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Physical Metallurgy of Cast Irons

 Springer

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*This book is dedicated to the memory of José
Antonio Pero-Sanz Elorz.*

Endorsement

“The second half of the twentieth century was seeing casting processes gradually lifted from the art of crafts status to that of a science—engineers are complementing and supplementing the craftsman, and for the first time books are being published treating casting processes on the level of an advanced engineering or scientific subject; for contrary to the opinions of many, no other branch of industrial engineering will lend itself more responsively or rewardingly to scientific treatment and control, although the road will not be easy because the start has been slow and the numbers of scientist and engineers engaged in the process were relatively few”

“Cast iron is second only to steel in total tonnage produced. Cast iron has certain metallurgical and economic characteristics to the engineer; perhaps the most important is its cheapness”.

H. F. Taylor, M. C. Flemings and J. Wulff
(*Department of Metallurgy,*
Massachusetts Institute of Technology (MIT), 1959).

Preface

The possibility of obtaining metallic parts by simply solidification, without the subsequent processes of forging, justifies the interest of cast irons as structural materials. The economic advantages derived from this kind of manufacture, as well as some of their intrinsic properties, explain the strong demand of this product. Cast irons, with an annual production of 73.2 million tonnes in 2015, are, after steels, the metallic material most used worldwide. Cast irons are followed (regarding the production) in weight importance by aluminum and alloys (58.3 million tonnes in 2015).

The relation among the world production of cast irons and the total production of steel has decreased in the last years, being this relation 4.58% in 2015 (Fig. 1).

The industry of cast irons generates more employments than the steel industry, even when the investment for each position is only the seventh part of the equivalent in the steel industry. Nowadays, it is estimated that around 4.5 million people work (worldwide) in the steel industry, while around 3.5 million people work in the cast irons industry. However, one position in the cast irons industry generates, at

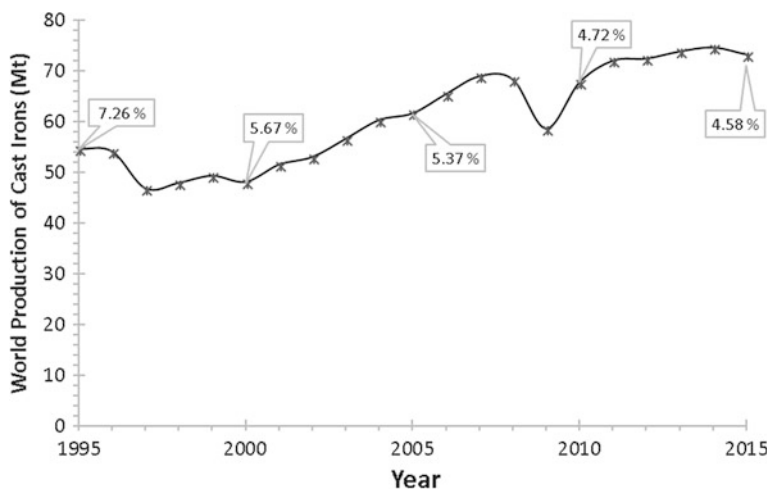


Fig. 1 World production of cast irons and their percentage in relation to steel production

least, other two or three in the metal mechanic industry. In short, the industry of cast irons has a strong impact in the horizontal integration of goods production.

The study of cast irons offers several facets: melting elaboration, physical chemistry of the equilibriums in liquid state, appropriate geometrical design of the parts, moulding technology, etc. Throughout the pages that compose this book, the physical metallurgy of cast irons is preferably studied with the objective of providing a criterion for the rational election of cast irons. That is, the relation between composition, metallographic structure derived from the composition and properties is studied, as well as the possibility of modifying the structure and properties by heat treatment.

It is assumed that the reader is familiarized with the constituents of the alloys, simples (solid solutions, intermetallic compounds, etc.) or compounds (eutectics, eutectoids); and that the reader knows and interprets the equilibrium diagrams. To study the previous fundamentals, as well as to know the fundamentals of solidification and transformations in solid state, the book of José Antonio Pero-Sanz Elorz, María José Quintana Hernández and Luis Felipe Verdeja González entitled *Solidification and Solid-state Transformation of Metals and Alloys* (Elsevier, 2017, first edition) is available for the readers.

From Chaps. 1 to 5, the metallographic structures of cast irons are studied. These chapters concern low and medium-alloyed cast irons, although the notions developed in these chapters will reach other types of cast irons. Chapter 5 is dedicated to the general properties resulted from the structure of grey cast irons.

Chapters 6 and 7 are devoted to malleable and ductile irons, while Chaps. 8 and 9 deal with the high-alloy cast irons. Chapter 8 is dedicated to the diagram Fe–C–Cr with the purpose of justifying several types of cast irons with corrosion resistance. White cast irons are first studied in Chap. 9 as an introduction to the alloyed cast irons used in applications where abrasion resistance is required. Chapter 9 continues with the explanation of high-alloy cast irons characterized by abrasion, corrosion or heat resistances.

Chapter 10 comprises exercises, problems and case-studies. This chapter could be of special interest for the readers after studying the book. Different situations, some of them real case-studies, will help the reader in the full understanding of the cast irons applications, with problems of moulding practice as well as exercises for studying the mechanical properties of cast iron parts. Finally, Chap. 11 is dedicated to the manufacture of cast irons in cupola furnace.

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Acknowledgements

Nearly 30 years after the first edition in Spanish (new revised edition in 2018) of the book of Prof. José Antonio Pero-Sanz Elorz, that was entitled *Materiales para la Ingeniería. Fundiciones Férrreas*, the new edition of the book, this time in English, is published as a small tribute to him. With the idea of reaching a larger public, the original book was translated into English, and more than 50 solved exercises were included with the purpose of facilitating the understanding of the document. The book, now entitled *Physical Metallurgy of Cast Irons*, will be a support for professors in the fields of metallurgy and materials science, but also will be interesting for industrial professionals and researchers.

In this new edition of the book, several people have collaborated, and we want to express our sincere gratitude for their support. We thank José Ignacio Verdeja González of the University of Oviedo (Oviedo, Asturias, Spain), and María José Quintana Hernández and Roberto González Ojeda of the Panamerican University (México City, Mexico) for their advices and support. We cannot forget the invaluable help of José Ovidio García García, we thank him for the micrographs and good attitude towards work. Moreover, we express our gratitude for the valuable collaboration, help and support to the companies Arcelor Mittal Spain and Fundyser (www.fundyser.com/, Gijón, Asturias, Spain).

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Oviedo, Asturias, Spain

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Fe–C System. Stable and Metastable Equilibrium Diagrams

1

Abstract

In this chapter, first, classification of the cast irons based on the Fe–C binary diagram is carried out. White cast irons are those that follow the metastable Fe–C diagram and give eutectics with ledeburite and cementite. Grey cast irons are those that follow the stable Fe–C diagram and give eutectics with graphite and austenite. In this first chapter, additions (graphitizing elements, inoculants, carbonogenous agents and silicon) used to facilitate either the metastable or the stable solidifications are also described.

1.1 Fe–C Equilibrium Diagram

In the first assumption, cast irons can be classified as *white cast irons* and *grey cast irons* according to the solidification. In this way, if the solidification followed the metastable equilibrium diagram (Fe–Fe₃C), a white cast iron would be obtained. If the solidification followed the stable equilibrium diagram (Fe–graphite), a grey cast iron would be obtained.

The equilibrium diagram showed in Fig. 1.1 is usually designed as Fe–C metastable diagram. This diagram describes the Fe–Fe₃C equilibrium.

In effect—for the industrial cooling rates—liquid formed by iron and 4.3% of carbon habitually solidifies at 1148 °C as a kind of eutectic aggregated called ledeburite. This aggregate comprises austenite (of 2.11% C) and cementite (of 6.67% C), whose weight percent in austenite and cementite are, respectively, 51.9 and 48.1% (as it is possible to be deduced from the metastable diagram in Fig. 1.1). However, in the sufficiently slow cooling rate, a liquid of that composition (specifically of 4.25% of carbon) can solidify following the stable diagram shown

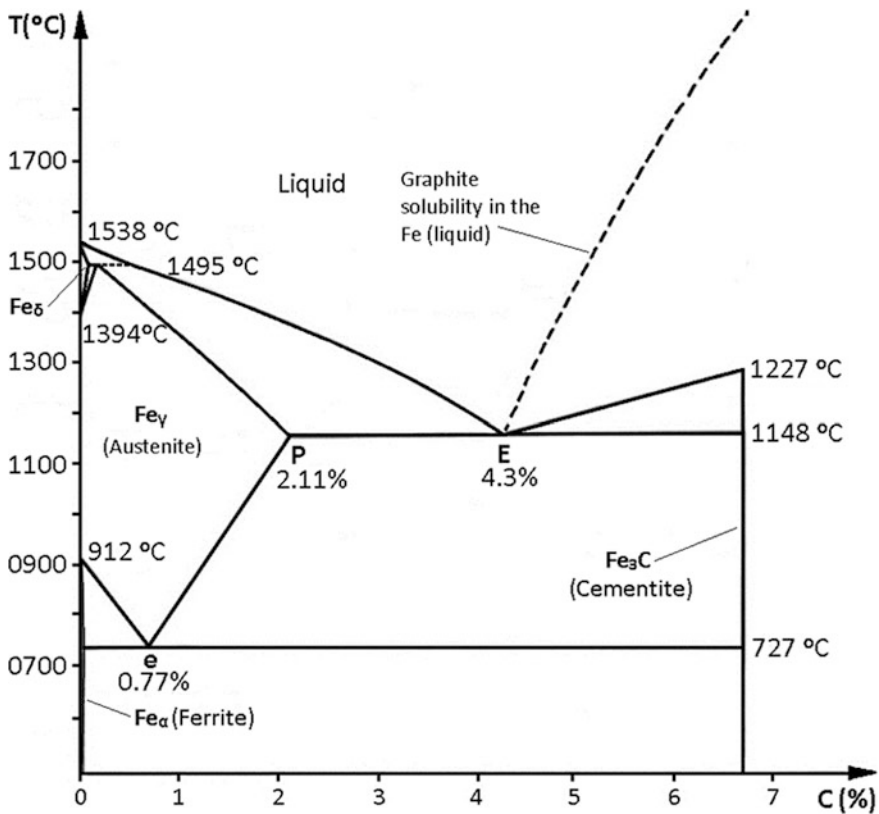


Fig. 1.1 Fe-C metastable diagram

in Fig. 1.2, at 1154 $^{\circ}\text{C}$, and gives a eutectic of carbon (in the form of graphite) and austenite (of 2.08% of carbon), in weight percent of 2.33 and 97.67%, respectively.

Frequently, in high massivity parts (rolling cylinders, wheels, thick plates) both types of eutectics could be obtained: ledeburite in the external zones of the part, and eutectic of graphite and austenite in the inner ones, which was cooled more slowly.

In Fig. 1.3, it is possible to see two homogeneous solidification curves for small amounts of eutectic liquids that were cooled at different rates. If the temperature falls fast, curve I, molten metal solidifies at 1148 $^{\circ}\text{C}$, and a eutectic of cementite and austenite is formed. Whereas, if the temperature falls very slowly (curve II in Fig. 1.3), solidification will happen at a higher temperature, 1154 $^{\circ}\text{C}$, and an aggregated formed by eutectic of graphite and austenite is obtained.

For a liquid with a composition near to 4.3 wt% C, there are two possibilities of eutectic solidification: following the stable diagram or following the metastable diagram. To obtain one or the other eutectic during the cooling period, it is required: first, descending down to the temperature of 1154 $^{\circ}\text{C}$ (to obtain the stable eutectic)—or descending down to the temperature of 1148 $^{\circ}\text{C}$ (to obtain the metastable eutectic)

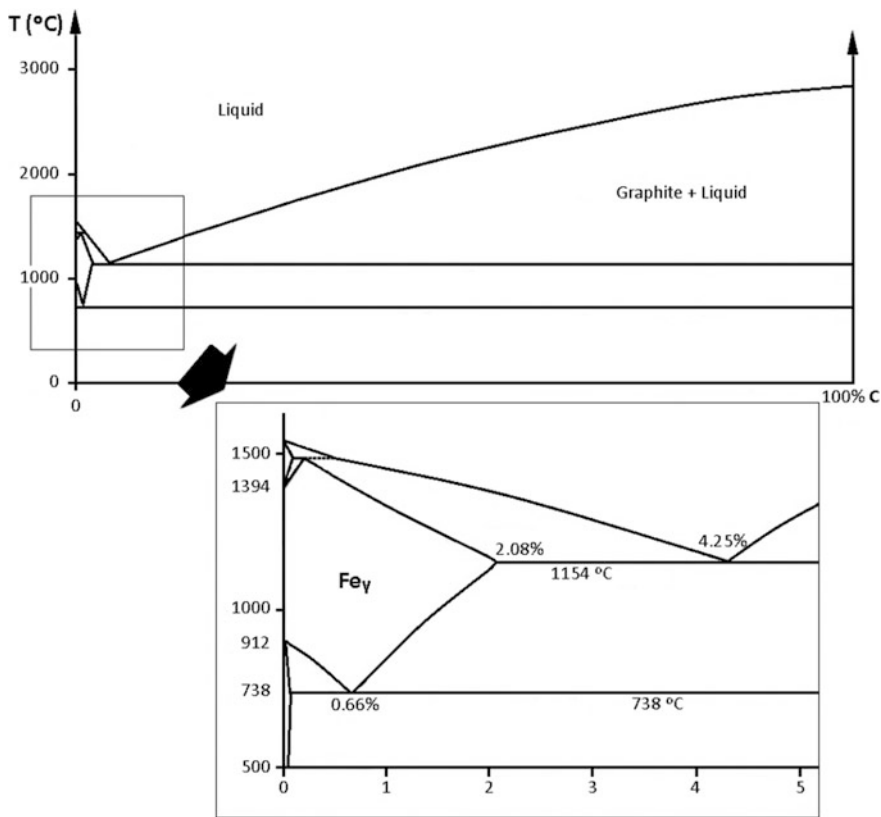
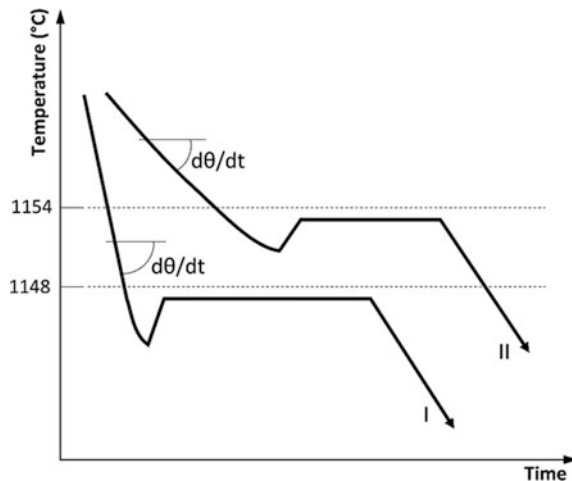


Fig. 1.2 Fe–C stable diagram

Fig. 1.3 Fe–C stable eutectic and Fe– Fe_3C metastable eutectic formation according to the cooling rate. Curve I: metastable eutectic. Curve II: stable eutectic



—and, besides, a certain undercooling; as it happens in all homogeneous solidification. Afterwards, latent heat that was released in the solidification period will rise the temperature once again due to the evolution of heat. The temperature will rise, at the most, up to 1154 °C.

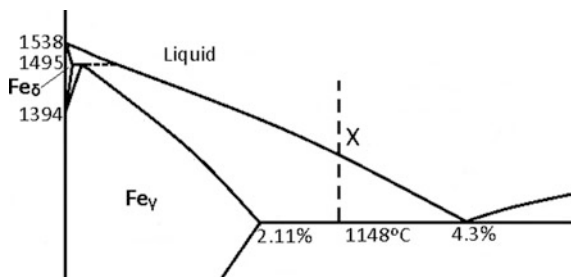
The molten metal does not solidify immediately when it reaches the corresponding temperature; a certain time is required to achieve the graphite or the austenite nucleation, which are drivers of the solidification. Cementite nucleation kinetics is faster than that of a group of carbon atoms to obtain graphite. In the appearance of cementite takes part the affinity between carbon and iron for obtaining the intermetallic compound Fe_3C . That is the reason for the less time required to obtain cementite than to achieve graphite.

It is understood that a binary liquid (composed only of iron and carbon) normally solidifies in the form of ledeburite (cementite and austenite), instead of giving the eutectic of graphite and austenite. To achieve the eutectic of graphite and austenite, a so slowly cooling rate that would made possible (in an interval of 6 °C, at temperatures between 1154 and 1148 °C) an enough holding time to achieve the formation of a cluster of carbon atoms as graphite would be necessary. In this way, if the cooling rate is fast and the temperature is lower than 1148 °C, the molten metal will give ledeburitic cementite an appearance previous to that of the graphite and austenite. The presence of ledeburitic cementite is related to the possibility of its appearance at temperatures lower than 1148 °C, and also due to the chemical affinity between iron and carbon to make up cementite.

Exercise 1.1: The time elapsed, at a constant temperature, for the complete solidification of a weight (P_1) of a binary eutectic white cast iron, in equilibrium conditions, is t_1 . An equivalent quantity (in weight) of another binary hypoeutectic white cast iron takes $0.41 \cdot t_1$ to complete the solidification, also in equilibrium conditions. It is requested:

1. Carbon content in the hypoeutectic white cast iron.

Fig. 1.4 Section of the Fe– Fe_3C diagram



Question

The carbon content in the hypoeutectic white cast iron is calculated. First, the hypoeutectic region of the Fe–Fe₃C metastable diagram is drawn (Fig. 1.4).

The eutectic fraction in the hypoeutectic white cast iron, X , is calculated through the lever rule, as follows:

$$\left(\frac{X - 2.1}{4.3 - 2.1} \right) \cdot P_1 \quad (1.1)$$

Then, as the eutectic fraction and the time required for the complete solidification are known in both white cast irons, the carbon content will be calculated as follows:

$$\frac{[(X - 2.1)/(4.3 - 2.1)] \cdot P_1}{P_1} = \frac{0.41 \cdot t_1}{t_1} \quad (1.2)$$

$$\left(\frac{X - 2.1}{4.3 - 2.1} \right) = 0.41 \quad (1.3)$$

$$X = 3\% \text{ C wt.} \quad (1.4)$$

2. Differences in minor segregation (dendritic) in both white cast irons.

Question

The differences in the minor segregation are

- in the eutectic cast iron: there is not segregation.
- in the hypoeutectic cast iron: there is segregation in the disperse, and eutectic constituent will appear (fluidity will be favoured). If the Scheil equation is used, which is as follows:

$$f_L = \left(\frac{c_0}{c_L} \right)^{\frac{1}{1-K}} \quad (1.5)$$

K : partition coefficient; Scheil equation is defined as the relation between the solute concentration (carbon) in the liquid and in the solid with which is in equilibrium.

In this case,

$$K(\text{carbon}) = \frac{2.11}{4.3} = 0.49 \quad (1.6)$$

$$f_L = \left(\frac{3}{4.3} \right)^{\frac{1}{1-0.49}} \simeq 0.49 > 0.41 \quad (1.7)$$

Note: The carbon diffusion in the austenite is very fast. So, there is no coring in cast irons as carbon element is concerned. But, there is coring with the rest of alloying elements and/or impurities.

3. Calculate the hardness of this white cast iron. Data: Pearlite's hardness: 24 HRC; Cementite's hardness: 68 HRC.

Question

The hardness of the white cast iron will be calculated, approximately, with the *rule of mixtures*:

$$\text{Hardness}_{\text{Cast Iron}} = \text{Hardness}_{\text{Pearlite}} \cdot f_{\text{Pearlite}} + \text{Hardness}_{\text{Cementite}} \cdot f_{\text{Cementite}} \quad (1.8)$$

where

$$\text{Hardness}_{\text{Pearlite}} = 24 \text{ HRC} \quad (1.9)$$

$$\text{Hardness}_{\text{Cementite}} = 68 \text{ HRC} \quad (1.10)$$

$$f_{\text{Pearlite}} = \frac{6.67 - 3}{6.67 - 0.77} = 0.622 (62.2\%) \quad (1.11)$$

$$f_{\text{Cementite}} = 1 - f_{\text{Ferrite}} = 0.378 (37.8\%) \quad (1.12)$$

And finally, the hardness of the hypoeutectic white cast iron is

$$\text{Hardness}_{\text{Cast Iron}} = 24 \cdot 0.622 + 68 \cdot 0.378 \simeq 41 \text{ HRC (high)} \quad (1.13)$$

4. Explain the main properties of the white cast irons regarding the micro-graphic structure.

Question

The model to explain the white cast irons behaviour could be a cementite sponge, whose empty spaces were filled with pearlite (transformed either from dispersed austenite or eutectic austenite). Consequently, (Fe_3C intermetallic compound is hard and brittle) their mechanical properties include low toughness, almost null elongation in the tensile test and high wear resistance. Their wear

behaviour determines their use in industrial applications such as mineral crushing, sieving and grinding operations; and also, explains the non-machinability of white castings. White cast irons are composites of the ceramic matrix (cementite) and metallic disperse (austenite, pearlite, bainite, martensite). They are ceramic matrix composites (CMC) according to their nature.

Exercise 1.2. The time elapsed, at constant temperature, for the complete solidification of a weight (P_1) of a binary eutectic grey cast iron, in equilibrium conditions, is t_1 . An equivalent quantity (in weight) of another binary hypoeutectic grey cast iron takes $0.42 \cdot t_1$ to complete the solidification, also in equilibrium conditions. It is requested:

1. Carbon content in the hypoeutectic grey cast iron.

Question

The simplified Fe–C stable diagram is enclosed (Fig. 1.5).

The *lever rule* is used to calculate the eutectic fraction in the hypoeutectic grey cast iron X:

$$f_L = \frac{X - 2.08}{4.25 - 2.08} \cdot P_1 \quad (1.14)$$

As the solidification time is proportional to the amount of eutectic constituent, it is obtained that

$$\frac{[(X - 2.08)/(4.25 - 2.08)] \cdot P_1}{P_1} = \frac{0.42 \cdot t_1}{t_1} \quad (1.15)$$

$$\left(\frac{X - 2.08}{4.25 - 2.08} \right) = 0.42 \quad (1.16)$$

$$X = 3\% \text{ C wt} \quad (1.17)$$

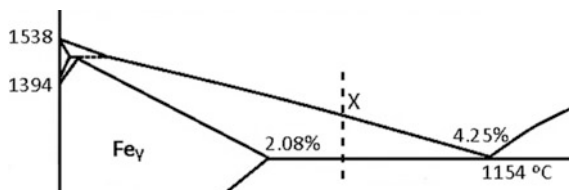


Fig. 1.5 Section of the Fe–C diagram

If the *lever rule* is used again, the graphite content can be calculated as follows:

$$\text{Graphite} = \left(\frac{3 - 2.08}{100 - 2.08} \right) = 0.009(0.9\%) \quad (1.18)$$

2. **Types of graphite that can appear regarding the cooling rate in one or another cast iron.**

Question

Regarding the cooling rate, the types of graphite that can appear are:

in the eutectic, graphite types A and B can appear; in the hypoeutectic, graphite type D (see Figs. 2.6 and 2.8) can be observed. The structure of the grey cast iron is like the structure of a pearlitic steel (matrix of austenite transformed into pearlite) with hollows (cracks) filled with graphite. A high-volume fraction of hollows implies a low mechanical strength. Moreover, if the hollows have a high size and angularity (notch effect), the mechanical strength will be low. In other words, the higher the carbon content, the lower the mechanical strength, but also the higher the castability (a more detailed explanation will be given in Chap. 5). It is, naturally, a MMC (metal matrix composite).

3. **For the same massivity (relation Volume/Area) in parts manufactured with both cast irons, what cast iron should have higher silicon content?**

Question

Equivalent massivities mean similar cooling rates. Slow cooling rates favour the stable solidification. If the carbon content diminishes, then the tendency to chill of the parts grows. This tendency to chill can be corrected with higher silicon contents.

4. **Compare the mechanical properties: strength, elongation, toughness; and others: wear and corrosion resistances, and machinability.**

Question

The properties of grey cast irons will be deeply detailed in Chap. 5. However, it can be said that lower carbon content (hypoeutectic grey cast iron) implies a higher strength, a higher elongation, and a better toughness. On the other hand, lower resistance to wear, lower resistance to corrosion and a worse machinability will be achieved with the lower carbon content.

1.2 Graphitizing Elements

In fact, for achieving the formation of graphite in the case of eutectic liquids and industrial cooling rates, even if they are slow, the presence of graphitizing elements, such as Si, P, Al, Ni or Cu (listed in descending order of efficiency) is required.

The presence of these elements in the liquid is effective due to both the dilution and the *affinity* (activity) effects. Graphitizing elements dissolve the pre-clusters of Fe and C necessities for the formation of cementite clusters. Consequently, the cementite kinetics is retarded, and the appearance of graphite is made possible. On the other hand, some elements—such as Si, P, Al—with an affinity for the iron (to form silicides, phosphides, aluminides) add, to the dilution simple effect above mentioned, a tendency to form graphite instead of cementite.

1.3 Inoculant Elements

Ferrosilicon and some compounds that are called *inoculants*—such as calcium silicides, zirconium alloys, strontium alloys, etc.—accelerate the graphite formation. That is because they facilitate the heterogeneous nucleation of the graphite, by epitaxy or crystallographic similarity. This effect is achieved even without being graphitizing elements strictly speaking as it happens with the most of these heterogeneous *clustering agents*, which are not graphitizing agents.

The inoculation increases the nucleation rate and the refining of the graphite particles; and it gives origin, also, to the formation of a higher number of eutectic cells. Some elements, as magnesium or boron, are in the origin of a spheroidal graphite morphology, instead of the typical laminar morphology.

The inoculants efficiency disappears with the time, so, after the inoculation, it is advisable to cast irons as soon as possible.

1.4 Carburigenous Elements

The elements with the aptitude to form more stable carbides than the cementite, or to stabilize the cementite as a complex carbide—such as titanium, zirconium, niobium, vanadium, tungsten, molybdenum, chromium, manganese—are called *anti-graphitizing* elements. Obviously, the presence of these elements in the liquid is unfavourable for the graphite nucleation (carbides are preferentially formed); and, therefore, they are harmful for the formation of the eutectic of graphite + austenite.

For example, *high-chromium alloyed cast irons*, which are characterized by their abrasion, corrosion and high-temperature resistances, always solidify following the Fe/C metastable diagram as will be studied in Chaps. 8 and 9.

1.5 The Influence of Silicon in Cast Irons

From all the elements that are used for achieving the graphite + austenite eutectic transformation, avoiding the appearance of ledeburite, silicon is the main low-cost graphitizing agent. Aluminium, for instance, is an energetic graphitizing element; but its addition reduces the castability and it usually produces surface defects in the parts. Phosphorus, despite its graphitizing nature, can produce cementite because of the formation of a ternary eutectic of phosphorus, iron, and cementite. Nickel and copper are slightly graphitizing elements—silicon, for instance, is five times more graphitizing agent (in weight) than copper—and their use can be explained, as we will see afterwards, when the graphitizing effect in the solid state is pursued.

The partition coefficient ($K = C_S/C_L$) in the Fe–Si solidification diagram has a value near to 1. That is why it is possible to achieve a uniform distribution of silicon in the liquid without segregations of this element.

Silicon percentages, which are required to avoid the ledeburite formation in the plain and low-alloyed cast irons, range between 2 and 6%.

High-silicon amounts should be used when the cooling rates rise (or the part size is thinner). On the other hand, the higher the amount of carbon in the melting, the faster the graphite formation kinetics, so more probable the appearance of the graphite results, and, consequently, less critical results the silicon.

Logically, the silicon presence modifies the lines and critical points in the stable and metastable binary diagrams of the Fe–C system. Binary eutectics, for instance, will not solidify at a constant temperature but in an interval of temperatures: because in the ternary system the presence of three phases (liquid + graphite + austenite, or liquid + cementite + austenite in the case of the ledeburite) means one degree of freedom.

Figure 1.6 shows the temperature's gap between stable and metastable solidification as a function of the silicon percentages.

With 0% silicon, achieving the stable eutectic results is difficult: it should be noticed that the temperature's gap between both eutectics is only of 6 °C. However, when the quantity of silicon in the cast iron is increased, the temperature's gap is also increased. This higher temperature's gap (between the stable and metastable

Fig. 1.6 Beginning temperatures of both stable and metastable eutectics as a function of the silicon amount (wt%)

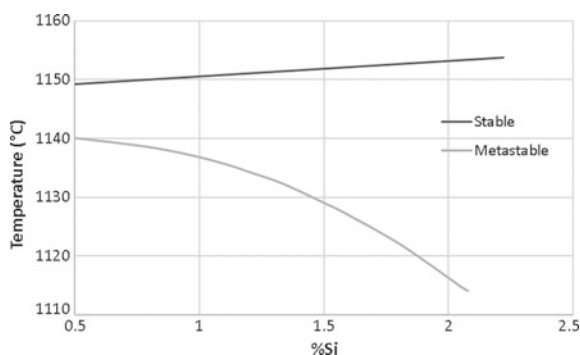
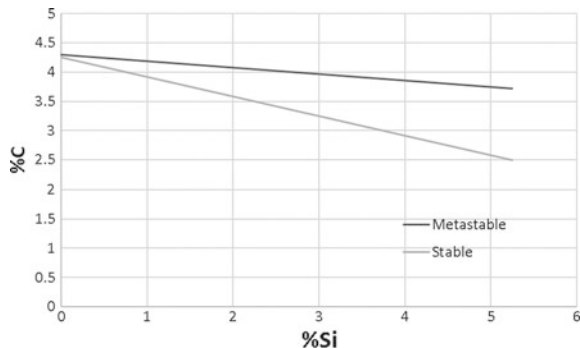


Fig. 1.7 Carbon contents both in the stable and metastable eutectics (wt%) as a function of the silicon



eutectics) results favorable when a eutectic of graphite and austenite is pursued. Therefore, when the silicon content is increased, to the graphitizing effect is added, favourably, the enlargement of the temperature's gap between both eutectics. Like this, the formation of the stable eutectic is possible even for faster solidification rates. Although, while increasing solidification rates, the ledeburite formation would be unavoidable.

The presence of silicon decreases the carbon contents in the eutectic, both in the stable and metastable diagrams, as it is shown in Fig. 1.7; also, phosphorus has a similar effect in the composition of the eutectics. It is usually called *equivalent carbon of a grey cast iron* (EC or C_{eq}) to the following sum of percentages:

$$EC(C_{eq}) = \% C + \% Si/3 + \% P/3 \quad (1.19)$$

The carbon content in the stable and metastable eutectics can be calculated as a function of the silicon and phosphorus percentage by means of the following expressions:

$$\% C \text{ stable eutectic} = 4.25 - \% Si/3 - \% P/3 \quad (1.20)$$

$$\% C \text{ metastable eutectic} = 4.3 - \% Si/9 - \% P/3.5 \quad (1.21)$$

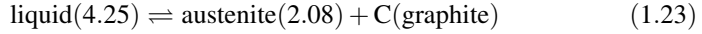
Exercise 1.3. In the grey iron Fe–4.25% C, calculate the minimum value of the interaction coefficient C–C, ε_C^C , for the grey solidification of the cast iron.

Question

In thermodynamics, it is called *activity* of an element i in solution (liquid, solid) to the tendency that has this element to leave the solution. In real solutions, the activity is equal to the product of the activity coefficient (γ_i) and its mole fraction (x_i), that is

$$a_i = \gamma_i \cdot x_i \quad (1.22)$$

When $\gamma_i > 1$, the tendency to leave the solution is strengthened. On the other hand, if $\gamma_i < 1$, the tendency diminishes. In the limit situation, when $\gamma_i \cdot x_i = 1$, the component tends to segregate, precipitate, as pure element. In the ternary equilibrium:



The formation of graphite imposes that

$$a_{\text{C}}^{\text{Liquid}} = a_{\text{C}}^{\gamma} = a_{\text{C}}^{\text{Graphite}} = 1 \quad (1.24)$$

That is,

$$a_{\text{C}}^{\text{Liquid}} = \gamma_{\text{C}}^{\text{Liquid}} \cdot x_{\text{C}}^{\text{Liquid}} = 1 \rightarrow \gamma_{\text{C}}^{\text{Liquid}} = 1/x_{\text{C}}^{\text{Liquid}} \quad (1.25)$$

It can be demonstrated that for an element i in solution:

$$\ln \gamma_i = \ln \gamma_i^0 + \sum \varepsilon_i^j \cdot x_j \quad (1.26)$$

where

- γ_i^0 is the activity coefficient of the element i in solid solution at infinite dilution, that is $x_i \rightarrow 0$ (Raoult's law, for C in the Fe, at 1154 °C, $\gamma_i^0 = 2.3$).
- ε_i^j are the interaction coefficients of first order between the different elements in solution.
- x_j are the mole fractions.

If the interaction coefficients are positives, $\varepsilon_i^j > 0$, the tendency of the considered element for leaving the solution is positive; and negative, $\varepsilon_i^j < 0$, in the opposite situation.

The carbon mole fraction and the activity coefficient of this element are calculated:

$$x_{\text{C}} \simeq \frac{4.25 \cdot 55.85}{12 \cdot 100} \simeq 0.2 \quad (1.27)$$

If the following equation is used:

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_{\text{C}}^{\text{C}} \cdot x_{\text{C}} \quad (1.28)$$

$$\ln 5 = \ln 2.3 + \varepsilon_C^C \cdot 0.2 \rightarrow \varepsilon_C^C \simeq 3.9 \quad (1.29)$$

Knowing that the cast iron 3.5% C–2.5% Si is eutectic, calculate the interaction coefficient C–Si, $\varepsilon_C^{\text{Si}}$.

