CHAPTER VI

Ingredients of and Materials Used in Steel

The elements entering into the composition of steel have been studied and investigated in many ways and their effects have been carefully noted. Many new alloying materials have been brought into use in the past few years. These were made available by the high temperature obtained in the electric furnace, as this enables them to be separated from the elements with which they were found, and combined with iron to make ferro-alloys that could be added to the steel in its making. Many other elements are being experimented with, and some of these give promise of adding new properties to steel or bettering the properties already recognized as good ones, and thus we may be able in the near future to still further improve it in quality.

These new alloying materials have given us steels which, for strength, cutting qualities, wearing qualities, and ability to withstand vibrational and torsional stresses, attain a higher standard of excellence than would have been considered possible a short time ago.

CARBON IN STEEL

Of all the alloying elements entering into steel, carbon is the most important, as it is the quantity and condition of the carbon in the metal that makes the distinction between iron and steel. The distinctive features of different grades of steel are due more to the variation of the carbon contents than to the differences in any or all of the other elements.

One of the wonders of metallurgy is the effect that a small per cent. of carbon has upon iron. Pure iron, that is, iron that has been electrolytically deposited, has a tensile strength of 45,000 pounds per square inch, and if we add a few tenths of 1% of carbon, the tensile strength immediately rises to 60,000 pounds, and with 1% it reaches 120,000 pounds per square inch. This is a quantity so small that it is out of all proportion to the mass in which it is distributed.

Carbon unites with chemically pure iron in all proportions up to 4½ per cent. The capacity of the iron for carbon can be increased by using manganese, and when a high percentage of manganese is added to steel the carbon content can be raised to 7 or 8 per cent. Manganese, silicon, phosphorus, sulphur, etc., may vary widely in quantity, but the carbon

usually decides the class in which the steel belongs; for the carbon gives greater hardness and strength to the steel, with less brittleness, than any other element.

To get the desired percentage of carbon into steel, various methods are used. In the melting in process, that is, adding the carbon to the steel when the metal is molten, the Bessemer, open-hearth, and crucible processes all use a different method. Besides this, there is the cementation process in which the carbon is put into the steel while in a solid state. Several methods are employed in this, and they consist of submitting the metal to the action of some carbonaceous material in the presence of heat.

In the Bessemer process, the charge of molten metal is put into the converter and air is blown through it. This air oxidizes out all of the silicon and manganese and nearly all of the carbon, the heat of combustion of these elements raising the temperature of the charge. The charge is then recarburized through an addition of molten spiegeleisen, after which the metal is poured into ingots.

In the open-hearth process, the charge usually consists of 50% pig iron and 50% of scrap, and these are melted up together. The pig iron usually contains from 3½ to 4% of carbon, and the charge is melted down and boiled until the carbon has been reduced by oxidation to the required amount. Tests are taken every half hour or so, to determine when the carbon has been reduced to the proper percentage, and when this is reached, the ferro-alloys are added to the bath and it is cast into ingots.

In the crucible process, muck iron and charcoal is charged, the crucible sealed up and the charge melted down. If the muck iron contains 0.10% of carbon, 100 pounds of muck bar and 15 ounces of charcoal, which is the form in which the carbon is put in the bath, will make a 1% carbon steel. With the muck iron higher or lower in carbon, the charcoal is diminished or increased to obtain the correct carbon content.

By the cementation process muck iron is changed into blister bars, or from a low to a high carbon metal by placing alternate layers of iron and charcoal in a furnace and covering the top with clay to prevent the charcoal from burning off. Much iron containing about 0.10% of carbon is usually used. By closing the furnace, heating it up slowly for a few days and then keeping it at a good yellow heat for about nine days, the iron has absorbed about 1% of carbon. This product is often used for making crucible steel by merely melting it down in the pot and adding the alloying materials that are desired to purify and strengthen the metal. This process is also used in Harveyizing armorplate, but in this case but two plates separated by one layer of charcoal are used, and about 30 days' time consumed; ten of which are used to slowly heat the metal up to the desired temperature, at which it is retained for ten more days, and the final ten days are consumed in allowing it to slowly cool. With this treatment the carbon has penetrated to a depth of from 1 to 1¼ inches and the surface of the plate will show about 2.50 per cent. of carbon when analyzed.

The Krupp process conducts illuminating gas over the surface of the armorplate instead of the charcoal. When the plate is at a good yellow heat, it decomposes this gas into carbon and hydrogen; the carbon being deposited on the plate in a finely divided state as soot, which is immediately absorbed by the metal, while the hydrogen escapes as a gas.

Both of these cementation processes are used with various modifications for carbonizing small pieces in special furnaces, and this subject is treated in detail under the chapter on Carbonizing. A low carbon iron or steel will absorb carbon from any carbonaceous material in the presence of heat; in fact, if two pieces of metal are heated to the proper temperature, one containing a high and the other a low percentage of carbon, the carbon will flow from the high to the low point. Its action under these conditions is very similar to the difference in potential of an electric current, which always flows from a highly charged body to that of a lower, until an equilibrium has been established.

