THE TERM CAST IRON, like the term steel, identifies a large family of ferrous alloys. Cast irons are multicomponent ferrous alloys, which solidify with a eutectic. They contain major (iron, carbon, silicon), minor (∼0.1%), and often alloying (∼0.1%) elements. Cast iron has higher carbon and silicon contents than steel. Because of the higher carbon content, the structure of cast iron, as opposed to that of steel, exhibits a rich carbon phase. Depending primarily on composition, cooling rate, and melt treatment, cast iron can solidify according to the thermodynamically metastable Fe-Fe₃C system or the stable Fe-Gr system. When the metastable path is followed, the rich carbon phase in the eutectic is the iron carbide; when the stable solidification path is followed, the rich carbon phase is graphite. Referring only to the binary Fe-Fe₃C or Fe-Gr system, cast iron can be defined as an iron-carbon alloy with more than 2% C. The reader is cautioned that silicon and other alloying elements may considerably change the maximum solubility of carbon in austenite (γ). Therefore, in exceptional cases, alloys with less than 2% C can solidify with a eutectic structure and therefore still belong to the family of cast iron.

The formation of stable or metastable eutectic is a function of many factors including the nucleation potential of the liquid, chemical composition, and cooling rate. The first two factors determine the graphitization potential of the iron. A high graphitization potential will result in irons with graphite as the rich carbon phase, while a low graphitization potential will result in irons with iron carbide. A schematic of the structure of the common types of commercial cast irons, as well as the processing required to obtain them, is shown in Fig. 1.

The two basic types of eutectics—the stable austenite-graphite or the metastable austenite-iron carbide (Fe₃C)—have wide differences in their mechanical properties, such as strength, hardness, toughness, and ductility. Therefore, the basic scope of the metallurgical processing of cast iron is to manipulate the type, amount, and morphology of the eutectic in order to achieve the desired mechanical properties.

Classification

Historically, the first classification of cast iron was based on its fracture. Two types of iron were initially recognized:

- **White iron**: Exhibits a white, crystalline fracture surface because fracture occurs along the iron carbide plates; it is the result of metastable solidification (Fe₃C eutectic)
- **Gray iron**: Exhibits a gray fracture surface because fracture occurs along the graphite plates (flakes); it is the result of stable solidification (Gr eutectic)

With the advent of metallography, and as the body of knowledge pertinent to cast iron increased, other classifications based on microstructural features became possible:

- **Graphite shape**: Lamellar (flake) graphite (FG), spheroidal (nodular) graphite (SG), compacted (vermicular) graphite (CG), and temper graphite (TG); temper graphite results from a solid-state reaction (malleableization)
- **Matrix**: Ferritic, pearlitic, austenitic, martensitic, bainitic (austempered)

This classification is seldom used by the floor foundryman. The most widely used terminology is the commercial one. A first division can be made in two categories:

- **Common cast irons**: For general-purpose applications, they are unalloyed or low alloy
- **Special cast irons**: For special applications, generally high alloy

The correspondence between commercial and microstructural classification, as well as the final processing stage in obtaining common cast irons, is given in Table 1. A classification of cast irons by their commercial names and structure is also given in the article “Classification of Ferrous Casting Alloys” in Volume 15 of the 9th Edition of Metals Handbook.

Special cast irons differ from the common cast irons mainly in the higher content of alloying elements (>3%), which promote microstructures having special properties for elevated-temperature applications, corrosion resistance, and wear resistance. A classification of the main types of special cast irons is shown in Fig. 2.

Principles of the Metallurgy of Cast Iron

The goal of the metallurgist is to design a process that will produce a structure that will yield the expected mechanical proper-

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**Table 1 Classification of cast iron by commercial designation, microstructure, and fracture**