Question

The carbon and silicon mole fractions and the carbon activity coefficient are calculated:

$$x_C \simeq \frac{3.5 \cdot 55.85}{100 \cdot 12} = 0.16 \quad (1.30)$$

$$x_{\text{Si}} \simeq \frac{2.5 \cdot 55.85}{100 \cdot 28.1} = 0.05 \quad (1.31)$$

$$\gamma_C^L = \frac{a_C^L}{x_C} = \frac{1}{x_C} = 6.25 \quad (1.32)$$

If the fundamental equation is used

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_C^{\text{Si}} \cdot x_{\text{Si}} \quad (1.33)$$

$$\ln 6.25 = \ln 2.3 + 3.9 \cdot 0.2 + \varepsilon_C^{\text{Si}} \cdot 0.05 \rightarrow \varepsilon_C^{\text{Si}} \simeq 7.6 \quad (1.34)$$

From the provided data, it is deduced that the carbon interaction with itself and the carbon interaction with silicon are positives, strengthening their presence the graphite formation.

Calculate for the 3% C cast iron the silicon content that is necessary for the stable eutectic solidification.

Question

The carbon mole fraction and activity coefficient are calculated:

$$x_C \simeq \frac{3 \cdot 55.85}{100 \cdot 12} = 0.14 \quad (1.35)$$

$$\gamma_C^L = \frac{a_C^L}{x_C} = \frac{1}{x_C} = 7.14 \quad (1.36)$$

If the fundamental equation is used

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_{Si}^{Si} \cdot x_{Si} \quad (1.37)$$

$$\ln 7.14 = \ln 2.3 + 3.9 \cdot 0.14 + 7.6 \cdot x_{Si} \rightarrow x_{Si} \simeq 0.078; \quad w_{Si} \simeq 3.9\% \quad (1.38)$$

And, in the case of 4% C cast iron?

Question

The carbon mole fraction and activity coefficient are calculated:

$$x_C \simeq \frac{4 \cdot 55.85}{100 \cdot 12} = 0.19 \quad (1.39)$$

$$\gamma_C^L = \frac{a_C^L}{x_C} = \frac{1}{x_C} = 5.26 \quad (1.40)$$

If the fundamental equation is used

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_{Si}^{Si} \cdot x_{Si} \quad (1.41)$$

$$\ln 5.26 = \ln 2.3 + 3.9 \cdot 0.19 + 7.6 \cdot x_{Si} \rightarrow x_{Si} \simeq 0.012; \quad w_{Si} \simeq 0.6\% \quad (1.42)$$

And, in the case of 2.5% C cast iron?

Question

The carbon mole fraction and activity coefficient are calculated:

$$x_C \simeq \frac{2.5 \cdot 55.85}{100 \cdot 12} = 0.12 \quad (1.45)$$

$$\gamma_C^L = \frac{a_C^L}{x_C} = 8.33 \quad (1.46)$$

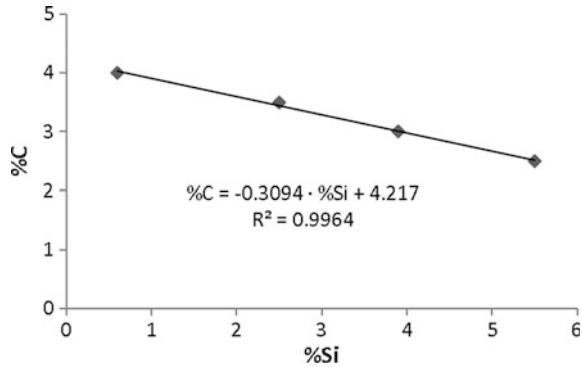
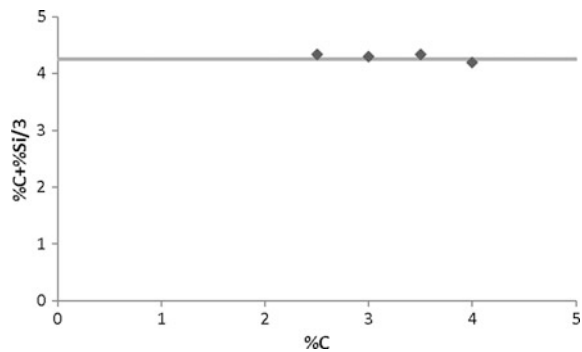
Applying the equation listed above:

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_{Si}^{Si} \cdot x_{Si} \quad (1.47)$$

$$\ln 8.33 = \ln 2.3 + 3.9 \cdot 0.12 + 7.6 \cdot x_{Si} \rightarrow x_{Si} \simeq 0.11; \quad w_{Si} \simeq 5.5\% \quad (1.48)$$

If we represent graphically the % C and % Si (Fig. 1.8).

In the same manner, we represent % C + % Si/3 and % C (Fig. 1.9).

Fig. 1.8 Representation of the % C and % Si**Fig. 1.9** Representation of the % C + % Si/3 and % C

That demonstrates

$$C_{\text{eutectic}} \simeq C + \text{Si}/3 \quad (1.49)$$

The cast iron 3.4% C–2.4% Si–0.24% P solidifies as stable eutectic. Demonstrate that the interaction coefficient C–P, $\varepsilon_{\text{C}}^{\text{P}}$, is positive and intermediate between the interaction coefficient C–C and C–Si.

Question

The carbon, silicon and phosphorous mole fractions are calculated:

$$x_{\text{C}} \simeq \frac{3.4 \cdot 55.85}{100 \cdot 12} = 0.16 \quad (1.50)$$

$$x_{\text{Si}} \simeq \frac{2.4 \cdot 55.85}{100 \cdot 28.1} = 0.048 \quad (1.51)$$

$$x_P \simeq \frac{0.24 \cdot 55.85}{100 \cdot 31} = 0.004 \quad (1.52)$$

If the principal equation is used

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_C^{Si} \cdot x_{Si} + \varepsilon_C^P \cdot x_P \quad (1.53)$$

$$\ln 6.25 = \ln 2.3 + 3.9 \cdot 0.16 + 7.6 \cdot 0.048 + \varepsilon_C^P \cdot 0.004 \rightarrow \varepsilon_C^P \simeq 5 \quad (1.54)$$

In the cast iron 3.5% C–2.1% Si, calculate the phosphorus percentage that is required for the stable eutectic solidification.

Question

The carbon and silicon mole fractions are calculated:

$$x_C \simeq \frac{3.5 \cdot 55.85}{100 \cdot 12} = 0.16 \quad (1.55)$$

$$x_{Si} \simeq \frac{2.1 \cdot 55.85}{100 \cdot 28.1} = 0.04 \quad (1.56)$$

If the following equation is used:

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_C^{Si} \cdot x_{Si} + \varepsilon_C^P \cdot x_P \quad (1.57)$$

$$\ln 6.25 = \ln 2.3 + 3.9 \cdot 0.16 + 7.6 \cdot 0.04 + 5 \cdot x_P \rightarrow x_P \simeq 0.016; \quad w_P \simeq 0.9\% \quad (1.58)$$

And, in the 3% C–3% Si cast iron?

Question

The carbon and silicon mole fractions are calculated:

$$x_C \simeq \frac{3 \cdot 55.85}{100 \cdot 12} = 0.14 \quad (1.59)$$

$$x_{Si} \simeq \frac{3 \cdot 55.85}{100 \cdot 28.1} = 0.06 \quad (1.60)$$

Applying the basic equation:

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_C^{Si} \cdot x_{Si} + \varepsilon_C^P \cdot x_P \quad (1.61)$$

$$\ln 7.14 = \ln 2.3 + 3.9 \cdot 0.14 + 7.6 \cdot 0.06 + 5 \cdot x_P \rightarrow x_P \simeq 0.026; \quad w_P \simeq 1.4\% \quad (1.62)$$

And, in the 2.5% C–4% Si cast iron?

Question

The carbon and silicon mole fractions are calculated:

$$x_C \simeq \frac{2.5 \cdot 55.85}{100 \cdot 12} = 0.12 \quad (1.63)$$

$$x_{Si} \simeq \frac{4 \cdot 55.85}{100 \cdot 28.1} = 0.08 \quad (1.64)$$

If the following equation is used:

$$\ln \gamma_i = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_C^{Si} \cdot x_{Si} + \varepsilon_C^P \cdot x_P \quad (1.65)$$

$$\ln 8.33 = \ln 2.3 + 3.9 \cdot 0.12 + 7.6 \cdot 0.08 + 5 \cdot x_P \rightarrow x_P \simeq 0.042; \quad w_P \simeq 2.3\% \quad (1.66)$$

Despite the approximations that were done, it is possible to demonstrate that

$$C_{\text{eutectic}} = 4.3 \simeq \text{Carbon}_{\text{total}} + \text{Si}/3 + \text{P}/3 \quad (1.67)$$

Exercise 1.4. Two cast irons have the following chemical composition:

- (A) 3.4% C–0.25% Si–0.6% Mn–0.03% S–0.05% P
- (B) 3.0% C–3.6% Si–0.6% Mn–0.03% S–0.30% P

Calculate the potentially white or grey behaviour of these cast irons and the possible micrographic structure. Which of the two cast irons would have a higher castability? And wear resistance?

Question

The equivalent carbon is calculated as follows:

$$EC \simeq \% C + \% Si/3 + \% P/3 \quad (1.68)$$

$$A: EC \simeq 3.4 + 0.25/3 + 0.05/3 = 3.5 < 4.3 \quad (1.69)$$

$$B: EC \simeq 3 + 3.6/3 + 0.30/3 = 4.3 \quad (1.70)$$

Cast Iron A has low silicon content. For that reason, this cast iron will have a great tendency to chill. It will solidify as hypoeutectic white cast iron, so the wear resistance will be good.

Cast Iron B has high-silicon content. Therefore, the solidification will be as eutectic grey iron. The castability will be excellent.

Exercise 1.5. A white cast iron has the following chemical composition: 4.26% C–0.9% Si–0.16% Mn–0.010% S–0.04% P–0.91% Cr. How can be justified the presence of primary cementite in the microstructure of this cast iron? Calculate the percentage.

Question

In the metastable eutectic, the eutectic equivalent carbon is calculated by applying the formula:

$$EC = 4.3 - \% Si/9 - \% P/3.5 \quad (1.71)$$

$$EC = 4.3 - 0.9/9 - 0.04/3.5 = 4.19 < 4.26 \quad (1.72)$$

Then, the cast iron is slightly hypereutectic ($4.26\% C > C_{\text{eutectic}} = 4.19\% C$), there are primary Fe_3C crystals. The amount of these crystals of primary Fe_3C is

$$Fe_3C_{\text{Primary}} = \frac{(4.26 - 4.19)}{(6.67 - 4.19)} \cdot 100 \simeq 2.8\% \quad (1.73)$$

The rest (97.2%) will be eutectic ledeburite.

Stable Eutectic—Graphite Morphologies

2

Abstract

This chapter is entirely dedicated to the stable eutectic, that of austenite and graphite. This eutectic is abnormal due to the significant differences in both the proportions and the melting temperatures of each constituent. This last aspect will have an important influence on the structure and properties of the eutectic. The type and size of the graphite will depend on both the amount of carbon and the cooling conditions. Five types of graphite will be identified. The presence of one or other kind of graphite will condition the properties of the grey cast iron.

2.1 Stable Eutectic

The eutectic of the Fe–C stable system, comprised of graphite + austenite, is an *abnormal* eutectic. That is because of the following reasons: first, due to the great difference between the proportions of each component (2.33 wt% of graphite and 97.67 wt% of austenite); and second, due to the noticeable differences between the graphite (2930 °C) and austenite (lower than 1394 °C) melting temperatures. These aspects (constituents' melting temperatures and weight proportions) largely affect the eutectic structure and properties.

In all eutectic, the first constituent that will solidify, will be the one who has the highest melting temperature. In this way, graphite undercooling, from 2930 to 1154 °C, is the force which drives the solidification (driving force). When a portion of graphite solidifies, then the adjacent liquid, locally, will become poor in carbon, and that is why, after that, the next constituent (austenite) will solidify in the necessary amount to keep the eutectic proportions in the remaining liquid.

Exercise 2.1. In a Fe–C binary alloy, with 5% C, calculate the weight percentages of the different types of graphite: pro-eutectic graphite, eutectic graphite, secondary graphite, eutectoid graphite and total graphite. (See stable diagram in Fig. 1.2.)

Question

By means of the lever rule:

At $1154\text{ }^{\circ}\text{C} + \delta T$ (pro-eutectic graphite):

$$C_{\text{pro-eutectic}} = \frac{5 - 4.25}{100 - 4.25} = 0.008(0.8\%) \quad (2.1)$$

At $1154\text{ }^{\circ}\text{C} - \delta T$ (eutectic graphite):

$$C_{\text{eutectic}} = C_{\text{total}} - C_{\text{pro-eutectic}} = \frac{5 - 2.08}{100 - 2.08} - 0.008 = 0.022(2.2\%) \quad (2.2)$$

At $738\text{ }^{\circ}\text{C} + \delta T$ (secondary graphite):

$$\begin{aligned} C_{\text{secondary}} &= C_{\text{total}} - C_{\text{pro-eutectic}} - C_{\text{eutectic}} = \frac{5 - 0.68}{100 - 0.68} - 0.022 - 0.008 \\ &= 0.01(1\%) \end{aligned} \quad (2.3)$$

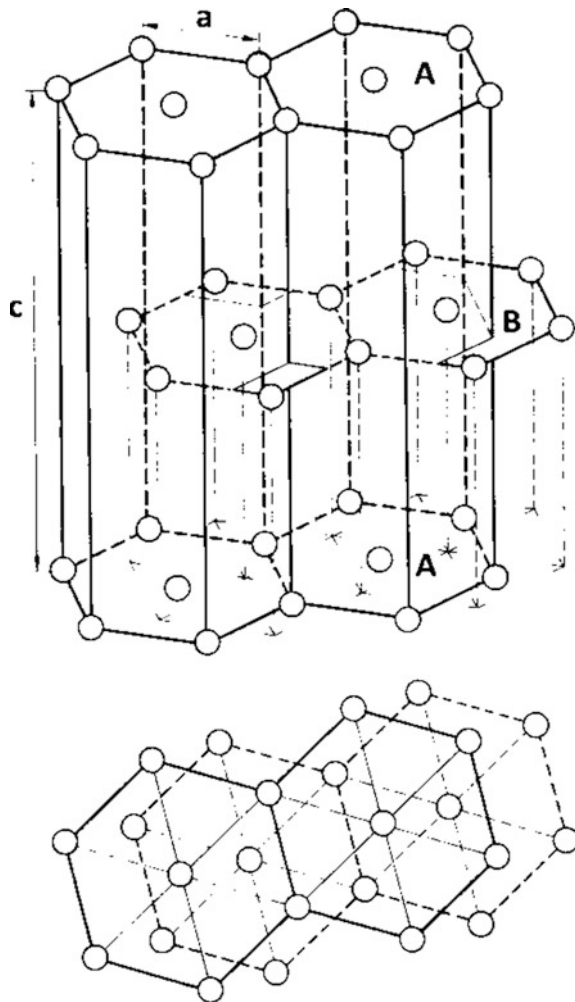
Total graphite:

$$\begin{aligned} C_{\text{total}} &= C_{\text{pro-eutectic}} + C_{\text{eutectic}} + C_{\text{secondary}} + C_{\text{eutectic}} = 0.008 + 0.022 + 0.01 + 0.01 \\ &= 0.05(5\%) \end{aligned} \quad (2.4)$$

Thus, *graphite is the driving constituent in the stable eutectic reaction*: its solidification kinetics results faster than that of the austenite due to the great undercooling above mentioned. Moreover, graphite is a good heterogeneous nucleation agent for the austenite (as well as, austenite is not a good clustering agent for graphite).

Graphite crystallizes in the hexagonal system (Fig. 2.1). Bonding energy of the atoms, which are placed in the same basal plane, is 100–120 kcal/mol, while the bonding energy between atoms of adjacent planes is significantly lower: 1–2 kcal/mol. Cell parameters, at a temperature of $20\text{ }^{\circ}\text{C}$, are: $a = 2.26\text{ }\text{\AA}$ and $c = 6.70\text{ }\text{\AA}$. Therefore, the relation c/a is higher than 1.63, so it results in an ‘overlaid’ structure, no compact, where atoms of the intermediate planes, B, are not tangent to the atoms of the basal planes, A. Crystals cleavage easily (that is the reason for the graphite’s lubricant good properties) and the thermal conductivity in

Fig. 2.1 Graphite crystallographic lattice



the parallel directions to the basal planes is 100 times higher than in the perpendicular direction.

Once the graphite nucleus was formed, it grows faster parallel to the (0001) basal plane than in the perpendicular direction to this plane. Growing is ramified and free, while the austenite does not solidify in the equivalent amount. This austenite will thoroughly cover the graphite flakes due to the great amount of austenite that solidifies, 97.77 wt%, in comparison with graphite.

The graphite flake (or lamellar), so covered, usually grows by edgewise extension, excepting if austenite also surrounded the edges (because of a fast formation of the austenite). Like this, for instance, for a high cooling rate, the eutectic cell will be a small flake of graphite—called graphite type D-, covered by austenite.

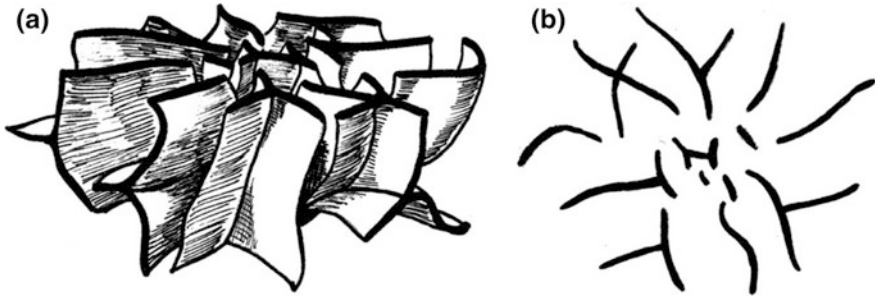


Fig. 2.2 **a** Eutectic graphite growing as warped flakes setting up a rosette. **b** Rosette cross section

The growing of those flakes, habitually at their ends, with the appearance of new branches during their growing, gives a warped surface, like a rosette surrounded by austenite (Fig. 2.2). The eutectic cell that solidified like this from the graphite nucleation is called *eutectic rosette*.

Exercise 2.2. Calculate the density of the graphite.

Question

Graphite is Hexagonal Compact-Packed (HC), with cell parameters: $a = 2.4612 \text{ \AA}$ and $c = 6.7079 \text{ \AA}$. $M_A^C = 12.01 \text{ g/mol}$

Graphite's density can be calculated as follows:

$$\rho_{\text{graphite}} = \frac{\text{no. of atoms cell} \cdot M_A \left(\frac{\text{g}}{\text{mol}} \right)}{\text{Volume Cell (cm}^3\text{)} \cdot N_A \left(\frac{\text{atoms}}{\text{mol}} \right)} \quad (2.5)$$

$$\begin{aligned} \text{Volume Cell (cm}^3\text{)} &= \frac{3\sqrt{3}}{2} \cdot a^2 \cdot c = \frac{3\sqrt{3}}{2} \cdot 2.4612^2 \cdot 6.7079 \text{ \AA}^3 \cdot \frac{1 \text{ cm}^3}{(10^8)^3 \text{ \AA}^3} \\ &= 1.056 \times 10^{-22} \text{ cm}^3 \end{aligned} \quad (2.6)$$

$$\rho_{\text{graphite}} = \frac{12 \text{ atoms} \cdot 12.01 \left(\frac{\text{g}}{\text{mol}} \right)}{1.056 \times 10^{-22} \text{ cm}^3 \cdot 6.022 \times 10^{23} \left(\frac{\text{atoms}}{\text{mol}} \right)} = 2.27 \text{ g/cm}^3 \quad (2.7)$$

Exercise 2.3. Calculate the density of the cementite.**Question**

Cementite is orthorhombic, with cell parameters: $a = 4.5165 \text{ \AA}$, $b = 5.0837 \text{ \AA}$ and $c = 6.7297 \text{ \AA}$. There are 12 iron atoms and 4 carbon atoms per unit cell. $M_A^C = 12.01 \text{ g/mol}$, $M_A^{Fe} = 55.85 \text{ g/mol}$.

Cementite's density can be calculated as follows:

$$\rho_{Fe_3C} = \frac{\text{no. atoms cell} \cdot M_A \left(\frac{\text{g}}{\text{mol}} \right)}{\text{Volume Cell (cm}^3\text{)} \cdot N_A \left(\frac{\text{atoms}}{\text{mol}} \right)} \quad (2.8)$$

$$\begin{aligned} \text{Volume Cell (cm}^3\text{)} &= a \cdot b \cdot c = 4.5165 \cdot 5.0837 \cdot 6.7297 \text{ \AA}^3 \cdot \frac{1 \text{ cm}^3}{(10^8)^3 \text{ \AA}^3} \\ &= 1.545 \times 10^{-22} \text{ cm}^3 \end{aligned} \quad (2.9)$$

$$\begin{aligned} \rho_{Fe_3C} &= \frac{12 \text{ atoms Fe} \cdot 55.85 \left(\frac{\text{g Fe}}{\text{mol Fe}} \right) + 4 \text{ atoms C} \cdot 12.01 \left(\frac{\text{g C}}{\text{mol C}} \right)}{1.545 \times 10^{-22} \text{ cm}^3 \cdot 6.022 \times 10^{23} \left(\frac{\text{atoms}}{\text{mol}} \right)} \\ &= 7.72 \text{ g/cm}^3 \end{aligned} \quad (2.10)$$

This density value is similar to the iron's density (7.97 g/cm^3).

Logically, some graphite nuclei appear inside of a eutectic liquid after a period, and their growth provides as much eutectic cells as graphite nuclei appeared. The number and morphology will depend on the graphite nucleation rate and the graphite and austenite associated growing rate. Definitely, it will depend on the liquid cooling rate.

Few graphite nuclei will be formed in the case of the eutectic liquid slow cooling rates. Therefore, few eutectic cells will appear, and they will be of a great size. Besides, the graphite rosette will reach larger sizes due to the absence of a premature cover of austenite during the thickness growth (that is because a slow cooling rate means a lower austenite solidification rate).

Reciprocally, if the liquid cooling rate was higher, the graphite nucleation rate would increase, and more eutectic cells would appear, so the eutectic cells, when the growth ends, will result smaller. Graphite will be curved and thinner, due to the exclusive growth in the basal plane and it will have been soon embedded, except at the ends, by austenite.

If we add certain heterogeneous clustering agents to the molten metal just before the pouring (for instance, Mg, Mg–Ni, Mg–Fe–Si, etc.), graphite can exceptionally adopt the spheroid shape (*graphite N*) as it can be seen in Figs. 2.3 and 4.5. This

Fig. 2.3 Spheroidal graphite growing way (see Fig. 4.5b)

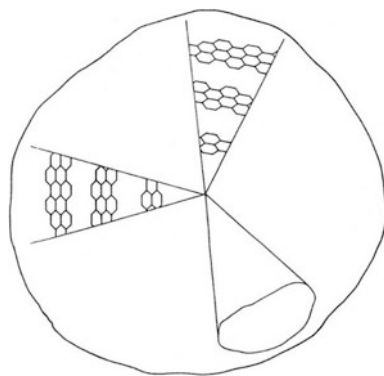
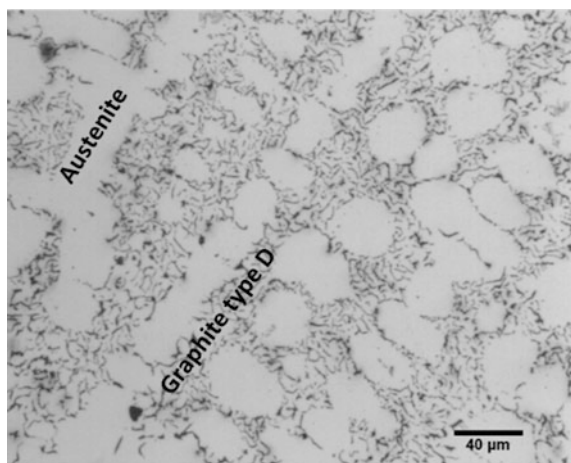


Fig. 2.4 Graphite type D between austenite dendrites. Sample simply polished, without etching



graphite N appears due to the radial growth, in sectors, when the growing rate in the direction of the *C* axis exceeds the growing rate in the direction of planar growth.

The addition of these inoculants to the liquid to achieve the spheroidization of the graphite produces undercooling in the stable eutectic. That is the reason for the higher silicon requirement in the spheroidal graphite grey cast irons than in the lamellar graphite cast irons.

If the undercooling was so fast that would produce a premature cover of the graphite during its growth, the rosette's formation would be avoided. In Fig. 2.4, it is possible to see, polished, without chemical etch, that dispersed austenite dendrites stand out over a eutectic whose graphite appears as punctual (graphite type D).

In the same cast iron, if the liquid undercooling was much faster, the metastable eutectic temperature would be achieved without giving time to the graphite appearance. In this case, cementite would solidify and, it would be obtained as ledeburite instead of the stable eutectic of austenite and graphite.

2.2 Lamellar Graphite Morphologies

Graphite can be directly observed over a polished sample by using a microscope, without chemical etching. When the sample is examined, usually at $100\times$, the *eutectic rosettes* morphology will not be observed if the cells are so big that the observation field cannot include a complete cell. This situation happens almost always in the eutectic grey cast iron. In this case, graphite, whose appearance can be observed in Fig. 2.5, is called *graphite type A*.

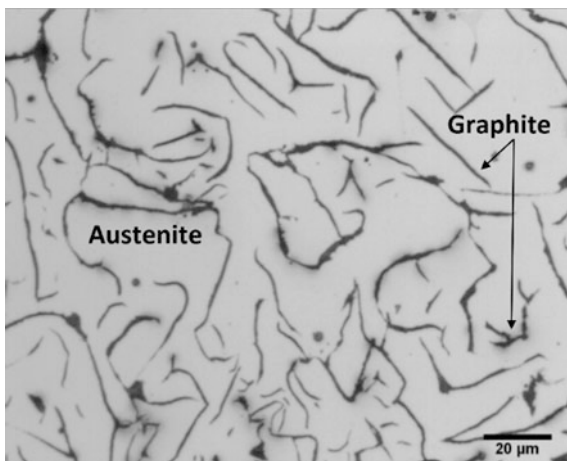
If the solidification was faster, due to a faster cooling rate, the number of eutectic cells will be higher. These cells will be of a lower size, and the observation at $100\times$ will allow to notice the rosettes (see Fig. 2.8b). This graphite is known as *type B*.

When the molten metal has *hypereutectic composition* ($\%C + (\%Si)/3 + (\%P)/3$ higher than 4.25%), solidification begins with the primary graphite formation in the range between the liquidus and the eutectic temperatures. This type of graphite grows freely inside of the liquid, without obstacles in its growth, and gives straight flakes whose thickness exceeds that of the subsequent eutectic graphite. This primary graphite is known as *graphite type C*. Sometimes is also called *kish graphite*, because—in the temperature range between liquidus and the eutectic—there is only this kind of solid that tends, due to its low density, to float in the surface.

Figure 2.6 shows different moments of a hypereutectic cast iron solidification: initially, the appearance of primary flakes until reaching the eutectic temperature, and finally, the solidification. When the solidification ends, there are, at least, two different morphologies of graphite: primary graphite *type C*, and eutectic graphite (which can be type A or type B depending on the cooling rate).

On the other hand, the solidification of the hypoeutectic cast irons begins with the appearance of primary austenite. This austenite continues to freeze in the corresponding temperature range liquidus–eutectic and when the eutectic temperature is reached the graphite rosettes and the eutectic austenite appear. The interaction

Fig. 2.5 Flake graphite type A. Sample simply polished, without etching



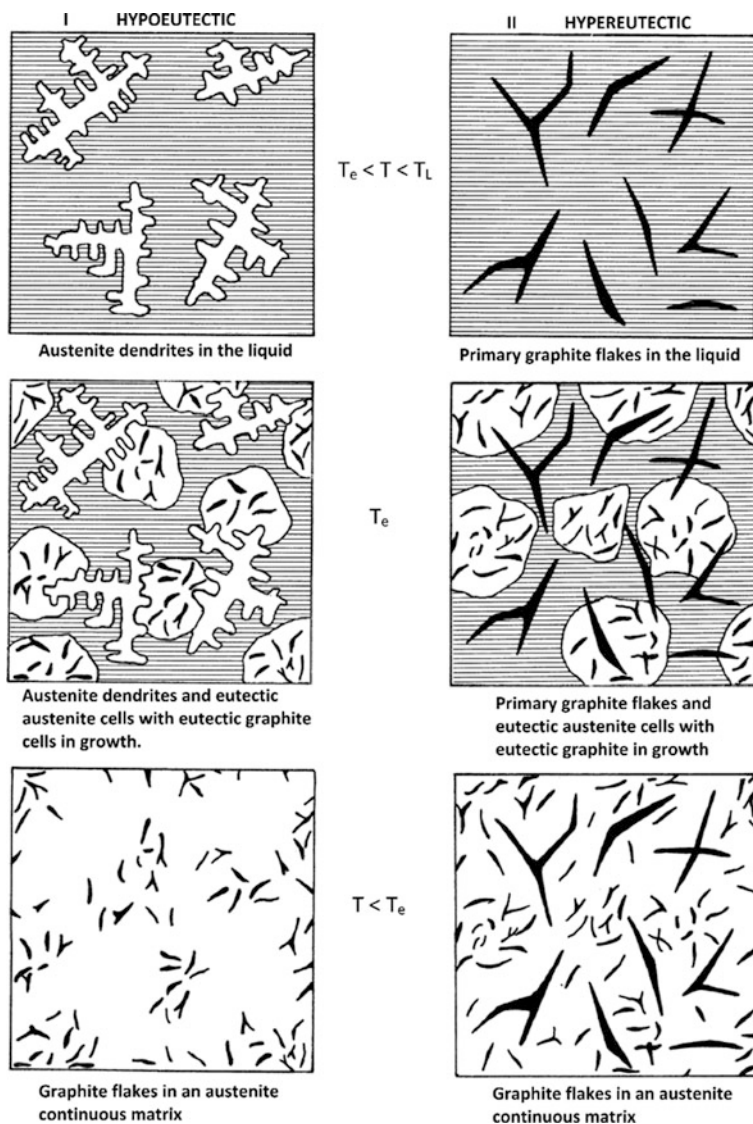
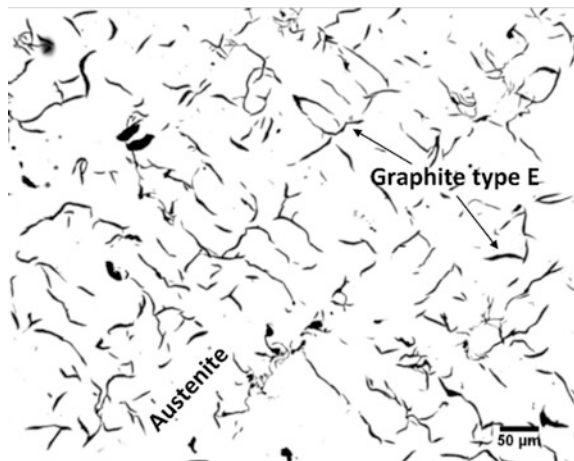


Fig. 2.6 Grey cast iron microstructure evolution during the solidification

between the primary austenite dendrites and the eutectic cells can be summarized in a microstructure of austenite (it is not possible to establish a difference between primary and eutectic austenite) and graphite.

Fig. 2.7 Sample slightly etched with Nital 2. In this way, it is possible to see the flake graphite type E in the interdendritic regions



When the cast iron is *very hypoeutectic*, that is to say, when the cast iron has low carbon content (higher amount of silicon would be required to avoid the appearance of ledeburite), the problem is that before reaching the eutectic temperature almost all the liquid will have solidified as primary austenite dendrites. The small amount of remaining eutectic liquid should be stored in the small interdendritic spaces. And this small amount of remaining eutectic liquid when solidifies without enough space for the properly development as rosettes, produces peculiar graphite morphology: *graphite type E*, which draws the interdendritic spaces as a rib (Figs. 2.7 and 2.8e).

In all grey cast irons, the microstructure constituents at the end of the stable solidification are the same: austenite matrix, and dispersed graphite. This peculiar microstructure well explains, as it can be read in Chap. 5, some of the common properties and applications of these materials: good castability, damping capacity and machinability. Grey cast irons' mechanical behaviour is like that of steels with small cavities filled with graphite (the spheroidal graphite has a lower notch effect if compared with lamellar graphite).

The broken section of these materials presents a colour fashion, given by the graphite, which explains the name of *grey cast iron*. Whereas, the broken section of the cast irons with ledeburite has a colour fashion rather bright, so these cast irons are called *white cast irons*.

Exercise 2.4. Considering the micrographic factors, indicate and explain which of the following grey cast irons would have a higher tensile strength? Which one would have a higher moulding ability?

