

L4 : METALLURGY OF CAST IRON

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INTRODUCTION

Cast iron is essentially an alloy of iron-carbon (carbon > 2%) containing other important elements such as Si, Mn, S & P. It also contains trace elements (< 0.1%) and alloying elements (> 0.1%) which modify the structure and properties of the resulting alloy markedly. The alloy is used in the as cast condition or after heat-treatment.

The different types vary from gray iron which is machinable to either mottled or white iron which is not easily machinable. White iron of suitable composition can be annealed to give malleable cast iron, whereas by suitable addition of indulging element (Mg or Ce) in a low S & P grey iron composition produces ductile iron or spheroidal graphite iron which is becoming competitors to steel. Yet another type of cast iron known as compacted graphite iron is a comparatively new member in the family of cast iron which has got intermediate properties between grey iron and ductile iron. Thus, cast iron is basically a mechanical mixture of graphite embedded in a metallic matrix such as ferrite, pearlite, bainite and martensite. Besides metallic matrix, the size, shape and distribution in which graphite is deposited depends on numerous factors, such as melting temperature, nucleation, cooling rate etc. but the basic forms are flake graphite, aggregate or temper carbon and nodules or spheroids. About two percent is the maximum carbon content at which iron can solidify as a single phase alloy with all the carbon in solution in austenite.

In addition to carbon, cast iron must also contain appreciable silicon, usually from one to three percent, and thus they are actually iron-carbon-silicon alloys. The high carbon content and the silicon in cast irons

makes them excellent casting alloys. Their melting temperature are appreciably lower than for steel. Molten iron is more fluid than steel and less reactive with molding materials. Formation of lower density graphite in the iron during solidification reduces the change in volume in the metal from liquid to solid and makes production of more complex casting possible. Cast irons, however, do not have sufficient ductility to be rolled or forged.

The various type of cast-iron can be produced by controlling two thing (i) melt chemistry and (ii) cooling rate. Table-1 list typical composition ranges for the most frequently determined elements in the five generic types of cast iron.

Table-1 : Range of compositions for typical unalloyed cast iron

| Type of iron | Percent (%) | | | | |
|---------------------------|-------------|---------|-----------|-----------|------------|
| | Carbon | Silicon | Manganese | Sulphur | Phosphorus |
| White iron | 1.8-3.6 | 0.5-1.9 | 0.25-0.8 | 0.06-0.2 | 0.06-0.2 |
| Malleable (Cast White) | 2.2-2.9 | 0.9-1.9 | 0.15-1.2 | 0.02-0.2 | 0.02-0.2 |
| Gray | 2.5-4.0 | 1.0-3.0 | 0.2-1.0 | 0.02-0.25 | 0.02-1.0 |
| Ductile | 3.0-4.0 | 1.8-2.8 | 0.1-1.0 | 0.02-0.25 | 0.02-1.0 |
| Compacted Graphite | 2.5-4.0 | 1.0-3.0 | 0.2-1.0 | 0.01-0.03 | 0.01-0.1 |

THE TYPES OF CAST IRON

The various types of cast iron can be classified by their microstructure particularly the form and shape in which the major portion of the carbon occurs in the iron. In general, as mentioned in Table-1, there are five basic types : white iron, malleable iron, grey iron, and ductile iron, and compacted graphite iron. In addition, there is a sixth classification, the high alloy irons, generally containing over three percent of added alloy, can also be individually classified as white, grey, or ductile iron.

A. White Iron

If the composition of iron is appropriate or the cooling rate of the metal is sufficiently rapid during solidification, the metal will solidify as white iron in which all carbon will combine with iron as iron carbide. This compound, also known as cementite, is hard and brittle and has a white crystalline fracture, Fig-1. It is essentially free of graphite. White iron has a very high compressive strength and excellent wear resistance, and it retains its hardness for limited periods even upto a red heat.

White iron can be produced in selected area of a casting such as on the periphery of a cam by causing localized rapid solidification of iron. White iron at the surface of the casting is called chill.

White iron does not have easy castability of the other irons because its solidification temperature is generally higher, and it solidifies with carbon in its combined form as iron carbide. Thus because of the absence of free graphite minimizing shrinkage towards solidification is absent. A region in a casting that solidified at an intermediate rate can contain both iron carbide and graphite. This structure is called mottled iron.

