

The Production, Microstructure, and Properties of Wrought Iron

Robert Walker VII

School of Mechanical and Materials Engineering, University of Surrey, Guildford, Surrey GU2 7XH, UK;
Robert.walker@surrey.ac.uk

Wrought iron was the first form of iron used by man to produce weapons and tools, with the exception of tiny supplies of meteoric material. It had the very important property that it could be hammered to shape; indeed, the word “wrought” means “that which has been shaped by forging, rolling or drawing”. One of the earliest references is in the Bible, Genesis 4:22, where Tubal Cain was described as “the one who forged all kinds of tools out of bronze and iron”.

Wrought iron has been defined by the American Society for Testing Materials (ASTM) as “a ferrous material, aggregated from a solidifying mass of pasty particles of highly refined metallic iron with which, without subsequent fusion is incorporated a minutely and uniformly distributed quantity of slag”. In many old artifacts the slag and iron are irregularly dispersed and form an intimate mechanical mixture.

The smelting of ore with charcoal must have been discovered independently in many parts of the world and there is evidence from the third millennium B.C.E. of production in Egypt and Anatolia, Turkey. Wrought iron was all forged by hand until waterpower was harnessed in the 13th century C.E. According to Dennis (1), wrought iron was the most important ferrous engineering material up to the middle of the 19th century, when the production in the United Kingdom alone was 2.5×10^6 tons per year. After 1856 its importance decreased owing to the increased production of Bessemer steel.

Wrought iron is still produced in small quantities, however, for blacksmiths to make articles such as horseshoes, railings, and decorative ironware.

Production of Wrought Iron from the Ore

The earliest wrought iron was produced directly from the ore in primitive charcoal-burning hearths or furnaces. These primitive furnaces could reach a maximum temperature of only 1150–1200 °C, so it was not possible to melt iron (mp 1535 °C) and they produced a pasty mixture of iron and slag.

The main reactants in the furnace were iron ore, charcoal, and oxygen. Oxygen in the air was introduced by a natural draft and the efficiency was later improved by siting the furnace on a hillside or at the bottom of a cliff where the wind would give an enhanced supply. The role of the charcoal was very important because it (i) acted as a fuel for the furnace, (ii) was a reducing agent for the ore, and (iii) functioned as a shield to reduce oxidation of the hot metal.

There are several possible reactions between charcoal and oxygen. The relative reactivities and free energies of these can be determined from the Richardson diagram, in which the negative standard free energy change is plotted against temperature for a number of oxides. Further details of these diagrams can be obtained from the paper by Richardson and Jeffes (2). At 1200 °C the free energy changes for the following

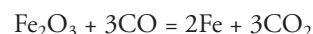
reactions are



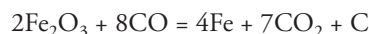
Hence both carbon monoxide and carbon dioxide may be present. Carbon dioxide can dissociate or combine with more carbon to give carbon monoxide



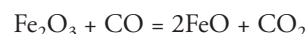
This carbon monoxide can react with hematite (Fe_2O_3), a constituent of iron ore, to give iron



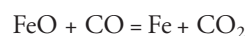
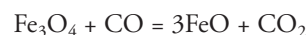
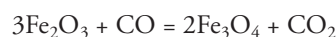
or



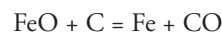
or it may give ferrous oxide, FeO,



A series of reactions can occur involving the production and reduction of magnetite, Fe_3O_4 :



The carbon may also react directly with the ferrous oxide to give iron:



The rates of these processes depend upon many factors such as the temperature and pressure within the furnace.

Other elements in the ore, present as impurities, are oxidized to form the slag, which is mainly fayalite, a silicate of iron (Fe_2SiO_4), and viscous at temperatures above about 1177 °C. Hence the metalworker would hammer the heated mixture of iron and slag to squeeze out the viscous slag and convert the porous iron into a more continuous form called a “bloom”, that is, “a lump of wrought iron after hammering and before rolling or otherwise working” (3). The term “blooming” referred to “a small charcoal fired hearth for the production of wrought iron direct from the ore” (3). These blooms, the blacksmith’s raw material, were heated and shaped as required.