<table>
<thead>
<tr>
<th>Commercial designation</th>
<th>Matrix(a)</th>
<th>Fracture</th>
<th>Final structure after heat treatment(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gray iron</td>
<td>P</td>
<td>Gray</td>
<td>Solidification</td>
</tr>
<tr>
<td>Ductile iron</td>
<td>F, P, A</td>
<td>Silver-gray</td>
<td>Solidification or heat treatment</td>
</tr>
<tr>
<td>Compact graphite iron</td>
<td>F, P</td>
<td>Gray</td>
<td>Solidification</td>
</tr>
<tr>
<td>White iron</td>
<td>P, M</td>
<td>White</td>
<td>Solidification and heat treatment(b)</td>
</tr>
<tr>
<td>Mottled iron</td>
<td>P</td>
<td>Mottled</td>
<td>Heat treatment</td>
</tr>
<tr>
<td>Malleable iron</td>
<td>F, P</td>
<td>Silver-gray</td>
<td>Heat treatment</td>
</tr>
</tbody>
</table>

(a) F, ferrite; P, pearlite; A, austenite; M, martensite; At, austempered (bainite). (b) White irons are not usually heat treated, except for stress relief and to continue austenite transformation.
The metallurgy of cast iron involves understanding the solidification process and the formation of graphite. The structure of cast iron depends on factors such as chemical composition, cooling rate, liquid treatment, and heat treatment. In the original cooling or through subsequent heat treatment, a matrix can be internally decarburized or carburized by depositing graphite on existing sites or by dissolving carbon from them.

Depending on the silicon content and the cooling rate, the pearlite in iron can vary in carbon content. This is a ternary system, and the carbon content of pearlite can be as low as 0.05% with 2.5% Si. The conventionally measured hardness of graphitic iron is influenced by the graphite content, especially in gray iron. Martensite microhardness may be as high as 66 HRC, but measures as low as 54 HRC conventionally in gray iron (58 HRC in ductile).

The critical temperature of iron is influenced (raised) by silicon content, not carbon content.

The following sections in this article discuss some of the basic principles of cast iron metallurgy. More detailed descriptions of the metallurgy of cast iron are available in separate articles in this Volume describing certain types of cast irons. The Section “Ferrous Casting Alloys” in Volume 15 of the 9th Edition of Metals Handbook also contains more detailed descriptions on the metallurgy of cast iron.

Gray Iron (Flake Graphite Iron)

The composition of gray iron must be selected in such a way as to satisfy three basic structural requirements:

- The required graphite shape and distribution
- The carbide-free (chill-free) structure
- The required matrix

For common cast iron, the main elements of the chemical composition are carbon and silicon. Figure 3 shows the range of carbon and silicon for common cast iron as compared with steel. It is apparent that irons...
Classification and Basic Metallurgy of Cast Iron / 5

The manganese content varies as a function of the desired matrix. Typically, it can be as low as 0.1% for ferritic irons and as high as 1.2% for pearlitic irons, because manganese is a strong pearlite promoter. From the minor elements, phosphorus and sulfur are the most common and are always present in the composition. They can be as high as 0.15% for low-quality iron and are considerably less for high-quality iron, such as ductile iron or compacted graphite iron. The effect of sulfur must be balanced by the effect of manganese. Without manganese in the iron, undesired iron sulfide (FeS) will form at grain boundaries. If the sulfur content is balanced by manganese, manganese sulfide (MnS) will form, which is harmless because it is distributed within the grains. The optimum ratio between manganese and sulfur for an FeS-free structure and maximum amount of ferrite is:

$$\% \text{Mn} = 1.7(\% \text{Si}) + 0.15$$ (Eq 2)

Other minor elements, such as aluminum, antimony, arsenic, bismuth, lead, magnesium, cerium, and calcium, can significantly alter both the graphite morphology and the microstructure of the matrix.

The range of composition for typical unalloyed common cast irons is given in Table 2. The typical composition range for low- and high-grade unalloyed gray iron (flake graphite iron) cast in sand molds is given in Table 3.

Both major and minor elements have a direct influence on the morphology of flake graphite. The typical graphite shapes for flake graphite are shown in Fig. 5. Type A graphite is found in inoculated irons cooled with moderate rates. In general, it is associated with the best mechanical properties, and cast irons with this type of graphite exhibit moderate undercooling during solidification (Fig. 6). Type B graphite is found in irons of near-eutectic composition, solidifying on a limited number of nuclei. Large eutectic cell size and low undercoolings are common in cast irons exhibiting this type of graphite. Type C graphite occurs in hypereutectic irons as a result of solidification with minimum undercooling. Type D graphite is found in hypoeutectic or eutectic irons solidified at rather high cooling rates, while type E graphite is characteristic for strongly hypoeutectic irons. Types D and E are both associated with high undercoolings during solidification. Not only graphite shape but also graphite size is important, because it is directly related to strength (Fig. 7).