B. Malleable Iron

By a special heat-treatment of white cast iron, iron carbide is separated into iron and free graphite. The free graphite in the microstructure takes the form of irregularly shaped nodules of graphite, Fig-2. This form of graphite is also called temper carbon because it is formed into solid state during heat-treatment. The iron is cast as white iron of suitable chemical composition. After the castings are removed from the mould, they are given a long heat-treatment starting at a temperature above 1650 (900°C). This causes the iron carbide to dissociate and the free carbon precipitates in the solid iron as graphite. The rapid solidification rate that is necessary to

form the white iron limits the metal thickness in the casting. The thickness of irons that can be cast white and still be annealed is increased by addition of bismuth and tellurium to the molten metal.

In general, the mechanical properties of cast iron is dependent both on the metallic matrix and the state of graphite. A wide range of mechanical properties can be obtained in malleable iron by controlling the matrix structure around the graphite, pearlite and martensitic matrices are obtained both by rapid cooling through the critical temperature and with alloy addition.

C. Gray Iron

The graphite morphology can be changed from one form to another over a wide range of graphite formations by altering the solidification cooling rate and/or the amount of nodularizing elements present such as magnesium or rare earths. When the composition of molten iron and its cooling rate are appropriate, the carbon in the iron separates during solidification and forms separate graphite flakes that are interconnected within each eutectic cell. The graphite grows edgewise into the liquid and forms the characteristic flake shape, Fig-3. When grey iron is broken, most of the fracture occurs along the graphite, thereby accounting for the characteristic grey colour of the fracture surface. Increasing cooling rate and/or increasing the effective nodularizing elements results in the following changes in the graphite formations : Type-A graphite, Type-B graphite, Type-D graphite (under cooled graphite), coral, compacted, deteriorated form of spheroidal and spheroidal graphite.

The properties of grey iron are influenced by the size, amount, and distribution of graphite flakes, and by the relative hardness of the matrix metal around the graphite. These factors are controlled mainly by the carbon and the silicon contents of the metal and the cooling rate of the

casting. Slower cooling and higher carbon and silicon contents tend to produce more and large graphite flakes, a softer matrix structure, and lower strength. The flake graphite provides grey iron with unique properties such as excellent machinability at hardness levels that produces superior wear resisting characteristics, the ability to resist galling, and excellent vibration damping resulting from a non-linear stress-strain relationship at relatively low stresses. Because of the nature of the graphite flakes in grey iron, i.e. long, flaky and interconnected with sharp tips, it has got high thermal conductivity.

D. Ductile Iron

Sometimes referred as nodular iron or spheroidal graphite (S.G) iron, ductile iron was introduced some 54 years ago in the year 1940's and become one of the most important cast engineering materials in the automotive and machine tool industries. Ductile iron possesses far superior mechanical properties compare to grey iron while exhibiting excellent castability unlike steel. Ductile irons have unconnected spheroidal particles of graphite Fig.4. This breaks the easy path of fracture and minimizes stress concentration. High strength, ductility and toughness are, therefore, achieved inherently.

It is possible to change the graphite morphology through judicious melt treatment from one form to another thus making the cast iron suitable for specific application. Several processes have developed for the production of S.G.Iron. This mode of solidification is obtained by adding a very small, but specific amount of magnesium to the molten iron of proper composition. The base iron is severely restricted in the allowable contents certain minor elements which can interfere with the graphite spherulite formation. The added magnesium reacts with sulphur and oxygen in the molten iron and changes the way the graphite is formed. Control procedures have been developed to make the processing of ductile iron very dependable.

The high carbon and silicon content of ductile iron provide the casting process advantages, but graphite spheroids have only a nominal influence on mechanical properties of the metal. Ductile iron like malleable iron exhibits a linear stress-strain relation, a considerable range of yield strengths, and as its name implies, ductility. Castings are made in a wide range of sizes with sections that can be either very thin or very thick.

The different grades are produced by controlling the matrix structure around the graphite either as cast or by subsequent heat-treatment. Alloy additions may be made to ductile iron to assist in controlling the matrix structure as-cast or to provide response to heat-treatment.