If a superior form of iron were required, piling would be carried out. This gave a laminated configuration of wrought iron and involved cutting the hammered blooms into lengths, arranging these in piles of five or seven perpendicular to each other, and bending them or using wire to hold them together. When heated to white heat they were hammered, which welded them together. Further heating and hammering squeezed out more liquid slag and eventually the remaining

slag was plastic and the composite material was shaped on an anvil. It is interesting to note that this technique was carried out by the ancient Egyptians and Indians as well as in the late Roman period.

Production of Wrought Iron from Pig or Cast Iron

The introduction of the blast furnace, in about 1500 C.E. in England, enabled higher temperatures to be attained in the furnace to give free-flowing molten iron suitable for casting. This is now mainly used rather than the ore to produce wrought iron. Pig iron, according to Chambers (4), is the "crude iron produced in the blast furnaces and cast into pigs which are used for making steel, cast iron or wrought iron". Principal impurities are carbon, silicon, manganese, sulfur, and phosphorus. Composition varies according to the ore used, the smelting practice and the intended use. The term *pig* refers to the shape of the channels or runners that direct the molten metal from the furnace into side channels called sows and then into smaller channels termed pigs.

Cast iron is a generic term for alloys of iron containing 2–4% carbon and other elements derived from the ore. It has been defined as "an iron-carbon alloy in which the carbon content exceeds the solubility of carbon in austenite at the eutectic temperature. Carbon content is usually above 2%" (4). Further details of the iron blast furnace are given in a comprehensive review elsewhere (5).

Cast or pig iron has the advantage of good castability and machinability with a wide range of strengths and many applications. Unfortunately it is brittle, owing to the presence of impurities, and so cannot be shaped by hammering at temperatures below the melting point. If these impurities are removed it is converted into wrought iron, which is tough and ductile with good weldability and forgeability. The differences in the composition of wrought iron and pig iron are considerable, as indicated in Table 1, and these are reflected in the differing mechanical properties (Table 2). In Scotland wrought iron was known as "malleable iron" until the Second World War.

The embrittling impurities in pig or cast iron could be removed by heating in a charcoal-fired "finery hearth", which used an air blast to decarburize the pig iron and also to oxidize the other elements. It differed from the blast furnace because there was no necessity to use an excess of charcoal to give the reducing atmosphere required for the reduction of

the ore. The finery fire gradually developed, and fire bricks were used to give a furnace called the Lancashire hearth in the UK, the South Wales process in Sweden, and the Walloon process by the Belgians.

An alternative procedure to remove the impurities was termed "puddling". This was carried out in a reverberatory furnace—that is, a furnace in which the charge is melted on a shallow hearth by flame passing above the charge and heating a low roof (4). In these the fuel and metal were kept separately, much of the heating was done by radiation from the roof, and the molten iron was puddled (i.e., agitated "by hand or mechanical means in an oxidizing atmosphere to oxidize most of the carbon silicon and manganese and thus produce wrought iron" [6]).

There were two different methods, those of Cort (1784), who used sand at the bottom of the furnace, and Hall (1820). Hall improved the technique by having iron oxide at the bottom; sand was added to the iron to give a slag with the iron oxide, and then hammer scale was introduced to give the very oxidizing environment required for the removal of the impurity elements.

The chemistry of the oxidation of the impurities can be explained by reference to the Richardson diagram (2). The sequence of oxidation is indicated by the free energies, the most reactive process occurring first. The order of oxidation for the impurities in cast iron is silicon, manganese, carbon, and then phosphorus. The reactions and relative free energies at 1000 °C are



Hence the silicon then the manganese, the carbon, and finally the phosphorus oxidize. According to Gregory, the reductions in concentration from the solid pig iron are silicon 1.88 to 0.20%, manganese 1.0 to 0.06%, carbon 3.27 to 1.20%, and phosphorus 0.85 to 0.14% and the sulfur decreased from 0.15% to nil (6).

The slag that is formed is mainly iron silicate and iron oxide and constitutes about 1–3% of the total weight. The composition depends upon the ore and it may contain 1.25–3% Al₂O₃, 0.5–3.9% CaO, 0.2–0.4% MgO, 1.25–8% P₂O₅, and 1–2% S (7). The slag is an essential ingredient of wrought iron.

It has been suggested that it is possible to distinguish wrought iron made by bloomery, finery, and puddling techniques from the analysis of the composition of the tap slags and large slag inclusions (8). An insight into the production of wrought iron from cast iron in the methods used prior to the industrial revolution has been given by work carried out at the Valley Forge in the USA (9).