- (A) 3.25% C–2.2% Si–0.5% Mn–0.1% S–0.2% P
- (B) 2.85% C–2.2% Si–0.7% Mn–0.1% S–0.1% P

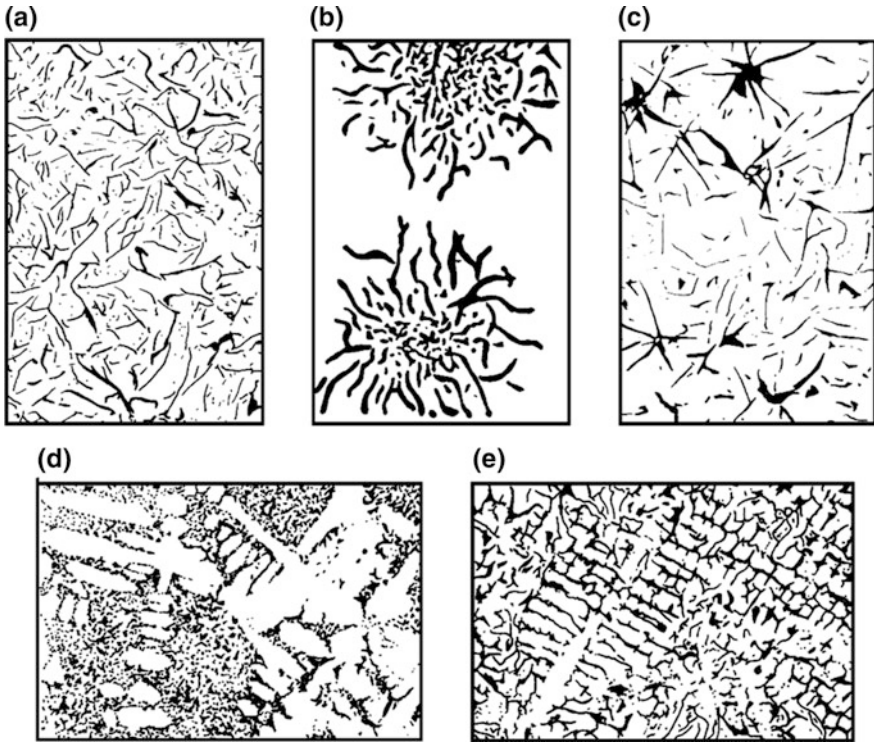


Fig. 2.8 Graphite morphologies observed at 100×

Question

The equivalent carbon is calculated as follows:

$$EC \simeq \%C + \%Si/3 + \%P/3 \quad (2.11)$$

$$A: EC \simeq 3.25 + 2.2/3 + 0.2/3 = 3.25 + 0.73 + 0.07 = 4.05 \quad (2.12)$$

$$B: EC \simeq 2.85 + 2.2/3 + 0.1/3 = 2.85 + 0.73 + 0.03 = 3.61 \quad (2.13)$$

Cast Iron A would be better for moulding of ornamental parts (better castability). It is slightly hypoeutectic and presents more flake graphite eutectic (higher notch effect) than B.

Cast Iron B would have better mechanical properties. It is clearly hypoeutectic and would present graphite types D or E (thin flakes or points).

Exercise 2.5. In lamellar pearlitic grey cast irons, when the higher carbon content, is the tensile strength higher or lower? Explain the answer.

Question

Increasing the carbon content implies a reduction in the resistant section of the cast iron matrix constituent and implies increasing the notch effect of the graphite flakes, and consequently, the tensile strength is reduced.

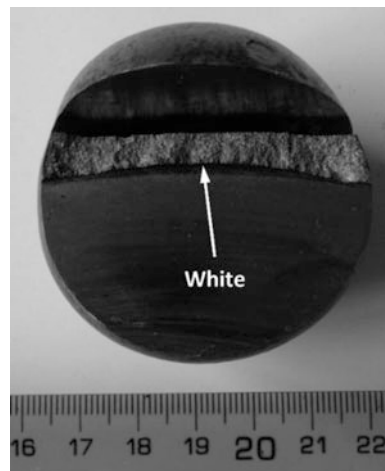
Historically, the first classification of cast irons was based on its fracture. Two types of iron were initially recognized:

- *White iron*: It exhibits a white, crystalline fracture surface because fracture occurs along the iron carbide plates; it is the result of the metastable solidification (Fe_3C eutectic). See Fig. 2.9.
- *Grey iron*: It exhibits a grey fracture surface because fracture occurs along the graphite plates (flakes); it is the result of stable solidification (graphite eutectic) See Fig. 2.10.

In Fig. 2.8, it is possible to see the international ranking for the different types of graphite, and the graphite's ranking according to its length appears in Table 2.1.

Apart from the flaky graphite shown in Fig. 2.8, and the spheroidal graphite, there are other morphologies of graphite. We remark the *compacted graphite*—intermediate between the flaky and the spheroidal graphite. Compacted graphite appears in nodules interconnected within the eutectic cells, and in this way, gives intermediate properties between those of the flaky graphite and the spheroidal graphite.

Fig. 2.9 Fracture surface of a white cast iron



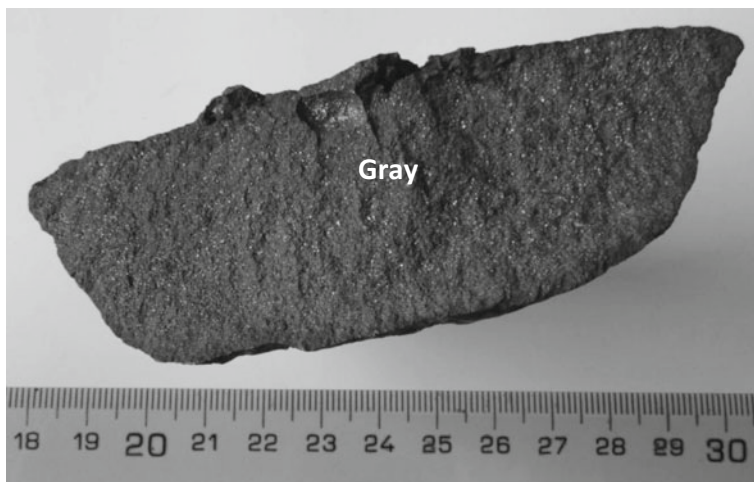


Fig. 2.10 Fracture surface of a grey cast iron

Table 2.1 Graphite sizes

Reference number	Particles size at 100× (mm)	Real size (mm)
1	>100	1
2	50–100	0.5–1
3	25–50	0.25–0.5
4	12–25	0.12–0.25
5	6–12	0.06–0.12
6	3–6	0.03–0.06
7	1.5–3	0.015–0.03
8	<1.5	<0.015

Exercise 2.6. What of the following chemical compositions would you choose for manufacturing in grey cast irons: high strength thick parts, ornamental parts, or equipment parts of large thickness?

- (A) 3.25% C–1.25% Si–0.5% Mn–0.25% P
- (B) 3.50% C–2.5% Si–0.5% Mn–1% P
- (C) 2.75% C–2.2% Si–0.5% Mn–0.1% P

Question

The equivalent carbon of each cast iron is

$$\text{A: EC} = 3.25 + 1.25/3 + 0.25/3 = 3.75 \quad (2.14)$$

$$\text{B: EC} = 3.5 + 2.5/3 + 1/3 = 4.66 \quad (2.15)$$

$$\text{C: EC} = 2.75 + 2.2/3 + 0.1/3 = 3.81 \quad (2.16)$$

↑ EC implies a low solidification interval and abundance of graphite. Castability is good.

↑ EC implies a low resistant section and notch effect because of the graphite. Consequently, the tensile strength is low.

Ornamental parts: Require low solidification intervals and excellent castability. Mechanical strength is a secondary property. The presence of phosphorus improves the castability and makes possible the appearance of steadite, which improves the wear resistance (toughness is reduced but it is not important in ornamental parts). The suitable chemical composition belongs to *Cast Iron B*.

High strength thick parts: Require high toughness. The small massivity factor (parts of small thickness) increases the tendency to chill of the cast iron (this question is solved with the presence of silicon). A low carbon (less graphite) improves the tensile strength. The suitable chemical composition belongs to *Cast Iron C*.

Equipment parts of large thickness: The importance of the equivalent carbon is low, because in high thickness parts the chilling risk is lower than in the other cases (the silicon content can be lower). A low equivalent carbon improves the tensile strength. The suitable chemical composition belongs to *Cast Iron A*.

Compromise Between Stable and Metastable Solidifications

3

Abstract

The solidification according to the stable or metastable diagrams will depend on both the composition, size of the parts to be cast and the superheating. In this way, we have seen in Chap. 1, the elements that favour one or other solidification. In this chapter, we will see the effect of the parts size and the superheating, and we will see that it is possible to obtain a cast iron with simultaneously both white and grey eutectics, known as mottled cast iron. The ternary eutectic composed of Fe_3P , Fe_3C and Fe (steadite) is also described in this chapter.

3.1 Composition and Massivity Factor (Section Sensitivity or Volume/Area Ratio)

The same cast iron, depending on the cooling conditions, can solidify as grey cast iron—with the structure of austenite and graphite—or as white cast iron following the metastable solidification—with ledeburite as matrix component. The stable solidification always means slow cooling rates of the liquid.

The cooling rate depends on multiples and varied factors, such as the casting temperature, latent heat of solidification, mould thermal diffusivity, method of mould's refrigeration, etc.

For the same cooling conditions, for instance chill moulding and air cooling, the higher the part size, the slower the liquid cooling rate will be—and therefore the stable solidification will be more probable. Or, to explain this assessment otherwise, then the higher the *massivity factor* of the part (V/A , where V is the part volume and A is the superficial area), the slower the cooling rate will be.

Therefore, and considering the questions mentioned in Sect. 1.5, if the chill of the grey cast irons in parts of small thickness (small value of V/A) is required to be avoided, a higher silicon content is necessary.

Also, due to the reasons mentioned in Sect. 1.5, and for parts with the same relation V/A , silicon content in the cast iron should be high when the carbon content is lower.

In the same way, it can be proved that in grey cast irons with high carbon content, silicon percentages can range in larger limits.

To control the influence of the section local changes in the tendency to the chill of a certain cast iron, the use of *step bars*, as it is shown in Fig. 3.1, is common.

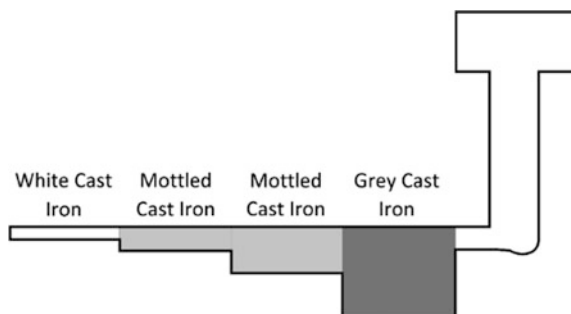
With the idea of illustrating the size influence, it is indicated, as an example in Fig. 3.1, an estimation of the structures that is possible to obtain from the same liquid cast iron. Logically, for a cast iron with the same carbon content and high silicon contents, it is possible to achieve a grey cast iron, even in the sections of small thickness in the *step bars*.

We talk about *mottled* cast iron when we can observe both graphite and ledeburite (as it is possible to see in Fig. 3.2) in the micrograph of a cast iron. This name is due to the reflections that are like the scales of a fish. These reflections are visible in the section of a metallographic specimen (polished and etched with Nital), when it is observed at first sight.

For the manufacture of the wheels of mine wagons (Fig. 3.3), cast irons of medium carbon (2.5–4% C) and low silicon (0.5–1% Si) contents are used. This cast iron is moulded in an energetically cooled metallic chill and is inappropriately called *as hardened*. In this way, it is possible to achieve a surface of white cast iron (with wear resistance to the rolling), the nucleus of grey cast iron (tougher than the white cast iron), and mottled cast iron in the intermediate region.

To illustrate the tendency of a cast iron (whose composition is well known) to chill, it is quite common to use as an alternative or complement to the step bar, the *wedge test*. With the idea of performing the *wedge test*, it is necessary to melt in sand a sample with the wedge shape (angle of 10° in the vertex). Then, an intermediate specimen is removed from the sample (in the lengthwise section). Over this

Fig. 3.1 Step bar used in the determination of the sensitivity of a cast iron according to the thickness



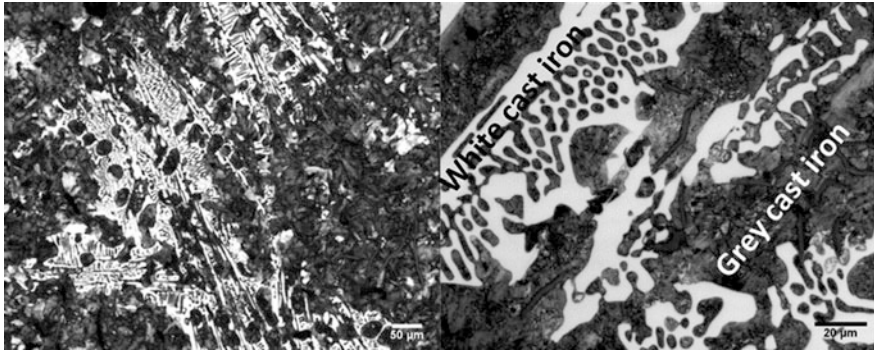


Fig. 3.2 Mottled cast iron (ledeburite in graphite)



Fig. 3.3 Mine wagon wheels

intermediate specimen, the Rockwell C hardness is calculated (as it is possible to see in the upper section in the right side of Fig. 3.4). The sudden drop in the hardness appears, logically, in the section which is in the left edge, when there is a change between the white cast iron and the grey cast iron.

Exercise 3.1. In a mottled cast iron with 3.25% C, 50% of the eutectic liquid has solidified according to the stable diagram (Fe–Graphite), and the remaining 50% according to the metastable diagram (Fe–Fe₃C). Calculate the proportions of graphite and ledeburite in the solidification structure. With the purpose of simplifying the problem, it is supposed that both eutectics coincide in temperature and chemical composition.

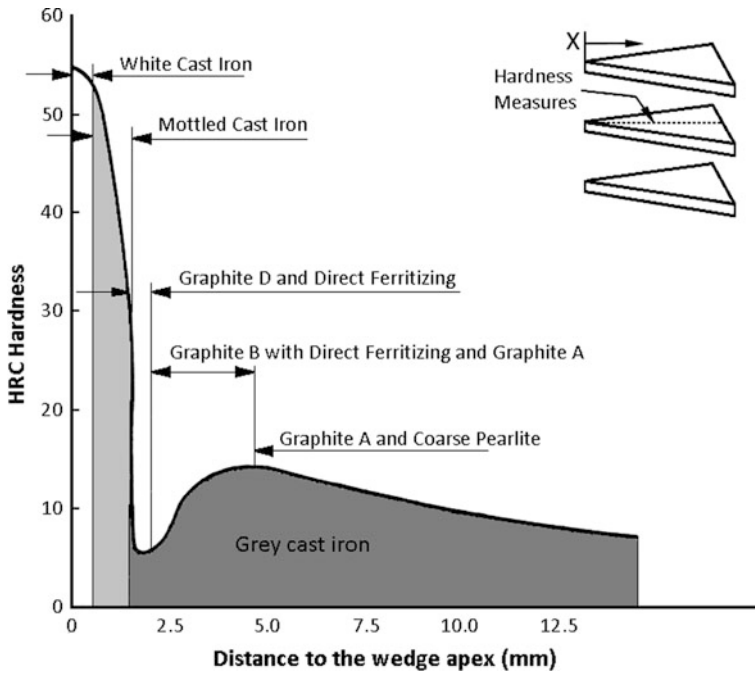


Fig. 3.4 Structures and hardness at different points of the section of a cast iron ASM wedge test part (ASM 1978)

Question

In 100 kg of white cast iron

$$\gamma_{\text{pro-eutectic}} = \frac{4.3 - 3.25}{4.3 - 2.11} = 0.48 \text{ (48\%)} \quad (3.1)$$

$$\gamma_{\text{eutectic}} = 0.52 \cdot \frac{6.67 - 4.3}{6.67 - 2.11} = 0.27 \text{ (27\%)} \quad (3.2)$$

$$\text{Fe}_3\text{C}_{\text{eutectic}} = 0.52 \cdot \frac{4.3 - 2.11}{6.67 - 2.11} = 0.25 \text{ (25\%)} \quad (3.3)$$

The amount of ledeburite in the case of that 50% would have solidified as white cast iron is

$$\text{Ledeburite} = 0.5 \cdot (\gamma_{\text{eutectic}} + \text{Fe}_3\text{C}_{\text{eutectic}}) = 0.26 \text{ (26\%)} \quad (3.4)$$

In 100 kg of grey cast iron

$$\gamma_{\text{pro-eutectic}} = 0.5 \cdot \frac{4.3 - 3.25}{4.3 - 2.11} = 0.48 \text{ (48\%)} \quad (3.5)$$

$$\gamma_{\text{eutectic}} = 0.52 \cdot \frac{100 - 4.3}{100 - 2.11} = 0.508 \text{ (50.8\%)} \quad (3.6)$$

$$C_{\text{eutectic}}^{\text{Graphite}} = 0.52 \cdot \frac{4.3 - 2.11}{100 - 2.11} = 0.012 \text{ (1.2\%)} \quad (3.7)$$

The amount of graphite in the case of that 50% would have solidified as grey cast iron is

$$\text{Graphite} = 0.5 \cdot C_{\text{eutectic}}^{\text{Graphite}} = 0.006 \text{ (0.6\%)} \quad (3.8)$$

Exercise 3.2. 4.5 kg of carbon–graphite are dissolved in 95.5 kg of molten iron. During the cooling, the carbon that is in excess separates from the eutectic as primary graphite, and two-thirds of the remaining carbon also separates as graphite (mottled cast iron).

- (A) Calculate the percentages of austenite, cementite and graphite at the end of the solidification. It should be supposed that the stable and metastable eutectics have carbon contents that are equivalents as well as for the eutectic austenite.

Question

Primary graphite:

$$C_{\text{graphite}}^{\text{Primary}} = \frac{(4.5 - 4.3)}{(100 - 4.3)} = 0.0021 \text{ (0.21 kg)} \quad (3.9)$$

So, there are 99.79 kg of eutectic that solidify following the stable diagram (2/3) and to the metastable diagram (1/3).

In the stable eutectic, the following relationship is verified:

$$\frac{\gamma}{C_{\text{Graphite}}} = \frac{100 - 4.3}{4.3 - 2.1} = \frac{95.7}{2.2} \quad (3.10)$$

And, the C_{Graphite} in the stable eutectic is

$$C_{\text{Graphite}} = 99.79 \cdot \frac{2.2}{100 - 2.1} = 2.24 \text{ kg} \quad (3.11)$$

As two-thirds of the carbon solidifies as grey cast iron:

$$C_{\text{Graphite}}^{\text{Eutectic}} = \frac{2}{3} \cdot 2.24 = 1.49 \text{ kg} \quad (3.12)$$

And, the amount of austenite in the eutectic is

$$\gamma_{\text{eutectic}}^{\text{stable}} = \frac{95.7}{2.2} \cdot 1.49 = 65 \text{ kg} \quad (3.13)$$

The carbon amount associated with the $\gamma_{\text{eutectic}}^{\text{stable}}$ is

$$C_{\text{stable}}^{\gamma} = 64.8 \cdot 0.021 = 1.36 \text{ kg} \quad (3.14)$$

Carbon and iron that solidify according to the metastable diagram are

$$\begin{aligned} C_{\text{metastable}} &= C_{\text{total}} - C_{\text{Graphite}}^{\text{Primary}} - C_{\text{Graphite}}^{\text{Eutectic}} - C_{\text{stable}}^{\gamma} = 4.5 - 0.21 - 1.49 - 1.36 \\ &= 1.44 \text{ kg} \end{aligned} \quad (3.15)$$

$$\begin{aligned} \text{Fe}_{\text{metastable}} &= \text{Fe}_{\text{total}} - \text{Fe}_{\text{stable}} = \text{Fe}_{\text{total}} - (\gamma_{\text{eutectic}}^{\text{stable}} - C_{\text{stable}}^{\gamma}) = 95.5 - (64.8 - 1.36) \\ &= 31.9 \text{ kg} \end{aligned} \quad (3.16)$$

In the metastable eutectic, the following relationship is verified:

$$\frac{\gamma}{\text{Fe}_3\text{C}} = \frac{6.67 - 4.3}{4.3 - 2.1} = \frac{2.37}{2.2} = \frac{52}{48} \quad (3.17)$$

In the metastable eutectic, the proportions of austenite and cementite are 52 and 48%, respectively.

The metastable liquid available is

$$\text{Liquid}^{\text{metastable}} = C_{\text{metastable}} + \text{Fe}_{\text{metastable}} = 33.5 \text{ kg} \quad (3.18)$$

In this way, the amount of Fe_3C in the metastable eutectic is

$$\text{Fe}_3\text{C}^{\text{eutectic}} = 33.5 \cdot 0.48 = 16.08 \text{ kg} \quad (3.19)$$

And, the amount of austenite in the eutectic is

$$\gamma_{\text{eutectic}}^{\text{metastable}} = 33.5 \cdot 0.52 = 17.42 \text{ kg} \quad (3.20)$$

Constituents of the cast iron:

$$C_{\text{Graphite}} = C_{\text{Graphite}}^{\text{Primary}} + C_{\text{Graphite}}^{\text{Eutectic}} = 1.7 \text{ kg} \quad (3.21)$$

$$\text{Fe}_3\text{C}^{\text{eutectic}} = 16.08 \text{ kg} \quad (3.22)$$

$$\gamma_{\text{total}} = \gamma_{\text{eutectic}}^{\text{metastable}} + \gamma_{\text{eutectic}}^{\text{stable}} = 17.42 + 64.8 = 82.22 \text{ kg} \quad (3.23)$$

(B) Proportions of graphite, cementite and pearlite below the eutectoid temperature (suppose metastable cooling).

Question

$$\gamma(2.1) \leftrightarrow \gamma(0.77) + \text{Fe}_3\text{C}$$

$$\gamma_{0.77} = \frac{6.67 - 2.1}{6.67 - 0.77} = \frac{4.56}{5.9} = 0.77 \quad (3.24)$$

$$\text{Pearlite}^{\text{Eutectoid}} = 82.22 \cdot 0.77 \text{ kg} = 63.31 \text{ kg} \quad (3.25)$$

$$\text{Fe}_3\text{C}^{\text{Pro-Eutectoid}} = \gamma_{\text{total}} - \text{Pearlite}^{\text{Eutectoid}} = 18.91 \text{ kg} \quad (3.26)$$

$$C_{\text{Graphite}}^{\text{Total}} = C_{\text{Graphite}}^{\text{Primary}} + C_{\text{Graphite}}^{\text{Eutectic}} = 1.7 \text{ kg} \quad (3.27)$$

$$\text{Fe}_3\text{C}^{\text{Eutectic}} = 16.08 \text{ kg} \quad (3.28)$$

Summarizing,

$$C_{\text{Graphite}}^{\text{Total}} = C_{\text{Graphite}}^{\text{Primary}} + C_{\text{Graphite}}^{\text{Eutectic}} = 1.7 \text{ kg} \quad (3.29)$$

$$\text{Fe}_3\text{C}^{\text{Total}} = \text{Fe}_3\text{C}^{\text{Eutectic}} + \text{Fe}_3\text{C}^{\text{Pro-Eutectoid}} = 35 \text{ kg} \quad (3.30)$$

$$\text{Pearlite}^{\text{Eutectoid}} = 63.3 \text{ kg} \quad (3.31)$$

(C) Fraction of area occupied by each constituent.

Question

Data: $\rho_{\text{Graphite}} = 2.25 \text{ g/cm}^3$; $\rho_{\text{Pearlite}} = 7.86 \text{ g/cm}^3$; $\rho_{\text{Fe}_3\text{C}} = 7.66 \text{ g/cm}^3$

$$V_{\text{Pearlite}} = \frac{\frac{P_{\text{Pearlite}}}{\rho_{\text{Pearlite}}}}{\frac{P_{\text{Pearlite}}}{\rho_{\text{Pearlite}}} + \frac{P_{\text{Graphite}}}{\rho_{\text{Graphite}}} + \frac{P_{\text{Fe}_3\text{C}}}{\rho_{\text{Fe}_3\text{C}}}} = \frac{\frac{63.3}{7.86}}{\frac{63.3}{7.86} + \frac{1.7}{2.25} + \frac{35}{7.66}} = \frac{8.05}{13.38} = 0.602 (60.2\%) \quad (3.32)$$

$$V_{\text{Graphite}} = \frac{\frac{P_{\text{Graphite}}}{\rho_{\text{Graphite}}}}{\frac{P_{\text{Pearlite}}}{\rho_{\text{Pearlite}}} + \frac{P_{\text{Graphite}}}{\rho_{\text{Graphite}}} + \frac{P_{\text{Fe}_3\text{C}}}{\rho_{\text{Fe}_3\text{C}}}} = \frac{\frac{1.7}{2.25}}{\frac{63.3}{7.86} + \frac{1.7}{2.25} + \frac{35}{7.66}} = \frac{0.76}{13.38} = 0.057 (5.7\%) \quad (3.33)$$

$$V_{\text{Fe}_3\text{C}} = \frac{\frac{P_{\text{Fe}_3\text{C}}}{\rho_{\text{Fe}_3\text{C}}}}{\frac{P_{\text{Pearlite}}}{\rho_{\text{Pearlite}}} + \frac{P_{\text{Graphite}}}{\rho_{\text{Graphite}}} + \frac{P_{\text{Fe}_3\text{C}}}{\rho_{\text{Fe}_3\text{C}}}} = \frac{\frac{35}{7.66}}{\frac{63.3}{7.86} + \frac{1.7}{2.25} + \frac{35}{7.66}} = \frac{4.57}{13.38} = 0.341 (34.1\%) \quad (3.34)$$

- (D) A micrograph of a mottled cast iron has a 4% of the area occupied with graphite, a 35% occupied with cementite and a 61% occupied with ferrite. Calculate the proportions (in weight) of austenite and cementite at the end of the solidification. Data: the proportions (in weight) of ferrite and cementite in the pearlite are 88 and 12%, respectively.

Question

$$\begin{aligned} P_{\text{Ferrite}} &= \frac{V_{\text{Ferrite}} \cdot \rho_{\text{Ferrite}}}{V_{\text{Ferrite}} \cdot \rho_{\text{Ferrite}} + V_{\text{Fe}_3\text{C}} \cdot \rho_{\text{Fe}_3\text{C}} + V_{\text{Graphite}} \cdot \rho_{\text{Graphite}}} \\ &= \frac{60.2 \cdot 7.86}{60.2 \cdot 7.86 + 34.1 \cdot 7.66 + 5.7 \cdot 2.25} \\ &= \frac{473.17}{747.21} = 0.633 (63.3\%) \end{aligned} \quad (3.35)$$

$$\begin{aligned} P_{\text{Fe}_3\text{C}} &= \frac{V_{\text{Fe}_3\text{C}} \cdot \rho_{\text{Fe}_3\text{C}}}{V_{\text{Ferrite}} \cdot \rho_{\text{Ferrite}} + V_{\text{Fe}_3\text{C}} \cdot \rho_{\text{Fe}_3\text{C}} + V_{\text{Graphite}} \cdot \rho_{\text{Graphite}}} \\ &= \frac{34.1 \cdot 7.66}{60.2 \cdot 7.86 + 34.1 \cdot 7.66 + 5.7 \cdot 2.25} \\ &= \frac{261.21}{747.21} = 0.35 (35\%) \end{aligned} \quad (3.36)$$

$$\begin{aligned}
 P_{\text{Graphite}} &= \frac{V_{\text{Graphite}} \cdot \rho_{\text{Graphite}}}{V_{\text{Ferrite}} \cdot \rho_{\text{Ferrite}} + V_{\text{Fe}_3\text{C}} \cdot \rho_{\text{Fe}_3\text{C}} + V_{\text{Graphite}} \cdot \rho_{\text{Graphite}}} \\
 &= \frac{5.7 \cdot 2.25}{60.2 \cdot 7.86 + 34.1 \cdot 7.66 + 5.7 \cdot 2.25} \\
 &= \frac{12.83}{747.21} = 0.017(1.7\%)
 \end{aligned} \tag{3.37}$$

Before, the eutectoid transformation:

$$\gamma_{0.77} = \frac{63.3 \cdot 100}{88} = 71.93 \tag{3.38}$$

$$(\text{Fe}_3\text{C})_{\text{eutectoid}} = \frac{63.3 \cdot 12}{88} = 8.63 \tag{3.39}$$

$$(\text{Fe}_3\text{C})_{\text{pro-eutectoid}} = 35 - 8.63 = 26.37 \tag{3.40}$$

$$\gamma_{2.11} \rightarrow \gamma_{0.77} + (\text{Fe}_3\text{C})_{\text{pro-eutectoid}}$$

If we call x to the austenite fraction at the eutectic temperature

$$x \cdot \frac{(6.67 - 2.11)}{(6.67 - 0.77)} = 71.93 \rightarrow x = 71.93 \cdot \frac{(6.67 - 0.77)}{(6.67 - 2.11)} = 93.07 \tag{3.41}$$

$$93.07 = 71.93 + (\text{Fe}_3\text{C})_{\text{pro-eutectoid}} \rightarrow (\text{Fe}_3\text{C})_{\text{pro-eutectoid}} = 21.1 \tag{3.42}$$

Then, the cast iron has

$$93.07\gamma_{2.11} + (35 - 8.63 - 21.1)(\text{Fe}_3\text{C})_{\text{eutectic}} \tag{3.43}$$

And, the carbon content in the mottled cast iron is

$$\frac{6.67 - C}{6.67 - 2.11} = \frac{0.9307}{1 - 0.017} \tag{3.44}$$

$$C = 2.35\% \tag{3.45}$$

3.2 Superheating

To achieve a better fluidity of the liquid, the molten is poured into the mould at a temperature higher than the liquidus. That filling temperature is known as *pouring temperature* and, in cast irons, it is, habitually of 1410–1450 °C.

Table 3.1 Superheating above the liquidus temperature for 2% Si and different carbon contents. Casting temperature: 1455 °C. Data from ASM (1978)

% Carbon	Liquidus temperature (°C)	Superheating above the liquidus temperature (°C)
2.52	1295	160
3.04	1245	210
3.60	1175	280

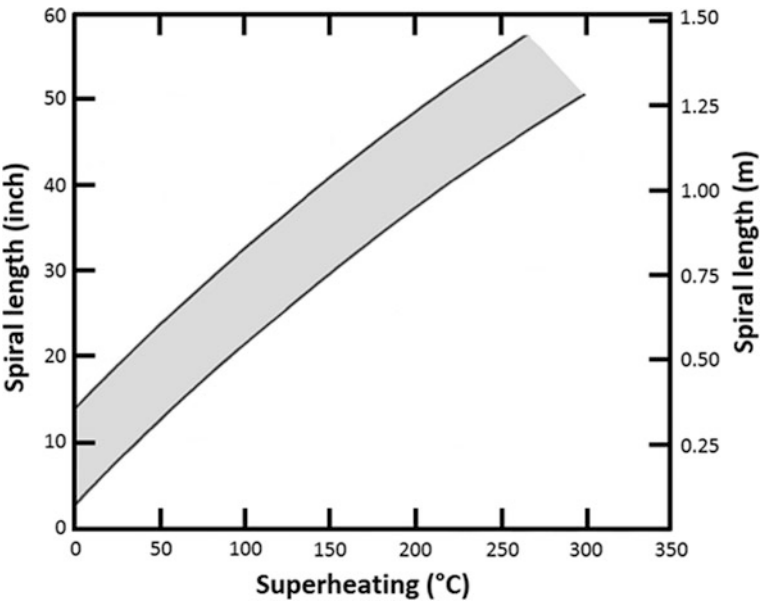


Fig. 3.5 Relation between fluidity and **superheating** in cast irons of 2.13–3.60% C and 2–2.10% Si. Adapted from ASM (1978)

As can be deduced from the Fe–C equilibrium diagram, the liquidus temperature decreases with the carbon content in the cast iron (Table 3.1), and that is why, for the same pouring temperature, the fluidity is higher in cast irons with high carbon content. The difference between the pouring temperature and the liquidus temperature is known as *superheating*. In Fig. 3.5, it is marked that, for the same molten, the castability grows with the superheating.

Even though the superheating improves the fluidity, it is convenient to advice about some negative effects of the superheating. On the one hand, the higher the superheating the higher the liquid contraction until the solidification begins, and therefore, the higher the shrinkage hole. On the other hand—and in relation with the compromise stable/metastable—it is verified that the superheating is favourable to the cast iron chilling, especially if the carbon content is low.

If a *superheated* liquid is cast inside of a step bar, as it is possible to see in Fig. 3.1, the cast iron can be *white* even in the zones of highest thickness; and, whether for big thickness the cast iron comes *grey*, it will be possible to see, preferentially, graphite type D. The types of graphite usually go from A (less superheating) to D (highest superheating).

In Fig. 3.6, the correlation that exists between the *superheating* and the tendency to chill is schematically shown for the same hypoeutectic casting.

The graphite nucleation rate, in the white cast iron, considerably decreases with the superheating.