COMPACTED GRAPHITE IRON

Compacted graphite cast iron is a new group of material produced in recent years, which has joined the family of commercially produced cast irons. It lies intermediate between flake graphite and nodular graphite and like each of those groups of materials, it is characterized by having a distinct graphite structure which is clearly recognizable under a microscope. The microstructure of compacted graphite consists of shortened, thickened flake with rounded ends. Scanning electron microscope has revealed that the compacted graphite particles are interconnected in a branched structure in a somewhat similar way to flake in grey iron and are not separated from one another as the spherulite in nodular irons.

Because of the graphite morphology, compacted graphite irons possess improved strength compared to flake graphite irons and approaching that of nodular graphite irons. They have, however, thermal conductivity as high as that of flake graphite irons, and so have an advantage over nodular graphite iron when combination of strength and good thermal conductivity is required.

For iron or similar general composition, the feeding requirements of C.G. irons are greater than those of normal flake graphite iron, but appreciably less than those of ductile iron. In several instances it has been possible to use conventional gray iron running and feeding system to produce sound castings in C.G. iron.

The major factor which control the fluidity of molten iron is the carbon equivalent (C.E.) of the iron. Therefore, there is no significant difference in fluidity between flake graphite iron, compacted graphite iron and spheroidal graphite iron of similar C.E. However, many flake graphite irons are produced at low C.E. content to obtain relatively high strength. Compacted graphite irons have strengths at least equal to the highest strength flake graphite irons, even when the C & Si contents of compacted graphite irons are much higher. Thus, for equivalent tensile strengths, compacted graphite iron have greater fluidity than flake graphite iron. Table-2 & 3 shows the comparative thermal conductivity and mechanical properties respectively.

Table - 2

| Type of iron | Thermal Conductivity Cl/cm. S.C. | |
|-----------------------|----------------------------------|---------------|
| | Medium Light Section | Heavy Section |
| ASTM A 48-74 Class 25 | 0.125 | 0.120-0.135 |
| ASTM A48-74 Class 45 | 0.113 | - |
| Compacted Graphite | 0.118 | 0.0105-0.120 |
| Spheroidal Graphite | 0.080 | 0.090 |

Table - 3

| Type of Iron | Approximate C.E. % | 0.1% offset Yield Strength | Tensile Strength | Elongation % |
|---------------------|-----------------------|-------------------------------|---------------------|-----------------|
| ASTM 48-75 Class 25 | 4.4 | 15,000 | 25,000 | < 1 |
| " " 30 | 4.2 | 20,000 | 30,000 | < 1 |
| " " 45 | 3.6 | 25,000 | 45,000 | < 1 |
| Compacted Graphite | 4.2 | 33-41,000 | 48-57,000 | 3-5 |
| Spheroidal Graphite | 4.2 | 38-47,000 | 60-70,000 | 7-12 |

MATRIX STRUCTURES

The matrix structure in cast irons are the same as found in steel. The various matrix, structures have a wide range in hardness so that each kind of iron have a wide range in properties depending on its matrix structure. Matrix structures, except those in some of the high alloys irons, can be changed by heat treatment.

a) Ferrite

This is a Fe-C solid solution in which appreciable Si and some Mn, Cu and Ni may dissolve. It is relatively soft (although dissolved Si makes it harder than in plain C steel), ductile, of low strength and with poor wear resistance, good fracture toughness, relatively good thermal conductivity and good machinability. A ferritic matrix can be produced as cast but is often the result of an annealing treatment.

b) Pearlite

This is a matrix of ferrite and cementite, which forms from austenite by a eutectic reaction and derives name from its mother of pearl appearance.