Microstructure

The microstructure of a sample is revealed by polishing the surface, etching it with a weak acid, and examining it with a microscope at a magnification greater than 10-fold. This can reveal much about the structure and fabrication history: the size and shape of the grains as well as the number and distribution of the phases are particularly important.

Table 1. Typical Composition of Wrought Iron and Pig Iron

| Material | Element (%) | | | | | |
|--------------|-------------|-----------|------|------|------|---------|
| | C | Si | S | P | Mn | Slag |
| Wrought iron | 0.02–0.08 | 0.10–0.20 | 0.02 | 0.10 | 0.01 | 0.1–1.0 |
| Pig iron | 3.5 | 1.5 | 0.06 | 1.0 | 1.0 | — |

NOTE: Data from ref 1.

Table 2. Typical Properties of Wrought Iron and Pig Iron

| Material | Ultimate Tensile Strength/MN m ⁻² | Elongation (%) | Yield Point/MN m ⁻² |
|--------------|--|----------------|--------------------------------|
| Wrought Iron | 350–370 | 25–38 | 300–590 |
| Pig Iron | 77–123 | nil | nil |

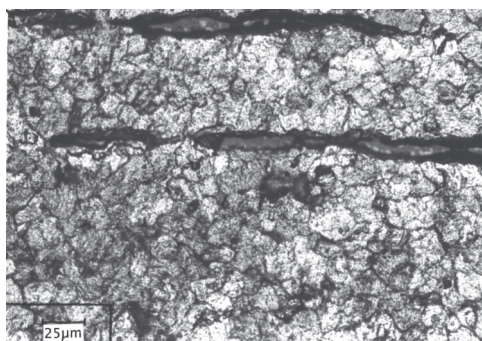


Figure 1. Microstructure of wrought iron showing regular ferrite grains indicative of an annealed condition or of hot-working and recrystallization.

Wrought iron consists mainly of ferrite, a nearly pure form of iron in which up to 0.05% carbon and other impurities such as phosphorus, manganese, and silicon are dissolved as a solid solution. The shape of the grains may be regular and roughly polyhedral, indicating either an annealed condition or hot-working and recrystallization, as shown in Figure 1. This represents a soft condition with low hardness and metal in this condition can easily be shaped. Alternatively they may be elongated and of an irregular size and shape if the material has been cold-worked. If the wrought iron has been rapidly cooled from the austenitic region, a Widmanstatten structure can be formed. This is a mix of ferrite grains that alternate with areas of pearlite, an aggregate of ferrite and carbide in the form of thin plates or lamellae. This structure does not easily accommodate deformation and so is brittle and not usually desirable because it cannot be shaped by hammering.

The slag in wrought iron is an important constituent and can be present as 1–3 wt % of the total. It is relatively inert, nonconducting, and glass-like and consists of iron silicate and iron oxide. It acts as a flux and assists in welding.

The slag is distributed as fibers elongated in the direction of rolling, and it is these fibers that distinguish wrought iron from steel. The appearance and microstructure of the slag depend upon the cross-section examined: the orientation of the stringers may be parallel to the surfaces so they appear as long lines, or perpendicular so they appear as dots or streaks, as shown in Figure 2. These regions of slag give the iron its anisotropic properties. The bonding between the ferrite matrix and the slag is unusual because it is mechanical and there is no continuous atomic relationship at the interface.

Properties

When heated during forge-welding, wrought iron does not melt but the slag fibers become molten, act as a flux, and protect the iron from oxidation and thus are very beneficial. Because the slag fibers do not have a uniform shape or size, wrought iron is very anisotropic. The greatest strength is in the direction of these threads, so it is important to have the correct orientation in order to achieve the optimum properties. This is illustrated by the fact that the strength is typically 400 MP m^{-2} parallel to the fibers but only 340 MP m^{-2} in a perpendicular direction and there is an even greater difference in the elongation of 40% and 10%. The fibers prevent internal

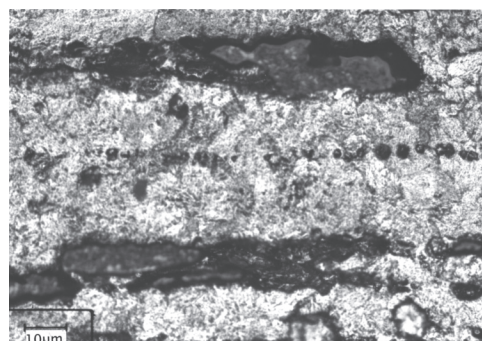


Figure 2. Microstructure of slag. Stringers parallel to the surface appear as long lines; those perpendicular to the surface appear as dots or streaks.

grain growth and consequent embrittlement and also tend to divert cracks during deformation and block corrosion pits.