The real causes of this behaviour are not clear at this moment. Possibly, this behaviour is explained as the superheating dissolves the atomic clusters of carbon that were achieved in the liquid and it delays and makes difficult the graphite nucleation in the solidification. Anyway, the chilling effect due to the superheating

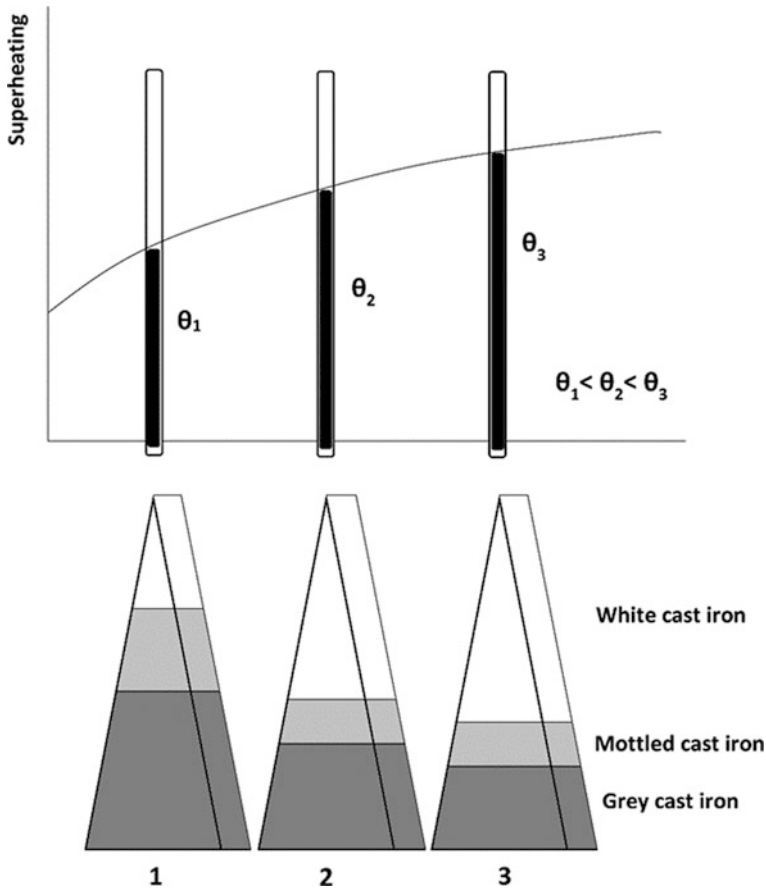


Fig. 3.6 Superheating influences the tendency to chill, for the equal wedges, of the same hypoeutectic cast iron

is like an *effective* increase of the cooling rate. This means that for the same external cooling conditions, chilling really takes place if the liquid temperature, at which liquid is poured into the mould, is increased.

In cast irons with low-carbon content, the addition of *inoculant* agents is usually convenient. These inoculant agents play the role of heterogeneous clustering agents and make up for the lower aptitude of the superheated liquid for the graphite germs clustering.

In the case of the cast irons with high carbon content, and consequently, those who are prone to solidify following the stable diagram, the unfavourable effects of the superheating should be considered.

3.3 A Eutectic of Iron Phosphide (Fe_3P), Steadite

When the phosphorus content in a cast iron (potentially grey cast iron) is higher than 0.07%, this element, whose partition coefficient Fe-P is very small (0.06), concentrates in the residual liquid during the solidification progress. Once the 950 °C is reached (below the stable eutectic of graphite and austenite), then the liquid solidification ends because a ternary eutectic of Fe_3P (42%), Fe_3C (31%) and Fe (27%) appears. This ternary eutectic is known as *steadite*. Figure 3.7 shows the steadite.

Figure 3.7 (right) shows at high magnification the steadite matrix appearance, whose morphology is usually called *fish bone*. Observed at less magnification, steadite occupies only a small fraction of the grey cast iron microstructure as shown in Fig. 3.7 (left).

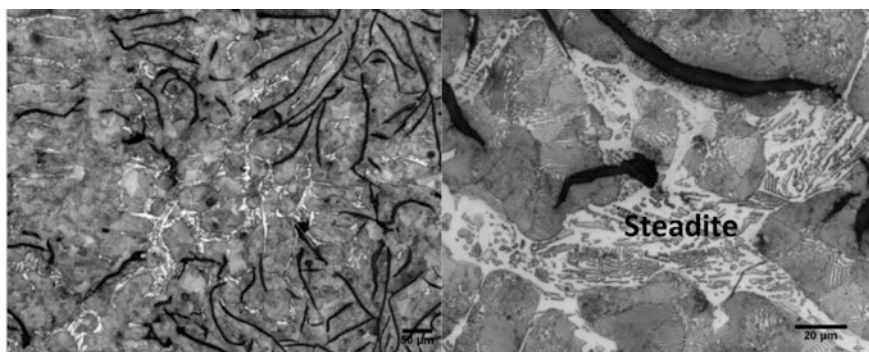


Fig. 3.7 Steadite. It is possible to see the wrapping morphology of the steadite, as a matrix component, drawing the boundaries of the pearlite

With high phosphorus contents (never higher than 1.8%), important contents of the low melting point ternary eutectic appear, and that is advisable because the liquid castability improves significantly. Steadite increases the wear resistance of the grey cast iron, but, on the contrary, the toughness gets worse.

Stable and Metastable Cooling Compromise in Solid State

4

Abstract

Transformations that can take place in the cooling of a molten cast iron, with the possibility of obtaining either a white or a grey cast iron, but also a mottled iron depending on several factors were studied in previous chapters. This chapter also studies the transformations that take place during the cooling in solid state, and in this way, the different matrix structures that can be obtained, either of equilibrium or non-equilibrium. The treatment known as ferritizing annealing is also studied as the transformation of cementite into graphite that takes place during this treatment can be used in the obtaining of nodular cast iron. Graphitizing risks in cast irons working at temperatures of around 450 °C are also pointed out as problems of scaling and growth can take place.

4.1 Introduction

In previous pages, it was mentioned that a certain cast iron can solidify following the stable equilibrium diagram—with the formation of graphite + austenite—or the metastable equilibrium diagram with the transformation of the eutectic liquid into ledeburite.

When at the end of the solidification of a cast iron we have austenite and graphite instead of ledeburite, the solidification followed the stable diagram and we have a grey cast iron. However, it is necessary to advise that the austenite can experience, during the subsequent cooling period between the eutectic and the eutectoid temperatures, the stable (Fig. 1.2) or the metastable transformations (Fig. 1.1).

The Fe–C stable diagram—dotted lines—and the Fe–C metastable diagram—full lines—are shown overlapped in Fig. 4.1, for 0% of silicon. The eutectoid stable transformation (austenite of 0.68% C $\rightarrow$ ferrite + graphite) happens at 738 °C,

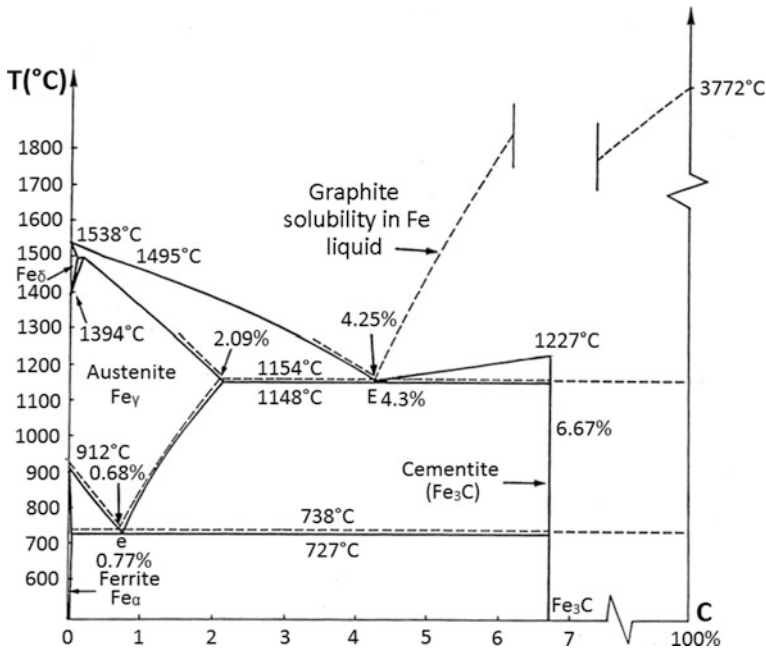


Fig. 4.1 Fe-C metastable diagram (continuous line) and Fe-C stable diagram (discontinuous line)

while the eutectoid metastable transformation (austenite of 0.77% C $\rightarrow$ ferrite + cementite) takes place at a lower temperature: 727 °C.

When silicon and phosphorus are present, the stable eutectoid has a carbon content which is equal to $0.68\% - (\% \text{Si})/3 - (\% \text{P})/3$. The carbon percentage in the metastable eutectoid is equal to $0.77\% - (\% \text{Si})/3 - (\% \text{P})/3$. On the other hand, both eutectoid transformations happen at a temperature that is not constant (transformation takes place in a temperature range). That situation can be explained if we apply the Gibbs's phase rule to systems of higher degree than the binary: the presence of three phases in equilibrium—*austenite + ferrite + graphite*, or *austenite + ferrite + cementite*—does not mean invariant transformation.

The presence of a third component—silicon—would make the use of the ternary Fe-C-Si stable and metastable diagrams necessary for following how the phases evolve during cooling. For instance, having sections of the ternary diagram Fe-C-Si for different silicon percentages as it is possible to see, for instance, for 2% of silicon, in Figs. 4.2 (stable diagram) and 4.3 (metastable diagram) is essential.

On the other hand, it is necessary to consider that cast irons usually contain other alloying elements, and it requires the use of phase diagrams of a higher order than the ternary. For that reason, it seems better studying the stable-metastable compromise with some simplifications.

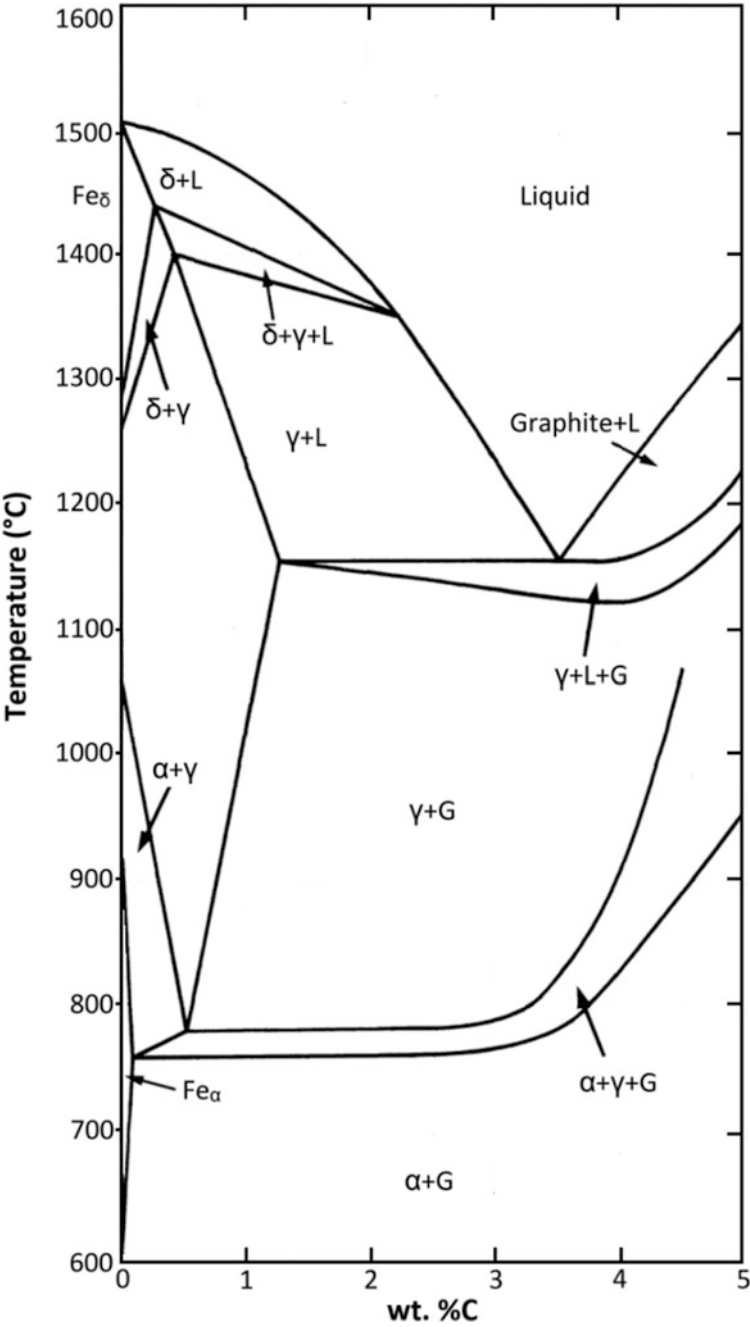


Fig. 4.2 Section of the Fe–C–Si stable diagram for 2% Si

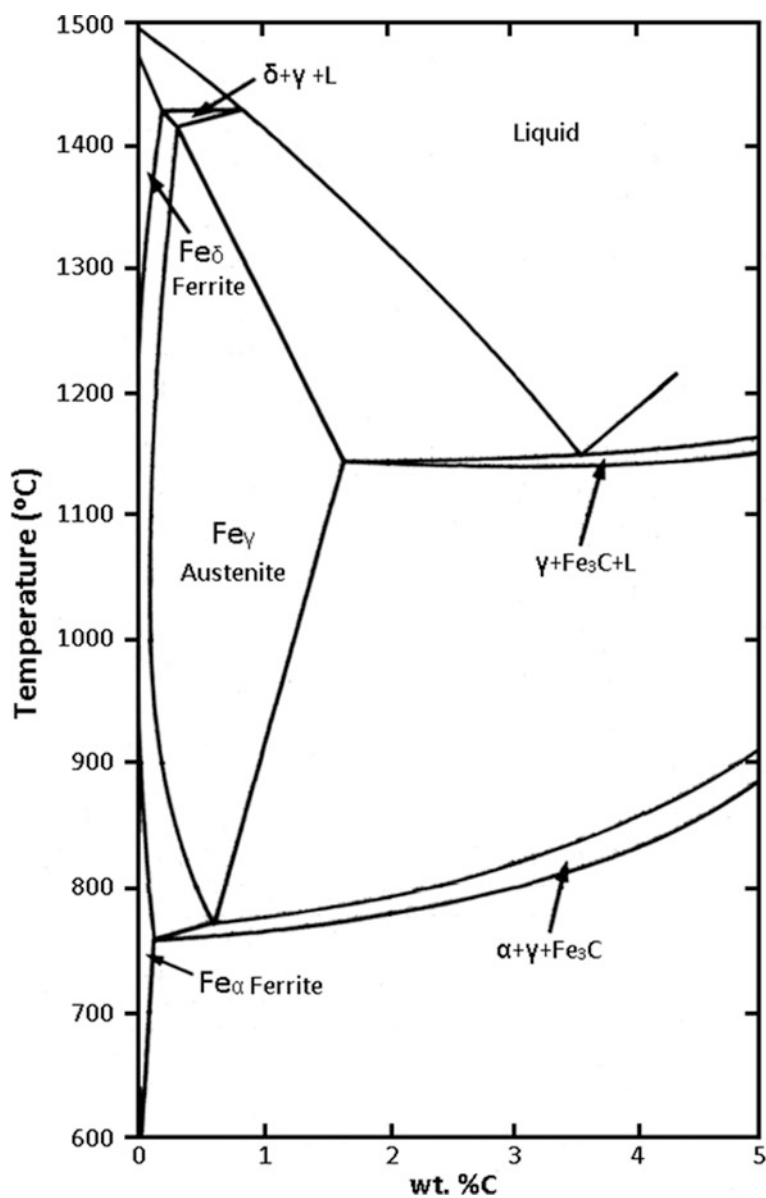


Fig. 4.3 Section of the Fe-C-Si metastable diagram for 2% Si

4.2 Cooling of Grey Cast Irons in Solid State: Matrix Structures

The compromise between stable and metastable transformations in the solid state can be understood through the observation of Fig. 4.4. In Fig. 4.4, for the sake of simplicity, it is accepted that the stable eutectoid transformation temperature is constant and equal to the metastable eutectoid temperature.

Suppose that a grey cast iron is cooled very slowly—following the stable diagram—between the eutectic and the eutectoid temperatures. Dissolved carbon in the austenite losses solubility in the austenite and, when this carbon is expelled from the lattice, it combines with other atoms to precipitate as pro-eutectoid graphite, in small amount, and sometimes with Widmanstätten morphology, inside carbon-depleted austenite.

Complementarily, a ferritizing process of the austenite is usually observed, which is called *direct ferritizing*, on the edges of the solidification lamellar graphite. That is due to that some carbon atoms of the austenite migrate by diffusion and they settle over the solidification of graphite—mainly if the graphite is of the B or D types. For this reason, the carbon-depleted austenite locally transforms into ferrite.

Direct ferritizing process is more probable when the carbon content is high—that is why it is difficult to find this process in graphite of type E, and when silicon content is also high. It is necessary to consider that austenite contains silicon in solid solution and due to its α -forming nature, this element rises to A_3 temperature.

γ -forming elements—such as copper, nickel and manganese—stabilize the austenite and hinder (or delay) direct ferritizing process. The presence of copper is useful because, apart from being γ -forming element, it delays the ferritizing process due to the *barrier effect* during the carbon diffusion. Other elements also produce a barrier effect, such as bismuth, lead, and tin. These elements—which are even alphagenic, unlike copper—are more effective than copper but give brittleness to cast iron.

When the eutectoid temperature is reached with a slow cooling in the interval **a** of the Fig. 4.4, the structure will be made of: solidification graphite, pro-eutectoid graphite—in small amount—a little of ferrite and eutectoid austenite.

If the cooling progresses as stable at the eutectoid temperature, which, in practice, has less probability than the opposite, eutectoid austenite will transform into ferrite and graphite. In the end, at room temperature, if cooling was fully stable from the solidification temperature, a micrographic structure of matrix thoroughly ferritic with graphite as disperse component will be obtained. Graphite is of different types: solidification graphite—the most abundant, pro-eutectoid graphite, eutectoid graphite and graphite that was formed in the interval **c** of Fig. 4.4 because of the carbon solubility loss in the ferrite.

However, if the transformation of the austenite at the eutectoid temperature takes place following the metastable diagram, meaning pearlitic, due to a faster cooling than in the stable transformation, then the matrix structure would be ferritic-pearlitic. Solidification graphite and pro-eutectoid graphite (in lower amount, even in some occasions negligible) would appear as disperse component.

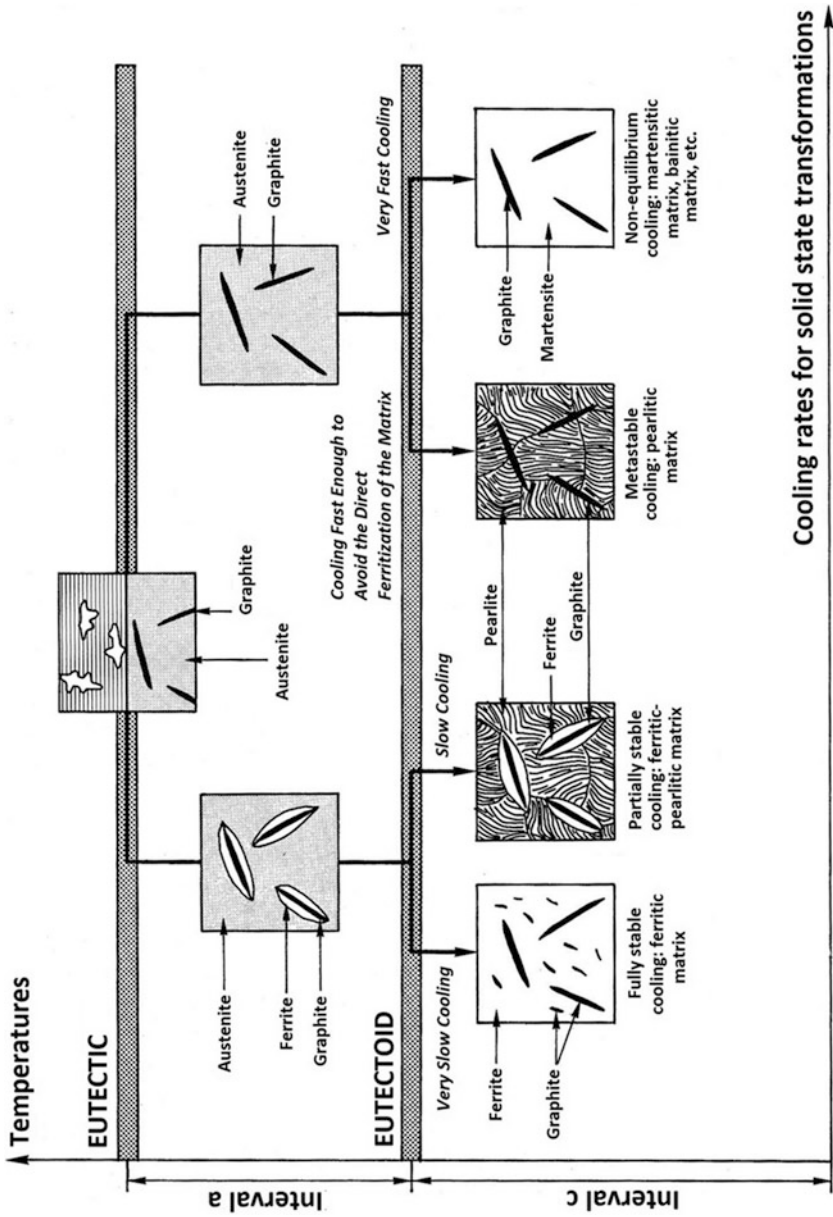


Fig. 4.4 Transformations of grey cast iron in solid state (below eutectic temperature). Compromise between the stable and metastable cooling

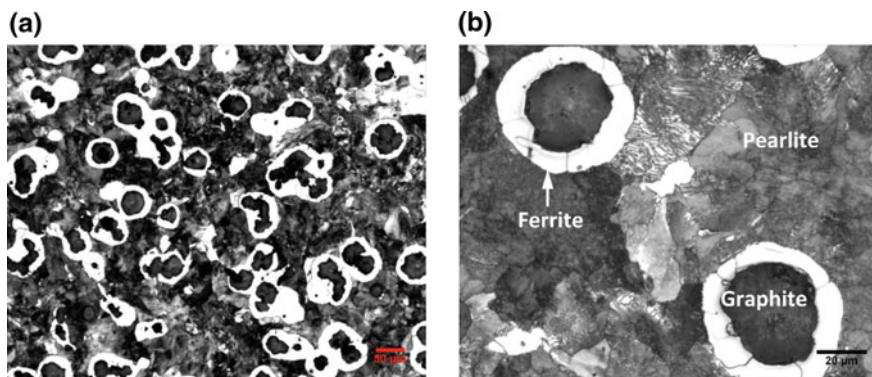


Fig. 4.5 **a** Spheroidal cast iron of ferritic–pearlitic matrix. Etched with Nital 2. **b** Above-shown micrograph in detail (direct ferritization in the graphite boundaries). Bullseye ductile iron

Direct ferritizing areas are not desirable in pearlitic cast irons or in the spheroidal cast irons (see Fig. 4.5) due to the unfavourable behaviour facing to wear.

Now, consider a cooling fast enough—metastable—to avoid direct the ferritizing of austenite matrix in the interval **a** of the Fig. 4.4. In this way, carbon solubility loss in austenite would not have produced graphite. It would produce pro-eutectoid cementite. If the cooling would have also followed the metastable diagram until the room temperature, the *pearlitic matrix* grey cast iron structure would have been obtained. These pearlitic grey cast irons, which are the most commonly used because of the good balance between low cost and properties, are called as *structural cast irons*.

4.3 Non-equilibrium Transformations. Low and Medium Alloy Elements

Analogously to steel's situation, austenite of a cast iron can also transform into bainite or martensite. That is, austenite can also experience non-equilibrium transformations below the eutectoid temperature. These non-equilibrium transformations happen when cooling rate from austenitic state exceeds critical cooling rate to transform austenite into pearlite.

Grey cast irons with martensite matrix are of interest when a high abrasion resistance and toughness higher than that of the white cast irons is required. To improve only mechanical strength, martensitic structures are seldom employed. Later on (Chap. 5), it will be mentioned that the improvement in that mechanical strength can be achieved by using pearlitic matrix grey cast irons: simply by achieving low equivalent carbon.

In Sect. 7.4, the utility of spheroidal grey cast irons with bainitic matrix (bainitic cast irons with flaky graphite have lost practical interest) is mentioned.

In any case, it is not convenient to obtain non-equilibrium structures by means of fast cooling rates. In effect, due to the high percentages of carbon in cast irons, their M_s point is very low, and therefore, cast irons are very prone to quench cracking.

It seems preferable to increase hardenability of austenite by means of alloying elements added to the cast iron, and in this way, obtain bainite or martensite structures using less severe cooling. As it is logic, for the same alloying elements content, the cast iron would give martensitic, bainitic or pearlitic structures, depending on the massivity.

If grey cast irons are alloyed only for increasing hardenability, then they are called *low and medium alloyed cast irons*. In some standards, this naming is used when the sum of silicon and other alloying element contents is lower than 5%.

Selected alloying elements should be those with high partition coefficient to achieve a uniform distribution in the liquid, without segregation problems.

Preferentially, it would be advisable the use of non-carbide-forming elements with the purpose of avoiding a possible tendency to chill during the solidification, although this tendency to follow metastable solidification can be counter-balanced with increasing silicon content. It should be kept in mind, however, that silicon is not favourable from the hardenability point of view.

In low or medium alloyed cast irons, nickel is usually employed in percentages from 2 to 4%. As alternative, or complementarily, due to the lower cost, manganese is used even when this element is slightly carburigen.

Molybdenum moves energetically the pearlitic nose of TTT curves to the left and facilitates the bainitic transformation. That is why to efficiently increase bainitic hardenability, it is quite common resorting to this element, although in percentages that are lower than 1%. Molybdenum is a strongly carbide-forming element and increasing silicon in the cast iron is advisable.

4.4 High Alloying and Transformations During the Cooling

When we compare the structures of non-alloyed cast irons (or those of low and medium alloyed cast irons) for different cooling rates, we can only observe: grey cast iron (graphite types A, B or D depending on the cooling rate), mottled cast iron or white cast iron. On the other hand, for the same grey cast iron, because of the different cooling rates, the possible matrices are: ferritic, ferritic-pearlitic, pearlitic, bainitic, martensitic as it is shown in Fig. 4.4.

Logically, it is possible to reduce the *intrinsic* cooling rate, for the same real cooling conditions (external), by means of the use of higher silicon contents. This way, the difficulty of directly obtaining, by slow cooling, a thoroughly ferritic matrix disappears when silicon percentages are of 6% (*Silal* cast iron) or greater.

Among grey cast irons, there are also some of them that have austenitic matrix. This happens with *high-nickel cast irons* when the amount of this element is higher than 20%. In these cast irons, solidification takes place in a stable way and, also,

because of the nickel γ -stabilizing behaviour, austenite does not transform during the cooling and continues as matrix component at room temperature. High-nickel cast irons are *grey* even for low silicon contents—for instance 1.5%—as nickel is γ -forming and graphitizing element as well.

4.5 Transformations by Heating

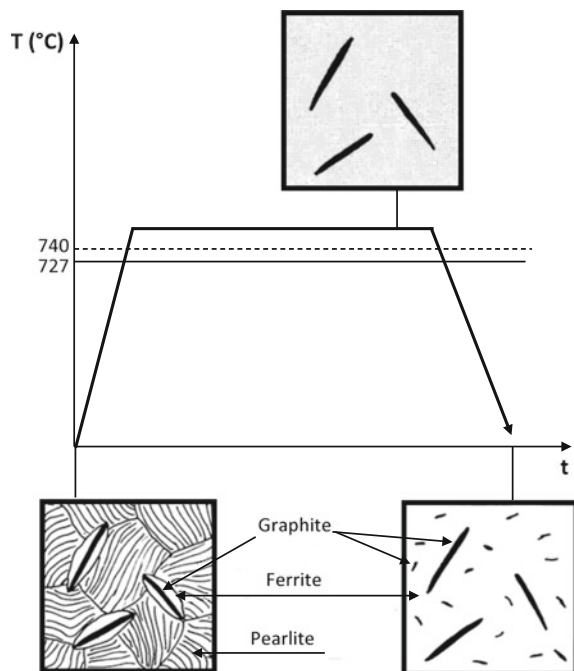
4.5.1 Indirect Ferritizing Due to Heat Treatment

In Fig. 4.6, the heat treatment cycle called *indirect ferritizing annealing* is shown. This treatment can be given to a grey cast iron of ferritic–pearlitic matrix if the thoroughly ferritic structure is desired.

The possibility of simultaneous stable and metastable equilibria in solid state can be kept in mind for achieving a full graphitization of the pearlite of that grey cast iron by means of heat treatment. Overcoming this simultaneous equilibrium requires direct ferritizing areas.

Carbon diffusion, from the decomposed pearlitic cementite (to give atoms of carbon and iron) to the solidification graphite, only takes place in times reasonably short whether it exists a strong gradient of carbon between both components, separated by directly ferritized areas.

Fig. 4.6 Indirect ferritizing annealing in a ferritic–pearlitic grey cast iron. Structures of the cast iron: cycle and evolution



Indirect ferritizing annealing is usually employed in spheroidal graphite cast irons. The holding time at temperatures of the order of the eutectoid—generally around 750 °C—allows the pearlitic cementite breaking down to give austenite and graphite. If the subsequent cooling from that temperature is very slow—following the stable diagram—it is possible to achieve that, at room temperature, graphite appears dispersed in a thoroughly ferritic matrix.

That possibility of transforming the cementite into graphite is normally used, also, with other purpose: obtaining *nodular cast irons*. If a white cast iron is held for a sufficiently long time at a temperature above the eutectoid, the metastable iron carbon present decomposes to form *graphite temper nodules* in an austenite matrix. If, then, cooling down to room temperature is sufficiently slow, austenite transforms into ferrite, with the excess carbon precipitating on the temper nodules. The result is a *ferritic malleable iron*. This material possesses many of the advantages of grey cast irons and as much greater ductility (20% more if compared with about 1% for ferritic grey iron). In addition, high yield and tensile strength can be obtained in malleable iron by subsequent heat treatments to produce *pearlitic malleable iron* or *quenched and tempered malleable iron*.

Some cast irons, potentially white (v. gr. the composition: 2.5% of carbon, 1% of silicon), that solidify giving ledeburite, can transform all cementite of that ledeburite into graphite (of nodular appearance) and into austenite enriched in carbon by means of an adequate heat treatment (which means holding times between 12 and 48 h at 900 °C). Depending on the way of carrying out the cooling from that temperature, more or less quickly, austenite can transform into martensite, pearlite or even ferrite if the cooling is slow enough. Strictly speaking, they are not grey cast irons because this name is reserved to those cast irons where graphite is obtained during the solidification, which is not this situation. They are called nodular cast irons, where nodular graphite is dispersed in a martensitic, pearlitic or ferritic matrix depending on the cooling rates (Sect. 6.3). In Fig. 4.7, the microstructure of a ferritic nodular cast iron can be observed.

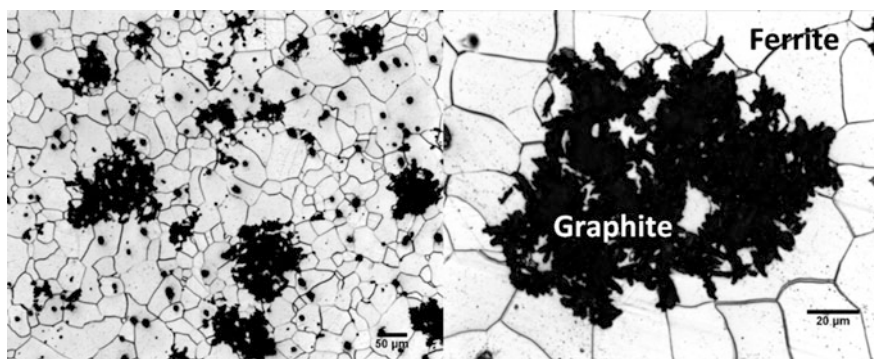


Fig. 4.7 Blackheart malleable cast iron of ferritic matrix (nodular graphite over background of ferrite). Etched with Nital 2

Exercise 4.1. First-stage graphitization annealing. Calculate the approximate time for the malleabilization annealing at 740 °C of a white cast iron (2.5% Si) with the purpose of achieving a pearlitic matrix malleable cast iron. Use the equation proposed by Flemings:

$$t_{\text{cr}} = \frac{f_{\text{Fe}_3\text{C}}^v \cdot C_{\text{Fe}_3\text{C}} \cdot l_0^2}{(C_{\gamma_2} - C_{\gamma_1}) \cdot D_C^{\gamma}} \quad (4.1)$$

The equation follows typical diffusion law $\langle x \rangle \simeq \sqrt{D \cdot t}$, that relates mean diffusion paths ($\langle x \rangle$), diffusion coefficient (D) and time (t).

$f_{\text{Fe}_3\text{C}}^v$	volume fraction of cementite.
$C_{\text{Fe}_3\text{C}}^v$	carbon content in the cementite (6.7%).
l_0	average distance between nodules of graphite (interlamellar distance of the ledeburite).
$C_{\gamma_2}, C_{\gamma_1}$	carbon concentrations in the austenite in equilibrium with Fe ₃ C and graphite, respectively.
D_C^{γ}	diffusion coefficient of the carbon in the austenite which is equal to: $D_C^{\gamma}(\text{cm}^2/\text{s}) = 0.21 \cdot \exp\left(-\frac{33800 \text{ cal}}{RT}\right)$; at $T = 1013 \text{ K}$; $D = 1.19 \times 10^{-18} \text{ cm}^2/\text{s}$.