### Table 2 Range of compositions for typical unalloyed common cast irons

<table>
<thead>
<tr>
<th>Type of iron</th>
<th>C</th>
<th>Si</th>
<th>Composition, %</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gray (FG)</td>
<td>2.5-4.0</td>
<td>1.0-3.0</td>
<td>0.2-1.0</td>
<td>0.002-1.0</td>
<td>0.02-0.25</td>
<td></td>
</tr>
<tr>
<td>Compacted graphite (CG)</td>
<td>2.5-4.0</td>
<td>1.0-3.0</td>
<td>0.2-1.0</td>
<td>0.01-0.1</td>
<td>0.01-0.03</td>
<td></td>
</tr>
<tr>
<td>Ductile (SG)</td>
<td>3.0-4.0</td>
<td>1.8-2.8</td>
<td>0.1-1.0</td>
<td>0.01-0.1</td>
<td>0.01-0.03</td>
<td></td>
</tr>
<tr>
<td>White</td>
<td>1.8-3.6</td>
<td>0.3-1.5</td>
<td>0.25-0.8</td>
<td>0.06-0.2</td>
<td>0.02-0.2</td>
<td></td>
</tr>
<tr>
<td>Malleable (TG)</td>
<td>2.2-2.9</td>
<td>0.9-1.9</td>
<td>0.15-1.2</td>
<td>0.02-0.2</td>
<td>0.02-0.2</td>
<td></td>
</tr>
</tbody>
</table>

Source: Ref 2
Alloying elements can be added in common cast iron to enhance some mechanical properties. They influence both the graphitization potential and the structure and properties of the matrix. The main elements are listed below in terms of their graphitization potential:

### Table 3: Compositions of unalloyed gray irons

<table>
<thead>
<tr>
<th>ASTM 48 class</th>
<th>Carbon equivalent</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>20B</td>
<td>4.5</td>
<td>3.1-3.4</td>
</tr>
<tr>
<td>55B</td>
<td>3.6</td>
<td>1.4-1.6</td>
</tr>
</tbody>
</table>

The classification is based on the thermodynamic analysis of the influence of a third element on carbon solubility in the Fe-C-X system, where X is a third element (see the section “Influence of a Third Element on Carbon Solubility in the Fe-C-X System” in the article “Thermodynamic Properties of Iron-Base Alloys” in Volume 15 of the 9th Edition of Metals Handbook). Although listed as a graphitizer (which may be true thermodynamically), phosphorus also acts as a matrix hardener. Above its solubility level (probably about 0.06%), phosphorus forms a very hard tertiary eutectic. The above classification should also include sulfur as a carbide former, although manganese and sulfur can combine and neutralize each other. The result of this reaction is referred to as a nucleating process, nucleation phenomena may sometimes override solubility considerations.

In general, alloying elements can be classified into three categories. Each is discussed below:

- Silicon and aluminum increase the graphitization potential for both the eutectic and eutectoid transformations and increase the number of graphite particles. They form solid solutions in the matrix. Because they increase the ferrite/pearlite ratio, they lower strength and hardness.
- Nickel, copper, and tin increase the graphitization potential during the eutectic transformation, but decrease it during the eutectoid transformation, thus raising the pearlite/ferrite ratio. This second effect is due to the retardation of carbon diffusion. These elements form solid solution in the matrix. Because they increase the amount of pearlite, they raise strength and hardness.
- Chromium, molybdenum, tungsten, and vanadium decrease the graphitization potential at both stages. Thus, they increase the amount of carbides and pearlite. They concentrate in principal in the carbides, forming (FeX),C-type carbides, but also alloy the aFe solid solution. As long as carbide formation does not occur, these elements increase strength and hardness. Above a certain level, any of these elements will determine the solidification of a structure with both Ga and FeC (mottled structure), which will have lower strength but higher hardness.