The actual mode of existence of the carbon in the metal is of great importance in the working and treating of steel, and several words have been coined to define its different conditions. Ferrite means carbonless iron, and its chemical abbreviation is Fe. Cementite consists of three atoms of iron combined with one atom of carbon, Fe_3C. Graphite is the carbon that is uncombined, as, when an excess of carbon is present in iron, all that will combine will be taken up by the iron and form cementite, while the balance will remain in a free state or as graphitic carbon. Pearlite is a very intimate mechanical mixture of ferrite and cementite, usually in alternate layers, and Austenite is a solid solution of carbon in iron. Martensite, Troostite, Sorbite, etc., are transition forms that are taken up under the chapter entitled "Hardening Steel."

The term solid solution refers to that association of substances which is neither chemical combination nor mechanical mixture. A solid solution has all of the properties of a liquid solution, such as salt or sugar when dissolved in water, except liquidity. It is distinguished from a chemical compound because of the fact that the constituents may vary in the proportions in which they are present, and that it is not a mechanical mixture may be told by microscopic observation. Glass is a familiar example of a solid solution.

In heating and cooling steel, the carbon assumes different forms, as well as when in different percentages. In heating and cooling a piece

of annealed steel that contains about 30% carbon or less, it goes through the changes graphically illustrated in Chart 1. With a steel containing not more than 0.90% of carbon, it is almost impossible to develop any graphitic carbon, as this is a eutectoid steel that contains about six times as much pure iron by weight as the weight of the cementite, and thus it is almost impossible to force the carbon into the graphitic state. The ability to produce graphitic carbon is greatly decreased as the carbon lowers in percentage.

Starting with a soft or annealed bar of low-carbon steel at atmospheric temperature, which has been designated zero on the chart, the temperature will rise uniformly until it reaches a point at about 1300° F. Here the temperature hesitates and remains stationary until certain internal conditions have been satisfied, when it again rises uniformly to about 1400° F., where the second transformation takes place in the metal, and the temperature again remains stationary until this has been completed, and it again rises uniformly to about 1550° F., where the third change takes place. These have been designated the recalescent points, and they have been named Ac1, Ac2, and Ac3. If suddenly cooled at the upper point, the steel will be made very hard, and the metal will be held in the condition it was placed by the applied heat.

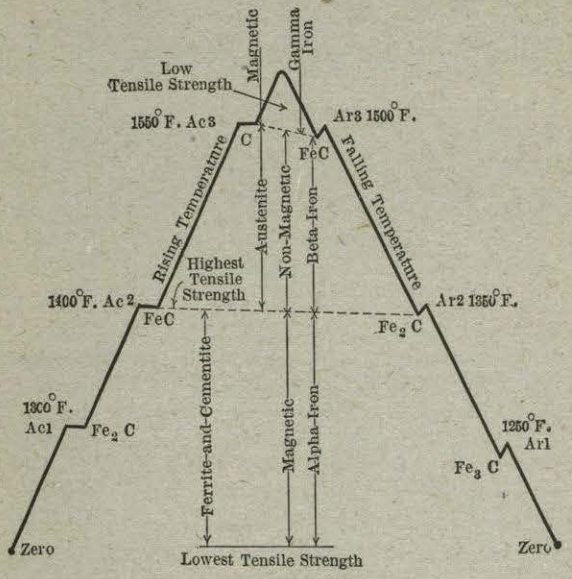

CHART 1.

If allowed to cool slowly or annealed, the temperature will drop uniformly until slightly below the temperature at which the transformation took place while the heat was rising, or about 1500° F., and the metal will then slightly rise in temperature. This point has been designated

Ar3. When the alterations in the structure and grain have been completed, the temperature again falls uniformly until it reaches a temperature of about 1350° F., at which point the second change takes place, that is the opposite of that on the rising temperature, and has been designated in Ar2. After the change has been completed at this point, it again lowers in temperature uniformly to the next point, or Ar1, at about 1250° F., and after this change takes place, it then gradually lowers to atmospheric temperature. These have been named the decalescent points.

While opinions differ on this point, what probably takes place is that while heating the steel up to Ac1 all the carbon is in the cementite form, or Fe_3C. When this point is reached, the heat that has been absorbed by the metal causes a partial decomposition to take place that results in the dropping of one atom of iron, and when the metal has completely assumed the form of Fe_2C, the temperature rises to Ac2, where it drops another atom of iron and the carbon assumes the form of FeC. With this change completed, the temperature again rises to Ac1, where the carbon goes into solid solution with the iron or the Austenite form.

On slowly cooling the metal from this point, the reverse action takes place, that is, at Ar3 the carbon absorbs one atom of the iron that has been dropped on the rising temperature, and the metal becomes FeC; while at the next point, or Ar2, it absorbs the second atom of iron that was dropped and takes the form of Fe_2C, while at Ar1 it absorbs the third atom of iron and again becomes Fe_3C, or cementite.

During these changes in the metal, the iron assumes three different conditions. While the temperature is rising up to Ac2 it is highly magnetic, and is called alpha (α) iron. At Ac2 it loses its magnetism and between Ac2 and Ac3 it is as non-magnetic as brass, and is called beta (β) iron. This change in magnetism is accompanied by a change in electric conductivity and specific heat. At Ac3 another change in electrical conductivity takes place and also in the crystalline form. Above Ac3 it is called gamma (γ) iron.