It is relatively hard, show moderate toughness, reduced thermal conductivity and good machinability. Several mechanical properties increase as the pearlite spacing decreases. The C content of pearlite in unalloyed steel is 0.8%. It is variable in cast iron depending on the iron composition and cooling rate. It can be as low as 0.5% in the high Si irons.

c) Bainite

This structure can be produced, as cast, in alloyed (Ni and Mo iron) when it is known as acicular iron or, more reliably, by an austemper heat-treatment Fig-5. This structure provides a high strength and improved wear resistance at a machinable hardness.

d) Austenite

This is a solid solution of carbon (2% max.) in γ -iron (f.c.c.). A high alloy content is required to retain this phase during cooling. It is non-magnetic and have excellent heat and corrosion resistance properties up to 800°C and a wide range of thermal expansivity depending on the Si content of the casting.

e) Carbide

White iron is readily identified by its massive primary carbides, Fig-6. This structure can occur in the matrix of other irons because of unusually rapid cooling at the end of solidification or because of the presence of carbide stabilizing elements. Massive carbide means that the grains of carbides are relatively thick and have a low length to width ratio. This is in contrast to the carbide lamellae of pearlite which are thin and long. The term primary identifies carbides that were formed during solidification from liquid iron, and not during subsequent cooling from

casting or heat-treatment. Massive carbides reduce machinability much more than do thin carbide plates that can be readily sheared by a cutting tool. Unless the carbide plates that can be readily sheared by a cutting tool. Unless the carbides are stabilized by alloys, they are generally be dissociated by a high temperature anneal.

f) Sulphide

The sulphur present in iron normally occurs as manganese sulphide. Since this compound solidifies at a temperature above the solidification temperature of the iron, manganese sulphide forms in separate particles that may be of geometric shape. The quantity normally present in commercial iron is not significant. Though the quantity normally present in commercial irons is not significant, it is always advisable to neutralize the sulphur content as manganese sulphide, and prevent the formation of the more harmful iron sulphide. This is achieved when the manganese content equals $1.7 \times \% \text{ sulphur} + 0.2$ or 0.3 . When sulphur content is not balanced by manganese, anomalous inverse chilling may occur, indicated by free carbide in the centre of otherwise gray section. Any excess of manganese over the amount required to neutralize the sulphur will stabilise the pearlite and slightly increase the hardness, without, however, forming free carbide. One percent manganese lowers the γ (austenite) to α ferrite transformation temperature by about 25°C .

Sulphur is usually present in amount from 0.03 to 0.07 percent and is a normally constituent of cast iron when present in amount less than 0.03 percent structural alterations from the conventional patterns may occur.

g) Phosphide

Phosphorus in an amount upto about 0.1% is soluble in iron. Larger amount form the microconstituent, steadite. This complex eutectic of iron and iron phosphide is the last constituent to solidify in iron and thus

occurs at the cell boundaries. With a content of 0.2% in grey iron, steadite is limited to the junctions of three cells and has a shape of a concave triangle. With about 1.5% of P in grey iron a complete network of steadite can form around the cell boundaries Fig.7. Steadite is sometimes improperly identified as a carbide but can be identified by etching with stead's reagent.

Phosphides are similar to carbides. They causes machining problems but they can not be eliminated by heat treatment. High P content has been associated with the segregation of Mo, Cr, V and W. This leaves areas of matrix depleted of these alloying elements and reduces the matrix strength. Embrittlement of ferrite spheroidal cast iron that has undergone cooling or long range annealing between 350°C and 550°C has been attributed to P segregation. Phosphide eutectic liquid at cell boundaries creates a mushy state that is difficult to feed. This condition creates high eutectic solidification forces in the outer solidifying shell, causing mould wall movement and requirement for feed metal in the final stages of solidification. This can lead to shrinkage porosity. An upper limit is usually specified for P for these regions except when it is used for a specific purpose such as promoting castability in low grade irons.

CHEMICAL COMPOSITION

Approach to the problem of graphitization in cast irons has been made on the basis of binary or ternary equilibrium diagrams involving Fe, Si and C. However, C.I. behaves much differently than pure iron. The metastability anomaly, by which the system can freeze either in the stable iron-graphite system or in a metastable iron-iron carbide system, is considerably enhanced in the case of cast irons. This is due to the presence of several elements with diverse influences on freezing. The quality and physical strength of C.I. depends on the size shape, distribution and orientation of graphite masses in the metallic matrix.

It has been established for sometime that various types of graphite bears a definite relation to each other. The condition which gradually change one graphite type to the other can be classified into two main sections - chemical factors and thermal factors. A combination of these two can give any size, distribution and orientation of graphite flake. The C.G. is formed by the manipulation of the same factors which cause normal graphitization in the compact and desirable form.

