

ASTM Metals Data Series™

DS70: Handbook of Steel Data: American and European

Introduction

The expression ferrous materials is used to mean the metallic element iron and the entire range of iron-based metallic alloys. There are a great many different ferrous materials, but they can be divided into three basic categories, namely wrought iron, steel and cast iron.

Wrought iron, which is no longer commercially produced, is a relatively pure iron containing non-metallic slag inclusions. Modern wrought iron products are actually made of low carbon steel.

Steels are iron-based alloys whose most important component element next to iron itself is carbon. The carbon contents of steels are low, usually below 1%, but the presence and amount of carbon in the steel have a major effect on its behavior in service. By far the most common type of steel is plain carbon steel, i.e. steel containing only iron and carbon plus small amounts of manganese and, usually, silicon or aluminum. The manganese, silicon and aluminum are added to compensate for the presence of the impurities sulfur, oxygen and nitrogen. Another important type of steel, the alloy steels, contain in addition to the above-mentioned elements, significant quantities of such elements as chromium, nickel and molybdenum, which distinguishes them from plain carbon steels. A specialized range of alloy steels, known as stainless steels, contain a minimum of 10.5% chromium. Tool steels, the final type to be considered here, are specialized carbon or alloy steels which are capable of functioning under the demanding service conditions associated with the working and shaping of metallic and non-metallic materials into desired forms. Some steel is used in the form of steel castings, but most steel objects are mechanically worked into their final forms and are thus categorized as wrought products.

Cast irons contain much higher carbon and silicon levels than steels, typically 3-5% carbon and 1-3% silicon. These comprise another category of ferrous materials, which are intended to be cast from the liquid state to the final desired shape.

Ferrous alloys dominate the world of construction materials. Their widespread applications are the result of a broad range of desirable material properties combined with favorable economics. Iron is the least expensive of all the metals and the second most abundant in nature.

This chapter supplies an introduction to the metallurgical aspects of ferrous materials, especially steels. Subsequent chapters provide data on many aspects of various ferrous materials. More details relating to the metallurgy of particular products are discussed in introductions to the sections on Carbon and Alloy Steels, Cast Steels, Cast Irons, Tool Steels and Stainless Steels.

Historical Aspects

Iron is one of the seven metals of antiquity, and is associated with the Roman god Mars and the planet of the same name. The first iron to have been used by humanity was probably meteoritic iron; this is readily identifiable because the so-called 'iron' meteorites are in fact iron-nickel alloys containing an average of about 8% nickel. Objects made from meteoritic iron are found among the archaeological artifacts left by many ancient cultures worldwide. Meteoritic iron, the metal from the sky, was used for utilitarian, decorative and ornamental purposes, and in some cases for objects with ceremonial functions.

However, most of the iron found in the archaeological record has been smelted from ores of iron, and the existence of this early material has led to the designation "Iron Age" for a particular stage of the evolution of societies, which began during the second millennium B.C. The first instances of iron smelting are not known, but it is possible that the earliest smelted iron was an inadvertent by-product of copper smelting operations. Here it was sometimes necessary to add iron oxide to the smelting furnace charge as a flux in order to lower the melting temperature of the silicate slag. Overly reducing conditions in the copper smelting furnace could have led to the subsequent reduction of metallic iron from the slag. Certainly smelted iron was in use by about 2000 B.C. and was relatively widespread by 1000 B.C. The original form in which smelted iron was used was wrought iron, a heterogeneous mixture of iron with silicate slag. Wrought iron was produced in bloomery furnaces by the solid state reduction of iron ore to metal, well below the melting temperature of iron. The product of this smelting operation was a bloom, a mixture of slag

and metallic iron which was hot hammered to remove as much slag as possible. With improvements in bellows and furnace technology, smelting temperatures increased until they were adequate to permit the production of liquid iron, in blast furnaces. This iron, which contained a high carbon content, could then be cast directly to useful shapes, as cast iron. Alternatively it could be converted to wrought iron by subjecting it to decarburization, initially by treating it in fining furnaces and later by the puddling process. Cast iron came into use in the western world some time in the 11th-13th centuries A.D., although it had been used since about 500 B.C. in China, where higher temperature furnaces were available much earlier than in the west.

