

THE EFFECT OF NON-METALLIC IMPURITIES ON
CEMENTITE DISTRIBUTION IN STEEL.

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It is a well known fact that non-metallic inclusions in iron and steel exert injurious and very undesirable effects upon the metal. Since it has been impossible entirely to eliminate their presence they have been the subject of much investigation and discussion.

Their weakening effect upon the steel is much more pronounced than can be explained by assuming that they are essentially the same in their effect as would be produced by cavities of the same size. Inclusions which may occupy a very small proportion of the cross sectional area of a given piece of steel very often prove fatal, whereas the total effective area of the metal lying between the inclusions would seem to be sufficient to withstand the strain. Their importance to the manufacturer and to the user of steel then is vastly greater than their size might at first indicate.

When pure hyper-eutectoid steel (steel containing more than 0.87 per cent carbon and generally called high carbon steel) is heated above its critical range it is composed of austenite. The upper limit of this range varies from 725° to 1125°C as the carbon content varies from 0.87 to 1.7 per cent. Austenite is essentially solid iron with carbon in the form of iron carbide (Fe_3C) dissolved in it. Iron carbide as a constituent of steel is called cementite. If the steel is slowly cooled nothing happens except that the austenite grains increase in size until the first recalescent point A_{r1} is reached. At this point the unsaturated austenite of higher temperature becomes saturated with cementite and the latter is thrown out of solution. As the temperature continues to fall the austenite continues rejecting cementite until the second recalescent point A_{r2} is reached when austenite of eutectic composition remains and is changed bodily into pearlite. Pearlite then is the mixture of eutectic composition stable below the A_{r2} point and consists of a conglomerate of carbonless iron (ferrite) and iron carbide (cementite).

Figure 1a is a photomicrograph of an annealed hyper-eutectoid steel which has been highly polished and etched with a solution of nitric acid in alcohol in order to show the grain structure. Each irregular cell-like area is a grain of this conglomerate, pearlite. The light network and areas between the pearlite grains represent the excess cementite above that required to form the eutectic and which was rejected to the grain boundaries as the steel cooled.

In the case of hypo-eutectoid steel (steel containing less than 0.87 per cent carbon) the iron or ferrite instead of cementite is in excess of that required for eutectic composition, consequently ferrite is thrown from solution as it cools through the critical range and the cooled steel consists of pearlite and ferrite. Figure 1b, shows a hypo-eutectoid steel in which the network and light areas are ferrite. The dark constituent is again pearlite.

In ordinary annealed hyper-eutectoid steel inclusions are generally found within the cementite areas. In the case of hypo-eutectoid steel they usually occur in the ferrite grains and ferrite network surrounding