The carbon content of steel usually varies between 0.10 and 2%. Metal having more than 2% is called cast iron and used as such. Until recently wrought iron was about the only useful iron product that contains less than 0.10% of carbon, but this is made by a working instead of a casting process. Now, however, so-called "ingot iron," consisting of about 99.9% of pure iron, with only a trace of carbon, is made commercially.

With a carbon content of from 0.10 to 0.30%, steel is soft and cannot be hardened enough to prevent cutting with a file. It is then called machinery, soft, or low carbon steel. With a carbon content of from 0.30 to 2% it can be hardened so as to cut other steels or metals, and is then called tool, half hard, hard or high-carbon steel, according to the carbon content. Exceptions to the above statement may be made in hard

steels, as a low-carbon steel can be made hard by either manganese, tungsten, or chromium, but it is true of soft steel.

Every increase in the percentage of carbon increases the hardness and brittleness, and therefore its liability to fracture when cold or when heated suddenly, while it reduces the elongation and reduction of area. The tenacity shows a relatively quick rise up to 0.90% of carbon, and a slow rise from there to 1.20% carbon, after which it decreases. The relative ductility decreases in an irregular curve with an increasing carbon content. These properties are graphically shown in the chart (Fig. 43), while the separation of the ferrite and carbon and the formation of graphitic carbon are shown by Fig. 44.

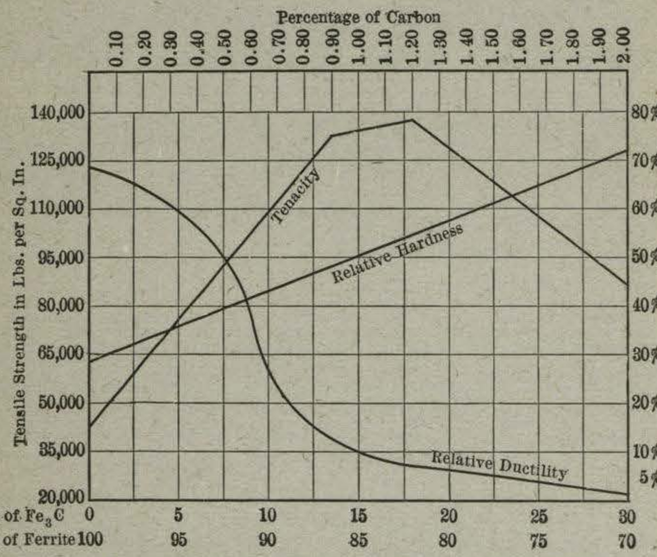

FIG. 43. — Effect of carbon on physical properties of steel.

The strength of steel is always secured at the sacrifice of some other desirable property, but the sacrifice is less in the case of carbon than with any other element. The tensile strength and elastic limit are raised considerably by hardening, and the higher the percentage of carbon the greater the degree of hardness that can be attained. But the greater the carbon content the less will be the elongation, as hardened high carbon steel is very brittle. This brittleness makes high carbon steel very easily damaged in heat treating or working, and the carbon content is usually kept as low as possible for the strength and hardness that is desired. "Sudden rupture" is a term which is especially applicable as a characteristic of carbon steel products, and a large amount of effort is being expended to discover either new ingredients, new methods of manufacture, or new ways of treating the metal that will overcome this characteristic.

Some investigations that have been carried on prove that beginning with pure steel, which has a tensile strength of 40,000 pounds per square inch, every increase of 0.01% of carbon, up to about 1%, increase the strength of acid open hard steel about 1000 pounds, and basic open hard steel 770 pounds per square inch. As the color method of determining the carbon content does not show all the carbon present, these figures, however, should be changed to 1140 and 820 pounds respectively, when the color method of analysis is used.

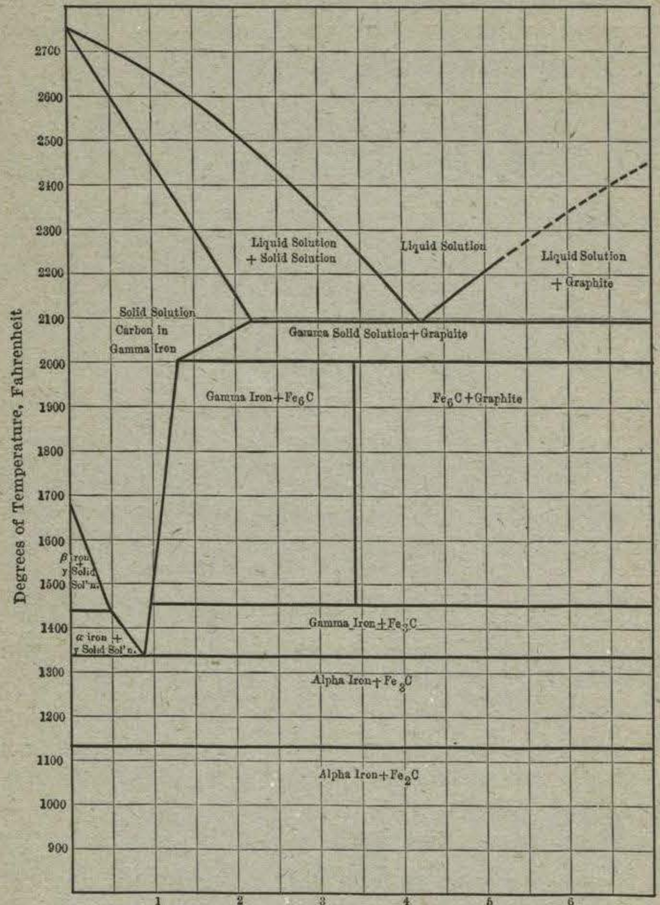

FIG. 44. — Effect of temperature on carbon.