The intentional addition of carbon to wrought iron to make steel was being carried out during the first millennium B.C. but once again the precise chronological and geographical origins are not yet known. A high production industrial version of the solid state carburization process, known as cementation, was widely used in the western world beginning early in the 17th century. For severe service applications this was supplemented in the mid-18th century by crucible steel, which was made by remelting cementation steel to produce a higher quality material. However, steel remained a relatively low volume, high cost product until the development of the mass production processes (the Bessemer process and the Siemens-Martin open hearth process) for producing steel from blast furnace iron in the mid-19th century. Prior to these developments wrought iron and cast iron, rather than steel, were the predominant ferrous materials in use for structural applications.

Iron and Steel Production

Iron is one of the most abundant elements in the earth's crust, where it is a major constituent of many minerals including oxides, sulfides, silicates and carbonates. Commercially viable ores are predominantly of the oxide or carbonate type, and metallic iron is reduced from such ores with relative ease. Most of the iron produced goes directly for conversion into steel, with minor amounts being modified for use as cast iron. Typical primary production operations involve the blast furnace reduction of iron ore to produce liquid pig iron, a metallic iron containing some 4% carbon. Liquid pig iron is subsequently treated in steelmaking furnaces where carbon and impurities are removed by preferential oxidation. The basic oxygen furnace is the technology most widely used for this purpose at present. Some steel is also produced by remelting scrap or combinations of scrap and ore (e.g. pre-treated pellets) in electric arc furnaces.

All steel is produced in the liquid state, so that before further processing it must be allowed to solidify. In commercial operations this solidification is carried out using two different practices. The molten steel may be teemed into tall rectangular molds to solidify as ingots, which are subsequently reheated and worked, usually by hot rolling, into semifinished products known as blooms, billets or slabs depending on their dimensions. More commonly, blooms, billets or slabs may be produced directly from liquid iron by continuous casting. In this process the liquid steel is poured into the top of an open-bottomed water-cooled mold while a strand of solid steel is withdrawn continuously from the bottom of the mold. Semifinished steel is converted into finished wrought products such as bars, sheets, strips, plates, structural shapes, wire, rails and tubular products using such operations as hot and cold rolling, drawing, forging and extruding. Many finished products require specific forms of heat treatment which, in combination with the forming operations, produce the specific combinations of properties desired for particular engineering applications.

Deoxidation and Desulfurization

Liquid steel coming from the steelmaking furnace contains high levels of dissolved oxygen which must be removed before the steel is cast, either in a continuous caster or as ingots. Typical deoxidants employed for this purpose are aluminum and silicon (in the form of ferrosilicon). The removal of oxygen from the steel is referred to as killing, thus the expressions "silicon-killed" and "aluminum-killed" steel. Fully killed steel is relatively homogeneous in its chemical composition and properties, and this practice is common in alloy steels and steels which are intended to be forged or carburized. Semi-killed steel has less deoxidant added than is the case for killed steel, and is typically used for low to medium carbon steels for structural applications. However some steels are not killed, and the oxygen remains in the steel where it reacts with carbon forming porosity (blowholes) of carbon oxide gases. These rimmed steels solidify with marked variations in chemical composition within the ingot. They have an outer rim of relatively pure iron, low in carbon, phosphorus and sulfur. These elements occur at higher than average levels in the center of the ingot, especially near the top. The higher purity outer rim makes these steels more suitable for the production of low carbon steel sheet with good surface quality. Capped steels are intermediate between rimmed and semi-killed steels, and are suitable for sheet, strip, wire and bars with carbon levels above 0.15%.

The sulfur in steel originates as impurities in coal, the material which, after it is converted to coke, is used as the fuel and reductant in the iron blast furnace. Conventionally, the addition of manganese compensates for the sulfur in steel, the sulfur being tied up as manganese sulfides, rather than iron sulfides which would be molten at hot rolling temperatures, causing the steel to be brittle or hot short. However manganese sulfide inclusions tend to degrade the fracture toughness, so modern blast furnace iron and steels are subjected to various types of desulfurization involving, for example, the injection of agents such as calcium carbide or calcium silicide into the molten iron or steel to remove the sulfur. Thus many modern steels have much lower sulfur contents than the levels which were acceptable several decades ago, and which are still reflected in the specifications for standard grades of steel.