Question

$$C_{\gamma_2} = 0.76; C_{\gamma_1} = 0.68; \quad (4.2)$$

$$T = 740 + 273 = 1013 \text{ K} \quad (4.3)$$

$$f_{\text{Fe}_3\text{C}}^v \simeq \frac{2.5 - 0.76}{6.7 - 0.76} = 0.29 \text{ (29\%)} \quad (4.4)$$

For an average distance between graphite nodules of 100 μm (0.01 cm) (Figs. 4.8 and 4.9)

$$t_{\text{cr}} = \frac{f_{\text{Fe}_3\text{C}}^v \cdot C_{\text{Fe}_3\text{C}} \cdot l_0^2}{(C_{\gamma_2} - C_{\gamma_1}) \cdot D_C^{\gamma}} = \frac{0.29 \cdot 6.7 \times 10^{-4}}{(0.77 - 0.68) \cdot 1.19 \times 10^{-8}} = 1.8 \times 10^5 \text{ s} \simeq 50 \text{ h} \quad (4.5)$$

If the distance between graphite nodules was divided by two ($l_0 = 50 \mu\text{m} = 5 \times 10^{-3} \text{ cm}$) the graphitization times would be reduced four times, $t_{\text{cr}} \simeq 13 \text{ h}$.

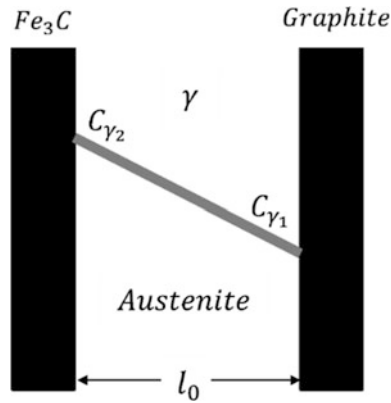


Fig. 4.8 Scheme of the graphitization annealing

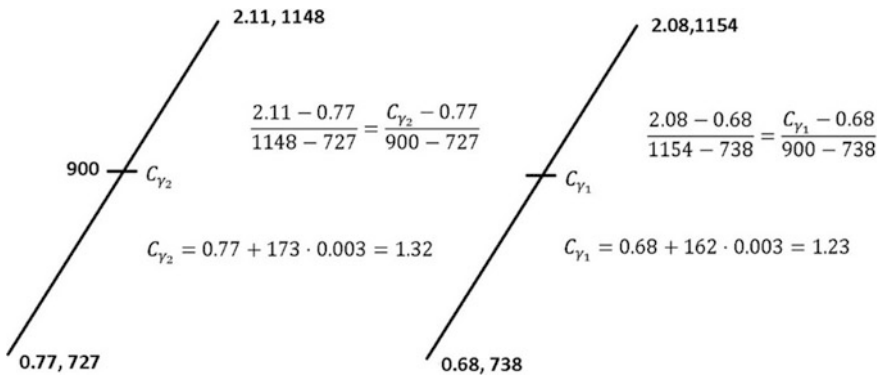


Fig. 4.9 Scheme of the calculations performed in the graphitizing annealing

If the annealing was performed at 900 °C (1173 K):

At 900 °C:

$$C_{\gamma_2} - C_{\gamma_1} = 1.32 - 1.23 \simeq 0.09 \quad (4.6)$$

$$D_C^{\gamma} = 0.21 \cdot \exp(-33800/2 \cdot 1173) \simeq 1.16 \times 10^{-7} \text{ cm}^2/\text{s} \quad (4.7)$$

$$f_{\text{Fe}_3\text{C}}^{\gamma} \simeq \frac{2.5 - 1.32}{6.7 - 1.32} = 0.22 \text{ (22\%)} \quad (4.8)$$

$$t_{\text{cr}} = \frac{f_{\text{Fe}_3\text{C}}^{\gamma} \cdot C_{\text{Fe}_3\text{C}} \cdot l_0^2}{(C_{\gamma_2} - C_{\gamma_1}) \cdot D_C^{\gamma}} = \frac{0.22 \cdot 6.7 \times 10^{-4}}{0.09 \cdot 1.16 \times 10^{-7}} = 14119 \text{ s} \simeq 4 \text{ h} \quad (4.9)$$

The time required for the treatment would be divided by 10.

Exercise 4.2. Second-stage graphitization annealing. To produce a ferritic iron through heat treatment, a cast iron is first heated up to a temperature slightly lower than that of the eutectoid with the purpose of achieving the diffusion of the carbon excess from the matrix towards the nodules without forming cementite. Enclosed figure describes schematically the kinetics of the isothermal transformation at a temperature T slightly below the stable (738 °C) and metastable (772 °C) transformation temperatures, for instance 700 °C (Fig. 4.10)

$$\begin{aligned} c_{\alpha_2} &\simeq 0.021 (\alpha \text{ in equilibrium with } \gamma, \text{ metastable diagram}) \\ c_{\alpha_1} &\simeq 0.020 (\alpha \text{ in equilibrium with graphite, stable diagram}) \end{aligned}$$

Question

The problem will be solved by applying Flemings equations:

$$g_\alpha = \frac{2\gamma\sqrt{D_C^\alpha \cdot t}}{l_0} \quad (4.10)$$

where g_α is the ferritized fraction, while γ is a parameter whose value can be obtained through the following equation:

$$F = \gamma e^{\gamma^2} \operatorname{erf}(\gamma) = \frac{1}{\sqrt{\pi}} \cdot \frac{(C_{\alpha_2} - C_{\alpha_1})}{(C_\gamma - C_{\alpha_2})} \quad (4.11)$$

Fig. 4.10 Scheme of the graphitizing annealing

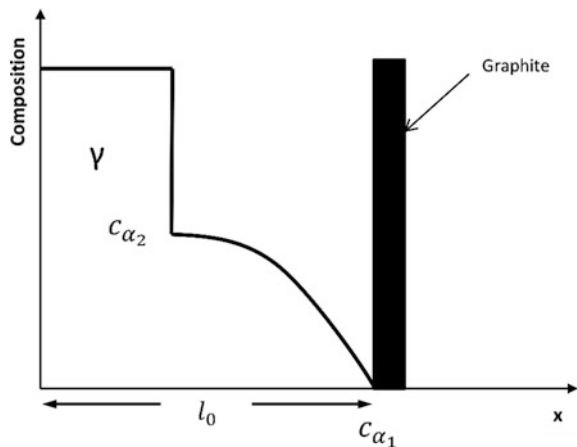


Table 4.1 Ferritization times as a function of the temperature and diffusion

T (°C)	D (cm ² /s)	$t_{\text{ferritization}}$ (h)
700	6.9×10^{-7}	$\simeq 13$
600	2.1×10^{-7}	$\simeq 42$
500	4.8×10^{-8}	$\simeq 185$
400	7×10^{-9}	$\simeq 1265$

For low values of γ :

$$\gamma e^{\gamma^2} \operatorname{erf}(\gamma) \simeq \gamma^2 \rightarrow \gamma^2 = \frac{1}{\sqrt{\pi}} \cdot \frac{(0.021 - 0.020)}{(0.77 - 0.021)} = 7.53 \times 10^{-4} \rightarrow \gamma = 0.028 \quad (4.12)$$

At 700 °C:

$$D_C^z = 0.02 \cdot \exp\left(\frac{-20000}{RT}\right) = 6.9 \times 10^{-7} \text{ cm}^2/\text{s} \quad (4.13)$$

In this way, the ferritized fraction equation gives the time required for the second-stage annealing:

$$g_z = \frac{2\gamma\sqrt{D_C^z \cdot t}}{l_0} \rightarrow t_{\text{second-stage annealing}} = \frac{1}{D_C^z} \cdot \left(\frac{g_z \cdot l_0}{2\gamma}\right)^2 \quad (4.14)$$

For $l_0 = 100 \mu\text{m}$ (average distance between graphite nodules):

$$\begin{aligned} t_{\text{second-stage annealing}} &= \frac{1}{6.9 \times 10^{-7} \text{ cm}^2/\text{s}} \cdot \left(\frac{1 \cdot 0.01 \text{ cm}}{2 \cdot 0.028}\right)^2 \\ &\simeq 4.62 \times 10^4 \text{ s} (\simeq 13 \text{ h}), \text{ for } g_z = 1 \end{aligned} \quad (4.15)$$

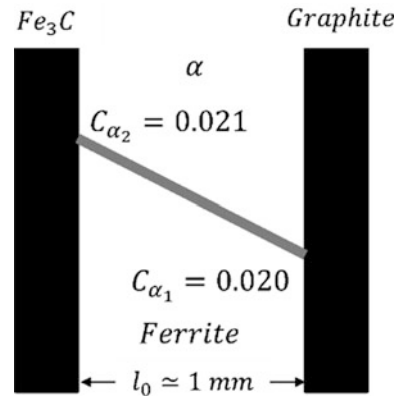
If the temperatures drop down to 600, 500, and 400 °C, the ferritization times will be those shown in the next Table 4.1 ($g_z = 1$) (Table 4.1):

4.5.2 Cementite Graphitization at 450 °C

To achieve the decomposition of the cementite, and then producing graphite, it is not necessary to reach the high temperatures that we have mentioned in the last section.

If we compare the stable and metastable diagrams in the range of temperatures comprised between the eutectoid and the room temperature, it is possible to notice in Fig. 4.6 that equilibrium constituents could be ferrite and cementite (metastable diagram) or ferrite and graphite (stable diagram). Therefore, this situation implicitly illustrates the possibility of changing from the metastable to the stable system,

Fig. 4.11 Scheme used in the calculations of the exercise



although, logically, graphitization would be slow because of having low temperatures for the cementite decomposition kinetics.

Cementite graphitization, as a consequence of long exposure times at moderated temperatures, 450–550 °C, can even happen in steels. For instance, in tubes of low carbon content for heat exchangers after 3000 h working, cementite decomposes into graphite and ferrite, and therefore the mechanical strength of the tube drops, and it fails due to the inner pressure produced by the vapour with a typical crack. With the idea of avoiding this kind of failure, standards for chemical composition of this sort of steel tubes usually recommend the presence of 0.5% of molybdenum to stabilize the cementite and avoid its decomposition into graphite.

Exercise 4.3: Using the same equation than in the last exercise, calculate the graphitization time of a steel of 0.15% C (heat exchange tubes in power stations) at 500 °C. Data: $D_C^{\alpha}(\text{cm}^2/\text{s}) = 0.02 \cdot \exp\left(-\frac{20000 \text{ cal}}{RT}\right)$ (Fig. 4.11).

Question

The method of solving the problem of the graphitization undertakes the Flemings equations:

$$g_{Fe_3C} = \frac{2\gamma\sqrt{D_C^{\alpha}t}}{l_0} \quad (4.16)$$

$$\gamma e^{\gamma^2} \text{erf}(\gamma) = \frac{1}{\sqrt{\pi}} \frac{(C_{\alpha_2} - C_{\alpha_1})}{(C_{Fe_3C} - C_{\alpha_2})} \quad (4.17)$$

where

g_{Fe_3C} fraction of transformed cementite
 l distance between colonies of pearlite

The other parameters are the same that in Exercise 4.2.

$$F = \gamma e^{\gamma^2} \operatorname{erf}(\gamma) = \frac{1}{\sqrt{\pi}} \frac{(0.021 - 0.020)}{(6.7 - 0.02)} = 8.45 \times 10^{-5} \quad (4.18)$$

For low values of $\gamma \Rightarrow \gamma e^{\gamma^2} \operatorname{erf}(\gamma) \simeq \gamma^2 \Rightarrow \gamma \simeq 9.2 \times 10^{-3}$

$$t = \frac{1}{D_C^z} \cdot \left(\frac{g_{\text{Fe}_3\text{C}} \cdot l_0}{2 \cdot \gamma} \right)^2 = \frac{1}{4.8 \times 10^{-8}} \cdot \left(\frac{1 \cdot 0.1}{2 \cdot 9.2 \times 10^{-3}} \right)^2 = 6.2 \times 10^8 \text{ s} \\ \simeq 19.5 \text{ years} \quad (4.19)$$

If the distance between pearlite nodules was 10 times lower (100 μm), the ferritization times would be around 0.2 years (around 1700 h).

One of the graphitization of the non-alloyed pearlitic grey cast irons drawbacks is the *growth* that is experienced by these grey cast irons if they are used at temperatures higher than 450 °C (in prolonged times at those temperatures), or after repeated cycles of heating and cooling. Growth is produced by the expansion that accompanies the graphitization, expansion and contraction at the transformation temperature and internal oxidation of the iron produced by gases. The process is based on: first, graphite of the hot surface disappears as CO_2 and then gases can accede to deeper zones where continue with the oxidation of the graphite, and also of the iron and silicon.

To improve the *heat resistance* of the typical grey cast irons at moderated operation temperatures (and to improve the resistance even up to 800 °C), it is common the use of cast irons with low silicon contents (1.5–2%, to limit the graphitization risks), and with chromium (1–2%, to stabilize the cementite and also to improve the behaviour of the ferrite facing to oxidation). In this way, for cyclical heating with holding times of even 500 h at 800 °C, a 2% of chromium can suppress the *growth*.

In addition to the internal oxidation that contributes to growth, after exposure at sufficiently high temperatures, it is usually the presence of roughness in the unalloyed grey cast irons. This is caused by a mix of iron oxides, which descale as *scales* and facilitate the oxidation penetration. The scale formed in air consists of a mixture of iron oxides. The important factor in scale formation is whether the scale is essentially adherent and protective to the base metal or tends to flake and permit continuous oxidation of the metal. Scaling resistance of common grey cast irons improves with silicon (content higher than 3%), chromium, aluminium and nickel additions. This resistance improvement is due to the previous formation of the oxide layer that is adherent and impenetrable to the gases action. In Chap. 9, which corresponds to highly alloyed cast irons, this question will be completed.

Growth and graphitizing risks of cast irons do not appear in the case of ferritic matrix grey cast irons—as is the case of the *Silal* cast iron (6% Si), or the highly alloyed cast irons of austenitic matrix (Niresist and Nicrosilal cast irons). In the last

two cases, there is not cementite, and for this reason, there is not graphitizing risk even at high temperatures. On his behalf, the silicon content (6%) in the Silal cast iron and the high-nickel content in the austenitic cast irons improve the scaling behaviour.

General Properties of Non-alloyed Grey Cast Irons (or Low Alloy) and Flake Graphite

5

Abstract

This chapter is entirely dedicated to the properties of the grey cast irons and the main uses of this kind of irons. Grey cast irons are metal matrix composites with several interesting properties that make them usable in several applications in different fields. Maybe two of the most relevant properties of grey cast irons are their low shrinkage and good castability. For that reason, they find application in ornamental parts, but also, in products that could be obtained directly by moulding taking advantage of this good castability as is the case of different parts used in the automotive industry.

5.1 Properties of Grey Cast Irons

It is convenient to mention, as introduction to the properties, that grey cast irons are a metal matrix composite, composed of graphite and a matrix material which, in turn, is usually made up by a *ceramic* intermetallic—cementite—and another constituent—ferrite—that is metallic. Grey irons are composites of metallic matrix (Metal matrix composites, MMC). White cast irons are composites of ceramic matrix (Ceramic matrix composites, CMC).

Cast irons are ferrous alloys that require for their manufacture *lower energy than steels* because with similar heat capacity, the melting point of cast irons is lower than the melting point of steels. Besides, cast irons present excellent castability and also give low shrinkage after cooling (solidification).

The higher the carbon content, the better castability of cast irons, because the interval of temperatures between the liquidus and the solidus diminishes. Some of them, those of eutectic composition, solidify at constant temperature.

Table 5.1 Linear shrinkage during the solidification (data from ASM 1978)

Cast iron type	Linear shrinkage (%)
Ductile cast iron	0.0–0.7
Grey cast iron	1.0
Malleable cast iron	1.0
Austenitic cast iron	1.3–1.5
White cast iron	2.0
Carbon steel	2.0
Alloyed steel	2.5

It is not advisable the practice of increasing the pouring temperature with the finality of improving the castability due to the *superheating* problems (mentioned in Sect. 3.2), but also, because the shrinkage would be increased.

Grey cast irons give little shrinkage (around 1% of linear shrinkage), lower than in steels and white cast irons, as it is possible to see in Table 5.1. The small shrinkage in the solidification is due to the density of grey cast irons (between 6.95 and 7.35 g/cm³, the lower the greater the carbon content), which is lower than the density of white cast irons (7.7 g/cm³), and lower than steel density (7.85 g/cm³).

This low density of grey cast irons is because of the graphite presence, which has a density of 2.2 g/cm³. In grey cast irons, graphite usually occupies a volume (or a fraction of area as observed in the microscope) between 6 and 10% of the total volume.

Exercise 5.1. A cast iron, in liquid state, at eutectic temperature has a density of 7.20 g/cm³. Immediately after the solidification, this cast iron has a density of 7.50 g/cm³. Calculate the volumetric change that takes place during the solidification. Are there contraction (shrinkage) or expansion during the solidification?

Question
Per gram:

$$\frac{\Delta V}{V} = \frac{V_S - V_L}{V_L} = \frac{\left(\frac{1}{7.50} - \frac{1}{7.20}\right)}{\left(\frac{1}{7.20}\right)} = \frac{0.133 - 0.139}{0.139} = -0.040 \text{ } (-4\%) \tag{5.1}$$

The cast iron has experienced contraction during the solidification. The linear shrinkage would be, approximately, the third part ($\simeq -1.3\%$).

Exercise 5.2. Demonstrate that in a eutectic grey iron there is no shrinkage (or contraction) in the transformation: liquid $\rightarrow$ solid.

Data : $\rho_{\text{Liquid}} \simeq 7.3 \text{ g/cm}^3$; $\rho_{\gamma} \simeq 7.6 \text{ g/cm}^3$; $\rho_{\text{Graphite}} \simeq 2.25 \text{ g/cm}^3$

Question

The fractions of austenite and graphite are calculated by means of the lever rule in the eutectic of the stable diagram:

$$f_{\gamma} = \frac{100 - 4.25}{100 - 2.08} = 0.978 \text{ (97.8\%)} \quad (5.2)$$

$$f_{\text{Graphite}} = \frac{4.25 - 2.08}{100 - 2.08} = 0.022 \text{ (2.2\%)} \quad (5.3)$$

If 100 g of liquid are considered,

$$100 \text{ g (l)} = 97.8 \text{ g } (\gamma) + 2.2 \text{ g (graphite)} \quad (5.4)$$

The volume of the three constituents or phases of the last equation are:

$$V_{\text{Liquid}} = \frac{100 \text{ g}}{7.3 \text{ g/cm}^3} = 13.70 \text{ cm}^3 \quad (5.5)$$

$$V_{\gamma} = \frac{97.8 \text{ g}}{7.6 \text{ g/cm}^3} = 12.87 \text{ cm}^3 \quad (5.6)$$

$$V_{\text{Graphite}} = \frac{2.2 \text{ g}}{2.25 \text{ g/cm}^3} = 0.98 \text{ cm}^3 \quad (5.7)$$

In this way,

$$V_{\text{Liquid}} = 13.70 \quad (5.8)$$

$$V_{\gamma} + V_{\text{Graphite}} = 12.87 + 0.98 = 13.85 \quad (5.9)$$

$$V_{\text{Liquid}} < V_{\gamma} + V_{\text{Graphite}} \quad (5.10)$$

It is possible to say that the solidification happens with a slight increase in volume. There is no, as it is common, contraction (shrinkage) in the liquid $\rightarrow$ solid transformation of the grey iron. However, the cast iron contracts, in liquid state from the pouring temperature down to the solidification temperature

(see Sect. 3.2). And this contraction (shrinkage) is not compensated with the expansion that takes place during the solidification. In this context, shrinkage (contraction) will appear if complementary liquid is not provided (risering).

The radical feature of grey cast irons is that these cast irons do not have ledeburite in their microstructure. Instead of having this component in the microstructure, grey irons have graphite embedded into a metallic matrix, which is very like steel.

The mechanical behaviour of a grey cast iron is like the steel one, but with large micro-fissures filled in with graphite. The cohesion between graphite and metallic matrix is almost non-existent. That is because of the great difference between the iron and the graphite expansion coefficients. And consequently, graphite comes off from the metallic matrix easily.

The model exposed above explains several properties of grey cast irons: the grey colour of the fracture, the ability for vibrations *damping* (the higher graphite content, the higher the vibrations damping), *machinability* is usually good, the tensile strength is moderate, and the elongation is low, there is a common dispersion in the microhardness values, etc.

Thermal conductivity of grey cast irons is approximately 46 W/m K, which is higher than the thermal conductivity of steels. Graphite has influence in this value, as it is good conductor. The ability for heat dissipation is, therefore, higher in grey cast irons—the higher the graphite content, the higher the heat dissipation, and flake graphite is better than spheroidal graphite—than in steels. To take advantage of this property, the ingot moulds for molten steels are manufactured in hypereutectic grey cast irons.

The *thermal shock resistance* of grey cast irons is also better for higher carbon contents.

The *coefficient of thermal expansion* in grey irons is, approximately, 13 $\mu\text{m/m } ^\circ\text{C}$ between 0 $^\circ\text{C}$ and 500 $^\circ\text{C}$, and 10.5 $\mu\text{m/m } ^\circ\text{C}$ between 0 $^\circ\text{C}$ and 100 $^\circ\text{C}$. Even though like the iron coefficient of thermal expansion, this coefficient is lower in the case of grey cast irons Fe_α : 13 $\mu\text{m/m } ^\circ\text{C}$; Fe_γ : 18 $\mu\text{m/m } ^\circ\text{C}$.

With the purpose of explaining the heat resistance, it is necessary to remember that we have noted about *growth* and *scaling* in the section dedicated to the study of the transformations of grey cast irons during heating (Sect. 4.5).

To achieve a good behaviour to *heat at high temperatures*, cast irons of matrix thoroughly ferritic or austenitic (of high alloy, instead of being of medium alloy cast irons) are used, as it will be detailed in Chap. 9. Ferrite or austenite matrices, without critical points from the room temperature to the melting point, are advantageous because they do not produce transformations during the cooling period.

The presence of graphite is equivalent to micro-notches, mainly in non-spheroidal cast irons. That is why, elongation in the tensile test of the lamellar grey cast irons is small (commonly lower than 0.6%). The previous existence of these *micro-notches* also clarifies the weak sensibility of these cast irons to the complementary influence of superficial mechanical notches. For that reason, being

careful with the presence of scratch marks, sharp angles, etc. is not as necessary in lamellar cast irons as in steels.

Toughness of grey cast irons is higher than the toughness of white cast irons. However, due to the notch effect sensibility (because of the flake graphite) toughness is not enough. Because of that, when a tough material is required, neither lamellar cast iron nor white cast iron should be used.

Hardness values are interesting to evaluate the resistance to wear of a grey cast iron. Furthermore, these measures provide a first criterion about their machining behaviour or machinability.

Brinell hardness test is the most usual one because allows for obtaining an average hardness value of the composite made up of the graphite and the matrix. As opposed to steels, in grey cast irons, there is no clear correlation between the hardness value and the tensile strength. This unequal behaviour in grey cast irons and steels seems reasonable due to the notch effect caused by the graphite flakes when testing in tension.

Rockwell C hardness is usually employed in the case of hard matrices (pearlite, bainite and martensite) to avoid possible deformations of the Brinell testing indenter. With the purpose of measuring the hardness of the matrix constituent—it is necessary to avoid that the indentation reaches the graphite—*Vickers micro-hardness test* is also used with load of 200 g, and then, by means of equivalence, the Rockwell C hardness is calculated.

To quantify the *massivity effect over the tendency to chill* and over the structures of a pearlitic cast iron, a test performed in a *wedge* sample (with shape and dimensions standardized, moulded with this cast iron) is used.

In the middle cross section of this sample, Rockwell C hardness is calculated at different points. Hardness values, from the wedge vertex, evolve as it is shown in Fig. 3.4, and provide information about the microstructure which is derived from each cooling rate at different points. Cooling rates, and therefore also solidification rates, change with the mass and are lower when the higher is the distance to the wedge's vertex.

In the vertex of the angle, cooling is faster, so a white cast iron is found, and the highest hardness of the entire wedge is measured at this point. Hardness drops fast due to the appearance of mottled cast iron in the adjacent section. The minimum in the curve can be found when graphite type D appears and the subsequent direct ferritization of the matrix takes place. Further to the right, hardness begins to increase because of the presence of graphite of types B and A, which are associated with a lower ferritization of the matrix in these points. The relative maximum belongs to fine graphite type A and pearlitic matrix. Over to the right of this maximum with graphite type A, the lamellar spacing increases, and therefore hardness drops slowly.

The preferable microstructure when wear resistance and tensile strength are pursued matches in the section of relative maximum hardness. Sections placed on the left side of the maximum have non-desirable structures when grey cast irons of thoroughly pearlitic matrix are looked for.

The relative similarity between these curves and the curves of the Jominy test for steels leads several authors to inappropriately call *hardenability* the tendency to chill of a grey cast iron.

Tensile strength is interesting in grey cast irons, especially in those sections of equipment which work under static loads in direct stress or in bending, such as autoclaves, pressure vessels, frameworks, diesel engine blocks, valves, levers, etc.

Tensile strength, R , depends on the graphite type, the amount of graphite and the matrix structure. It is possible to point out, from a generic point of view, that tensile strength drops when the carbon content in the cast iron grows. Graphite reduces the cross section of the matrix constituent, which supports the tensile load, and on the other hand, the notch effect of the flake graphite decreases the toughness.

Tensile behaviour of cast irons is like that of metal matrix composite and is equivalent to steels with microcracks in their entire mass. Thus, tensile strength values, R , in grey cast irons are lower than the tensile strength values in steels. For instance, the tensile strength of a certain grey cast iron of 3.7% carbon and 2.5% silicon, with matrix thoroughly pearlitic, is 137 MPa (20 ksi, 14 kg/mm²). For its part, pearlitic steel, even of coarse pearlite, has a tensile strength of at least 800 MPa (116 ksi, 82 kg/mm²) when tested in tension.

Most of the grey cast irons for general purposes have tensile strengths, R , comprised between 150 and 450 MPa.

On the other hand, the same pearlitic cast iron can have different R_m values according to the *part size*. In this way, for the same carbon content, which determines the amount of graphite in the grey iron, increasing the massivity modulus (Volume/Area) is equivalent to diminishing the solidification rate. For this reason, the eutectic rosettes will be higher, the graphite type A will be coarse and longer, and interlamellar spacing in the pearlite will be higher and softer with lower tensile strength.

The combination of morphological changes, in both graphite and pearlite, gives thus a *lower tensile strength, for the same grey iron, in the larger sections*.

Reciprocally, for the same cast iron, the R value will be higher in the small sections. In this way, the evolution of the strength with the size will follow an analogous curve to the one that was shown in the hardness profile (Fig. 3.4), and in the thinner sections the cast iron could be white or mottled, as well.

When, with an unalloyed or low-alloyed pearlitic grey cast iron, we intend to assess a given tensile strength R , and parts of different sizes are moulded, *the increase in the massivity modulus can make advisable a readjustment in the composition of the grey cast iron* (decreasing the carbon content, and therefore, increasing if necessary the silicon content).

See in Fig. 5.1 the diameter effect over the tensile strength, calculated from tensile specimens taken out from the centre of the bars for three different classes of grey cast iron.

The minimum thicknesses that can be achieved without the chilling of the cast iron are shown in Table 5.2 for different classes of grey cast iron.

Fig. 5.1 Influence of the section over the tensile strength by tensile stress of cylindrical samples in three different classes of grey cast iron

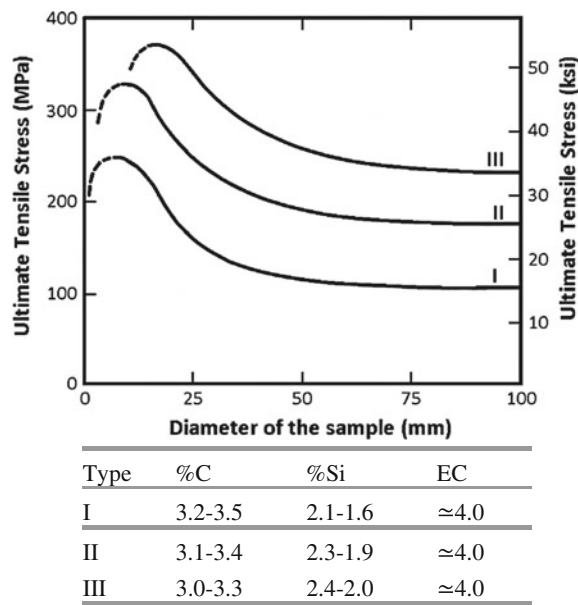


Table 5.2 Minimum average sections recommended for grey cast irons

ASTM class	Minimum thickness (mm.)	Relationship V/A ^a (mm.)
20	3.2	1.5
25	6.4	3.0
30	9.5	4.3
35	9.5	4.3
40	15.9	7.1
50	19.0	8.4
60	25.4	10.7

^aThe relationship V/A belongs to square plates

Class is understood, according to the American Society for Testing Materials standard (internationally accepted), as the tensile strength *R*, expressed in ksi, or the tensile strength value divided by 0.7 when *R* has been calculated in kg/mm² (or *R*/6.9 if the strength *R* is measured in MPa).

The result of the mechanical tests in a grey cast iron, which had the same composition but performed in samples moulded in different diameters, will not be always representative of the calculated property if the result is not accompanied by the diameter of the sample that was used.

Exercise 5.3. With the purpose of calculating the class of a grey iron, Winte proposed an equation that links the tensile strength *R* (ksi) with the chemical composition (carbon and silicon in weight %) and the diameter of

the casting appendix (d in inches), above which the tensile strength has been proposed. The appendix should have an equivalent massivity to the one of the moulded parts. The equation is

$$R(\text{ksi}) = 162.37 + \frac{16.61}{d} - 21.78\% \text{ C} - 61.29\% \text{ Si} + 14.16 \cdot (\% \text{ Si})^2 \quad (5.11)$$

Calculate the value of the mechanical strength, R , as a function of the diameter, d , in the following cast irons:

Cast Iron A: 3.2% C–2.1% Si (EC = 3.9).

Cast Iron B: 3% C–1.5% Si (EC = 3.5).

Cast Iron C: 3.5% C–2.4% Si (EC = 4.3).

Question

The class of a cast iron will depend on the diameter of the casting appendix (Fig. 5.2), on the massivity. To the real representation of the class of the moulded part by means of the appendix, both should have similar massivities, similar cooling rates.

Demonstrate that for a plate of $L = w = 12$ in. and $t = 1 \frac{1}{8}$ in., a sample (appendix) of 2 in. in diameter and $L = 22$ in. could represent the class of the cast iron.

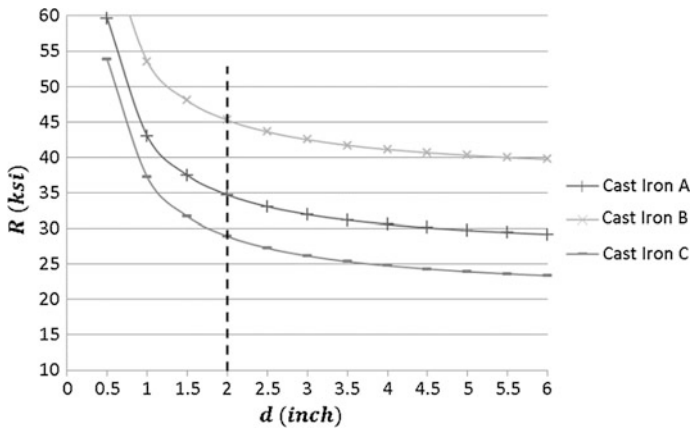


Fig. 5.2 Representation of the class as a function of the diameter of the appendix

Question

It would be enough with equivalent massivities:

$$\left(\frac{V}{A}\right)_{\text{plate}} = \frac{12 \cdot 12 \cdot 1.125}{2 \cdot 12 \cdot 12 + 4 \cdot 12 \cdot 1.125} = \frac{162}{342} = 0.473 \quad (5.12)$$

$$\left(\frac{V}{A}\right)_{\text{appendix}} = \frac{\pi \cdot 1^2 \cdot 22}{2 \cdot \pi \cdot 1 \cdot 22 + 2 \cdot \pi \cdot 1^2} = \frac{22}{46} = 0.478 \quad (5.13)$$

Both the massivity of the plate and the massivity of the appendix are similar. In this context, the class of the cast iron would depend on the equivalent carbon, as the figure above mentioned indicates.

In the proposed equation, the presence of silicon in the grey iron appears expressed by the terms: $61.29 \cdot \%Si + 14.61 \cdot (Si)^2$. How can be reasoned this influence?

Question

The silicon influence in the strength of the cast iron crosses a minimum that derived the equation and equalized to zero is

$$-61.29 + 2 \cdot 14.16\% Si = 0 \rightarrow \%Si \simeq 2.2 \quad (5.14)$$

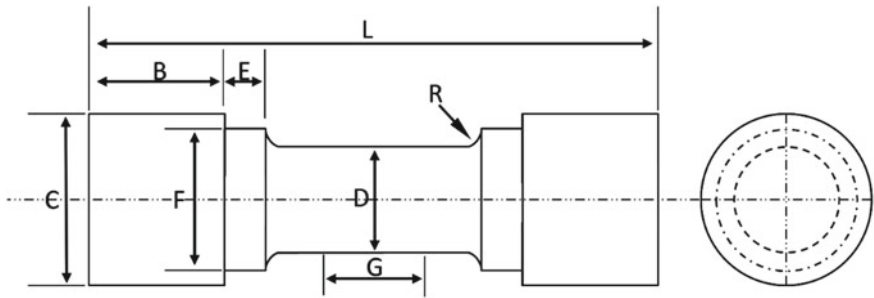
If the silicon content is diminished below that value, the total carbon (CT) should be increased. In this context, the graphite proportion is increased, and the class of the cast iron is deteriorated. With higher silicon contents, the situation is the opposite. The same conclusion is reached if CT is replaced with EC in the equation:

$$CT = EC - \frac{Si}{3} \rightarrow R = 162.37 + \frac{16.61}{d} - 54.03\% Si + 14.16 \cdot (\%Si)^2 - 21.78 \cdot EC \quad (5.15)$$

Increasing the class of the cast iron is equivalent to rising the silicon content (>1.9%) and diminishing the EC (with equivalent massivities).