The other important properties of wrought iron are toughness, weldability, forgeability, and malleability. Because it can be rolled, drawn, or forged it was heated and hammered on an anvil or other base to the required shape. Blacksmiths still use it to produce horseshoes, railings, and ornamental ironwork.

Because it recovers rapidly from overstrain and accommodates sudden shock without damage, it has been widely employed for engineering applications such as lifting chains, crane hooks, anchors, and railway couplings. It was extensively employed in the production of armor plates, some of which were massive: those made in Sheffield in 1856 were $400 \times 90 \text{ cm}$ and 11 cm thick and weighed 3600 kg, while others made in 1873 were 25 cm thick!

One major improvement of properties was to increase the tensile strength and hardness by carburizing or “steeling” the iron. This involved the diffusion of carbon into the surface of the wrought iron. The rate of this is negligible at room temperature but is significant when the iron at about $1200 \text{ }^\circ\text{C}$ is in contact with white-hot charcoal and carbon monoxide. The rate of diffusion at different temperatures can be calculated using the Arrhenius equation

$$D_{\text{coeff}} = D \exp(-Q/RT)$$

where D_{coeff} is the diffusion coefficient, D is the diffusion constant, Q is the activation energy, R is the gas constant, and T is the absolute temperature.

If the iron is held at $950 \text{ }^\circ\text{C}$ for 9 h the carbon concentration at a depth of 1.5 mm is 0.5%, but at $1150 \text{ }^\circ\text{C}$ it is much higher, 2%. This gives a considerable increase in the tensile strength which can increase from $350\text{--}370 \text{ MN m}^{-2}$ to about 950 MN m^{-2} with 1.2% carbon. More details of the development of carburization and examples of its use in ancient times were described by Madden et al. (10).

Corrosion Resistance

Many ancient wrought iron artifacts have been recovered from the sea, indicating that the metal must have good corrosion resistance. These objects, such as guns and anchors, often have a surface appearance that is characteristic of wood, as shown in Figure 3. This is due to highly heterogeneous way



Figure 3. An ancient wrought iron anchor recovered from the sea. Note the wood-like appearance of the surface.



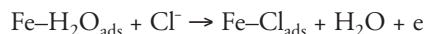
Figure 4. The ancient Delhi Pillar, made by forge-welding pieces of wrought iron. Its surface is remarkably free of corrosion.

in which the iron matrix tends to corrode while the inert slag fibers are not attacked. Chilton and Evans have described this effect; they defined the different zones and suggested that the presence of sulfur increased the attack (11).

In warm dry conditions wrought iron can very efficiently resist corrosion. The oft-quoted example is the Delhi Pillar in India, dated 4th century C.E. It is 7.373 m high and 0.416 m in diameter and estimated to weigh more than 6096 kg (Fig. 4). This masterpiece of engineering was made by forge-

welding pieces of wrought iron. Further details are given elsewhere (12, 13). The surface condition of the Pillar is remarkable and the original Sanskrit writing is clearly visible.

One of the major influences on the rate of corrosion of iron is the presence of chloride ions. These can initiate attack on the surface to give pitting and the corrosion becomes auto-catalytic. The first stage is probably adsorption onto the surface



Ferrous chloride is then formed



and this is followed by decomposition into the more stable hydrated ferric oxide or rust



Hence during the formation of rust the chloride is released and the corrosion can continue (14).

The National Federation of Iron and Steel Manufacturers, submitting evidence in 1931 on the wrought iron trade, stated that "owing to its ability to resist all forms of corrosion resulting from atmospheres, damp and alternative wet and dry conditions, it possesses exceptionally high lasting properties."

Ancient Artifacts

Among the oldest artifacts recovered is an iron plate made by hammering to give a welded structure. It was found in the Great Pyramid of Gizeh, Egypt, and dated about 2900 B.C.E. (15). The many articles recovered from graves include an iron cube at Knossos, Greece, dated 1800 B.C.E., finger rings of 1500 B.C.E. from Pylos, Greece, and an Egyptian axe of 900 B.C.E.