Pure Iron and its Allotropy

Pure metallic iron is of very limited usefulness for engineering applications as it has a very low strength and poor resistance to corrosion. Its density (specific gravity 7.87) is slightly lower than that of copper, and its melting temperature is 1540°C (2804°F), slightly above that of nickel and well above copper and aluminum. However the most significant characteristic of iron is its allotropy. Between room temperature and its melting temperature pure solid iron undergoes two changes of crystal structure, known as allotropic phase transformations, so that it has one type of crystal structure at high and low temperatures and another at intermediate temperatures. Below 912°C (1674°F) iron exists with a body-centered cubic (bcc) crystal structure, with its atoms packed as shown in Fig. 1.1. This material is known as alpha (α) iron.

Figure 1.1 Crystal structures of iron.

At much higher temperatures, from 1395°C (2545°F) up to the melting temperature, iron also has the bcc crystal structure and in this temperature range it is referred to as delta (δ) iron. However, at intermediate temperatures, between 912°C and 1395°C (1674 and 2545°F), the crystal structure of iron is face-centered cubic (fcc), with atom packing shown at the right side of Fig. 1.1; this is known as gamma (γ) iron. Thus if iron is slowly heated from room temperature to above its melting point, several phase changes (phase transformations) occur, and on subsequent slow cooling back to room temperature the reverse changes occur. Note that this applies only to slow cooling; if cooling rates are too high the behavior can be different as discussed below.

Iron-Carbon Alloys

The presence of carbon and alloying elements in iron make the allotropic behavior more complex, but in so doing they create the opportunity for an even wider range of microstructures and properties. The effects of carbon are the most significant in this respect. Carbon dissolves in the bcc iron forming a solid solution known as ferrite but the solubility of carbon is very low, with a maximum of only 0.025%C at 725°C (1337°F) in α -ferrite, and only 0.09%C at 1495°C (2725°F) in δ -ferrite. (Common practice is to use the expression ferrite synonymously with alpha (α) ferrite, and to use the full expression delta (δ) ferrite to refer to the high temperature phase.) On the other hand, in the fcc γ -iron the solubility of carbon is much greater, reaching a maximum of 2.1%C at a temperature of 1150°C (2100°F); the fcc solid solution of carbon in fcc iron is known as austenite. Both ferrite and austenite are interstitial solid solutions, that is, the carbon atoms dissolve in the iron by locating themselves in interstitial sites between the iron atoms which are arranged on the bcc or fcc crystal lattice. Fig. 1.2 shows the fcc structure of austenite with some of the lattice interstitial sites occupied by carbon atoms. Ferrite and austenite are referred to as phases since they are physically homogeneous and structurally distinct constituents of the microstructure of the alloy. Other phases which can occur in ferrous alloys will be discussed below.

Figure 1.2 Carbon dissolved interstitially in fcc austenite. Carbon atoms are represented by black circles and iron atoms by white circles.

The temperature ranges over which the bcc and fcc crystal structures are stable are dramatically affected by the presence of carbon. Carbon lowers the lower limit of stability of the fcc phase from 912°C (1675°F) to as low as 725°C (1337°F) and raises the upper limit from 1395°C (2545°F) to as high as 1495°C (2725°F), as shown in Fig. 1.3, with the exact limits depending on the amount of carbon present.

Figure 1.3 Effects of the addition of carbon to pure iron.

This complexity of phase behavior and phase stability can be dealt with most easily by making use of a phase diagram; Fig. 1.4 shows the phase diagram for the effect of carbon on iron. The left end side of this diagram

represents pure iron, with increasing carbon content toward the right. Temperature increases toward the top of the diagram. Before considering this diagram in detail, it is important to be aware that phase diagrams apply to conditions of equilibrium, that is the thermodynamically stable state which is achieved only after there has been sufficient time for the atoms to move around and re-organize themselves into the stable phase or phases which are predicted by the diagram. Equilibrium can require long times to achieve, especially when temperatures are low since the diffusion process by which atoms move is slow at low temperatures where the thermal energy in the system is low.