In unalloyed gray iron, the typical ranges for the elements discussed above are as follows:

- **Carbon**: 0.04-0.12%
- **Chromium**: 1.3-1.8%
- **Molybdenum**: 0.2-0.6%
- **Vanadium**: 0.1-0.2%
- **Nickel**: 0.5-1.0%
- **Copper**: 0.05-0.5%
- **Tin**: 0.04-0.08%

The cooling rate, like the chemical composition, can significantly influence the cast structure and therefore the mechanical properties. The cooling rate of a casting is primarily a function of its section size. The dependence of structure and properties on section size is termed section sensitivity. Increasing the cooling rate will:

**Fig. 6**: Characteristic cooling curves associated with different flake graphite shapes. \( T_{eq} \), equilibrium temperature.

**Fig. 7**: Effect of maximum graphite flake length on the tensile strength of gray iron. Source: Ref 3.
An increased graphitization potential are used as inoculants. The main effects of inoculation are:
- Increase the chilling tendency; this may result in higher hardness, but will decrease the strength
- Increase the chilling tendency; this may result in higher hardness, but will decrease the strength
- Refine both graphite size and matrix structure; this will result in increased strength and hardness
- Graphite shape changes from type D or E to type A
- A finer structure, that is, higher number of eutectic cells, with a subsequent increase in strength

As shown in Fig. 9, inoculation improves tensile strength. This influence is more pronounced for low-CE cast irons.

Heat treatment can considerably alter the matrix structure, although graphite shape and size remain basically unaffected. A rather low proportion of the total gray iron produced is heat treated. Common heat treatment may consist of stress relieving or annealing to decrease hardness.

Ductile Iron (Spheroidal Graphite Iron)

Composition. The main effects of chemical composition are similar to those described for gray iron, with quantitative differences in the extent of these effects and qualitative differences in the influence on graphite morphology. The carbon equivalent has only a mild influence on the properties and structure of ductile iron, because it affects graphite shape considerably less than in the case of gray iron. Nevertheless, to prevent excessive shrinkage, high chilling tendency, graphite flotation, or a high impact transition temperature, optimum amounts of carbon and silicon must be selected. Figure 10 shows the basic guidelines for the selection of appropriate compositions. As mentioned previously, minor elements can significantly alter the structure in terms of graphite morphology, chilling tendency, and matrix structure. Minor elements can promote the spheroidization of graphite or can have an adverse effect on graphite shape. The minor elements that adversely affect graphite shape are said to degenerate graphite shape. A variety of graphite shapes can occur, as illustrated in Fig. 11. Graphite shape is the single most important factor affecting the mechanical properties of cast iron, as shown in Fig. 12.

The generic influence of various elements on graphite shape is given in Table 4. The elements in the first group—the spheroidizing elements—can change graphite shape from flake through compacted to spheroidal. This is illustrated in Fig. 13 for magnesium. The most widely used element for the production of spheroidal graphite is magnesium. The amount of residual magnesium, Mg_{residual}, required to produce spheroidal graphite is generally 0.03 to 0.05%. The precise level depends on the cooling rate. A higher cooling rate requires less magnesium. The amount of magnesium to be added in the iron is a function of the initial sulfur level, S_{in}, and the recovery of magnesium, η, in the particular process used:

\[
Mg_{\text{added}} = \frac{0.75 S_{\text{in}} + Mg_{\text{residual}}}{\eta} \quad \text{(Eq 4)}
\]

A residual magnesium level that is too low results in insufficient nodularity (that is, a low ratio between the spheroidal graphite and the total amount of graphite in the structure). This in turn results in a deterioration of the mechanical properties of the iron, as illustrated in Fig. 14. If the magnesium content is too high, carbides are promoted.