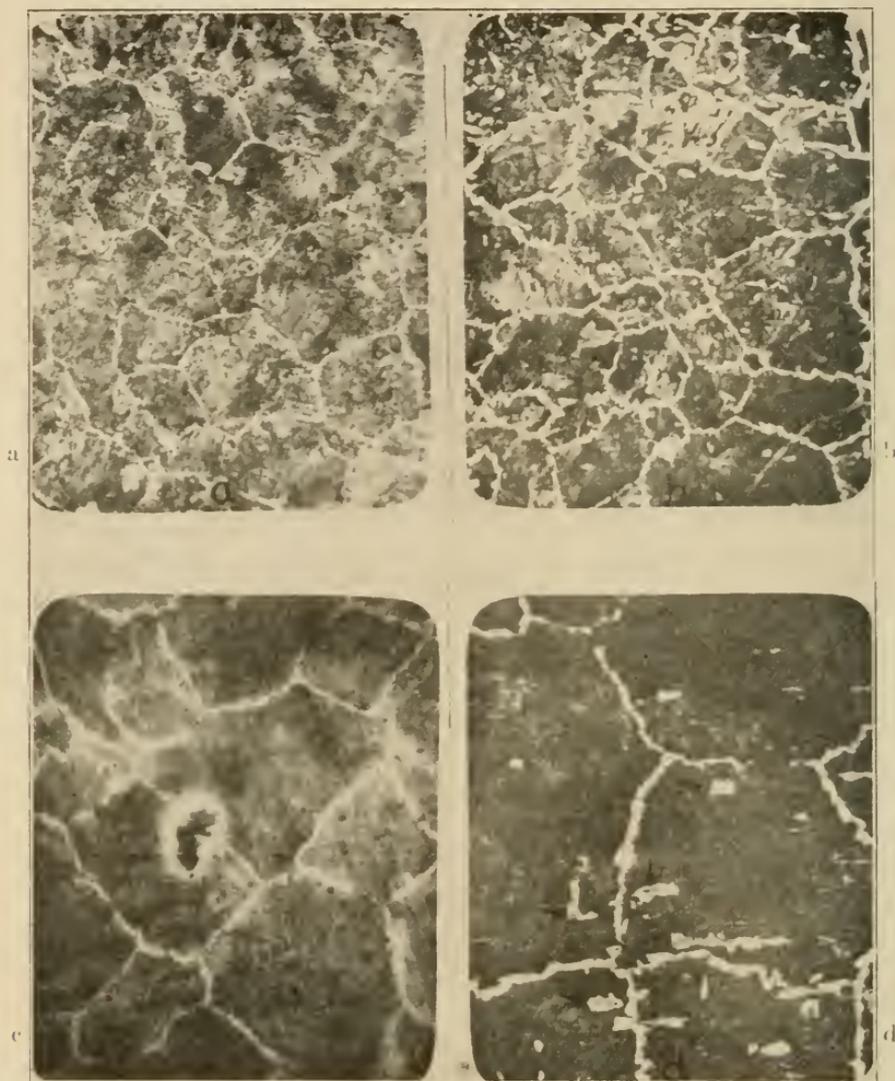


Fig. 1. a, Pearlite grains (dark) and cementite (light) in annealed hyper-eutectoid steel; b, pearlite grains (dark) and ferrite (light) in annealed hypo-eutectoid steel; c, inclusion surrounded by cementite in hyper-eutectoid steel; d, inclusions surrounded by ferrite in hypo-eutectoid steel, a and b etched with nitric acid, c and d with hydrochloric acid. $\times 80$.

pearlite grains but rarely in the pearlite grains themselves. Figure 1c is a rather striking example of an inclusion surrounded by cementite in hyper-eutectoid steel. Figure 1d, shows a hypo-eutectoid steel. It

will be noted that practically all the inclusions occur in the light ferrite areas.

Segregation about inclusions cannot be destroyed by ordinary heat treatment, such as would break up ordinary grain formations. Besides being areas of little or no strength they then act as obstacles to the proper thermal treatment of the metal.

Whether inclusions are the cause of the segregation of cementite in hyper-eutectoid and ferrite in hypo-eutectoid steel or whether their co-existence is the result of some common and deeper seated cause has been the subject of considerable discussion.

Stead¹ pointed out that in the case of hypo-eutectoid steel the inclusions surrounded by ferrite generally occur in areas rich in phosphorus and he held that the phosphorus is the real cause of the ferrite segregation and that the presence of the inclusions is merely incidental. He believed that the inclusions themselves are not the cause of this segregation.

Howe² expressed the opinion that the presence of the inclusions within the ferrite or cementite areas is due to the tendency of the steel in the process of cooling to reject both inclusions and the ferrite or cementite to the grain boundaries.

Brearly³ and Ziegler⁴ suggested that the inclusions might act as nuclei for ferrite or cementite crystallization in a manner similar to a string suspended in a sugar solution.

Work in this laboratory⁵ has led to the conclusion that the cause of ferrite and cementite segregation about inclusions is due to the fact that the inclusion itself or some reaction product of it with the surrounding steel is soluble to a slight extent in the metal at high temperatures and that this introduction of a third component into the solid solution system of iron and iron carbide so alters solubility relations that supersaturation is reached at a higher temperature in the metal immediately surrounding the inclusion than in the rest of the steel. If there is a zone, however narrow, lying about the inclusion and containing even a trace of any dissolved material from the inclusion, this foreign material should alter the solubility of the excess ferrite or cementite in the austenite next the inclusion and thus cause a local condition of supersaturation first in this region. The excess constituent then would separate here first. After separation had started it would continue about these spots as nuclei as the steel cooled farther and consequently the inclusions would be imbedded in the cementite or ferrite.