Note: Figs. 5.1, 5.3 and Table 5.2 should be considered in the resolution of this section of the exercise.

The cooling rate, like the chemical composition, can significantly influence the as-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



	Dimensions (mm)	Tensile Test. Sam- ple A	Tensile Test. Sam- ple B	Tensile Test. Sample C
G	Minimum parallel length	13	19	32
D	Diameter	12.7 ± 0.25	19.1 ± 0.4	31.7 ± 0.05
R	Minimum fillet radius	25	25	50
A	Minimum length of the lowed section	32	38	57
L	Minimum total length	95	100	160
C	Approximate diameter in the end section	22.2	31.8	47
E	Minimum length of the flange	6	6	8
F	Flange diameter	16 ± 0.5	25 ± 0.5	36 ± 0.5
B	Length of the external section	A	A	A

*Variable section according to the kind of grip of the tensile test equipment. If the sample is threaded, then the inside diameter should not be lower than F.

Fig. 5.3 Samples of grey cast iron used in the tensile test according to the American Society for Testing Materials (Reprinted, with permission, from ASTM A 48-76 Standard Specification for Grey Iron Castings, copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428) standard

and properties on the section size is termed section sensitivity. Increasing the cooling rate will

- Refine both graphite size and matrix structure; this will result in increased strength and hardness.
- Increase the chilling tendency; this may result in higher hardness but will decrease strength.

Consequently, composition may be tailored in such a way as to provide the correct graphitization potential for a given cooling rate. For a given chemical composition and as the section thickness increases, the graphite becomes

coarser, and the pearlite/ferrite ratio decreases, which results in lower strength and hardness. Higher equivalent carbon (EC) has similar effects.

Compare the tensile strength of a grey cast iron of class 20 with that of the pearlite. How can be justified the difference that can be observed? How can be increased the class of a cast iron?

Question

A class 20 cast iron has a tensile strength (R_m) of 20 ksi (14 kg/mm², or 140 MPa). Tensile strength of an annealed pearlite (coarse interlamellar spacing) is around 800 MPa, that is to say 5/6 times higher. Pearlite in a pearlitic grey cast iron is full of hollows/cracks filled in with graphite ($\simeq 2$ wt% $\simeq 7$ vol%). The more abundant and longer the hollows/cracks, the lower the tensile strength of the cast iron.

To increase the class of the cast iron, the carbon content should be diminished (and subsequently the graphite content is reduced). This question makes necessary an increase in the silicon content with the purpose of avoiding the chilling of the grey cast iron.

Note: C-graphite volume fraction in the eutectic grey iron:

$$\rho_{\text{graphite}} = 2.25 \frac{\text{g}}{\text{cm}^3}; \rho_{\text{cast iron}} = 7.3 \text{ g/cm}^3$$

The weight of graphite in 100 g of cast iron is calculated by means of the binary Fe–C diagram:

$$\frac{\text{Weight}_{\text{graphite}}}{100 \text{ g (cast iron)}} \simeq \frac{4.25 - 2.08}{100 - 2.08} = \frac{2.17}{97.92} = \frac{2.22}{100} \quad (5.16)$$

The volume fraction of C-graphite is

$$\begin{aligned} f_v(C - \text{graphite}) &= \frac{V_{C-\text{graphite}}}{V_{\text{cast iron}}} = \frac{\text{Weight}_{\text{graphite}}/\rho_{\text{graphite}}}{100 \text{ g (cast iron)}/\rho_{\text{cast iron}}} = \frac{2.22/2.25}{100/7.3} \\ &= 0.072 (7.20\%) \end{aligned} \quad (5.17)$$

Exercise 5.4. The general equation that describes the fracture toughness is

$$K_C \simeq \sigma \cdot \sqrt{\pi \cdot c} \quad (5.18)$$

where

- c is the size of the defect (critical half length of the crack),
- σ is the stress and
- K_C is the material fracture toughness or stress intensity factor.

A grey cast iron has a stress intensity factor of around $6 \text{ MPa}\sqrt{\text{m}}$. Which would be the critical size of the crack in a cast iron of class 20? And, in a cast iron of class 60?

Question

The size of the cracks (graphite) in a class 20 (140 MPa of tensile strength) cast iron would be

$$a_C = \frac{1}{\pi} \left(\frac{6}{140} \right)^2 \simeq 0.00058 \text{ m} = 0.58 \text{ mm}$$

(5.19)

$2 \cdot a_C \simeq 1 \text{ mm} \rightarrow$ cracks with a size of around millimetres, which is equivalent to the maximum graphite sizes found in Table 2.1. It could be obtained a class 60 whether the graphite flakes size is divided by 10 (ref. 5 in Table 2.1).

In Fig. 5.3, the commonly used dimensions for the American specimens (ASTM A48) utilized in the tensile strength test are shown. The standard indicates that the tensile strength obtained in the test should be followed by the letter A, B or C according to the sample that was employed.

Table 5.3 Approximate relation between the tensile strength of the grey cast iron and transverse strength calculate by means of the ASTM 438 standard (Reprinted, with permission, from ASTM 438, Standard Test Method for Transverse Testing of Grey Cast Iron, copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428)

Molten bar		A	B	C
Nominal diameter of the sample (mm.)		22.4	30.5	50.8
Distance between supports (mm.)		305	457	610
Tensile strength (approximately)		Corrected transverse strength (approximately)		
ksi	MPa	kg	kg	kg
20	138	408	816	2720
25	172	465	907	3080
30	207	522	998	3450
35	241	578	1089	3760
40	276	635	1179	4130
45	310	694	1270	4400
50	345	760	1361	4890
60	414	873	1542	5670

To know the quality of a grey cast iron, the three-point bending test over cylindrical samples, as-cast condition and without machining, is commonly used. This test is faster and cheaper than the tensile strength test.

In the three-point bending test each kind of sample—A, B or C—is placed between horizontal supports. These supports are situated with a separation that depends on the kind of sample (see Table 5.3). The sample is subjected in the centre to the action of growing loads until the break. The values that are obtained in the test are the total strength required for the break of the sample and the deflection in the breaking moment. The maximum tensile stress in the surface of the beam (specimen) when it breaks is called the *modulus of rupture (MOR)*, σ_R , which is approximately equal to $1.7 \sigma_{TS}$ ($1.7 \cdot R$).

Exercise 5.5. Obtain the expressions for the modulus of rupture (MOR) in the case of three-point bending test (circular cross-sectional specimen). According to the data provided by Table 5.3, calculate the MOR of the cast irons mentioned in that table (class 20–60) for the specimens' type B ($L = 457 \text{ mm}$, $D = 30.5 \text{ mm}$). Represent graphically MOR as a function of R , and demonstrate that the MOR value tends to the boundary value of $\text{MOR} = 1.7 \cdot R$.

Question

In the three-point test, for $0 < x < L/2$ (left side of the specimen), the bending moment of the force $F/2$, referred to a plane at the centre of the sample, acts in counterclockwise direction, and is, therefore, positive (Fig. 5.4):

$$M(x) = \left(\frac{F}{2} \right) \cdot x \quad (5.20)$$

Fig. 5.4 Scheme of the three-point bending test

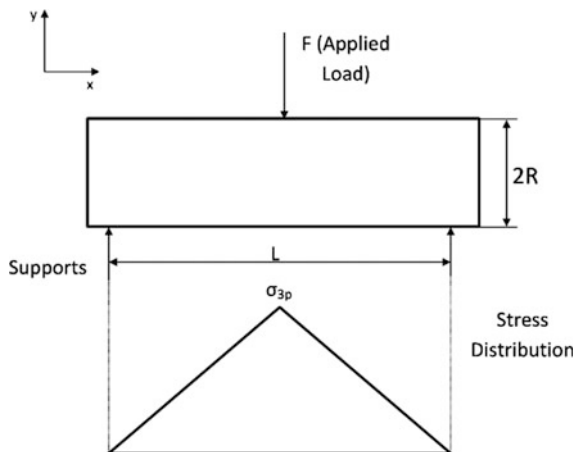
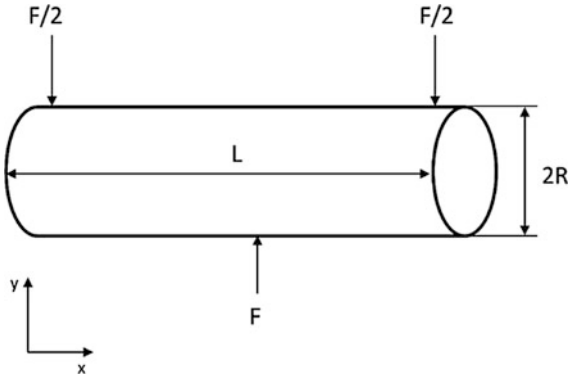


Fig. 5.5 Cylindrical specimen

and when $x = L/2$, then,

$$M\left(\frac{L}{2}\right) = \frac{FL}{4} \quad (5.21)$$

At the central part of the specimen and inside the zone working in traction the stress equation is

$$\sigma = \frac{M(x)y}{I} = \frac{FL}{4} \cdot \frac{y}{I} \quad (5.22)$$

The maximum value of σ is obtained when $y = 2R$ in the case of the rectangular cross section:

$$\sigma_{\max} = \frac{FL}{8} \cdot \frac{2R}{I} \quad (5.23)$$

Substituting the value of I (axial inertial moment for an area element referred to an axis located in the transverse plane) for a circular area (Fig. 5.5):

$$I = \frac{\pi R^4}{4} \rightarrow \sigma_{\max} = \frac{4}{8} \cdot \frac{FL2R}{\pi R^4} \quad (5.24)$$

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{FL}{\pi R^3} \quad (5.25)$$

From the values of F expressed in Table 5.3:
Class 20:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{816 \text{ kg } 457 \text{ mm}}{\pi (30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 328 \text{ MPa} \gg 138 \text{ MPa} = R \quad (5.26)$$

Class 25:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{907 \text{ kg } 457 \text{ mm}}{\pi(30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 365 \text{ MPa} \gg 172 \text{ MPa} = R \quad (5.27)$$

Class 30:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{998 \text{ kg } 457 \text{ mm}}{\pi(30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 402 \text{ MPa} \gg 207 \text{ MPa} = R \quad (5.28)$$

Class 35:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{1089 \text{ kg } 457 \text{ mm}}{\pi(30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 438 \text{ MPa} \gg 241 \text{ MPa} = R \quad (5.29)$$

Class 40:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{1179 \text{ kg } 457 \text{ mm}}{\pi(30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 474 \text{ MPa} \gg 276 \text{ MPa} = R \quad (5.30)$$

Class 45:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{1270 \text{ kg } 457 \text{ mm}}{\pi(30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 510 \text{ MPa} \gg 310 \text{ MPa} = R \quad (5.31)$$

Class 50:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{1361 \text{ kg } 457 \text{ mm}}{\pi(30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 547 \text{ MPa} \gg 345 \text{ MPa} = R \quad (5.32)$$

Class 60:

$$(\text{MOR})_{3p} = \sigma_{3p} = \frac{1542 \text{ kg } 457 \text{ mm}}{\pi(30.5 \text{ mm}/2)^3} \cdot \frac{9.8 \text{ N}}{\text{kg}} = 620 \text{ MPa} \gg 414 \text{ MPa} = R \quad (5.33)$$

$(\text{MOR})_{3p}$ is represented in front of the class of the cast iron (Fig. 5.6).

The strength that is necessary to apply to produce the breaking by bending is commonly more useful than tensile strength (strength/area of the section), because grey cast irons rarely work at pure tensile. Besides, the strength values for the breaking by means of transverse bending maintain a correlation with the tensile strength as it is possible to see in Table 5.3.

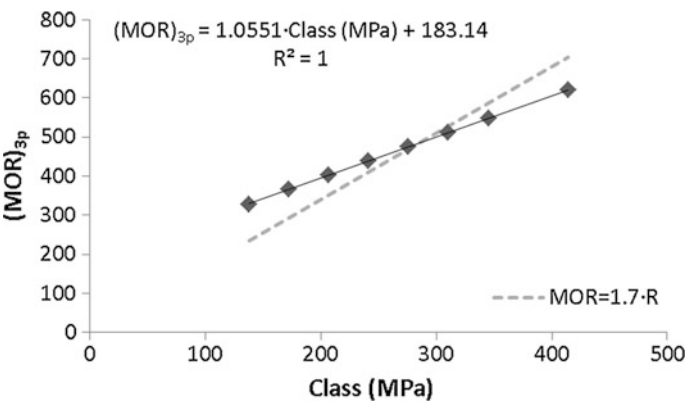


Fig. 5.6 Representation of $(MOR)_{3p}$ class of the cast iron

In Table 5.4, the equivalences between the more frequent mechanical properties of the grey cast irons of pearlitic matrix, measured over as-moulded samples *B* (of 30.5 mm or 1.2 in. of diameter) and the transverse bending test are shown. It can be checked that the higher the transverse strength (by bending), the higher the tensile strength (consequently, the lower the values of equivalent carbon), and also the higher the hardness, Young’s modulus, and shear modulus. Some applications of grey cast irons in the automotive industry are indicated for different *classes* in Table 5.5.

For metals (or any plastic solid), the strength measured in compression is the same as that measured in tension, Fig. 5.7. But for “brittle” solids, as grey irons, this is not so; for these, compressive strength is roughly 3 or 4 times higher than tensile strength. That is due to the lesser notch effect of graphite flakes in compression than in tension. And, for that reason, the only negative contribution is that because of the microcracks (filled in with graphite) the effective section of the matrix component is

Table 5.4 Mechanical properties of the more commonly used pearlitic grey cast irons

ASTM class	Tensile strength		Torsional strength	Compressive strength	Transversal Load. Sample B	Hardness	Young’s modulus	Torsion constant
	ksi	MPa	MPa	MPa	MPa	kg	HB	GPa
20	22.0	152	179	572	839	156	66–97	27–39
25	26.0	179	220	669	987	174	79–102	32–41
30	31.0	214	276	752	1145	210	90–113	36–45
35	36.5	252	334	855	1293	212	100–119	40–48
40	42.5	393	393	965	1440	235	110–138	44–54
50	52.5	362	503	1130	1638	262	130–157	50–55
60	52.5	431	610	1293	1678	302	141–162	54–59

Table 5.5 Applications of the grey cast irons in the automotive industry (according to the specification of the Society of Automotive Engineers J431)

ASTM class	SAE degree	Use
<i>Cast irons for common uses</i>		
18	G1800	Cast iron parts of different uses without treatment or annealed (strength is not a decisive feature)
25	G2500	Small engine blocks, cylinder heads, air-cooled cylinders, pistons, clutch discs, oil pumps bodies, gearboxes, clutch housing, brake drums for low power
30	G3000	Diesel and Otto engine blocks, cylinder heads, steering, differential crankcases, pistons, brake drums and clutch discs for medium strains
35	G3500	Diesel engine blocks, blocks and cylinder heads in lorries and tractors, large steering, crankcases in tractors, big gearboxes
40	G4000	Engine block, liners and pistons in diesel engines
<i>Cast irons for high power uses</i>		
25	G2500a	Brake drums and clutch discs for medium power, where high carbon content is required to avoid the presence of heating cracks
35	G3500a	Brake drums and clutch discs for high power, where hot-tearing resistance and high mechanical strength are essential requirements
35	G3500c	Drum brake for very high power
40	G4000d	Camshaft (see Case-Study in Chap. 10)

reduced. On the other hand, the compressive strength, as occurs with the tensile strength, grows when the class is increased, and therefore, when the carbon is reduced.

As also opposed to the steels and other metallic materials, see Fig. 5.7, grey cast irons do not follow the Hooke's law. Therefore, the Young's modulus obtained by means of the tensile test does not turn out constant. The stress/strain ratio decreases with the deformation as it is possible to see in Fig. 5.8.

It is commonly used as *Young's modulus* or *secant modulus* of a grey cast iron, the slope of the straight line that connects the origin of the tensile curve and the point of one-fourths of the tensile strength. Sometimes, less frequently, it is employed as Young's modulus the slope of the tangent line to the tensile curve at the origin (in this case is known as tangent modulus).

Young's modulus of grey cast irons can change considerably more than in other metallic materials. For low carbon content and flakes of lower size, the strain/stress ratio grows, and so the modulus increases. As for steels, Young's modulus calculated in tension is higher than the one obtained by torsion (see Table 5.4).

Because of the *good castability* of grey cast irons, it is possible to mould parts of thin walls, such as finned tubes employed in heat exchangers (Fig. 5.9), pump impellers, propellers for boats (ancient boats) (Fig. 5.10), boilers, boosters, etc.

To achieve a good castability, the interval of solidification should be as lower as possible. Or that which is the same, high values of equivalent carbon (summation of $\%C + \%Si/3 + \%P/3$).

Fig. 5.7 Stress–strain curve and strain elongation for different materials

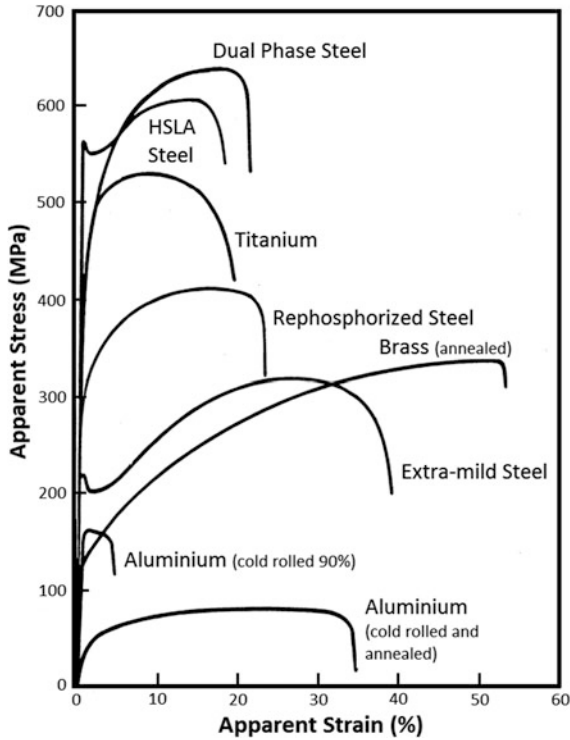
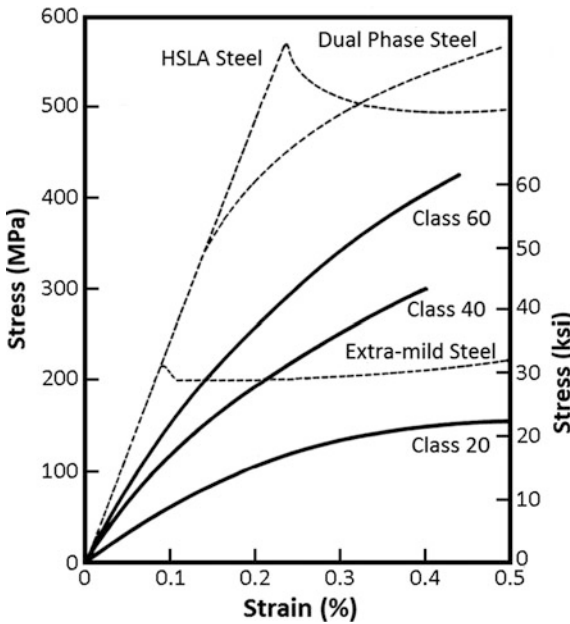


Fig. 5.8 Stress–strain curve —until 0.4% of elongation— of various lamellar grey cast irons (full lines) and some steels for the automotive industry (dotted lines)



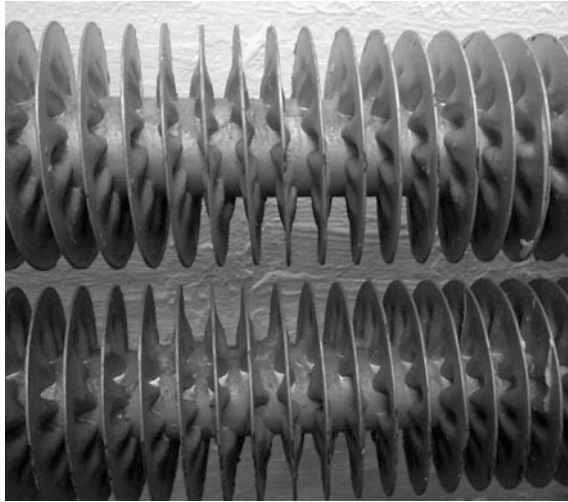


Fig. 5.9 Finned tube used in heat exchangers

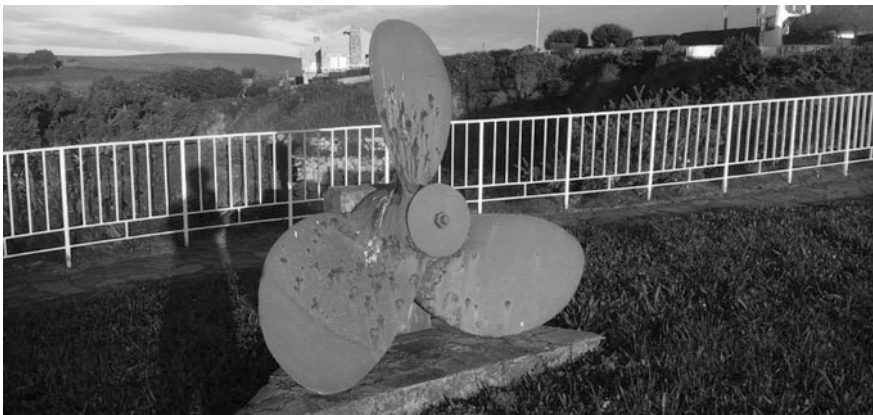


Fig. 5.10 Grey cast iron propeller used in an ancient boat

In this way, ornamental objects of grey cast iron—sculptures, cannons (Fig. 5.11), lampposts (Fig. 5.12), manhole covers (Fig. 5.13), anchors (Fig. 5.14), bandstand (Fig. 5.15), etc. are made from cast irons of equivalent carbon 4.25%, that is to say, eutectic. With the same purpose, hypereutectic cast irons can be used because pro-eutectic graphite does not impair the castability.

Hypereutectic cast irons will have lower tensile strength, because of the presence of graphite *C*, but this loss of mechanical features is irrelevant in the case of ornamental parts.



Fig. 5.11 Cannons of grey cast iron (placed in Puerto de Vega, Asturias, Spain)



Fig. 5.12 Lamppost of grey cast iron



Fig. 5.13 Manhole cover of grey cast iron



Fig. 5.14 Anchors for boats

Phosphorus in small amount can be also added to improve the castability. Phosphorus has a double effect: increases the equivalent carbon content and induces the appearance of the ternary eutectic of low melting point, *steadite* (responsible of a higher wear resistance and a lower toughness of the cast iron as well).

Conventional grey cast irons have a good corrosion resistance (higher than that of steels). Corrosion products remain trapped in the graphite skeleton, and in this way, the damage of the deepest zones is avoided.



Fig. 5.15 Bandstand of grey iron

Because of the good behaviour in water piping (both drinkable water and sewage), grey cast irons are used in subterranean pipes and outdoors pipes. The first water piping system was installed in 1455 in Germany. The use of grey cast irons in piping was spread out to other countries. For instance, between 1664 and 1668, a pipe of 7.9 km was installed to supply water to Versailles (France). Nowadays, to improve the corrosion resistance, many grey cast iron pipes are usually delivered with a bituminous coating.

In liquid and gases piping or in vessels, a good *tightness* is interesting with the purpose of avoiding the leaks or the losses of the gases or liquids (respectively) that circulate inside of the pipe. The lack of tightness in certain materials is consequence of the presence of interlinked porosity.

For the piping of oxidizing liquid, for instance, water, the tightness shortage is not too alarming: the oxides formation produces a soon covering of interstices. However, for oxidizing gases (mainly if the working conditions exceed the temperature of 450 °C), the interlinked porosity will also favour the *growth* (ref. Sect. 4.5.2).

The interlinked porosity mainly depends on the amount of graphite, and for that reason depends on the equivalent carbon of the cast iron. It should be considered that grey cast irons are composites of graphite and steel, whose coefficient of thermal expansion at high temperatures is significantly different, and for that reason,

graphite comes off easily from the matrix. Consequently, *the higher the carbon content, the higher the possibility of interlinked porosity.*

It is checked out that *avoiding porosity* is achieved with low graphite content, and for that reason low *equivalent carbon* is required (at the most 3.8%). The tightness of cast irons can be improved if phosphorus percentage is diminished (when phosphorus percentage exceeds 0.25%, interlinked porosity usually appears). To improve the soundness of grey cast irons, the reduction of the silicon content is advantageous (silicon should not be excessively reduced because of the possible chilling risks). As sulphur is concerned, it is recommended a maximum content of 0.12%.

The probability of interlinked porosity enhances with the number of eutectic cells. This happens, for instance, when a strong inoculation with calcium was performed. However, the effect of other inoculants that do not diminish the size of the eutectic cells can be even beneficial for the porosity control (for example, strontium). Logically, the graphite morphology has influence, so spheroidal graphite cast iron has more tightness than the flake's one.

Finally, shrinkage should be considered because of its influence in the tightness (although shrinkage in lamellar grey cast irons is only 1%, there is nearly zero shrinkage in spheroidal grey cast irons).

In this respect, macro-shrinkage is easily avoided (more than micro-shrinkage) if the following aspects are considered: an appropriate design, directional solidification and risers. Regarding the design, having a homogeneous wall thickness is convenient in pipes and other parts. Solidification shrinkage problems usually appear when there are changes of section, and in the joints between sections of different diameters (for example, in pipes of multiple joint). With the purpose of reducing micro-shrinkage, the use of cast irons with small interval of solidification (or equivalently, high equivalent carbon content) is reasonable. But in previous lines, we have already justified—for other reasons—the mistake of using (with the purpose of a good tightness) cast irons of high carbon content. Definitely, the reduction of micro-shrinkage should not be tackled from the compositional perspective; it should be tackled from the moulding practice point of view. For instance, the amount of gases dissolved in the liquid should be minimal, the internal stresses during the solidification should be avoided and the solidification should be directional.

Generally, grey cast irons are easily mechanized. However, occasionally, machining problems can appear because of the presence of surface defects (sand, defects linked with the design of the part or moulding practice defects): the existence of internal shrinkage in entering angles and in section changes, also the presence of white or mottled microstructures in thin sections and outgoing angles are unfavourable during the boring operations.

Graphite considerably influences the good machinability behaviour of grey cast irons. There are two aspects that explain this good behaviour: first, graphite breaks the shavings (as happens in free-machining steels with lead, tellurium or MnS inclusions) due to the discontinuity in the matrix caused by the graphite; second, graphite plays the role of tool lubricant. Definitely, *the machinability of the grey cast irons is higher than the machinability of the steels with the same hardness.*

Table 5.6 Grey cast irons machinability (data from ASM 1978)

Matrix microstructure	ASTM class	Yield stress (MPa)	Hardness (HB)	Cutting speed ^a (m/min)
Bainite	50	407	263	46
Alloyed fine pearlite	40	310	225	95
Ferrite (annealed)	–	108	100	293
Coarse pearlite without alloying	35	241	195	99

^aCutting speed: lowering 3280 cm³ produces a wear of 0.75 mm, in a carbide tool of only one cutting edge

The amount and kind of graphite—apart from the nature of the matrix: ferritic, coarse pearlite, fine pearlite, bainitic (Table 5.6)—have influence in the machinability, and in the quality of finishing. Generally, the quality of finishing is better when the equivalent carbon is high without reaching the hypereutectic value: that is because the coarse flakes of lamellar graphite C give a worse superficial quality, and for that reason the presence of graphite C is not recommended when a careful machinability is desired (for instance, threads). Within cast irons of hypoeutectic equivalent carbon, the fine flakes of graphite D, which are not desired in other situations (involves direct ferritizing), provide the best quality of finishing. Spheroidal cast irons have a machinability that is like the machinability of lamellar cast irons with the same hardness.

The wear resistance is excellent in both grey cast irons and white cast irons.

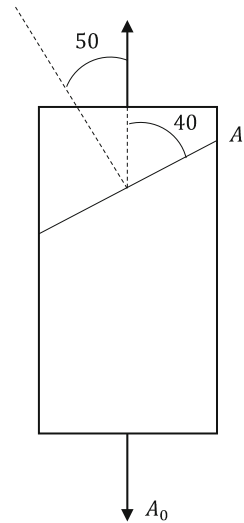
The excellent wear resistance of white cast irons (ref. Sect. 9.1) makes that this kind of cast irons cannot be machined. The wear resistance of grey cast irons (the same as the machinability) depends on the type of graphite and the matrix nature. Graphite types B and D are not recommended because of the appearance of soft ferritized areas usually in the boundaries. For that reason, the matrix will present non-homogeneous hardness areas with the associated uneven wear. Pearlitic cast irons of graphite type E are interesting because they do not make favourable the ferritizing process, and also the cast iron has higher mechanical resistance as a consequence of the low carbon content (slightly hypoeutectic).

Wear resistance can be improved in grey cast irons through thermal treatment (hardening of the matrix)—induction or flame scarfing are sometimes employed in the local hardening of the guides in benches of machine tool—or by means of the use of an appropriate chemical composition (matrix structure will be bainitic or martensitic only by moulding and air cooling).

Thermal treatment of nitriding can be also used in the hardening of grey cast irons. This can be done when the grey cast iron has a suitable composition. For instance, a grey cast iron of 1.6 Cr wt%, 1.4 Al wt%, 2.6 C wt% and 2.5 Si wt% could be nitrided.

It is necessary to mention that brazing with appropriated filler metal should be used as welding technique in low-alloyed grey irons. Previously, superficial graphite should be removed, if not, and because of the low surface energy solid/gas,

Fig. 5.16 Scheme of the problem



graphite would not be wetted by the alloying metal and the joint would be imperfect.

Removing the superficial graphite can be achieved by means of different methods, such as the electrochemical dissolution, mechanical dragging or simply burning of the graphite with an oxidizing flame. Graphite removal is easy when its morphology is nodular or spheroidal.

Exercise 5.6. A cylinder of cast iron 0.50 in. in diameter by 2 in. long is tested in compression. Failure occurs at an axial load of 50000 lb on a plane inclined 40° to the axis of the cylinder. Calculate the shearing stress on the plane of failure. The same cylinder of cast iron is pulled in tension. Give your estimate of the failure load and the plane of failure (Fig. 5.16).

Question

$$A = \frac{A_0}{\cos 50} = \frac{A_0}{\sin 40} \quad (5.34)$$

Shear stress on the plane of failure:

$$\tau = \frac{P}{A} \cdot \cos 40 = \frac{P}{A_0} \cdot \sin 40 \cdot \cos 40 \quad (5.35)$$

$$A_0 = \frac{\pi \cdot (0.5)^2}{4} \text{ in}^2 \quad (5.36)$$

$$\tau = \frac{50000}{\frac{\pi \cdot (0.5)^2}{4}} \cdot \sin 40 \cdot \cos 40 \cdot \frac{1 \text{ ksi}}{1000 \text{ psi}} \simeq 125 \text{ ksi} \quad (5.37)$$

In tension, the failure stress will be 3 or 4 times lower (30–40 ksi). The plane of failure (cleavage plane) will be at 90° of the tension direction, and it will take place through the flakes of cementite (cleavage, brilliant colour) or along the graphite flakes (grey colour).

Abstract

The main advantage of cast irons is the possibility of obtaining near-shape parts by moulding, without forging after solidification. The term *malleable* refers to the possibility of conferring more deformability to the cast irons through heat treatment in solid state. Two kinds of ferritic malleable irons will be described in this chapter, white and black heart malleable cast irons. Malleablizing treatment in *white heart malleable cast irons* is based on the decomposition of the cementite into iron and carbon atoms, diffusing then the carbon towards the periphery where it oxidizes, being modified the chemical composition of the initial white cast iron. In the case of *black heart malleable cast irons*, the chemical composition of the original white cast iron is not modified, and cementite is decomposed into carbon, which transforms into nodular graphite, and austenite, which allows obtaining either pearlitic or ferritic matrix depending on the cooling conditions after its transformation.

6.1 Malleable Cast Irons

Malleable does not seem a good name for a cast iron. Because of the high carbon content, cast irons do not have the deformability features that can explain (at temperatures lower than the eutectoid) the name *malleable*. On the other hand, the theoretical possibility of deforming white or grey cast irons above the eutectoid temperature, in gamma state at 900–950 °C, do not have practical interest because of the technical difficulties that imply.

The use of cast irons is advantageous just for the obtaining of directly near-shape parts by moulding, without the requirement of forging after solidification. Generally, mechanical properties of as-cast parts are, however, insufficient for certain

applications. For that reason, the advantage of malleable cast irons is that despite being cast irons, they can subsequently improve their properties, namely, ductility. The name of these cast irons refers to the possibility of *malleablizing* or conferring *more deformability*, by means of heat treatment in solid state to parts previously obtained through casting.