Probably Bessemer steel would show lower figures than this and crucible or electric steel higher figures. This is doubtless due to the fact that some processes of steel making remove the oxides and occluded gases better, or to a greater extent, than others, and it has been pretty well demonstrated that these are injurious to the strength and life of steel.

alter these figures, but with all other conditions equal they will probably hold good.

That the maximum strength is placed at about 1% carbon is probably due, to a great extent, to the fact that the crystalline constituents form an intimate mixture near the eutectoid proportions, and hence the crystallization is very small comparatively. With more carbon (cementite) present the pearlite grains are surrounded with a network of cementite, while with less the pearlite grains are surrounded with a network of ferrite, and both of these decrease the cohesive force inherent in the metal.

One of the oldest theories as to what made high-carbon or tool steel harden was that the carbon in unhardened steel was partially in the graphitic and uncombined form, and when it was hardened all the carbon assumed the combined form. The most generally accepted theory, however, assumes that the hardness is due partly to the presence of the solid solution of carbon in iron, and partly to the iron being in the gamma or beta forms. This solid solution of carbon in gamma or beta iron is exceedingly hard and it is preserved in the steel by quenching from above the critical temperature.

MANGANESE

Manganese occurs in nature principally in the form of manganese dioxide (MnO_2), which is commonly called black oxide of manganese, but occasionally it is found in other compounds, such as braunite, manganite, carbonate, etc. Some of its compounds with oxygen and hydrogen are distinctly acids while others are distinctly basic, and it is in connection with the base-forming elements that it is of interest in steel making. For use in steel making the dioxide is separated from its oxygen, in the presence of charcoal or coke, either in the blast furnace or in an electric furnace. It looks like cast iron, is brittle and hard, and is combined with iron to form ferro-manganese. Sometimes silicon is added to form ferro-silicon-manganese.

Manganese is an element that is always found in steel, but its true properties and effects were not known until about twenty years ago, when they were discovered by R. A. Hadfield, a metallurgist and steel maker of Sheffield, England. Its effect when added to steel up to 2% with various percentages of carbon is best shown by Fig. 45, the actual mode of existence of the carbon in the steel being very important.

When more than 2% and less than 6% of manganese is added, with the carbon less than 0.5%, it makes steel very brittle, so that it can be powdered under a hand hammer. From 6% of manganese up, this brittleness gradually disappears until 12% is reached, when the former strength returns and reaches its maximum at about 14%. After this a decrease in toughness, but not in transverse strength, takes place, until 20% is reached, after which a rapid decrease again takes place. Manganese may affect the tensile strength and ductility of steel, either indirectly by retarding the formation of blow-holes, or directly by entering into chemical combination with the metal.

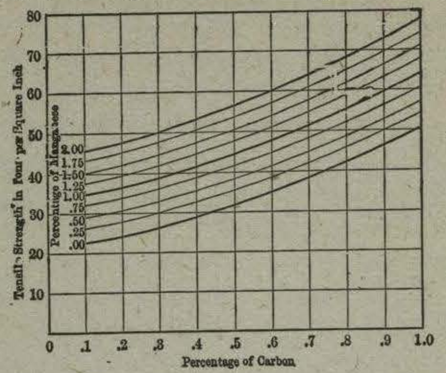

FIG. 45. — Effect of manganese below 2 per cent.

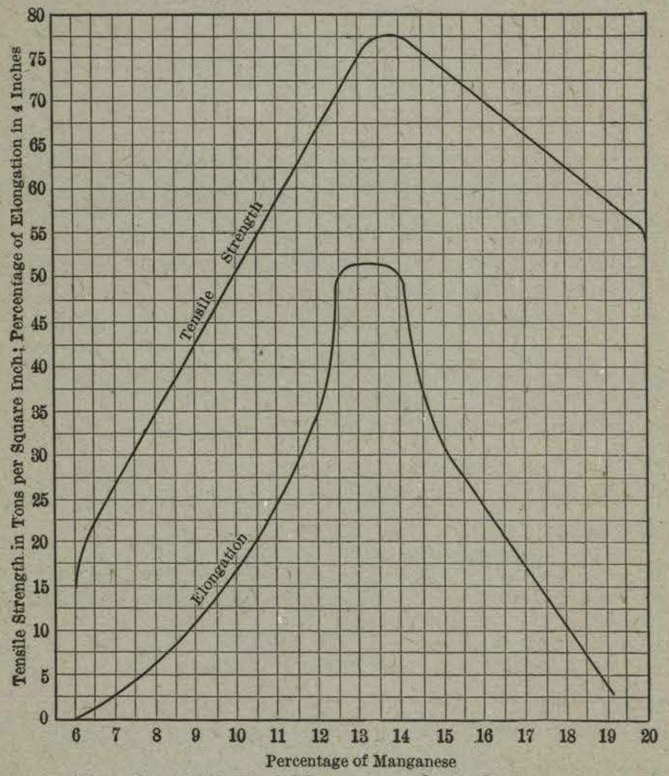

FIG. 46. — Effect of Manganese above 6 per cent.

