbuilders, Jan. and Feb. 1913.

Steel heated to a point short of incipient fusion is overheated, but heated to above that point is technically described as burnt.

It will be understood from these definitions that the word "burning" is not a very appropriate term to use, but, as it has been so firmly established, it is too late to-day to suggest a more scientific one.

It is clear that steel can be "burnt" in an atmosphere free from any oxidising gases: in hydrogen and nitrogen gases, in vacuum, or when surrounded by a neutral, non-oxidising slag or cinder.

Much error of interpretation has been made and published about so-called burnt steel. This is explained by the fact that in steel-works practice it is only the material which has been broken up at the rolls or forge after excessive heating that has been examined; indeed, the breaking up of steel in that manner has been taken as indicative of burning. Shattering of the material has usually prefaced examination. When burnt steel after cooling was examined near the point where it broke up, at the rolls or hammer, it is not surprising that oxidised surfaces of grains of steel were readily detected, and the conclusion deduced that the oxidising gases of the heating furnace had actually penetrated the solid material, with the consequent formation of oxide between the crystals.

Stead and others, who have examined, under the microscope, polished sections of similar material, arrived (it is now believed erroneously) at the conclusion that the oxidising gases, when the steel was still in the furnace, did pass between the crystalline grains and oxidised their surfaces. That the gases did do so is undoubted, but the penetration occurred after the material had been shattered at the forge and not when the steel was in the furnace.

On purely theoretical grounds, based on the behaviour of steels as they cool from the liquid to the solid state, it seemed absolutely certain that on heating the same steels up to the point of complete liquefaction, the same changes would occur, but in the reverse order. At the point when incipient fusion is effected, if the steel be maintained for a long enough period to admit of equilibrium being established, the liquid portion should have the same composition as the last portion to freeze in the steel ingot—a liquid rich in carbon and phosphorus. On heating up steel that had been forged into bars, with the original constituents evenly distributed, as the heat rose the austenite crystals would become larger and larger, and when the solidus or point at which the last parts become solid in freezing, and the first parts become liquid on heating up, was passed, the liquefied part would form into minute globules throughout the whole mass of steel. In course of time these would coalesce and form larger globules, and when they approached the junctions of the large crystals they would flow round them, forming very thin and fine liquid envelopes. On cooling down slowly, diffusion of the carbon would follow, and would pass into the purer portion of the metal or that part which had not become liquid on heating.

The envelopes of the crystals in the cold steel would be rich in phosphorus, and, if the steel did not contain more than 0·5 per cent. carbon, would appear in the ferrite boundaries of the crystals. When steel is heated to considerably above the solidus, the liquid

sometimes liquates to the outside, or gravitates downwards to the lower side of the heated steel. As the liquid flows out from between the crystal boundaries, the crystals fall together, so that actual crystalline cavities rarely, if ever, form. The steel, however, unless it is well supported on a rigid bed, may bend when in the fire, and the crystals may then separate and make actual fissures. Fig. 186 represents a piece of "burnt" soft steel which broke in use. The very dark part represents a fissure probably made by forging when the crystals were enveloped with liquid. The half-tone band running through the middle of the ferrite envelope represents a concentration of phos-

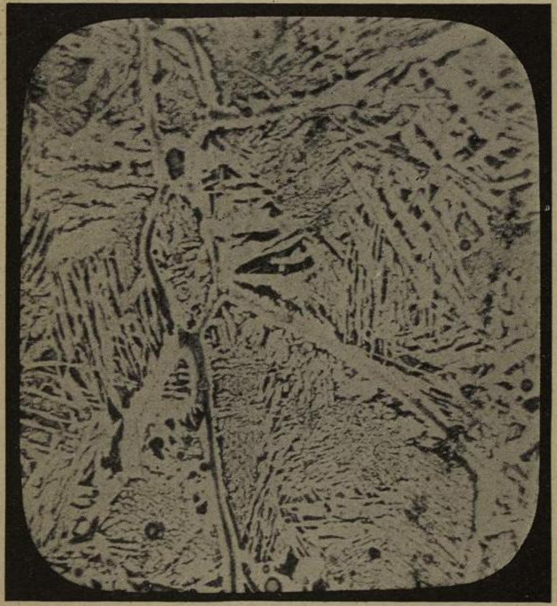

FIG. 186.—"Burnt" soft steel showing fissures.

phorus: it is the portion which was melted during the excessive heating, and at the time it was melted also contained an excess of carbon. In order to determine and show the changes above referred to, which theory dictates, a steel containing 0·5 per cent. phosphorus and 0·3 per cent. carbon was selected. The object of having so much phosphorus present was to enable one to clearly show the position of the liquid where it formed. It was known that phosphorus and carbon always associate at high temperatures, and that whilst carbon diffuses rapidly as the steel cools, phosphorus is exceedingly sluggish in that respect. It seemed certain, therefore, that if such steel were heated above the solidus, and were then suddenly quenched, one would retain the phosphorus-rich parts where they were concentrated. The photographs, pp. 248–49, illustrate the result of the trials:—

Fig. 177 represents the original steel as cast, and fig. 178 the same steel polished and heat-tinted. The white portions are the phosphorus-rich parts.