Under the direction of Dr. E. G. Mahin the writer undertook to study the effect produced upon cementite distribution in hyper-eutectoid steel when artificial inclusions of known composition were placed in the metal.

¹ J. Iron Steel Inst., 97, 287 (1918).

² "The Metallography of Steel and Cast Iron", 280.

³ Proc. Sheffield Soc. Eng. Metallurgists, 1919.

⁴ Rev. metall., 8, 655 (1911).

⁵ J. Ind. Eng. Chem., 11, 739 (1919).

Ibid., 12, 1090 (1920).

Small blocks were cut from a bar of ordinary commercial high carbon steel of the following composition; carbon, 1.2; manganese, 0.30; phosphorus, 0.02; sulphur, 0.03; silicon, 0.20 per cent.

The method of preparing these specimens was the same as previously used in the study of inclusions in low carbon steel. This consisted in drilling holes through the blocks. At the same time rods of several alloys and special steels were turned on the lathe to a diameter slightly larger than the holes. After cleaning both rods and holes with an alcohol ether mixture the rods were driven into the holes and hammered until the contact between the two pieces was very intimate.

The alloy or special steel insert now occupied the same relation to the main body of high carbon steel as a natural inclusion might occupy in the same position.

The specimens so prepared were heated well above the transformation range of the steel for varying periods of time after which they were allowed to cool slowly in the furnace. After this treatment a section was cut from each specimen perpendicular to the axis of the insert so that the zone about the contact between it and the main body of the piece might be subjected to examination for evidence of cementite segregation.

In order to study in a more definite manner the effect upon carbon distribution produced by the localization of a few of the more common elements generally found in ordinary commercial steels inserts were made of several specially prepared steels.

Number 1 was a plain carbon steel containing about 0.5 per cent carbon. The other seven were of identical composition except that to each had been added some element in excessive amount. For example to number 2 had been added silicon and to number 3 phosphorus, etc. The amount of the added element found in each of the entire set follows:

- No. 1 Plain 0.5 per cent carbon steel.
- No. 2 Plain 0.5 per cent carbon steel plus 4.0% silicon.
- No. 3 Plain 0.5 per cent carbon steel plus 1.06% phosphorus.
- No. 4 Plain 0.5 per cent carbon steel plus 1.46% manganese.
- No. 5 Plain 0.5 per cent carbon steel plus 1.34% copper.
- No. 6 Plain 0.5 per cent carbon steel plus 0.84% chromium.
- No. 7 Plain 0.5 per cent carbon steel plus titanium.
- No. 8 Plain 0.5 per cent carbon steel plus 1.36% sulphur.

Several non-ferrous alloys also were used for inserts. Among them were aludel, an alloy of aluminium and nickel; copel, an alloy of copper and nickel; and chromel, an alloy of chromium and nickel.

The specimen with the insert of plain carbon steel and which contained no excessive amount of any element showed no tendency to cause the separation of cementite. It was found however that the diffusion from some of the other inserts into the adjacent steel had a tendency to cause cementite to segregate in this region while with other inserts containing other elements this tendency did not manifest itself under the conditions of the experiment. A few photomicrographs will show the nature of this effect.

Figure 2*b*, shows the appearance of the specimen containing the high silicon insert after it had been heated at 950°C. for three hours. There is a narrow but well defined band of cementite about the insert.