Chemical factors affecting the formation of graphite in cast irons are those which are introduced by the presence of various elements other than iron. Each such element is effective in influencing graphitization to a greater or less extent. Its individual effect may be increased or minimized because of the presence of any other element or group of elements. Consequently, the classification of these elements based on their individual effects is seldom rigorously followed.

In pure Fe-Si-C alloys it was always found that both C and Si content profoundly influence graphitization. Increasing C content increases not only the amount of eutectic at the expense of primary austenite, but also the readiness and degree graphitization. Si is known to replace a third of its own weight in carbon. Rahder has shown that it is dissolved in the austenite as Fe_3Si . It decreases the solubility of carbon in austenite. Attempts by Owen to detect its presence in the carbide have yielded negative results.

Si increases the eutectic temperature, and according to Norbary, it also extends the range of eutectic freezing. Si presence facilitates the process of graphitization. Si is, therefore, generally regarded as a strong graphitizer. Chrome, however, has reported that whereas a low-Si white iron becomes completely soft after the malleablizing process, a high Si gray iron retains considerable pearlite after a similar thermal treatment.

C & Si together decide the relative amount of primary austenite, and increase in their contents increasing the amount of eutectic and hence reducing the influence of those elements which segregate into the eutectic. The presence of more primary austenite gives very restricted interdendritic spaces for the formation of graphite flakes. The greater the amount of C & Si, the fewer the primary dendrites and the resulting graphite flakes are characterized by their random orientation and comparatively unhindered growth.

Boyles found that graphitization in pure Fe-Si-C alloys always results in the formation of type-D graphite. This was due to an extreme urge of the eutectic to graphitize. Fe showed that it was the presence of S, Mn and H₂ which made the commercial cast irons behaves so differently from the pure ternary alloy. It was decisively shown that both S and H₂ are carbide stabilizer and that introduction of either one of them in pure alloys or in vacuum - melted, low S cast irons results in a rapid increase in size of graphite flake. This increase was maximum in presence of an optimum carbide stabilising action, intensification of which gradually increased the flake size. Further concentration of S or H₂ may even cause solidification of white iron. The carbide stabilising action of S has been corroborated by many other workers. In industrial practice, presence of 's' greatly aids in producing completely white iron casting and the presence of hydrogen causes hard spots and inverse chills.

The increase in flake size due to the initial additions of carbide stabilizers, was due to their ability to delay graphitization by making the carbide more persistent. This prevented a rapid graphitization. Further additions, however, decrease the availability of C for the formation of flake graphite. Both the elements are segregated into the eutectic where they exert all their influence. Hence, for the same content of H₂ and S, a low-si, Low-C iron is more susceptible to their influence.

Addition of Mn considerably modifies the effect of S, a complex series of solid solutions of FeS and MnS are formed with continued additions of Mn. As the MnS content of the solid solution is increased, its melting point is raised. The complex sulphide may even freeze before the freezing of the austenite starts, and may results in ladle desulphurization due to its gravity flotation to the top of the melt. S, when thus excluded from the freezing eutectic because of the presence of Mn, does not influence graphitization.

Cowan has shown that hydrogen is introduced into the metal from the moisture of the blast or due to prolonged contact with the atmosphere at high temperature. Zapffe has shown that its presence causes hard spots and inverse chills in cast irons. Morrogh, Norbwey and other have shown that hydrogen can be flashed out by bubbling CO₂ through the melt.

Thus three elements - S, Mn and H₂ - change the pure ternary alloys into cast irons. Boyles thoroughly investigated the influence of this trio and found that their manipulation can give any type or combination of types of graphite flakes.

Some additional elements are added to the cast irons to improve the physical properties of the metallic matrix. Such alloying elements include Ni, Cu and Cr.

TYPE OF INOCULANT

Inoculation of cast iron is a process that involves controlling the solidification behaviour of the austenite-graphite eutectic and avoiding the formation of the austenite - carbide eutectic in gray, ductile and compacted graphite cast irons. The purpose of inoculation is to provide potent substrates for the effective heterogeneous nucleation of the graphite phase in the iron - carbon eutectic. However, the maximum effects produced by an inoculation occur within seconds of the addition being made and considerable loss of the

effects occur within an extremely short time after addition. In recent years this has stimulated considerable effort into methods whereby inoculant can be added at a much latter stage in the casting sequence thus avoiding the risk of loss of the effect of inoculation during ladle transport and pouring. These methods have referred to as "late inoculation". The requirement of the inoculating materials and the forms in which they are available for late inoculation may differ considerably from those of ladle inoculation.