The presence of antispheeroidizing (deleterious) minor elements may result in graphite shape deterioration, up to complete graphite degeneration. Therefore, upper limits are set on the amount of deleterious elements to be accepted in the composition of cast iron. Typical limits are given below (Ref 6):
<table>
<thead>
<tr>
<th>Element</th>
<th>Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>0.1</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.02</td>
</tr>
<tr>
<td>Bismuth</td>
<td>0.002</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.01</td>
</tr>
<tr>
<td>Lead</td>
<td>0.002</td>
</tr>
<tr>
<td>Antimony</td>
<td>0.003</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.03</td>
</tr>
<tr>
<td>Tellurium</td>
<td>0.02</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.1</td>
</tr>
<tr>
<td>Zirconium</td>
<td>0.1</td>
</tr>
</tbody>
</table>

These values can be influenced by the combination of various elements and by the presence of rare earths in the composition. Furthermore, some of these elements can be deliberately added during liquid processing in order to increase nodule count.

Alloying elements have in principle the same influence on structure and properties as for gray iron. Because a better graphite morphology allows more efficient use of the mechanical properties of the matrix, alloying is more common in ductile iron than in gray iron.

**Cooling Rate.** When changing the cooling rate, effects similar to those discussed for gray iron also occur in ductile iron, but the section sensitivity of ductile iron is lower. This is because spheroidal graphite is less affected by cooling rate than flake graphite.

**The liquid treatment of ductile iron** is more complex than that of gray iron. The two stages for the liquid treatment of ductile iron are:

- Modification, which consists of magnesium or magnesium alloy treatment of the melt, with the purpose of changing graphite shape from flake to spheroidal
- Inoculation (normally, postinoculation, that is, after the magnesium treatment) to increase the nodule count. Increasing the nodule count is an important goal, because a higher nodule count is associated with less chilling tendency (Fig. 15) and a higher as-cast ferrite/pearlite ratio.

**Heat treatment** is extensively used in the processing of ductile iron because better advantage can be taken of the matrix structure than for gray iron. The heat treatments usually applied are as follows:

- Stress relieving
- Annealing to produce a ferritic matrix
- Normalizing to produce a pearlitic matrix

**Compacted Graphite Irons**

Compacted graphite irons have a graphite shape intermediate between spheroidal and flake. Typically, compacted graphite looks like type IV graphite (Fig. 11). Consequently, most of the properties of CG irons lie in between those of gray and ductile iron.

**Chemical composition effects** are similar to those described for ductile iron. Carbon equivalent influences strength less obviously than for the case of gray iron, but...
more than for ductile iron, as shown in Fig. 17. The graphite shape is controlled, as in the case of ductile iron, through the content of minor elements. When the goal is to produce compacted graphite, it is easier from the standpoint of controlling the structure to combine spheroidizing (magnesium, calcium, and/or rare earths) and antispheroidizing (titanium and/or aluminum) elements. Additional information is available in the article "Compacted Graphite Irons" in Volume 15 of the 9th Edition of Metals Handbook.

The cooling rate affects properties less for gray iron but more for ductile iron (Fig. 18). In other words, CG iron is less section sensitive than gray iron. However, high cooling rates are to be avoided because of the high propensity of CG iron for chilling and high nodule count in thin sections.

Liquid treatment can have two stages, as for ductile iron. Modification can be achieved with magnesium, Mg + Ti, Ce + Ca, and so on. Inoculation must be kept at a low level to avoid excessive nodularity.

Heat treatment is not common for CG irons.

Malleable Irons

Malleable cast irons differ from the types of irons previously discussed in that they have an initial as-cast white structure, that is, a structure consisting of iron carbides in a pearlitic matrix. This white structure is then heat treated (annealing at 800 to 970 °C, or 1470 to 1780 °F), which results in the decomposition of Fe₃C and the formation of temper graphite. The basic solid state reaction is:

$$\text{Fe}_3\text{C} \rightarrow \gamma + \text{Gr}$$  \hspace{1cm} (Eq 5)

The final structure consists of graphite and pearlite, pearlite and ferrite, or ferrite. The structure of the matrix is a function of the cooling rate after annealing. Most of the malleable iron is produced by this technique and is called blackheart malleable iron. Some malleable iron is produced in Europe by decarburization of the white as-cast iron, and it is called whiteheart malleable iron.