Fig. 46 shows the effect of more than 6% of manganese on the tensile strength and elongation.

Steel with from 10 to 15% of manganese and less than 0.50% of carbon is very hard and cannot be machined or drilled in the ordinary way; yet it is so tough that it can be twisted and bent into peculiar shapes without breaking. This makes a steel that is only suitable for casting into the desired shape. A process has recently been patented however, for casting this steel into ingots, and then subjecting them to a heat treatment that enables them to be mechanically worked; that is rolled, forged, etc., and this might possibly be extended to machining operation.

Manganese in the form of a ferro-alloy containing about 80% of manganese is added to a heat of steel at the time of tapping, so that it may seize the oxygen which is dissolved in the bath and transfer it to the slag as oxide of manganese. Manganese prevents the coarse crystallization that the impurities would otherwise induce, and steels low in phosphorus and sulphur require less manganese than those having comparatively high and percentages.

Manganese has a greater affinity than iron for both sulphur and oxygen, and is therefore used in steel making as a deoxidizer and to neutralize the sulphur. Manganese oxide (MnO) and manganese sulphide (MnS) are formed, the first of which passes almost entirely into the slag and the second of which will pass partly into the slag if time is allowed. About four times as much manganese is needed as there is sulphur present, as it does not always catch all of the sulphur; thus if any great amount of sulphur is present a considerable amount of manganese is desired to counteract its effect. If the bath is kept liquid enough and enough manganese is present, but little oxygen or sulphur will be found combined with the iron, which is desirable as they are very injurious to the metal. The length of time and the care required, however, make it commercially impractical to reduce the oxygen and sulphur to a trace in this way. Therefore manganese is used to reduce them to commercial percentages, and other materials are used to still further remove them for the finer grades of steel. Manganese sulphide weakens steel greatly if segregated together with phosphide of iron, especially if the metal is rolled, as this magnifies the sulphide by spreading it out during rolling.

Manganese is not only useful to cleanse the bath of impurities, but it has other properties that aid in making steel better. The amount that can be left in the steel varies with the amount of various other ingredients that are added to the metal, and this is especially so of carbon. In effect it behaves in practically the same manner as carbon, as also does nickel. With a given carbon content the introduction and increase of manganese causes a series of structural changes similar to those that occur in carbon steels, that only contain small percentages of manganese.

While the action of these three elements upon iron is of the same kind, it is not of the same strength, as the equivalent of 1% of total carbon, that contains the maximum amount of hardening carbon, is 7.25% of manganese and 17.55% of nickel. All three of these cause a structural change in the metal from pearlite, that includes the sorbitic, to martensite, that includes the troostitic, and then to the polyhedral structure, and with none of them is a special carbide formed. Chromium has an analogous effect, but not as complete, as a double carbide of iron and chromium forms and this is not maintained in solution in the iron without tempering.

The critical temperature to which it is safe to heat steel is raised by manganese, owing to its resisting the separation of the crystals in cooling from liquid, and conferring the quality of hot ductility. It also assists in producing more uniform alloys, and tends to make steel crystals smaller by making the metal plastic, and thus counteracting the tendency toward crystallization that phosphorus causes, although the metal is more liable to crack when heating or suddenly cooling it from a red heat. The good qualities more than offset the bad, and it is a very useful factor in steel making if the proper percentages are used. It atones for many evils in steel by healing it up and producing a smoothly rolled surface.

In the ordinary steels this percentage is usually from 0.70 to 1.00%, while in many of the special alloys it runs from 0.30 to 0.50%. In the high-speed steels the manganese content is from 0.10 to 0.30%, and in steels for carbonizing this should be kept below 0.20%. When in very large amounts (from 6.0 to 15.0%) it reverses the effects of rate of cooling upon the ductility of steel; slow cooling making manganese steel brittle, while quick cooling makes it extremely ductile.

Magnetic qualities are not materially effected when the manganese is kept below 7.50%. When 8%, or more, is present, however, the magnetic attraction becomes *nil*. Manganese decreases the electric conductivity in greater proportions than any other element, except nickel. Thus third rails, or similar steels, must be given their hardness by materials other than nickel or manganese. A peculiar fact that was brought out by some experiments was that a pure nickel-iron alloy that contained from 12 to 13% of nickel was highly magnetic, but by the addition of 5% of manganese this metal became as non-magnetic as brass. While manganese steels are known to be non-magnetic, it was not known that manganese would have this effect upon nickel, which also makes a non-magnetic steel when added in certain proportion.

To sum up, manganese alloys with iron in all ratios, it being reduced from its oxides at a white heat by carbon. Its presence increases the power of carbon to combine with iron at a very high temperature (about 2550° F.), and almost entirely prevents its separation into graphitic carbon at the lower temperatures. Manganese permits a higher total carbon by raising the saturation point, and it is easily separated from iron by oxidation, as it is even oxidized by silica. While it does not counteract the cold shortness caused by phosphorus, it does prevent to some extent the red and yellow hot shortness caused by sulphur.