It is generally believed that in the solidification of gray cast iron carbon precipitates from the liquid iron on nuclei that are present in the liquid. If insufficient nuclei are present the tendency is for the carbon to build upon existing nuclei rather than from new ones. One of the functions of inoculation is to increase, through addition to the molten phase, the number of nuclei upon which the precipitating carbon can build. The result is more type A graphite particles of smaller average size than would be present if no inoculation is used. In other words, one of the reason to inoculate iron is to establish more centers of nucleation.

Another reason to inoculate gray cast iron is for chill control. This especially is important in the case of low carbon equivalent irons. Because of the usually low Si content of these irons, graphite precipitation at the eutectic temperature is slow. This allows the iron to undercool considerably before nucleation starts. Very often, the undercooling is so great, that there is no time for any graphite to precipitate. The carbon then remains in the combined form as iron carbide resulting in a highly chilled iron. Proper inoculation either reduces or eliminates the chill depending on the amount used, the composition of iron, and the speed with which the iron solidifies. Proper inoculation will provide sufficient centres of nucleation to slow down the solidification rate so equilibrium conditions of solidification will take place. Each nucleus when it is formed generates some heat of crystallization which warms up the liquid iron, thus decreasing the rate of solidification.

A third reason for inoculating gray cast iron is to control the graphite structure. In case of ductile iron, or spheroidal graphite cast iron, adequate graphite nucleation is just as important in preventing under cooling as it is in gray cast iron. Without proper inoculation, carbide can be present, resulting in casting with inferior ductility and machinability properties. In addition, the graphite formed from subsequent decomposition of these carbides may be irregular in shape, giving the appearance, in some instance, of iron treated with insufficient nodularizing alloy. Suitable inoculation normally prevents these conditions from occurring by providing sufficient nucleation centres for normal solidification to take place. In general, the greater the degree of nucleation in ductile cast iron, the greater the number, and smaller and more uniform in size and shape will be the graphite spheroids. There will also be less tendency for carbides to precipitate during solidification. If as cast ductile iron is to be achieved readily, in other than the in mold process of manufacture, proper and adequate inoculation is of prime importance.

CARBONOUS INCULANTS

Graphite is regarded as an inconsistent inoculant. This is probably due to the failure to appreciate that the term graphite may include a wide range of materials, which although carbonous, are certainly not composed of truly crystalline graphite. In order for carbon to produce a useful inoculating effect when added in gray iron in the ladle it must consist primarily of highly crystalline graphite.

The graphite (basal planes oriented to give layered hexagonal crystalline structure) with its well developed crystal structure can provide sites for the nucleation of eutectic graphite when added to gray cast iron in the ladle whereas carbon without this structure being well developed may be unable to function as nuclei.

Many proprietary inoculants based on graphite consist on high purity graphite mixed with crushed ferrosilicon so that the benefits of chill removal by graphite, and the strengthening action in conjunction with further chill removal due to the ferrosilicon are combined into one addition. For special purposes small amount of Ti or zirconium silicide can be included in order to control fissures due to nitrogen in irons of abnormally high N_2 content.

High Silicon Inoculants

High purity ferrosilicon has very little inoculating effect when added in the ladle. With the exception of calcium silicide, high silicon inoculants are based on ferrosilicon alloys containing 75-80% Si or occasionally 45-50% Si. All the ladle inoculants based on ferrosilicon depends on their contents of one or more of the minor elements Al, Ca, Sr, Ba, Ti, Mg, Zr, Ce or other rare-earth elements to stimulate their inoculating effects. Mn is sometimes included to lower the melting point of ferrosilicon and thus facilitate solution.