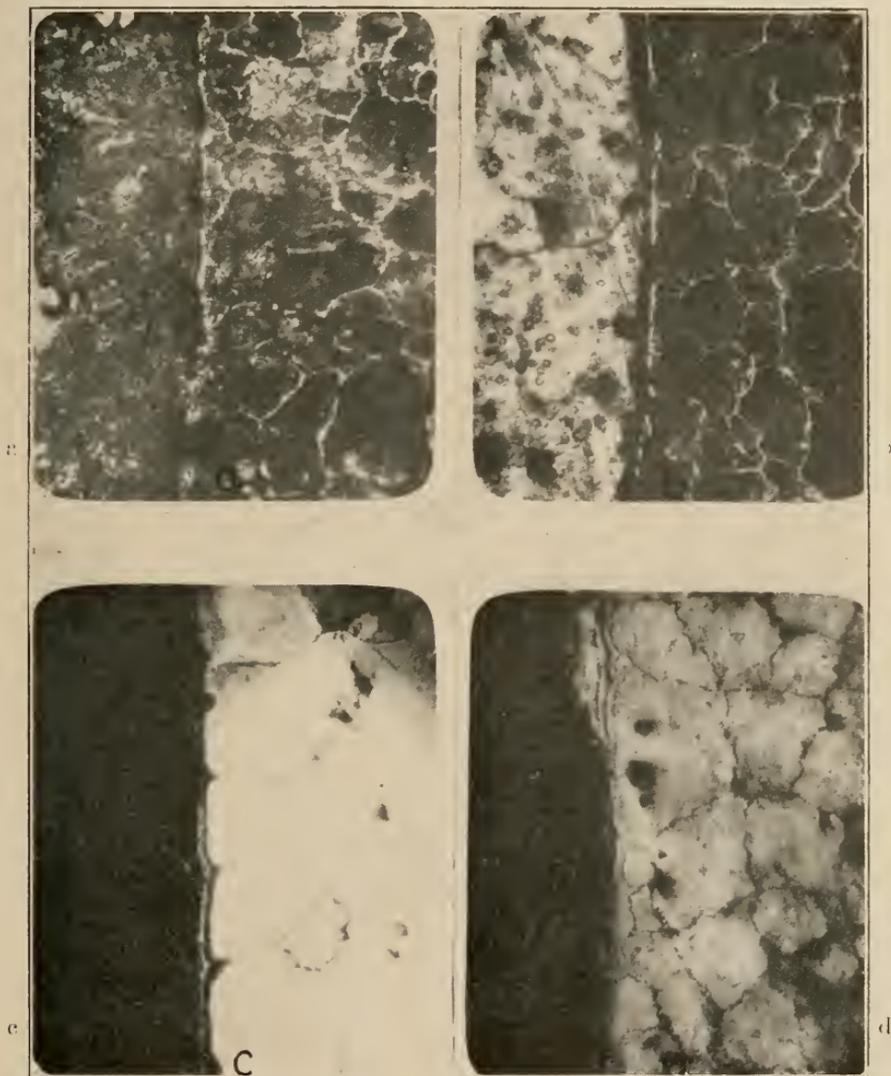


Fig. 2. a, Cementite segregated about high phosphorus insert in hyper-eutectoid steel; b, cementite segregated about high silicon insert in hyper-eutectoid steel; c, cementite segregated about alumel insert in hyper-eutectoid steel; d, cementite segregated about copel insert in hyper-eutectoid steel. a and b etched with nitric acid, c and d with sodium picrate. $\times 80$.

The width of this zone corresponds to the depth to which the material from the insert had penetrated into the surrounding steel. This diffused material was probable iron silicide.

Figure 2*b*, shows the high-phosphorus insert. Here again the extent to which the phosphorus had penetrated into the steel is marked by a zone of cementite. This was heated at 900 for two hours.

The other steel inserts containing manganese, copper, chromium, titanium, and sulphur showed this tendency to cause cementite segregation to only a very limited extent or not at all.

Figure 2, *c* and *d*, respectively, show the specimens containing almel and copel inserts. Cementite has collected about the insert in both cases. These specimens were etched with sodium picrate which causes cementite to appear dark.

From the results of these few experiments it would seem that inclusions in hyper-eutectoid steel must have a certain slight solubility in the austenite at high temperatures, and that the concentration of the dissolved matter is therefore greatest in the immediate vicinity of the inclusion. Such a condition of localized dissolved impurities probably has the effect of starting cementite crystallization first about the inclusion, thus breaking down the state of cementite supersaturation that always occurs in hyper-eutectoid steel cooling through the critical range. And since each inclusion is a center of contamination and furnishes a continuous supply of impurity to the surrounding steel no amount of heat treatment can eliminate its effect.