Manganese retards the formation of blow-holes, though not to the extent that silicon does, by preventing the oxidation of carbon, and thus the formation of carbonic oxide. It also increases the solubility of the gases in the steel while solidifying. It probably raises the elastic limit and slightly increases the tensile strength; adds fluidity to the metal; increases hardness; increases fusibility when present in considerable quantity, and gives greater plasticity and mobility to the metal at forging heats. Some recent investigations, however, make it doubtful that it diminishes ductility to any extent.

SILICON

Silicon is the second most important element in the solid part of the earth's crust, oxygen being first, and forms 27.21% of it. It is never found in the free state of nature, but, having a powerful affinity for oxygen, it occurs chiefly as silicon dioxide (SiO_2), which is commonly called silica, and in the form of silicates in combination with oxygen and such metallic elements as sodium, potassium, aluminum, and calcium. Silica will neutralize any base with which it comes in contact when molten, and all metallurgical slags are silicates thus formed. The silicon used in steel making has to be separated from the oxygen of the silica and united with iron to make ferro-silicon. Sometimes manganese is added to this to form ferro-silicon-manganese.

Many contradictory statements have been made as to the effect of silicon on steel. When the silicon is high in Bessemer steel it is an indication that the metal has been blown too hot, and the metal is apt to be brittle. The percentage varies considerably, according to the heat of the charge, and this causes irregularities which may account for the difference of opinion. The melting point and specific weight of pig iron are governed chiefly by the silicon and the carbon, which are the principal elements. To obtain strength and density the silicon and carbon should both be low. The hardness should be controlled by a careful adjustment of the sulphur, manganese, and phosphorus, together with a study of their effect on the final condition of the carbon. In making castings high and low silicon irons should never be mixed. To get the best results in the steel the silicon should be eliminated as much as possible from the iron and a definite quantity added in the form of high percentage ferro-silicon, or ferro-manganese-silicon. This gives a very different effect from that of silicon left in the process of manufacture.

If silicon is added to steel in such a manner as to cause it to enter into solution as silicide, it confers upon the metal valuable properties; but if it forms a silicate it is injurious in many ways, even to the point of being dangerous. This latter seldom occurs, or at least occurs only to a slight degree, as the silicates of iron, manganese, etc., dissolve into each other very readily and form a slag; although manganese silicate probably occurs more frequently and causes more failures in steel than is generally supposed.

Silicon, having a great affinity for oxygen, it seizes this wherever found, and carries it off into the slag, whether in the form of gases, oxides, or dissolved oxygen. This prevents the formation of blow-holes, and makes the steel harder and tougher. Thus it is better able to withstand wear or crushing from continual pounding. This is only so, however, when the silicon has been eliminated as far as possible from the pig iron and is again added to the steel bath in the form of ferro-silicon or silicon spiegel. Otherwise the steel is liable to show brittleness and irregularity of percentage.

One steel maker found that if the percentage of manganese plus 5.2 times the percentage of silicon were made to equal 2.05, the metal would be entirely free from blow-holes, but the pipe would be large; if the total was made to equal 1.66%, the pipe would be smaller and numerous minute blow-holes would appear, but not enough to harm the steel for the use to which it was to be put. He also found that 0.0184% of aluminum would give the same result as the 1.66% of manganese and silicon.

In the Bessemer converters the silicon increases the temperature of the bath. Thus the lower the percentage of the silicon in the pig iron the shorter will be the blow. At the end of the blow, 0.2% of silicon is added to rid the bath of the gases. Thus the percentage of silicon is usually under 0.2 in Bessemer steel, and for steel rails many engineers are limiting it to 0.1%.

During the "killing" in the crucible process the steel absorbs silicon from the crucible and thus becomes sound by throwing off the gases. The graphite crucibles used in this country give up more silicon than the clay crucibles used in Europe, and consequently allowances have to be made when charging. Too long "killing" makes the steel harsh, brittle, and weak, owing to its absorbing too much silicon. Crucible steels nearly always contain more than 0.2% of silicon.

The influence of silicon on the results of quenching is similar to that of carbon in many ways. It is also dependent upon the coexisting amount of carbon and manganese. It neutralizes the injurious tendency of manganese to some extent.

An increase in the percentage of silicon slightly raises the tensile strength and lowers the elongation and reduction of area. Up to a content of 4%, silicon increases the tensile strength about 80 pounds per square inch for every 0.01%. Beyond this amount a weakening of the metal seems to take place. Without a considerable percentage of manganese, silicon steels show very low shock resistance, whether annealed or quenched. With 0.20% of silicon the tensile strength is increased about one-third more than 0.01% of carbon would increase it. Beyond a content of 5.0% silicon steels are but little used for any purposes.

Steels containing a little less than 1% of carbon and from 1 to 2% of silicon have been used quite successfully for hard-tool steels. Below a content of 1% silicon ceases to have an influence on quenching and the metal may be classed as a special carbon steel. Some makers of steel try to keep the silicon as low as possible, but many of the best steels contain from 0.20 to 0.80%. With the carbon content low the silicon may be raised to a fairly high figure, but with the carbon high the silicon should be kept low. It should also be kept low when the phosphorus is high.

Silicon steels are extremely fibrous with a remarkable resistance to shock in the direction of lamination, but practically no resistance in a direction perpendicular thereto. This quality makes them especially adapted for leaf springs.