The most commonly used silicon-based inoculant for ladle inoculation is 75% silicon ferrosilicon usually containing between 1-2% Al and 0.2-1.0% Ca. It is perhaps questionable if the inoculants would be as effective if these two elements (Al & Ca) are not present. Strontium ferrosilicon is a special case in which it is necessary to reduce the Ca and Al contents to very low levels in order to obtain the full benefits from the Sr.

Cooling Rate

The stability of carbide is sensitive not only to chemical variations but also to thermal treatment. The thermal factors operating during freezing of the melt control graphitization during the freezing of the eutectic. The

rate of cooling of the melt and particularly the eutectic is the most important factor. It seems to control the temperature of initiation of graphite, the duration of graphitization and the degree of undercooling the rate of cooling is important. The greater the rate of cooling, the lower the temperature of graphite formation, the shorter its duration and the more severe the undercooling.

The effect of rate of cooling on graphitization has been studied by many workers, including Schneidewind, Solton, D.Amico, Long, Plawowsky, Morrough and Norbury. Some of their conclusions are :

- o The greater the rate of cooling, lower the eutectic arrest point, and the shorter the duration of graphitization.
- o The greater the rate of cooling, the more severe the undercooling and the finer the grains
- o With greater undercooling, melt become viscous and the growth of the graphite flake is seen to be hindered
- o The greater the rate of cooling, the finer the graphite pattern
- o Very fast rates of cooling give rise to metastable product
- o With gradual variation in the rate of cooling, a gradual and ordered change in the graphite pattern takes place
- o In each iron, every type of graphite is formed at a definite temperature. Elevating the temperature of graphitization gives longer and coarser flakes; decreasing the temperature of graphite formation brings about finer and more numerous flakes.
- o The eutectic freezing of cast irons can be made to occur over an extended period of time or over an extended range of temperature

These conclusions, which are compiled from various sources, are in close agreement and emphasize the fact that graphitization depends upon the time temperature conditions.

It is well established that flake graphite grows in contact with the liquid iron, with the austenite portion of the eutectic on either surface of the platelet of eutectic graphite. Type A and D graphite are interconnected. The spheroidal graphite eutectic solidification is not as well understood. It appears that graphite grows in contact with the melt but separated or divorced from the austenite. The amount of undercooling of the melt influences the rate of growth and type of graphite obtained; the state of nucleation affects the undercooling and consequently the rate of growth. The greater the undercooling, the more rapid the rate of growth. The effect of undercooling on the graphite or eutectic structure of gray iron is shown in Fig-1. In general, Type A graphite solidifies after only a very limited undercooling, the degree of undercooling increases for Type B and still more for Type D graphite. This indicates the presence of effective substrates for Type A and less potent ones for Type B and D for normal section sizes. The growth rates of different type of graphite follow directly from the amount of undercooling, assuming no growth restriction. With limited undercooling, Type A graphite grows relatively slowly; the growth rate is much more rapid with Type D graphite since the molten iron is sufficiently undercooled that much of the heat of fusion is absorbed by the remaining liquid without requiring the transport of heat from the system.

When drastic undercooling is obtained, the metastable austenite-carbide or Fe_2C eutectic forms. This is called chilling effect so changes the properties of iron that its prevention is one of the primary reasons for the addition of potent substrates for graphite nucleation or inoculation of the irons.

The rate of cooling of the liquid iron which is increased with decreasing section size also causes supercooling and lead, particularly in the absence of effective substrates, to chilling or the formation of white iron. The faster the cooling rate, the more likely the formation of white iron. The presence of effective substrates through inoculation can reduce chilling even at rapid rates of cooling.

The effect of the presence of effective substrate for graphite nucleation or rapid rate of cooling in ductile iron bears some relation to the behaviour of gray iron. Very rapid cooling rates of the absence of these effective substrates can lead to sufficient undercooling so that the austenite-carbide eutectic or white iron forms. The presence of effective substrates or rapid cooling short of what will produce chilling, acts to increase the number of graphite spheroids and to improve their nodularity. It is well known that molten ductile iron poured into light sections will have both a higher modularity and more numerous nodules than the same molten iron poured into heavy sectioned castings. Since compacted graphite irons are intermediate between gray and ductile, one would expect intermediate behaviour. Chilling could ensue at a rapid rates of cooling without potent substrates. Lighter sections could well favour greater nodularity.