Figure 1.4 The iron-iron carbide phase diagram.

If the system is subjected to a rapid change of temperature the atoms may be unable to diffuse fast enough to keep up with any phase changes which are demanded by the phase diagram. As a result, during rapid temperature changes the phase diagram does not accurately predict the phase behavior; a different type of diagram is used for rapid changes of temperature, as discussed below. Understanding of all these diagrams is of great importance since steels are virtually always heat treated in some manner to develop their properties, and the diagrams allow the consequences of heat treatment to be predicted and understood.

The phase diagram is basically a map which predicts which phases are stable for any alloy with a given carbon content at a given temperature, i.e. as represented by a point on the phase diagram. Each such point lies either in a single-phase region, e.g. the austenite region, or in one of the two-phase regions which exist between the single-phase regions. The single-phase solid solutions are readily apparent on Fig. 1.4, with α -ferrite in the region GQPG and δ -ferrite in region AJKA. The borders of these regions (e.g. the lines QPG and JKA) represent the limits of solid solubility of carbon. This diagram also illustrates the fact that the carbon solubility is much greater in austenite than in ferrite, the limits of the austenite phase being JIEHGJ with a maximum of 2.1% C at point E.

There are other two phases shown on this phase diagram. One of these is the liquid solution of carbon in iron, which occurs at high temperatures, across the top of the diagram. The lower boundary of this region shows how the freezing temperature (or more accurately the liquidus temperature, the lowest temperature at which the entire material is liquid) of iron-carbon alloys changes with carbon content. For example it shows how at carbon contents in the cast iron range, between 3% C and 5% C, this temperature is low, reaching 1150°C (2100°F) at about 4.3% C. The low freezing temperature is a major reason why cast iron products can be produced with relative ease and low cost. The other phase shown on the phase diagram, at the right hand end within the boundary ONMDO, is iron carbide or cementite, a compound with the formula Fe₃C, corresponding to 6.67% C (note that percentages on phase diagrams are conventionally given in weight percent; Fe₃C contains 25 atomic percent carbon, which corresponds to 6.67 weight percent carbon). The crystal structure of cementite is orthorhombic, giving it a very high hardness, strength and brittleness in contrast to the soft ferrite and austenite phases.

Between any two single-phase regions, in a horizontal sense on the phase diagram, are two-phase regions, for example a steel with a carbon content of 0.4% at a temperature of 760°C (1400°F) lies in the two-phase region with ferrite on the left and austenite on the right. Thus the diagram predicts that this steel at this temperature would consist of a mixture of ferrite and austenite. By constructing an artificial horizontal line across the two-phase region at the temperature of interest, the relative amounts of ferrite and austenite, as well as their carbon contents can be predicted. Thus for the 0.4% C steel at 760°C, the left (ferrite) end of the horizontal line intersects the ferrite solubility limit line PG at about 0.01% C, read from the composition scale across the bottom of the diagram, so this is the predicted carbon content of the ferrite. Correspondingly, the right (austenite) end of the artificial horizontal line intersects the austenite solubility limit line HE at about 0.7% C, which is the predicted carbon content of the austenite. The horizontal position of the alloy composition, 0.4% C, relative to the two ends of the line, 0.01% C and 0.7% C, permits the relative amounts of ferrite and austenite to be determined; the closer the overall alloy composition is to the austenite end of the line, the more austenite is present in the steel's microstructure. In this case, there is somewhat more austenite than ferrite present because the alloy composition, 0.4% C, is somewhat closer to 0.7% than to 0.01%. In this manner, the phase diagram is used to predict the equilibrium phase structure of any alloy at any temperature, including which phases are present, their individual phase compositions (i.e. their carbon contents) and their relative amounts.