Parts that can be treated are white cast irons. If a grey cast iron was used, the flake graphite would impede (because of the notch effect) that the cast iron, once *malleablized*, had the elongation and toughness characteristics that can be achieved after the malleabilization process. To the above mentioned, the negative influence of the graphite during the diffusion that requires the heat treatment would be added.

As said, malleable iron is a cast ferrous metal that is initially produced as white cast iron, then is heat treated to convert the carbon-containing phase from iron carbide to a nodular form of graphite usually called temper carbon. There are two types of ferritic malleable iron, *black heart*, and *white heart* malleable cast irons. Only the black heart type is produced in the United States.

6.2 White Heart Malleable Cast Iron

Malleablizing heat treatment has as objective the cementite decomposition (both the ledeburitic and the pro-eutectoid cementite) into γ -iron and carbon atoms. Therefore, with the purpose of *malleablizing* parts of white cast iron, these parts must be of small thickness (no higher than 20 mm). Like this, carbon atoms, and also carbon atoms dissolved in the austenite, can diffuse until the part surfaces, and there, carbon can oxidize as CO_2 . To achieve this process is also required an oxidizing atmosphere in the place where the heat treatment is performed.

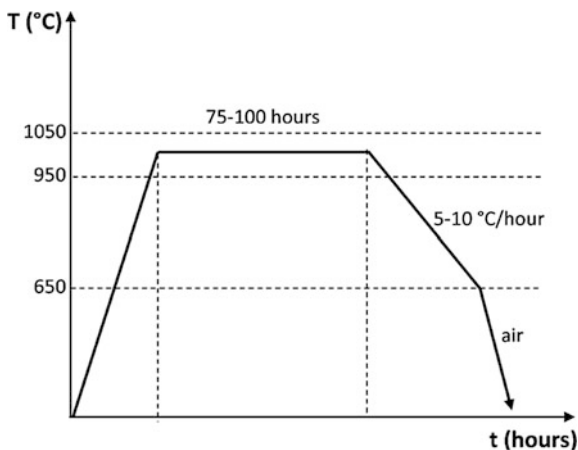
The final structure of the parts is ferrite, which is suitable to be fusion welded and metallically coated (for instance, galvanizing or tin-plating). Mechanical strength and tensile elongation of the parts are equivalents to the ones of moulded ferritic steel.

Note that moulding parts of ferritic steel would require pouring temperatures higher than 1538 °C. On their behalf, the malleablized parts were poured at temperatures that were considerably lower because of their initial composition of hypoeutectic cast irons.

The malleablizing process is mainly an oxidizing annealing (Fig. 6.1). Before the heat treatment, white cast iron parts are usually packed up in boxes with a material that provides oxygen, such as iron oxide. Afterwards, parts are heated at a temperature of 950–1050 °C and then are held between 75 and 100 h. This is to ensure that all cementite splits up into carbon and iron atoms. Simultaneously, decarburizing the austenite is also expected, which at the heat treatment temperature can have between 1.4 and 1.7 wt% C in solid solution.

Thus, the reactions that are mentioned take place at this temperature and remains gamma iron with some carbon in solid solution (austenite), because its migration towards the part surfaces is not complete:

Fig. 6.1 Heat treatment cycle used for obtaining white heart malleable cast iron



$\text{Cementite} + \text{O}_2 \rightarrow \text{CO}_2 + \text{Fe}_\gamma$ (with C in solid solution) at 950 – 1050 °C

$\text{Austenite} + \text{O}_2 \rightarrow \text{CO}_2 + \text{Fe}_\gamma$ (with C in solid solution) at 950 – 1050 °C

Not every carbon dissolved in gamma iron reach the surface of the part by diffusion, and for that reason, from this temperature down to temperatures lower than the eutectoid, the cooling should be very slow (from 5 to 10 °C per hour).

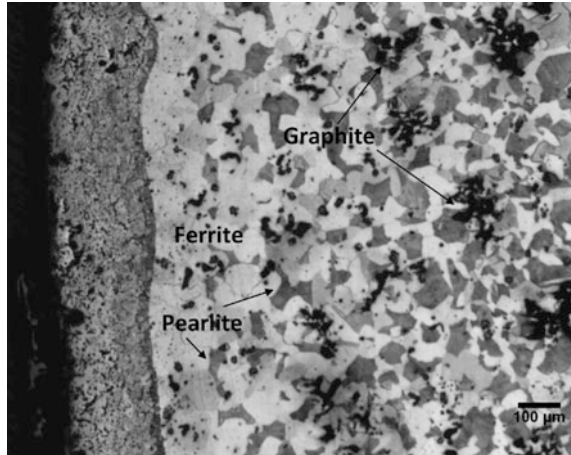
If the part is cooled like this down to 650 °C, the carbon migration towards the part surfaces will favour its conversion into CO_2 , and specially, the formation of pro-eutectoid and eutectoid (pearlitic) cementite is avoided. Under these conditions, the outside of the part, with decarburized austenite, will easily transform into ferrite, even in metastable cooling. However, the inner zones of the part, whose austenite did not eliminate all its carbon, would produce pearlite.

Reached the temperature of 650 °C, parts are presumably ferritized and the boxes can be removed from the furnace. The total duration of the treatment is normally around 6 days: one for heating, three of maintenance at high temperature and two days of cooling from the high temperature down to 650 °C (Fig. 6.1).

With the heat treatment that was already mentioned, it is possible to achieve a microstructure thoroughly ferritic at room temperature. See Fig. 6.2, dark ring of ferrite and core of pearlite. Sometimes, some nodules of graphite are also registered in the centre of the part when the size is higher than 7 mm. These nodules are formed by combination of carbon atoms, produced by cementite decomposition at the heat treatment temperature, which are impeded to diffuse towards the outsides of the part.

The *composition of the original white cast iron* must be hypoeutectic. That is because less carbon should be removed. The common percentages of this element range within 2.9 and 3.3%. Lower values would compromise the castability. Silicon improves this property and favours the decomposition of the cementite. However, silicon content should be restricted with the purpose of avoiding the possibility of a

Fig. 6.2 White heart malleable cast iron. The malleablizing treatment was based on a heating up to 1060 °C in 8 h; holding at that temperature for 80 h; and cooling down to room temperature in 12 h



stable solidification (grey or mottled iron). Habitually, silicon ranges within 0.45 and 0.75%. The same happens with sulphur content that should be low (maximum 0.20%), to avoid the formation of FeS–Fe eutectic that would melt down during the heat treatment. Manganese must compensate sulphur (1.72% S + 0.15%) with the purpose of achieving the combination of manganese with sulphur to obtain MnS. Phosphorus content should be also low. The maximum percentage of phosphorus should be lower than 0.15% to avoid the formation of steadite that also would melt down at the heat treatment temperatures.

The following values are representatives of the mechanical properties of the white heart malleable cast iron: 350 MPa of tensile strength (higher than the one of a ferrite without silicon), 5–15% of elongation (in very thick walls an elongation of 25% could be achieved) and Brinell hardness of 150 HB.

White heart malleable cast iron is used in parts of small thickness and complex shapes whose manufacture by means of solidification would result advantageous in comparison with forming through forging. Nowadays, sintered alloys compete advantageously with the white heart malleable cast irons for a lot of applications.

Exercise 6.1. Calculate the rough malleabilization time of a part of white cast iron (3% C-0.5% Si), at 1000 °C, with the purpose of obtaining a white heart malleable cast iron in a thickness of 2 mm. Suppose that the ferritized area has carbon contents within 0.02 and 0.1 %.

$$\text{Data : } D_C^{\gamma} (\text{cm}^2/\text{s}) = 0.2 \cdot \exp(-142000 \text{ J}/\text{RT})$$

Question

The profile concentration–penetration (C_x, x) of carbon is obtained by solving the second Fick's law of the diffusion in non-stationary regime. The result is

$$\frac{C_S - C_x}{C_S - C_0} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (6.1)$$

where

$C_S = 0.02$ is the carbon content in the surface of the part,
 $C_x = 0.1$ is the carbon content when $x = 2$ mm of distance from the surface of the part (ferritized area),
 C_0 is the carbon content in the austenite at 1000 °C,
 x is the distance from the surface and
 t is the treatment time.

The first step is calculating C_0 by means of the metastable diagram at 1000 °C and using similar triangles (Fig. 6.3):

$$\frac{1148 - 1000}{2.1 - C_0} = \frac{1148 - 727}{2.1 - 0.77} \quad (6.2)$$

$$2.1 - C_0 = \frac{148}{317} \rightarrow C_0 = 1.63 \quad (6.3)$$

The analytical solution is

$$\frac{0.02 - 0.3}{0.02 - 1.63} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \rightarrow \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \simeq 0.17 \quad (6.4)$$

If we go to Table 6.1 where the values of the error function are shown,

$$\frac{x}{2\sqrt{Dt}} \simeq 0.15 \rightarrow x = 0.3\sqrt{Dt} \quad (6.5)$$

At 1000 °C,

Fig. 6.3 Representation of the %C as a function of the temperature

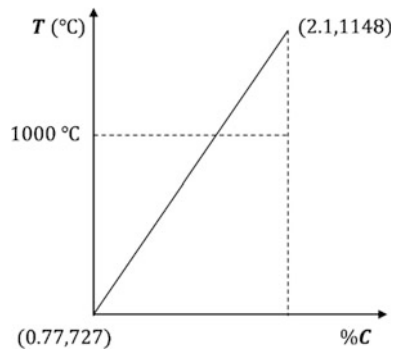


Table 6.1 Error function values

<i>z</i>	erf (<i>z</i>)	<i>z</i>	erf (<i>z</i>)	<i>z</i>	erf (<i>z</i>)
0	0.00000	0.55	0.56332	1.20	0.91031
0.05	0.05637	0.60	0.60386	1.30	0.93401
0.10	0.11246	0.65	0.64203	1.40	0.95229
0.15	0.16800	0.70	0.67780	1.50	0.96611
0.20	0.22270	0.75	0.71116	1.60	0.97635
0.25	0.27633	0.80	0.72410	1.70	0.98379
0.30	0.32863	0.85	0.77067	1.80	0.98909
0.35	0.37938	0.90	0.79691	1.90	0.99279
0.40	0.42839	0.95	0.82089	2.00	0.99532
0.45	0.47548	1.00	0.84270	2.50	0.99959
0.50	0.52050	1.10	0.88021	3.00	0.99997

$$D_C^{\gamma} = 0.2 \cdot \exp\left(-\frac{142000}{8.31 \cdot 1273}\right) \text{cm}^2/\text{s} = 2.96 \times 10^{-7} \text{cm}^2/\text{s} \tag{6.6}$$

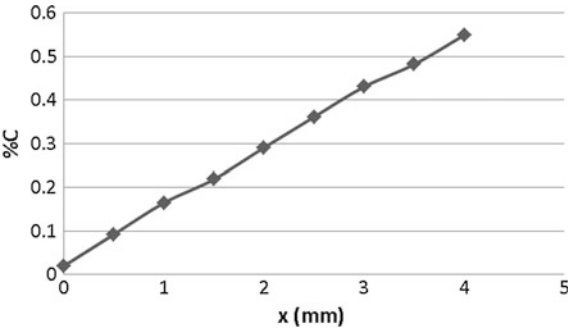
And finally,

$$x = 0.3\sqrt{Dt} \rightarrow t = \frac{x^2}{0.3^2 \cdot D} = \frac{0.2^2}{0.3^2 \cdot 2.96 \times 10^{-7}} = 417 \text{ h } (\simeq 17 \text{ days}) \tag{6.7}$$

The duration of the treatment is in this case 2 times higher than the conventional treatment that is performed with the purpose of achieving a white heart malleable cast iron (6–7 days). Enclosed to this exercise the profile concentration–penetration for a malleabilization treatment of 17 days at 1000 °C is shown (Fig. 6.4). See in Fig. 6.2, an example of white heart malleable cast iron.

Exercise 6.2. A microstructure like that one of the ferritic steels can be obtained in the contour of a white cast iron by decarburization (oxidation). By carburization (case-hardening) of steel in solid state, could be obtained in the surface of the part a microstructure like that one of a white cast iron?

Fig. 6.4 Representation of the %C as a function of the distance *x*



Question

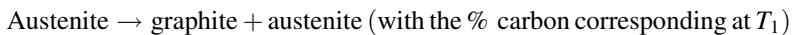
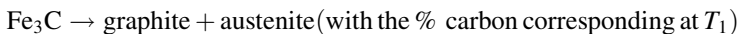
No. The maximum carbon content, which could be achieved in the proposed situation, is that one that saturates the austenite at the treatment temperature. There are neither ledeburite nor pro-eutectoid cementite in the microstructure of a case-hardened steel. In any case, lampblack (carbon dust) will appear in the contour of the part.

6.3 Blackheart Malleable Cast Iron

The heat treatment for malleablizing a white cast iron by means of transformation of cementite into graphite, *without modifying the chemical composition of the cast iron*, provides a metallic material that is usually known as blackheart malleable cast iron. This process that is used in the malleabilization of cast irons was first employed in USA, in Newark, in 1830.

The heat treatment is performed in neutral atmosphere, or in controlled atmosphere, to avoid that the carbon that was obtained from the cementite decomposition was oxidized again. Exactly, the opposite to what happens when a white heart malleable cast iron is manufactured.

In this case, the chemical composition of the original white cast iron is not modified, and the chemical reactions for the malleabilization, in austenitic state, at temperatures T_1 of 890–950 °C, are mentioned below:



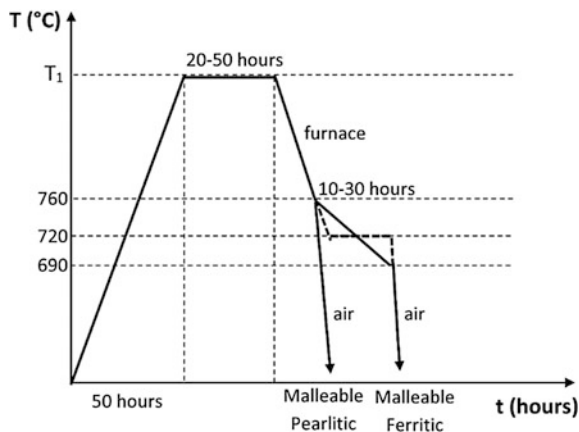
Graphitization could be achieved in lower times at temperatures (T_1) higher than 950 °C, but graphite would grow as lamellar, and this kind of graphite is unfavourable for toughness. With temperatures in the range 850–950 °C nodular morphologies are obtained. These morphologies give good toughness.

The time at the temperature T_1 lasts between 20 and 50 h depending on the carbon content of the white cast iron part. The lower the carbon content and the higher the silicon content (it should be remembered that is a graphitizing element), the lower the heat treatment duration. Obviously, as said, silicon content should be controlled with the purpose of avoiding stable solidification (mottled or grey iron) at the end of the solidification whether the silicon percentage is very high.

Adequate silicon content should be ensured (within precautionary limits) to the castability loss counteract that implies the low carbon content in the original white cast iron. Silicon and carbon usually keep the next relation:

$$3.5\% < \text{C}\% + \text{Si}\% < 3.9\%$$

Fig. 6.5 Heat treatment cycle used for obtaining blackheart malleable cast iron



Silicon percentages range between 1.25 and 1.55%.

Sulphur, manganese and phosphorus percentages are those that were mentioned in the white heart malleable cast iron situation.

The carbon content is lower in blackheart malleable cast irons than in the white heart malleable cast irons. In the first one cementite transforms into graphite. For that reason, the mechanical properties (tensile strength, elongation), as happens in grey cast irons, are better when the graphite content diminishes.

Carbon content is commonly comprised within 2.1 and 2.8%. These values advise us to obtain the cast iron in an electric furnace. In cupola furnaces, achieving carbon contents lower than 2.8% is complicated because the cast iron easily absorbs carbon because of the contact between the liquid cast iron and the coke.

The heat treatment cycle for achieving a blackheart malleable cast iron is represented in Fig. 6.5: 50 h in heating, from the room temperature up to the temperature T_1 ; between 20 and 50 h of holding time at T_1 —lower time and for that reason cheaper than obtaining the white heart malleable cast iron—; and different cooling rates depending on the required matrix, although, in any case, the cooling down to 760 °C is done as fast as the thermal inertia of the furnace allows.

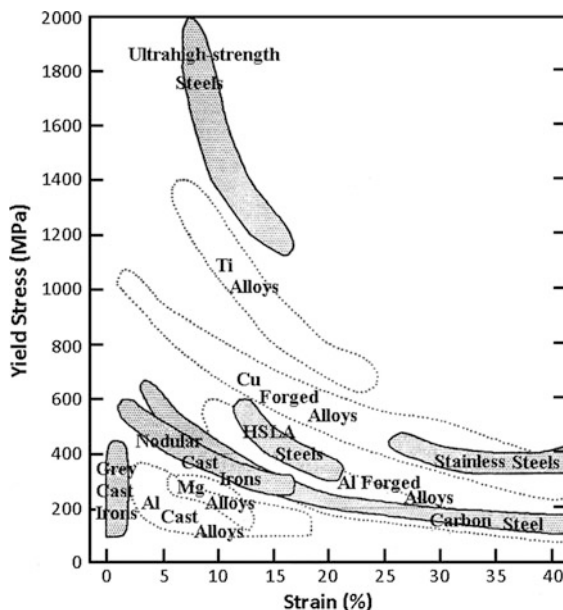
6.3.1 Ferritic Blackheart Malleable Cast Iron

Achieving a thoroughly ferritic matrix requires a very slow cooling down to temperatures below the eutectoid. The reason is that transformations will follow the Fe–C stable diagram.

Descending from 760 to 690 °C should take between 10 and 30 h. This slow cooling is sometimes replaced, with the purpose of diminishing the operation time, by an isothermal holding at 720 °C that is called second graphitization. The first graphitization would be that performed at 890–950 °C.

Once obtained a ferritic matrix, parts are air cooled.

Fig. 6.6 As opposed to other materials, lamellar grey cast irons do not have yield strength



The blackheart malleable cast iron, of ferritic matrix, Fig. 4.7, has a tensile strength between 250 and 375 MPa, yield strength between 160 and 250 MPa (*lamellar grey cast irons do not have yield strength*) see Fig. 6.6, and elongation that can even reach 25%. Nevertheless, in the worst situation, elongation is higher than in the grey cast irons situation.

In these malleable cast irons, as happens in grey cast irons and as opposed to steels, tensile strength evolves in the same way that elongation: the higher the tensile strength (that means a low amount of graphite), the higher the elongation.

Ferritic blackheart malleable cast iron is used in the automotive industry, expansion joints in bridges, pressure valves, etc.

The presence of ferrite would make supposing that these malleable cast irons could be fusion welded, but it is not possible because after melting, ledeburite would be obtained in the subsequent solidification. Blackheart malleable cast irons have the same composition that the original white cast iron.

Ferritic malleable cast irons are susceptible of heat treatment. In this way, by means of austenization at 840–870 °C, and subsequent air cooling it is possible to achieve a pearlitic matrix. The tensile strength would be of 550 MPa and the elongation of 3–4%. This possibility of heat treatment also justifies the use of a case-hardening which transform the matrix constituent into martensite.

6.3.2 Blackheart Malleable Cast Iron of Pearlitic Matrix

The pearlitic matrix can be directly obtained after the first-stage malleabilization treatment. Simply by air cooling from the temperature of 760–780 °C, the eutectoid austenite will transform into pearlite, by following the Fe–C metastable diagram.

When the cooling between the temperature T_1 and 760–780 °C is very slow, then unfavourable areas of ferrite can appear, because of the *direct ferritization*, in the boundaries of the nodular graphite (Fig. 6.7).

The properties of the blackheart malleable cast irons of pearlitic matrix and the ones of ferritic matrix are related between them, as the pearlitic and the ferritic steels properties are related between them.

Pearlitic cast irons have more tensile strength than the ferritic cast irons— R_m of the pearlitic, between 400 and 600 MPa—also more hardness and lower ductility. Their elongation is usually between 10 and 2%. But, as opposed to the ferritic blackheart cast irons, R_m and elongation (%) evolve in the contrary direction as happens in steels (R_m diminishes when elongation grows).

Pearlitic cast irons have a good *damping capacity* (damping capacity is the ability of a material to quell (absorb) vibrations and to dissipate the energy as heat, or simply the relative ability to stop vibrations or ringing; or can be also defined as the internal energy dissipation at large stresses and strains). By the contrary, these cast irons have a lower machinability than the ferritic cast irons. Pearlitic cast irons have an excellent wear resistance and provide a suitable behaviour to alternating stresses that could produce fatigue.

The pearlitic blackheart malleable cast iron can be thermally treated. For instance, after the first malleabilization annealing, it can be oil-quenched. The times required for martensite (formed during the oil-quenching) tempering are usually of 2 h, or even more, to achieve microstructure uniformity. The globulization of cementite in a pearlitic cast iron is also possible by means of a subcritical annealing. These structures of globular pearlite, which are obtained with lower costs, compete

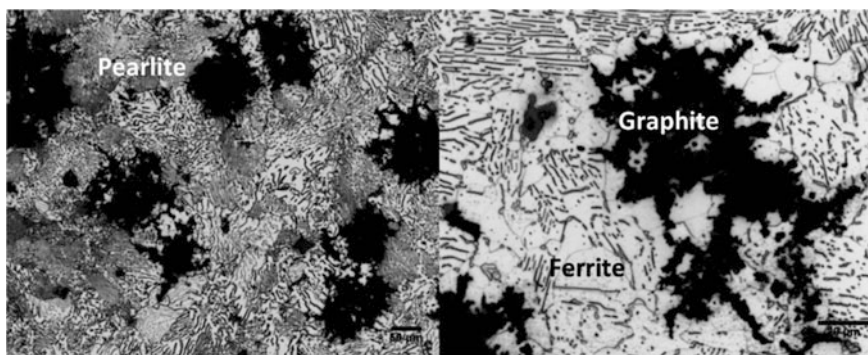


Fig. 6.7 Blackheart malleable cast iron. Direct ferritization areas between the nodular graphite and the pearlite. Nital 2 etched

in their applications with the structures of tempered martensite. Obviously, these structures of globular pearlite have a lower toughness.

The castability and excellent properties that can be achieved after the malleabilization (for obtaining nodular graphite) justify the large field of industrial applications. These cast irons are usually competitive with steels in some parts of agricultural vehicles, railway elements and some automotive components (gear assemblies, connecting rods, pistons, camshafts and generally complex shape parts) that are advantageously obtained through casting, which is cheaper than forming (forging) usually required for steel components.

White heart malleable cast irons cannot be used in broadly applications. That is consequence of the thickness limitations, the difficulty for being manufactured by mass production, the expensiveness of the malleabilization (due to the time-consuming heat treatment) and the lower mechanical strength.

The great series of blackheart malleable cast irons usually have not thicknesses higher than 40 mm. However, great quantity of parts until 100 mm thickness and 150 kg weight are also produced. Malleable cast iron parts advantageously compete with sintered parts.

Exercise 6.3. Demonstrate that the tendency to the graphitization of a blackheart malleable cast iron of pearlitic matrix can be corrected or attenuated with the addition of 2% Cr.

Data : $\varepsilon_C^{\text{Cr}} = -5.87$

Question

Chromium is α -forming element, although for lower contents than 5% diminishes the temperature A_3 . In Fig. 8.6, it is shown how the eutectoid temperature is moved towards above and left. For instance, at 740 °C, the carbon content in the eutectoid austenite with 2% chromium would be, approximately, 0.76. From the equations:

$$\ln \gamma(C) = \ln \gamma^\circ(C) + \varepsilon_C^C \cdot x_C \text{ (austenite without chromium)} \quad (6.8)$$

$$\ln \gamma'_{\text{Cr}}(C) = \ln \gamma^\circ_{\text{Cr}}(C) + \varepsilon_C^C \cdot x_C + \varepsilon_C^{\text{Cr}} \cdot x_{\text{Cr}} \text{ (austenite with chromium)} \quad (6.9)$$

By differencing both equations,

$$\ln \frac{\gamma'}{\gamma} = \varepsilon_C^{\text{Cr}} \cdot x_{\text{Cr}} \quad (6.10)$$

For the chromium, $\varepsilon_C^{\text{Cr}} = -5.87$; $x_{\text{Cr}} = 0.02$ (Fe and Cr atomic weights are similar)

$$\ln \frac{\gamma'}{\gamma} = -5.87 \cdot 0.02 = -0.12 \quad (6.11)$$

$$\frac{\gamma'}{\gamma} = 0.89 \quad (6.12)$$

$$\gamma \cdot x_C = \gamma' \cdot x'_C \quad (6.13)$$

$$\frac{x_C}{x'_C} = \frac{0.69}{x'_C} = 0.89 \quad (6.14)$$

$$x'_C = 0.76 \quad (6.15)$$

That is, the carbon content in the austenite (stable diagram) would be increased from 0.68 to 0.76; carbon would hardly diffuse into the austenite from the Fe_3C to the graphite. Destabilizing the cementite would be very difficult and the growth would be minimal. It should be also considered that chromium favours the metastable solidification.

Exercise 6.4. Why or why not seems right the following chemical composition for a blackheart malleable cast iron: 2.5% C–0.15% Si–0.5% Mn–0.15% S– < 0.1% P?

Question

The typical chemical composition of a blackheart malleable cast iron is

$$\%C \rightarrow 2.1-2.8\%$$

$$\%Si \rightarrow 1.25-1.55\%$$

The summation of the carbon and silicon percentages should verify the following relation:

$$3.5\% < \%C + \%Si < 3.9\%$$

Regarding the rest of alloying elements of the cast iron, the next relationships will be established:

$$\%Mn \rightarrow 1.72\%S + 0.15\% = 0.41 < 0.5$$

$$\%S \rightarrow < 0.2\%$$

$$\%P \rightarrow < 0.15\%$$

Table 6.2 Restrictions satisfied and not

%C	%Si	%C + %Si	%Mn	%S	%P
✓	↓	↓	✓	✓	✓

Table 6.2 shows, for the proposed chemical composition, which of the restrictions above mentioned are satisfied and which not.

This chemical composition does not seem adequate for manufacturing a blackheart malleable cast iron. That is because the silicon content is very low. Adequate silicon content is important because it allows for reducing the treatment times and also compensates the castability loss that implies the low carbon contents in the original white cast iron. The upper limits should be adjusted with the purpose of avoiding grey cast irons or mottled cast irons at the end of the solidification.

Exercise 6.5. Why or why not can be welded by autogenous welding a blackheart malleable cast iron? And a white heart malleable cast iron?

Question

Autogenous welding is a kind of joint where the part edges are heated up to the melting point by means of the heat that is produced by the combustion of a certain gas. Normally, it is a process of fusion welding without external soldering.

The presence of ferrite would make supposing that the blackheart malleable cast irons could be fusion welded. Nevertheless, this is not possible because after the local melting, ledeburite will be formed in the subsequent cooling. That is consequence of that all blackheart malleable cast irons (independently of the matrix) have the same chemical composition that the original white cast iron.

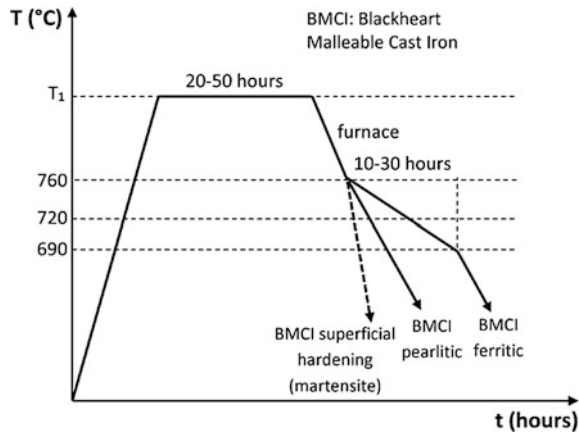
Blackheart malleable cast irons have after the malleabilization treatment a microstructure mainly ferritic (low carbon content) with a chemical composition different from the original white cast iron, and for that reason can be fusion welded.

Exercise 6.6. It is possible to read in a catalogue that a blackheart malleable cast iron (BMCI) can be hardened. Is this information a catalogue mistake?

Question

It is not a mistake because blackheart malleable cast irons are susceptible to heat treatment (Fig. 6.8). In this way by austenization at 840–870 °C followed by air cooling, a pearlitic matrix (with improvement in the properties) can be achieved.

Fig. 6.8 Structures that can be obtained in a blackheart malleable cast iron



This possibility of heat treatment explains that sometimes these cast irons are subjected to superficial hardening with the purpose of achieving a hardening of the matrix constituent consequence of its transformation into martensite.

Spheroidal Graphite Cast Irons (or Ductile Cast Iron)

7

Abstract

The main disadvantage of grey cast irons, regarding the mechanical properties, is the notch effect caused by the flakes of graphite. A model proposed to describe the grey cast irons is a steel with cavities filled with graphite. If this lamellar graphite is transformed into spheroidal graphite, mechanical properties will improve. This chapter is, for that reason, dedicated to the cast irons with spheroidal graphite, and particularly to the austempered ductile irons (ADI). ADI irons are spheroidal graphite cast irons of bainitic matrix with growing interest consequence of the excellent mechanical properties that make them competitive with steels.

7.1 Chemical Composition

During the solidification of a grey cast iron, graphite with spheroidal shape can be formed by the addition of heterogeneous nucleating agents, such as magnesium–nickel or magnesium–iron–silicon. These nucleating agents favour, through epitaxy or crystallographic similarity, the spheroidal shape of the nucleated graphite, when there are no traces of titanium, lead, tin, arsenic and bismuth.

For obtaining spheroidal graphite, it is necessary to begin from very pure raw materials, with sulphur contents lower than 0.01%—it is compulsory to reduce the content in this element until this value before the addition of the nucleating agents—and phosphorus contents lower than 0.04% to avoid the reactions and interferences with the magnesium action. The cast iron can be manufactured in smelting pot, in electric furnace or in induction furnace.

Magnesium action is simply clustering. The effective amount of magnesium incorporated into the chemical composition of the alloy, once solidified, is nearly irrelevant (0.03–0.05% Mg). But magnesium produces undercooling during the eutectic solidification, with the subsequent tendency to chill, and for that reason the silicon content—between 2.4 and 2.8%—should be higher than in lamellar grey cast irons. The equivalent carbon of the spheroidal graphite cast irons is convenient to be slightly hypereutectic—4.3–4.8% C—to improve the castability, and making possible the moulding of complex geometry parts. Carbon common percentages, between 3.5 and 3.8% C, emerge higher than in non-alloyed grey cast irons.

Graphite, former constituent of the stable eutectic, is formed in the liquid in favourable growing conditions as spider web, radial shape (Fig. 2.3). Probably, the nucleation and growing of the austenite are delayed, and in that conditions the appearance of spheroids is made possible, well developed, before being surrounded by the proportional amount of austenite. Once formed these eutectic cells, and before of the liquid exhaust, graphite spheroids grow through a reaction like the peritectic: by diffusion of carbon atoms from the liquid to the graphite nodule, through the austenite wrap.

Experimentally, it is possible to verify that *increasing the solidification rate diminishes the size of these graphite nodules*. This is logical because of the formation of higher number of graphite nuclei, and therefore higher number of eutectic cells. In very fast cooling rates, there are chilling risks (mentioned in relation to the lamellar graphite grey cast irons). All about the massivity factor previously mentioned is valid in this case.

Because of the silicon graphitizing behaviour, it is possible to appreciate a refining of the graphite spheroids when silicon content is increased in the cast iron.

Volume increase produced in the solidification of graphite with spheroidal shape approximately compensates the shrinkage in the liquid–solid transformation. Therefore, in these cast irons, *the shrinkage is nearly non-existing*, lower than 0.7%—while in grey cast irons the shrinkage would be of around 1%, and in the case of white irons and non-alloyed as-cast steels would be of around 2%—and makes unnecessary the risers.

Once the solidification ended, a microstructure of graphite spheroids dispersed in the metallic matrix of austenite is achieved. In the cooling, from this eutectic temperature down to the room temperature, different austenite transformations can give ferritic, pearlitic, bainitic or martensitic matrices.

In *medium alloy* cast irons, the percentage of carburigen elements should be limited because they are antigraphitizing agents, that are the cases of chromium (added with the purpose of improving the heat behaviour), molybdenum (added to move the pearlitic nose and promote bainitic transformations) and manganese (stabilizer of the pearlite). Habitually, molybdenum and chromium percentages are lower than 0.3%. Manganese percentage is usually lower than 1%. The same as in lamellar graphite grey cast irons, contents in alloying elements *should be adjusted according to the massivity factor* and desired matrix structures.

Austenite does not undergo transformations during the cooling of *spheroidal graphite cast irons highly alloyed with nickel* and so, spheroidal graphite cast irons with *austenitic matrix* can be obtained at room temperature. For some applications where corrosion resistance is required (for instance, in valves, chemistry pipes, shipbuilding industry) austenitic matrix cast irons with a 15–35% of nickel are commonly used.

Exercise 7.1. A non-alloyed ductile cast iron has the following chemical composition: 3.5% C–2.4% Si–0.025% Mg and irrelevant contents in P, S, Cr, Mo, Al, Cu, Ti, Sn, Co, V, Pb, Nb and W. Demonstrate that, thermodynamically, this cast iron can solidify as spheroidal graphite cast iron.

Data: $\gamma_0 = 2.3$; $\varepsilon_C^C = 3.9$; $\varepsilon_C^{Si} = 7.6$; $\varepsilon_C^{Mg} = 6.8$.