Ferro-silicon, as now made in the electric furnace, with a silicon content between 30 and 60%, is very brittle and liable to disintegrate spontaneously, even though made of comparatively pure material. With the silicon in any percentage from 30 to 40 and 47 to 65, it gives off quite large quantities of hydrogen phosphide gas, especially when attacked by moisture in any form. This is generated from calcium phosphide, which in turn is formed from the calcium phosphate, that is present in the quartz and anthracite, when it is submitted to the high temperature of the electric furnace. Smaller amounts of hydrogen arsenide are also evolved, and both of these are highly poisonous. When the ferro-silicon disintegrates, the amount evolved is greater, owing to the largely increased surface that is exposed.

Several fatal accidents by explosions and poisoning have been caused from these gases since ferro-silicon has been manufactured in the electric furnace. Most of these have occurred when shipping it on boats, as there is then more moisture to attack it. When the silicon content is below 30 or above 65% these gases do not appear to evolve in amounts that are dangerous. As it is not really necessary to use the alloys between these percentages for the manufacture of any of the iron products, unless it be for basic furnace steel, their use, if not their manufacture, should be prohibited. Where absolutely necessary to use them, the ferro-silicon should be broken up into usable sizes and completely exposed to the air for at least one month before shipping. It should then be stored in a place where there is plenty of ventilation to carry off the gases. Ferro-silicon made in a blast furnace, however, does not give off any of these gases, and there is a movement started in Europe by the electric furnace ferro-silicon makers to abandon the manufacture of this alloy in the dangerous percentages.

PHOSPHORUS

Phosphorus always occurs in nature in the combined condition, in the form of phosphates, derived from orthophosphoric acid H_3PO_4, or in the form of organic compounds. It unites with metals to form phosphides. It forms two oxides, namely, P_2O_3 and P_2O_5, and also forms compounds of the same character and analogous composition to arsenic, antimony, and bismuth. It is consequently placed in the same chemical group as these.

It is always encountered in reducing iron ores, and is a very difficult element to remove entirely from the finished iron and steel product. In these materials it must be reduced to as low a percentage as possible, as phosphorus is without doubt the most injurious element that is found in steel, notwithstanding the fact that in the past many experiments have been carried on that apparently proved that phosphorus, up to about 0.12%, strengthened steel. When these same steels were put into actual use, however, failures occurred, and the cause was nearly always traceable to the phosphorus.

In the rolling mills phosphorus does not show any bad effect, as the heat under which the steel is worked seems to overcome this, but when the metal has become cooled and is subjected to sudden shock or to vibrational stresses, it breaks very easily. The lower the temperature and the higher the atmosphere the easier will the breaks occur. This has led to the term, "cold-shortness," as applied to the effect of phosphorus on steel.

Phosphorus diminishes the ductility of steel under gradually applied load, as shown by the reduction of area, elongation, and elastic ratio when specimens are pulled apart in the ordinary static strength testing machines. But when the steel is tested in rotary or alternating vibration testing machines, as well as with a pendulum impact machine, the decrease in ductility and toughness is shown to a greater degree. Phosphorus also reduces deflection, and the rigidity thus imparted might be considered an advantage for structural purposes except for the metal's weakness at low temperatures and when subjected to shocks.

Phosphorus steels are so capricious that they may show a reasonably high static ductility and still show very brittle when shock tests are applied. Therefore the safest rule to apply is to have the phosphorus in all steel products as low as possible. It is a very poor steel that contains 0.10% of phosphorus. The ordinary grades contain as much as 0.08%, and the high-grade steels should have less than 0.04%, while in the very best steels it should be even lower than this. In fact, this has been reduced to below 0.01% in some of the electric furnace steels, and occasionally a mere trace is all that is left in the finished product.

Phosphorus gets into the metal by entering the blast furnace with the ores in the form of metallic phosphates, — the form in which it is usually found in nature, — and mainly as phosphate of lime, which occurs as a natural mineral named apatite. Many metallic oxides unite with it to form salts, especially iron and magnesium oxides and lime, but in the presence of silica, which is a stronger acid, it is driven out of the slags and returned to the iron until the silica has been satisfied with bases.

In steel, phosphorus has a tendency to cause coarse crystals to form, and this tendency is increased with each percentage of carbon. It forms the phosphide, Fe_3P, and this forms a series of alloys with iron. The eutectic of this series contains 64% of this phosphide, which equals 10.24% of phosphorus. A certain percentage of phosphorus will dissolve in pure iron and no eutectic will form to produce brittleness, but when carbon is added, each increase in percentage exerts an influence on the phosphorus that causes it to precipitate from the solid ferrite solution and take the eutectic form. Therefore the more pure the iron and the less cementite that is in the steel, the less will be the brittleness that is caused by phosphorus, while each increase in the percentage of carbon increases the tendency of the eutectic to form and the steel to assume a coarser crystallization, which makes it both weaker and more brittle.

Phosphorus is removed from steel to a different degree by the different processes of manufacture. Thus Bessemer steel usually contains the highest percentage of phosphorus, while the other steels contain gradually decreasing percentages in the order in which they are named: acid open-hearth; basic open-hearth; crucible; electric. The acid open-hearth furnace requires materials low in phosphorus, while in the basic it is removed by adding a sufficient amount of lime to the slag, and in electric furnaces it is removed by using the proper flux.