In India the development of iron technology can be traced back to 1300 B.C.E. in several geographic regions (12). The metal was used until about 600 B.C.E. to make specific items such as hunting tools and domestic items. Then, as more material became available, the use expanded to include swords, elephant goods, and plowshares by 100 B.C.E. and later, the Delhi Pillar. It is surprising to note that Alexander the Great had sufficient quantities to build a bridge over the River Euphrates.

In Thailand during the period 300–400 C.E. there was competent forging and welding and in some instances the cutting edges of articles had been hardened by cementation (16). The making of medieval Damascus swords, referred to in 9th-century Islamic texts, involved a high level of sophistication (17).

Growth in local areas was impressive. By the time of the Crusades the industry in the small area of the Weald of Sussex was able to use the water, wood, and ore in the region to make an estimated 50,000 horseshoes for the Crusade of King Richard I to the Holy Land.

The theory of corrosion and preservation of iron artifacts has been reviewed elsewhere with more details (18).

Summary

The progress of civilization and success in warfare from prehistory have been very dependent upon the ability to produce and use metals, initially bronze in the Bronze Age

and then wrought iron during the Iron Age. The earliest wrought iron was produced in small quantities and used for specialized applications such as weapons and decoration. Later it became more available and in the 19th century it was widely employed in the manufacture of girders for bridges, seaside piers, and buildings. It is now widely employed in the manufacture of decorative gates and railings as well as of horseshoes.

The early process was very labor intensive and involved the direct reduction of the ore. This was superseded by the indirect production from cast iron after introduction of the blast furnace in the 16th century, and production increased: 2,841,534 tons of puddled iron were made in England in 1882.

Wrought iron consists of a nearly pure form of iron, ferrite, and about 1–3 wt % slag. The slag is in the form of fibers made of iron silicate and iron oxide and these give it the anisotropic properties with the greatest strength in the direction of the fibers. The corrosion resistance is particularly good in atmospheric environments. Wrought iron objects recovered from the sea often have the appearance of wood due to the fibers.

At first the industry tended to be localized where there were deposits of iron ore and a supply of wood for the charcoal production. Later, sources of water power also became important. Although the peak production was in the middle of the 19th century, wrought iron is still widely used because it is easy to shape. However, articles must be individually made by forging, which is a comparatively arduous process.

Literature Cited

1. Dennis, W. H. *Metallurgy of the Ferrous Metals*; Pitman and Sons: London, 1963; p 124.
2. Richardson, F. D.; Jeffes, J. H. E. *J. Iron Steel Inst.* **1948**, *160*, 261.
3. Gale, W. K. V. *The Iron and Steel Industry: a Dictionary of Terms*; David and Charles: Devon, England, 1971.
4. Walker, P. M. B. *Chambers Science and Technology Dictionary*; W. and R. Chambers: Edinburgh, 1988.
5. Treptow, R. S.; Jean, L. J. *J. Chem. Educ.* **1998**, *75*, 43.
6. Gregory, E. *Metallurgy*; Blackie: London, 1949; p 24.
7. Bashford, G. R. *The Manufacture of Iron and Steel*; Chapman and Hall: London, 1960; p 293.
8. Rostokov, W.; Dvork, J. *Aeromaterials* **1990**, *4*, 153–166.
9. Schenk, H. R.; Knox, R. *MASCA J.* **1985**, *3*, 132–141.
10. Madden, R.; Muhly, J. D.; Wheeler, T. S. *Sci. Am.* **1977**, *237*, 122–131.
11. Chilton, J. P.; Evans, U. R. *J. Iron Steel Inst.* **1955**, *181*, 113–122.
12. Prakash, B.; Tripalti, V. *Met. Mater.* **1986**, *2*, 568–579.
13. Salvi, D. M. *New Sci.* **1985**, *105*, 43.
14. Walker, R. *Br. Corros. J.* **1996**, *31*, 69–71.
15. Gayar, S. E. L.; Jones, M. P. *Hist. Metall.* **1989**, *23*, 75–83.
16. Wright, J. H. *Bull. Hist. Metall.* **1972**, *6*, 24–27.
17. Wadsworth, J.; Kum, D. W.; Sherby, O. D. *Metal. Prog.* **1986**, *129*, 61–67.
18. Walker, R. J. *J. Chem. Educ.* **1982**, *59*, 943–947.