The composition of malleable irons must be selected in such a way as to produce a white as-cast structure and to allow for fast annealing times. Some typical compositions are given in Table 2. Although higher carbon and silicon reduce the heat treatment time, they must be limited to ensure a graphite-free structure upon solidification. Both tensile strength and elongation decrease with higher carbon equivalent. Nevertheless, it is not enough to control the carbon equivalent. The annealing time depends on the number of graphite nuclei available for graphitization, which in turn
depends on, among other factors, the C/Si ratio. As shown in Fig. 19, a lower C/Si ratio (that is, a higher silicon content for a constant carbon equivalent) results in a higher temper graphite count. This in turn translates into shorter annealing times.

Manganese content and the Mn/S ratio must be closely controlled. In general, a lower manganese content is used when ferritic rather than pearlitic structures are desired. The correct Mn/S ratio can be calculated with Eq 2:

\[
\text{CE} = \text{constant}
\]

Influence of C/Si ratio on the number of temper graphite clusters at constant carbon equivalent. Source: Ref 10.

![Fig. 19 Influence of C/Si ratio on the number of temper graphite clusters at constant carbon equivalent. Source: Ref 10.](image)

The liquid treatment of malleable iron increases the number of nuclei available for the solid-state graphitization reaction. This can be achieved in two different ways, as follows:

- By adding elements that increase undercooling during solidification. Typical elements in this category are magnesium, cerium, bismuth, and tellurium. Higher undercooling results in finer structure, which in turn means more Fe₃C interface. Because graphite nucleates at the γ-Fe₃C interface, this means more nucleation sites for graphite. Higher undercooling during solidification also prevents the formation of unwanted eutectic graphite.

- By adding nitride-forming elements to the melt. Typical elements in this category are aluminum, boron, titanium, and zirconium.

The heat treatment of malleable iron determines the final structure of this iron. It has two basic stages. In the first stage, the iron carbide is decomposed in austenite and graphite (Eq 5). In the second stage, the austenite is transformed into pearlite, ferrite, or a mixture of the two. Although there are some compositional differences between ferritic and pearlitic irons, the main difference is in the heat treatment cycle. When ferritic structures are to be produced, cooling rates in the range of 3 to 10 °C/h (5 to 18 °F/h) are required through the eutectoid transformation in the second stage. This is necessary to allow for a complete austenite-to-ferrite reaction. A typical annealing cycle for ferritic malleable iron is shown in Fig. 23. When pearlitic irons are to be produced, different schemes can be used, as shown in Fig. 24. The goal of the treatment is to...

![Fig. 20 Influence of the Mn/S ratio on the shape of temper graphite. Bracketed elements are dissolved in the matrix. Source: Ref 10.](image)

![Fig. 21 Influence of the Mn/S ratio on the number of temper graphite clusters after annealing. Source: Ref 10.](image)

![Fig. 22 Influence of bar diameter on the tensile strength (a) and elongation (b) of blackheart malleable iron. Source: Ref 11.](image)
achieve a eutectoid transformation according to the austenite-to-pearlite reaction. In some limited cases, quenching-tempering treatments are used for malleable irons.

**Special Cast Irons**

Special cast irons, as previously discussed, are alloy irons that take advantage of the radical changes in structure produced by rather large amounts of alloying elements. Abrasion resistance can be improved by increasing hardness, which in turn can be achieved by either increasing the amount of carbides and their hardness or by producing a martensitic structure. The least expensive material is white iron with a pearlitic matrix. Additions of 3 to 5% Ni and 1.5 to 2.5% Cr result in irons with (FeCr),C carbides and an as-cast martensitic matrix. Additions of 11 to 35% Cr produce (CrFe),C₃ carbides, which are harder than the iron carbides. Additions of 4 to 16% Mn will result in a structure consisting of (FeMn),C, martensite, and work-hardenable austenite.

Heat resistance depends on the stability of the microstructure. Irons used for these applications may have a ferritic structure with graphite (5% Si), a ferritic structure with stable carbides (11 to 28% Cr), or a stable austenitic structure with either spheroidal or flake graphite (18% Ni, 5% Si). For corrosion resistance, irons with high chromium (up to 28%), nickel (up to 18%), and silicon (up to 15%) are used.

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