Phase diagrams can also be used to predict the changes (transformations) which occur during heating and cooling, as long as the temperature changes are slow as explained above. For example, one typical heat treatment given to a

0.2%C steel consists of slowly cooling from a temperature in the austenite region of the phase diagram, say 900°C (1650°F). In this case, the phase diagram predicts that when the austenite temperature falls below the line GH, about 865°C (1590°F), ferrite begins to form in the austenite. As the temperature continues to decrease, more and more ferrite forms so that by the time the steel reaches a temperature just above the horizontal 725°C (1337°F) boundary, line HP, about three-quarters of it has transformed to ferrite, while the rest remains austenite. On cooling through the 725°C (1337°F) temperature line, the ferrite remains unaffected, while all of the remaining austenite transforms to a mixture of ferrite and cementite. There is little change during further slow cooling to room temperature so that the final microstructure of the steel consists mainly of ferrite, with a small amount of cementite. The morphology of such a microstructure will be discussed below, along with further examples of the use of phase diagrams.

It is important to remember that all of these heat treatments which involve the cooling of austenite occur completely in the solid state. Austenite is a solid, as are its transformation products when it is cooled. This type of heat treatment is typically carried out after the material has been formed into its final or near-final shape.

This phase diagram in Fig. 1.4 shows the phase behavior of iron-carbon alloys with compositions up to 6.67%C; it is therefore called the iron-iron carbide (Fe-Fe₃C) phase diagram. It is equally possible to show a phase diagram which covers the full range of carbon contents from pure iron to pure carbon, however carbon contents of greater than 6.67% are not relevant to useful ferrous alloys. The ranges of carbon content applicable to plain carbon steels and to cast irons are shown in Fig. 1.4 below the bottom of the diagram.

In reality, the Fe-Fe₃C phase diagram shown in Fig. 1.4 is a metastable phase diagram rather than a true equilibrium phase diagram. Since graphite is thermodynamically more stable than iron carbide, an equilibrium phase diagram would have iron at one end and graphite at the other and iron carbide would not be shown. However iron carbide formation is kinetically favored over graphite formation, and the conversion of iron carbide to graphite is normally extremely slow. For example, iron carbide is present in steels which are more than 3000 years old. For this reason the Fe-Fe₃C system is applied to most ferrous alloys as if it were an equilibrium diagram. The boundaries of the iron-rich phases (□, □, □) are not appreciably different in the Fe-Fe₃C phase diagram and the Fe-C (graphite) phase diagram. However alloying elements can have a significant influence on whether Fe₃C or graphite forms; this is particularly important in cast irons as discussed in Chapter 4.

There are a number of other important features on the phase diagram in Fig. 1.4. The point at 0.8%C, 725°C (1337°F) is called the eutectoid point, while the eutectic point is at 4.3%C, 1150°C (2100°F). The latter point is important for cast irons, while the former applies to steels. Steels with the eutectoid composition, 0.8%C, are referred to as eutectoid steels, steels with less carbon are called hypoeutectoid steels while those with more carbon are called hypereutectoid steels. Most steels are hypoeutectoid; in particular, those with carbon contents below about 0.15%C are referred to as mild steels. Very important for steel heat treating is the line PN, called the eutectoid temperature, also referred to as the lower critical temperature or the A₁ temperature. This is the first transformation line reached on slowly heating steel from room temperature, i.e. the temperature at which austenite first begins to form during slow heating. The line GH represents the temperature at which the last ferrite disappears from hypoeutectoid steels on heating so that the entire microstructure then consists of austenite; this is referred to as the A₃ temperature or upper critical temperature. Note that unlike the A₁ temperature, the A₃ temperature depends on the carbon content of the steel. For hypereutectoid steels the corresponding temperature line is the line HE (known as the A_{cm} temperature), the temperature at which the last cementite disappears on heating. The A₂ temperature is the Curie temperature of the ferrite, while the temperature given by line JI, the lowest temperature at which □-ferrite is stable, is called the A₄ temperature.

In fact, for real heating and cooling processes, which occur at finite rates, and bearing in mind the need for sufficient time for atoms to diffuse as discussed above, these phase transformations do not occur at exactly the same temperatures on heating as they do on cooling. Specifically the transformation temperatures on heating are higher than on cooling, the extent of the discrepancy (or hysteresis) increasing at higher cooling or heating rates. For this reason they are distinguished in the terminology as Ar and Ac temperatures, the r and c referring to the French words refroidissement and chauffage for cooling and heating respectively. Thus for example the Ac₁ temperature is higher than the Ar₁ temperature. In this way slight departures from equilibrium are represented.