Fig. 179 is a photograph of the cast steel after forging to a bar. The long lines are the elongated parts rich in phosphorus.

Fig. 180 represents the forged steel bar after heating and cooling in a 3-ton ladle of blast-furnace slag, the initial temperature of which was about 1350° C. The phosphorus had, during slow cooling, completely diffused throughout the steel.

Fig. 181 represents the same steel as the last, after heating to, and quenching from, a temperature sufficient to cause incipient fusion. The white parts indicate portions rich in phosphorus and carbon.

Fig. 182 is the same as fig. 181 after heating to 1000° C. and cooling slowly. The carbon has diffused out of the phosphorus-carbon-rich portions, leaving behind phosphorus-rich white ferrite.

These confirm fully the purely theoretical deductions above enumerated.

The conclusion arrived at by Stead, is that overheating does no permanent harm to steel, unless there has been an internal evolution of gas, leading to a lowering of the specific gravity. Overheated steel can always be restored by simple heat treatment.

Fig. 187.—Welded-up blowhole cavity containing sulphide inclusions.

The question as to the effect of "burning" on the mechanical properties of steel is receiving careful consideration.

Welding. — In a recent research by Stead on the welding up of blowholes in steel ingots, it was shown that when perfectly clean surfaces of steel are brought into absolute contact and are heated to 900° and upwards in an atmosphere of hydrogen gas, the surfaces crystallise together, and a true weld is effected.

The definition of welding was advanced: "That welding consists in the crystallising together of two juxtaposed surfaces," and the proof of welding is that the crystals along the joint of union are common to the pieces united, *i.e.* the crystals are composed of portions of the metal of the two separate faces.

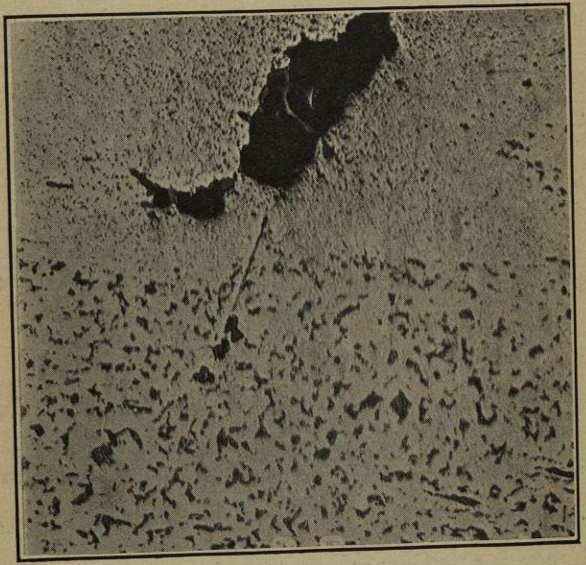

Fig. 188.—Surface blowhole in a forging showing unreduced oxide black surrounded by reduced oxide containing fine oxide inclusions.

Fig. 187 illustrates this. The metal on each side of an imaginary line drawn between the two arrows represents the sides of a closed-up blowhole cavity in a rolled bar from a honeycombed ingot. The crystals along this line are common to the metal of the original faces. The elongated dark patches represent the sulphide inclusions.

Trials with portions of honeycombed ingots in which there were no segregations proved that on forging at a temperature a little above 1000° C. the walls of the blowholes welded up perfectly.

When the blowholes extend to the surface of the ingot during heating, the inside of the cavities becomes coated with oxide, and this prevents the metallic surfaces coming into contact. In cases where the carbon in the steel is high, and after the oxidised walls of the cavities are closed so as to meet, and the temperature of the metal is maintained at about 900° more or less, for a sufficient length of time, the carbon of the steel diffuses to the oxide and reduces it to the metallic state, and the iron so reduced crystallises to the walls of the metal below where the scale existed, and a good weld is produced. This weld, however, never extends completely to the surface; it is only in the deep-seated portions where the coating of oxide is thin that welding is complete.

As the carbon cannot reduce the manganese oxide which constitutes a small portion of the oxide, this remains as dust-like, globular inclusions in the body of the reduced iron. Fig. 188 illustrates this.