One of the latest methods consists of using an oxidizing slag in such a way that it will combine with the phosphorus and form a phosphate, and then adding a reducing material to the slag that will convert this phosphate into a phosphide. The reducing material is usually ground coke that floats on top of the slag and reduces the phosphate without interfering with the molten metal below. Owing to the strong combination of the phosphide, the phosphorus cannot be separated out by the iron, without first being changed back to phosphate, and this is impossible in a reducing atmosphere.

One charge that was dephosphorized in the Heroult electric furnace, when taken from a Bessemer converter, analyzed: phosphorus, 0.10%, sulphur, 0.16%, manganese, 0.10%, carbon, 0.07%, and silicon, traces. A 15-ton charge of this was put in the Heroult furnace and a black slag composed of 400 pounds each of mill scale and lime was added. This made an oxidizing slag that became fluid when the molten metal below was thoroughly oxidized, and all the phosphorus passed into the slag as phosphate of lime (CaO). Ground coke was then added to the top of the slag, and this reduced the phosphates there into calcium phosphide (P_2Ca_3). Without removing the slag the required amounts of carbon, silicon, manganese, etc., were added. That there was no return of phosphorus to the steel is shown by the analysis of the final product, which was, phosphorus 0.005%, sulphur, 0.005%, with the carbon ranging from 0.05 to 1.50%, and the manganese and silicon as desired.

A high phosphorus steel is sometimes used for the third rail in an electric railway, as phosphorus will increase hardness without decreasing electric conductivity as much as other ingredients would, and it also decreases the purity of the iron less than any other material. This gives the rails the necessary hardness and purity to withstand the abrasive wear caused by the contact shoes, without greatly lessening the conductivity.

Phosphorus in cast-iron reduces the melting point, makes the metal more fluid, and prolongs the period of solidification. This is made useful in such work as art castings, where a detail of figure is of more importance than strength, as the metal fills every minute crevice in the molds. By keeping the metal in a pasty state for a long time, or retarding solidification, the phosphorus allows the graphite to be expelled from the solid solution and occupy spaces between the particles of iron. This action causes the metal to expand and press into every tiny cavity in the mold, and the higher the percentage of phosphorus the longer will the solidification be delayed. Certain chemical conditions caused by too much phosphorus, too little silicon, etc., might overcome this by exerting a tendency to keep the carbon in the combined form. A decreased shrinkage because of this expansion may also be caused when the phosphorus separates from its solution in the ferrite and forms a eutectic. Phosphorus also increases the tendency toward segregation.

SULPHUR

Sulphur is one of the elements of the earth that is found in large quantities in the free state, especially in volcanic regions, as well as combined with metals in the form of sulphides. It is given off from the fuels used in reducing the iron ores and refining steel, and at the higher temperatures it combines with the oxygen of the air to form a dioxide, SO_2. Part of this is liable to be trapped in the metal unless precautions are taken or slags used to remove the sulphur.

When in steel in the form of sulphide, it causes the metal to crack, tear, and check in rolling, forging, heat treating, or hot working, and, therefore, the term of "hot-shortness" has been applied to its effect on steel. This is the opposite of the effect of phosphorus. Its effect on the properties of steel when cold has not been accurately determined, but it seems certain that the effect is not detrimental to any extent.

When steel is heated beyond a dull red, sulphur in the sulphide form is said to cause a crystallization to take place, and when high temperatures are reached the grain becomes very coarse, as the sulphur is dissociated and forms into a gas that diffuses between the iron crystals, thus separating them and preventing perfect cohesion. When contraction by cooling takes place this may cause microscopic cracks, or even cracks large enough to be seen by the naked eye. These, of course, weaken the metal. Sulphur and phosphorus increase the tendency toward segregation.

Sulphur takes two forms in steel, one of which is sulphide of iron, and the other sulphide of manganese. Iron sulphide (FeS) usually forms when the sulphur is high and the manganese low, as sulphur has a greater affinity for manganese than for iron. Until the manganese is satisfied, sulphide of iron is not liable to occur, and this latter form does not often occur in commercial steels. It is more brittle than manganese sulphide, and at the proper temperatures for rolling steels is in a liquid state, so that there is no cohesion between it and the molecules of steel. Instead of coming together in drops, as manganese sulphide does, it spreads out in webs or sheets, which are very pale in color and usually completely surround the manganese sulphide. These cover a comparatively large area, and the effect of iron sulphide is thus very injurious to steel, as it is very weak and liable to break along these webs or sheets. Owing to its liquid state iron sulphide is very liable to cause trouble at the rolling temperatures, whether this temperature be used for rolling or when forging, welding, or heat-treating the steel.

Sulphide of manganese (MnS) is formed by the uniting of manganese and sulphur, and it is invariably found in steel; this being the form that sulphur takes in all the good grades of steel, and if there is enough manganese present all of the sulphur in the metal will assume this form. It usually forms in globular spots, but when the metal is rolled or hammered, these generally elongate and under the microscope they show a pale state or dove gray color.

Opinion differs as to the injurious effect of manganese sulphide upon steel, but, however this may be, it is not as injurious as iron sulphide. It has been melted in coke-fired assay furnaces that would not melt mild