Question

Carbon and silicon mole fractions are approximately calculated:

$$x_C = 0.035 \cdot \frac{55.85}{12} = 0.16 \quad (7.1)$$

$$x_{Si} = 0.024 \cdot \frac{55.85}{28.1} = 0.05 \quad (7.2)$$

In the graphite solidification, it can be checked that

$$a_C^{Liquid} = \gamma_C^{Liquid} \cdot x_C^{Liquid} = 1 \quad (7.3)$$

$$\gamma_C^{Liquid} = \frac{1}{x_C^{Liquid}} = \frac{1}{0.16} = 6.25 \quad (7.4)$$

If the next equation is used,

$$\ln \gamma_i = \ln \gamma_i^0 + \sum \varepsilon_i^j \cdot x_j \quad (7.5)$$

$$\ln \gamma_C^{Liquid} = \ln \gamma_i^0 + \varepsilon_C^C \cdot x_C + \varepsilon_C^{Si} \cdot x_{Si} + \varepsilon_C^{Mg} \cdot x_{Mg} \quad (7.6)$$

$$\ln 6.25 = 1.83 < \ln 2.3 + 3.9 \cdot 0.16 + 7.6 \cdot 0.05 + 6.8 \cdot x_{Mg} \simeq 1.83 + 6.8 \cdot x_{Mg} \quad (7.7)$$

$$x_{Mg} = 0.005 \rightarrow w_{Mg} < 0.2\% \quad (7.8)$$

The graphitizing element, Mg, which was inoculated in the cast iron, makes possible the graphite spheroidal nucleation.

Exercise 7.2. In the case of the spheroidal graphite cast iron of the Exercise 7.1 alloyed (0.3% Cr–0.4% Mo) with the purpose of achieving bainitic hardenability after the austempering. The spheroidal graphite cast iron would continue grey?

Data: $\varepsilon_C^{\text{Cr}} = -5.9$; $\varepsilon_C^{\text{Mo}} = -1.66$.

Question

Cr and Mo are, approximately,

$$x_{\text{Cr}} = 0.003 \cdot \frac{55.85}{52} = 3.2 \times 10^{-3} \quad (7.9)$$

$$x_{\text{Mo}} = 0.004 \cdot \frac{55.85}{95.9} = 2.3 \times 10^{-3} \quad (7.10)$$

$$x_{\text{Mg}} = 0.0025 \cdot \frac{55.85}{24.3} = 5.7 \times 10^{-4} \quad (7.11)$$

If the following equation is used,

$$\ln \gamma_i = \ln \gamma_i^0 + \sum \varepsilon_i^j \cdot x_j \quad (7.12)$$

$$\ln \gamma_C^{\text{Liquid}} = \ln \gamma_i^0 + \varepsilon_C^{\text{C}} \cdot x_{\text{C}} + \varepsilon_C^{\text{Si}} \cdot x_{\text{Si}} + \varepsilon_C^{\text{Mg}} \cdot x_{\text{Mg}} + \varepsilon_C^{\text{Cr}} \cdot x_{\text{Cr}} + \varepsilon_C^{\text{Mo}} \cdot x_{\text{Mo}} \quad (7.13)$$

$$\begin{aligned} \ln 6.25 = 1.83 &\simeq \ln 2.3 + 3.9 \cdot 0.16 + 7.6 \cdot 0.05 + 6.8 \cdot 5.7 \times 10^{-4} \\ &- 5.9 \cdot 3.2 \times 10^{-3} - 1.66 \cdot 2.3 \times 10^{-3} = 1.82 \end{aligned} \quad (7.14)$$

The graphitizing behaviour and the spheroidal clustering of the grey iron (provided by silicon and magnesium) would not be thermodynamically in risk. Demonstrate that there is risk in the case of increasing the chromium percentage up to 1%.

$$x_{\text{Cr}} = 0.01 \cdot \frac{55.85}{52} = 0.01 \quad (7.15)$$

$$\begin{aligned} \ln 6.25 = 1.83 &> \ln 2.3 + 3.9 \cdot 0.16 + 7.6 \cdot 0.05 + 6.8 \cdot 5.7 \times 10^{-4} \\ &- 5.9 \cdot 0.01 - 1.66 \cdot 2.3 \times 10^{-3} = 1.78 \end{aligned} \quad (7.16)$$

There would not be chilling risks in the cast iron.

Exercise 7.3. A part of 1 • 3 • 7 inches is manufactured in grey iron of spheroidal graphite: 3.6%C–2.5%Si. Considering the enclosed graph (Fig. 7.1), calculate the dimensions that a cylindrical riser with diameter equal to the height (compact riser, $D = h$) should have with the idea of ensuring the soundness of the part.

Question

First, the relation A/V is calculated:

$$\left(\frac{A}{V}\right)_{\text{casting}} = \frac{2 \cdot (7 \cdot 3) + 2 \cdot (7 \cdot 1) + 2 \cdot (3 \cdot 1)}{7 \cdot 3 \cdot 1} = \frac{42 + 14 + 6}{21} = 2.95 \simeq 3 \quad (7.17)$$

This value is too high, and for that reason, the casting (part) will tend to solidify easily (low massivity).

The volume of the casting is calculated:

$$V_{\text{casting}} = 21 \text{ in.}^3 \quad (7.18)$$

If it is supposed that exists volume shrinkage of 2% (minimal volume of the riser):

$$\Delta V = V_{\text{riser}} = 21 \cdot 0.02 = 0.42 \text{ in.}^3 \quad (7.19)$$

In the case of a cylindrical compact riser ($D = h$):

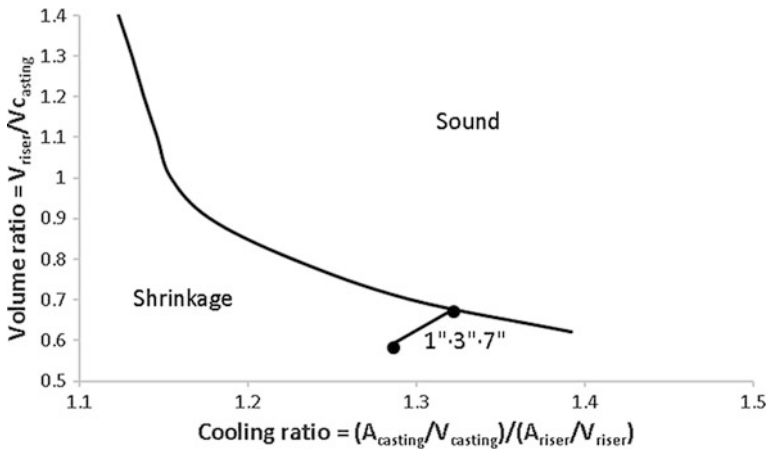


Fig. 7.1 Graph to be used in the calculation of the riser dimensions, where $A_{\text{casting}}/V_{\text{casting}}$ is the casting cooling rate, while $A_{\text{riser}}/V_{\text{riser}}$ is the riser cooling rate (data from Flinn 1963)

$$0.42 = \frac{\pi D^3}{4} \quad (7.20)$$

$$D = 0.81 \text{ in.} \quad (7.21)$$

The following relation is calculated:

$$\begin{aligned} (A/V)_{\text{riser}} &= \frac{2\pi R h + 2 \cdot \pi R^2}{\pi R^2 h} = \frac{2\pi R(h + R)}{\pi R^2 h} \\ &= \frac{2[D + (D/2)]}{(D/2)D} = \frac{6D/2}{D^2/2} = \frac{6}{D} = \frac{6}{0.81} = 7.41 \end{aligned} \quad (7.22)$$

Solidification times per the *Chvorinov equation* are

$$t_s = \text{cte} \cdot \left(\frac{V}{A}\right)^2 \quad (7.23)$$

Solidification times for the riser and casting are in this case

$$t_{\text{riser}} = \text{cte} \cdot \left(\frac{1}{7.41}\right)^2 < t_{\text{casting}} = \text{cte} \cdot \left(\frac{1}{3}\right)^2 \quad (7.24)$$

$$\frac{t_{\text{riser}}}{t_{\text{casting}}} = \frac{\left(\frac{1}{7.41}\right)^2}{\left(\frac{1}{3}\right)^2} < 1 \quad (7.25)$$

The rising fundamental's law is broken. For that reason, redefining the riser with the purpose of avoiding that the riser solidification happens before the casting solidification is necessary. If we choose according to the enclosed graph (Fig. 7.1) a cooling ratio of 1.3,

$$\frac{(A/V)_{\text{casting}}}{(A/V)_{\text{riser}}} = 1.3 \rightarrow (A/V)_{\text{riser}} = \frac{(A/V)_{\text{casting}}}{1.3} = \frac{3}{1.3} \simeq 2.3 \quad (7.26)$$

$$(A/V)_{\text{riser}} = \frac{6}{D} \rightarrow D = \frac{6}{2.3} = 2.6 \quad (7.27)$$

Finally, the relation $V_{\text{riser}}/V_{\text{casting}}$ will be

$$\frac{V_{\text{riser}}}{V_{\text{casting}}} = \frac{\pi \cdot R^2 \cdot h}{7 \cdot 3 \cdot 1} = \frac{\pi \cdot 1.3^2 \cdot 2.6}{7 \cdot 3 \cdot 1} = 0.66 \quad (7.28)$$

Values of $V_{\text{riser}}/V_{\text{casting}} > 0.66$ allow for sound castings (parts).

7.2 General Properties of Ductile Cast Irons

The density of these cast irons, which is around 7.1 g/cm^3 , changes with the increase of carbon content (diminishing) and the high graphitizing degree (diminishing) as well. A ductile cast iron of high carbon content and matrix thoroughly ferritic can reach a density of 6.8 g/cm^3 .

Returning to the proposed model used in the explanation of the grey iron mechanical behaviour—steel with numerous hollows filled with graphite—tensile strength is lower in comparison with the same matrix without hollows. This reduction is consequence of the notch effect that is higher in flake graphite cast irons than in spheroidal graphite cast irons. The cross section of the metallic matrix is also reduced because of the presence of cavities (the higher the carbon content, the lower the cross section). Spheroidal graphite will produce (as happens with flake graphite) a reduction in the cross section but its notch effect will be less marked.

For these two reasons, the *ductility* and toughness of spheroidal graphite cast irons, despite being lower than in steels, are better in comparison with cast irons of flake graphite. This better aptitude to plastic deformation justifies the name of *ductile cast iron*, which is usually employed in the spheroidal graphite cast irons designation. *Percent elongation in the tensile test* is important: spheroidal graphite cast irons of ferritic matrix (A_T) can reach the 25%.

Spheroidal cast irons as also happen in malleable cast irons, and as opposed to grey cast irons of flake graphite, *have yield strength*.

Exercise 7.4. The following data were collected from an 18 mm diameter test specimen of a ductile cast iron ($l_0 = 35.0 \text{ mm}$) (Table 7.1):

$$S = \frac{\text{Load (N)}}{\text{Area (mm}^2\text{)}} = \frac{F \text{ (N)}}{\left(\frac{\pi}{4}\right) \cdot (18 \text{ mm})^2} \quad (7.29)$$

$$e = (l - l_0)/l_0 \quad (7.30)$$

Table 7.1 Data to be used in the representation of the stress–strain curve

Load (N)	Gauge length (mm)	Stress (MPa)	Strain (mm/mm)
0	35	0	0.0
20,000	35.0185	78.6	0.00053
45,000	35.0370	176.8	0.00106
70,000	35.0555	275.1	0.00159
85,000	35.20	334.0	0.0057
100,000	35.60	393.0	0.017
115,000	36.56	451.9	0.045
126,000	39.00 (max. load)	495.1	0.114
120,000	42.52 (fracture)	471.6	0.215

After fracture, the gauge length is 42.42 mm and the diameter is 16.35 mm. Plot the data and calculate:

- The 0.2% yield strength.
- Tensile strength (R_m).
- Young's modulus (GPa).
- Elongation (%).
- Reduction in area (%).
- The true stress at fracture (MPa).
- The modulus of resilience (MPa).

Question

In Fig. 7.2, the data are plotted:

A zoom in the initial zone (Fig. 7.3).

- The yield strength at 0.2% ($S_y^{0.2\%}$) is calculated by means of a parallel to the straight line belonging to the elastic zone for 0.002 mm/mm of strain, and where cuts the curve of tensile test is obtained in the Y-axis the yield strength:

$$S_y^{0.2\%} = 325 \text{ MPa} \quad (7.31)$$

- The tensile strength is calculated as the maximum in the tensile test curve:

$$S_r \text{ or } R_m = 495.1 \text{ MPa} \quad (7.32)$$

- The Young modulus (E) is calculated by means of the slope of the elastic area in the tensile test curve:

$$E = \frac{(275.1 - 0) \text{ MPa}}{(0.00159 - 0) \left(\frac{\text{mm}}{\text{mm}}\right)} = 173000 \text{ MPa} = 173 \text{ GPa} \quad (7.33)$$

Fig. 7.2 Representation of the stress–strain curve

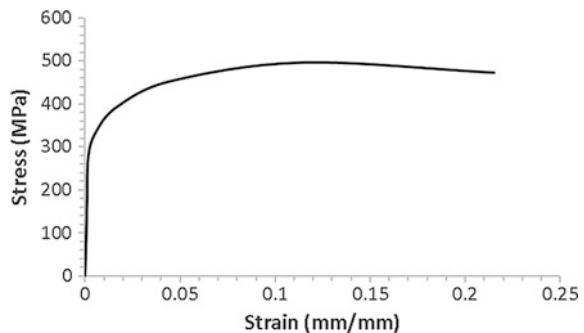
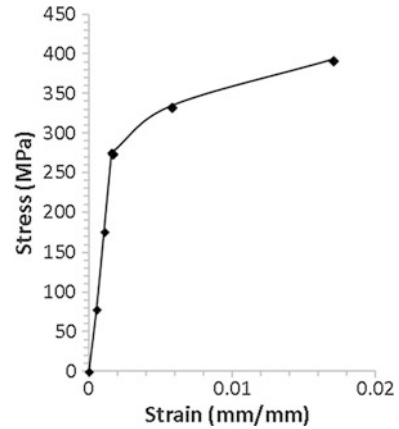


Fig. 7.3 Zoom in the initial zone of the stress–strain curve



(d) The elongation (%) is

$$A_T(\%) = \frac{(42.42 - 35)}{35} \cdot 100 = 21.20\% \quad (7.34)$$

(e) The reduction in area (%) is

$$\begin{aligned} \text{Reduction in area } (\%) &= \frac{\text{Area}_{\text{initial}} - \text{Area}_{\text{final}}}{\text{Area}_{\text{initial}}} \cdot 100 \\ &= \frac{(\pi/4) \cdot 18^2 \text{ mm}^2 - (\pi/4) \cdot 16.35^2 \text{ mm}^2}{(\pi/4) \cdot 18^2 \text{ mm}^2} \cdot 100 = 17.49\% \end{aligned} \quad (7.35)$$

(f) The true stress at fracture (MPa) (σ_u^r) is

$$\sigma_u^r = \sigma_u(A_T + 1) = 495.1 \cdot (0.2120 + 1) = 600 \text{ MPa} \quad (7.36)$$

(g) The modulus of resilience (absorbed energy in the elastic zone by unit volume) is calculated from the S–e curve, yielding begins near 275 MPa. Thus,

$$\begin{aligned} \text{Modulus of Resilience } (\text{J/m}^3) &= \left(\frac{1}{2}\right) \cdot \sigma_y \cdot A_y \\ &= 0.5 \cdot 275.1 \text{ MPa} \cdot 0.00159 \text{ m/m} = 0.22 \text{ MJ/m}^3 \end{aligned} \quad (7.37)$$

Tensile strength in spheroidal graphite grey cast irons is higher than in lamellar graphite cast irons: double, at least, for identical matrix. *Compression strength* is the same or even a 20% higher than tensile strength. However, in cast irons of flake graphite, compression strength reaches values three or four times higher than tensile strength (Chap. 5). The name *degree of a spheroidal graphite cast iron* is used in the designation of ductile cast irons and comprises three parameters: *tensile strength* (or *class*), yield strength and elongation.

As opposed to the lamellar graphite grey irons behaviour, where it was mentioned the practical inexistence of a *correlation between hardness and tensile strength*, the relation between both properties, HB and R_m , in the case of spheroidal cast irons is important, as it is possible to see in Table 7.2, which also includes the elongation.

Spheroidal cast irons present *lower ability for vibrations damping* than lamellar graphite cast irons, whose relation between surface and volume of the graphite is very high in lamellar graphite cast irons. In the hardness range of 160–240 HB, for instance, damping capacity is 0.12 times that of a class 30 lamellar graphite cast iron.

Furthermore, because of the morphological differences between one and other kind of graphite, *thermal conductivity* of spheroidal cast irons is lower—and the *electric conductivity* is higher—than in lamellar graphite cast irons.

The *coefficient of linear expansion* is similar in comparison with lamellar graphite cast irons (11.2 $\mu\text{m}/\text{mm K}$ between 20–100 °C, and 13.5 $\mu\text{m}/\text{mm K}$ between 20–500 °C).

Machinability is excellent and almost identical to the machinability of lamellar grey cast irons of the same hardness.

General properties—structure, mechanical properties and applications—of the most common degrees of ductile cast iron (395, 476, 536 ASTM Standards) are shown in Table 7.3. Their good characteristics of strength and toughness, combined with machinability and low manufacturing cost, make spheroidal cast irons a

Table 7.2 Mechanical properties for some ductile cast irons (data from ASM, specimen from a 25 mm keel block)

Cast iron	Elongation (%)	Hardness HB	Yield strength (MPa; ksi)	Tensile strength (MPa; ksi)
60–40–18, annealed	19–25	160–185	(303; 44)–(358; 52)	(421; 61)–(489; 71)
65–45–12, annealed	14–21	170–210	(331; 48)–(400; 58)	(462; 67)–(572; 83)
80–55–06, as-cast	6–12	185–235	(386; 56)–(483; 70)	(579; 84)–(731; 106)
100–70–03, air-quenched	4–10	215–265	(476; 69)–(627; 91)	(703; 102)–(923; 134)
120–90–02, oil-quenched	3–8	240–300	(669; 97)–(924; 134)	(827; 120)–(1117; 162)

Table 7.3 Structures, mechanical properties and applications of some prototypes USA of ductile cast iron

ASTM	Class	Description	Hardness ^a		Tensile strength ^b min. ^b	Yield strength ^b min. ^b	Elongation (50 min.) ^b		Common uses	Typical applications	Typical chemical composition				
			HB				%				CT ^c	Si	Mn	P	S
A395	60–40–18	Annealed ferrite	143–187		414	276	18		High temperature and pressure vessels	Valves and connectors used in vapour and chemical plants, electric equipment, engine blocks, pumps, carcasses, gears, pump bodies, clamps and cylinders.	>3.00	<2.50 ^d	–	<0.08	–
A476	80–60–03	As-cast cast iron	<201		552	414	3		Drying rolls in paper factories for temperatures below 230 °C		>3.00 ^e	<3.00	–	<0.08	<0.05
A536	60–40–18	Ferritic, can be annealed	–		414	276	18		Parts with shock resistance at low temperatures	Vessels used in high-pressure applications, as pump carcasses and valves					
	65–54–12	Mainly ferritic, directly by casting or annealed	–		448	310	12		General uses	Parts of equipment with shock strength and fatigue resistance					

(continued)

Table 7.3 (continued)

ASTM Class	Description	Hardness ^a		Tensile strength min. ^b MPa	Yield strength, min. ^b MPa	Elongation (50 min.) ^b %	Common uses	Typical applications	Typical chemical composition			
		HB							CT ^c	Si	Mn	P S
80–55–06	Ferritic–pearlitic, as-cast	–		552	379	6	General uses	Crankshafts ^f , gears and rolls	The A536 standard does not specify the composition, which is subordinated to the mechanical properties			
100–70–03	Mainly pearlitic, can be normalized	–		689	483	3	Optimal combination of strength, wear resistance and superficial hardening	Gears and pieces of equipment of high resistance				
12–90–02	Martensitic, oil-quenched and low tempering	–		827	621	2	Wear resistance and high tensile strength	Sprockets, gears, rolls and sliding guides				

^aMeasure in previously determined places of the molten part
^bCalculated by means of a standard sample took from a molten ingot separately, as is established in the corresponding specifications
^cTotal carbon (CT)
^dThe limit of silicon content can be increased as 0.08% per each 0.01% of diminishing in the phosphorus content until a total of 2.75% of silicon
^eThe equivalent carbon (CE) is of 3.8–4.5%: $CE = CT + 0.3 \cdot (Si + P)$
^fSee case study in Chap. 10

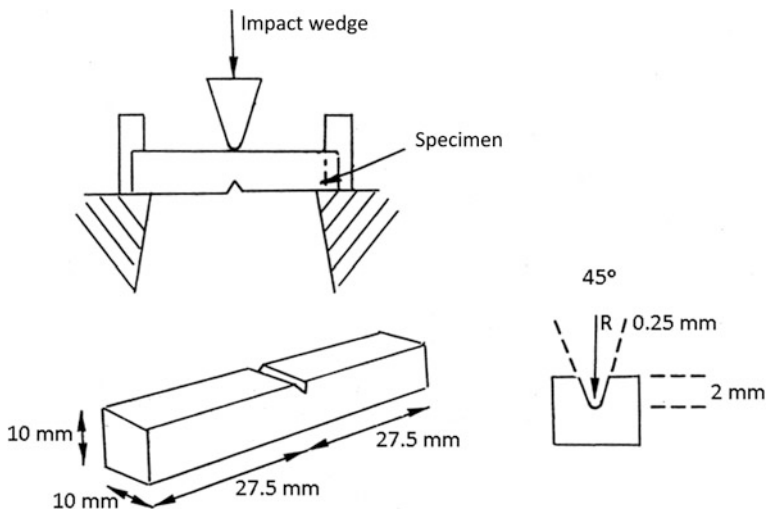


Fig. 7.4 Scheme of the three-point bending test

structural material that can compete with steels in some applications. Automotive industry consumes more than half of spheroidal graphite cast irons production.

Exercise 7.5. The three-point bending test (Fig. 7.4) performed by impact is used in the calculation of the toughness (resilience) of these materials. The result of the test gets worse with the impact speed, the decreasing of the temperature and the use of notched specimen. The energy that was absorbed by the specimen was measured in Jules.

Enclosed figure (Fig. 7.5) summarizes the absorbed energy as a function of the temperature in a ductile iron, also depending on the heat treatment (annealing, normalizing, quenching + tempering and austempering, Table 7.4). Calculate at room temperature ($\approx 25^\circ\text{C}$) the absorbed energy as a function of the treatment that was performed.

Question

The absorbed energy at room temperature (25°C) as a function of the heat treatment is shown in Table 7.5.

Curve F shows that the austempering treatment improves the tensile properties and also gives the highest toughness at room temperature.

As a comparison, building steel, ferritic-pearlitic, which is possible to be welded, has toughness at least 10 times higher than the ductile cast iron at room temperature. Building steel has a ductile-brittle transition temperature, for an absorbed energy of 27 J, of dozens of degrees below room temperature (sub-zero).

Fig. 7.5 Charpy impact energy as a function of the temperature (ASM 1978)

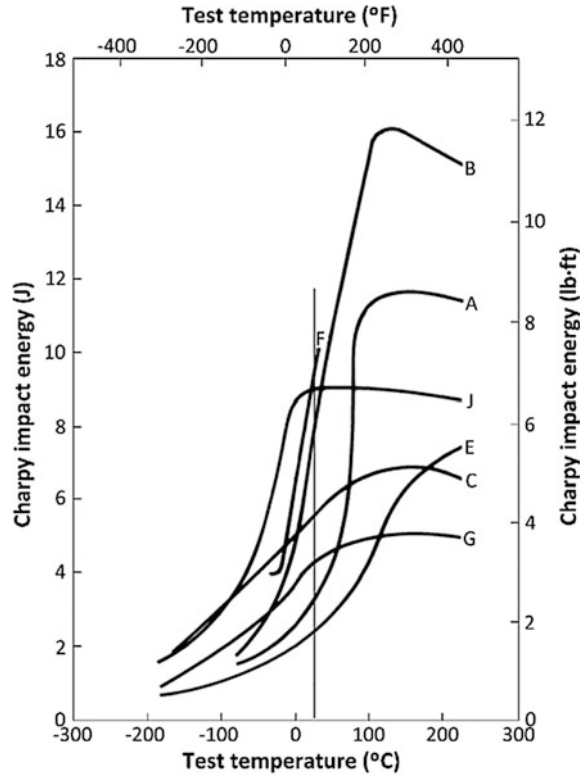


Table 7.4 Type of sample, characteristics and treatment (ASM 1978)

Sample ^a	Heat treatment	Tensile strength		Yield strength		Elongation in 50 mm or 2 in. (%)
		MPa	ksi	MPa	ksi	
A	As-cast	535	78	335	49	13.0
B	Subcritical annealing	430	62	315	46	23.6
C	Quenching + tempering	635	92	530	76	8.8
J	Quenching + tempering	750	108	580	84	9.4
G	Quenching + tempering	1,050	152	790	115	4.1
E	Quenching + tempering	780	113	470	68	8.2
F ^b	Austempering (700 °F)	930	135	650	95	11.5

^aAnalysis: 3.65% C, 0.52% Mn, 0.065% P, 2.48% Si, 0.08% Cr, 0.78% Ni, 0.15% Cu

^bAnalysis no available; data from non-published works directed by the International Harvester Co.

Table 7.5 Absorbed energy as a function of the heat treatment

Sample	Heat treatment	Absorbed energy (J)
A	As-cast	3
B	Subcritical annealing	8
C	Quenching + tempering	5.5
J	Quenching + tempering	9
G	Quenching + tempering	4.25
E	Normalizing + tempering	2.25
F	Austempering (370 °C)	9.5

Exercise 7.6. The phenomenon of fatigue happens when a part in service is subjected to repeatedly applied cycles of load–unload, causing the nucleation and growing of cracks, which can finally be responsible for the part failure. Fatigue increases with the number of cyclic loads, but also with the amplitude of the cycle load–unload, and the presence of internal stresses (notch effect) that favours the incubation of cracks (section changes, surface defects, machining scratches, inclusions, etc.).

Paris, Gomez and Anderson established the rate of crack growth, described by the following relationship:

$$\frac{da}{dN} = A \cdot (\Delta K)^m \quad (7.38)$$

- a : half-length of crack.
- N : number of cycles.
- ΔK : amplitude of the critical factor of stress intensities:
 $\Delta K \simeq (\sigma_M - \sigma_m) \cdot \sqrt{\pi \cdot a}$; being σ_M and σ_m the maximum and minimum stresses, respectively, in each cycle of load.
- m : exponent of the Paris equation.
- A : constant of the equation.

Enclosed figure (Fig. 7.6) shows the mathematical expression of Paris for growing of cracks as a function of ΔK . The time in service of the part will be fixed by the amplitude of the zone II, which belongs to the stable growing of the crack.

Separating variables, N and a , by integration of the equation above mentioned, the following equation is found:

$$N_f = \frac{2 \cdot \left[a_0^{(1-0.5m)} - a_C^{(1-0.5m)} \right]}{(m-2) \cdot A \cdot (\Delta \sigma \sqrt{\pi})^m} \quad (7.39)$$

Being a_C and a_0 the critical size of crack and the initial size of crack, respectively, N_f the number of alternative cycles of load–unload before the catastrophic break.

For a crankshaft of ductile cast iron working under rotating bending, calculate N_f by means of the following data:

$$A \simeq 10^{-13}; \quad m = 2.5; \quad \Delta\sigma = \sigma_M - \sigma_m = 200 \text{ MPa } (\pm 100 \text{ MPa})$$

Initial size of cracks: $200 \mu\text{m} = 2 \times 10^{-4} \text{ m}$ (proportional to the nodule's size of spheroidal graphite). $K_C \simeq 35 \text{ MPa}\sqrt{\text{m}}$

Question

The critical size of crack is

$$35 \text{ MPa}\sqrt{m} = 100\sqrt{\pi \cdot a_C} \rightarrow a_C \simeq 0.04 \text{ m (40 mm)} \quad (7.40)$$

Using the equation here with the above formulation,

$$N_f = \frac{2 \cdot \left[(10^{-4})^{(1-0.5 \cdot 2.5)} - (4 \times 10^{-2})^{(1-0.5 \cdot 2.5)} \right]}{(2.5 - 2) \times 10^{-13} \cdot (200\sqrt{\pi})^{2.5}} \simeq \frac{4 \cdot 7.77}{(200\sqrt{\pi})^{2.5}} \times 10^{13} \\ \simeq 1.3 \times 10^8 \text{ cycles} \quad (7.41)$$

The possible time in service depends on the following:

- The size of the initial defects: the lower and the shorter, the better for the part.
- The $\sigma_M - \sigma_m$: the lower the amplitude of the load cycles $\sigma_M - \sigma_m$ (supported stresses), the better for the part.
- The toughness of the material, K_C : the higher the toughness, the lower the rate of cracks propagation da/dN (plastic blunting).

Demonstrate that if the applied cycle load is twofold ($100 \text{ MPa} \rightarrow 200 \text{ MPa}$), the number of cycles before the cracking of the part because of fatigue is divided, practically, by 10. What would happen if $\Delta\sigma$ is doubled from 200 up to 400 MPa (rotating bending)?

Question

$$35 \text{ MPa}\sqrt{m} = 200\sqrt{\pi a_C} \rightarrow a_C \simeq 0.01 \text{ m (20 mm)} \quad (7.42)$$

$$N_f = \frac{2 \cdot \left[(10^{-4})^{(1-0.5 \cdot 2.5)} - (10^{-2})^{(1-0.5 \cdot 2.5)} \right]}{(2.5 - 2) \times 10^{-13} \cdot (400\sqrt{\pi})^{2.5}} \simeq \frac{2}{0.5} \cdot \frac{(10 - 3.16)}{(400\sqrt{\pi})^{2.5}} \times 10^{13}$$

$$\simeq 2 \times 10^7 \text{ cycles} \quad (7.43)$$

And, if it is threefold? $a_C \simeq 0.004 \text{ m}$ ($\simeq 4 \text{ mm}$).

Question

$$N_f = \frac{2 \cdot \left[(10^{-4})^{(1-0.5 \cdot 2.5)} - (0.004)^{(1-0.5 \cdot 2.5)} \right]}{(2.5 - 2) \times 10^{-13} \cdot (600\sqrt{\pi})^{2.5}} \simeq 6.5 \times 10^6 \text{ cycles} \quad (7.44)$$

Exercise 7.7. Creep test is used with the purpose of calculating the heat strength/resistance of a certain material under constant stress. The maximum permissible deformation speed ($\dot{\epsilon}$) is measured with the finality of that under temperature, working time and applied stress (T, t, σ), the deformation does not exceed 1%.

Under stationary creep, it can be demonstrated that the relation between $\dot{\epsilon}, t, T, \sigma$ is of the following type:

$$\dot{\epsilon} \propto \frac{1}{t} = A \cdot \exp\left(\frac{-Q}{RT}\right) \cdot \sigma^m \quad (7.45)$$

This relation is known as exponential stationary creep law, where m is an exponent commonly within the range of 3 and 8; Q , is the activation energy in the case of the stationary creep ($\dot{\epsilon} = \text{cte}$).

In the last equation, taking logarithms and reordering variables, T, t and σ , the following equation is obtained:

$$\sigma = f(\text{LMP}) = f[T \cdot (c + \log t_r)] \quad (7.46)$$

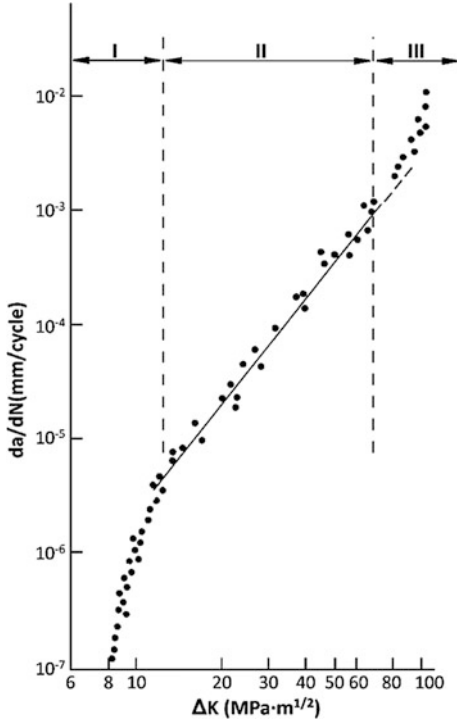
where LMP is the Larson–Miller parameter.

Enclosed figure (Fig. 7.7) shows the tensile strength as a function of the Larson–Miller parameter, in the case of ductile cast irons. The LMP parameter is

$$\text{LMP} = 10^{-3} \cdot T \cdot (20 + \log t_r) \quad (7.47)$$

where T is the temperature in $^{\circ}\text{R}$ and t_r is the broken time in hours.

Fig. 7.6 Representation of the Paris equation



Calculate the maximum stress that can be admitted by a part at 1000 °F(≈ 540 °C) after working for 100000 h:

Question

$$LMP = (1000 + 460) \cdot [20 + \log 10^5] \times 10^{-3} \simeq 36.5 \tag{7.48}$$

With this value of LMP in the enclosed figure (Fig. 7.7), $\sigma = 3.5$ ksi (≈ 24.5 MPa).

Calculate the maximum permissible temperature for working under 4 ksi for 10000 h:

Question

$$LMP(\sigma = 4 \text{ ksi}) \simeq 36 \tag{7.49}$$

$$36 = T(^{\circ}R) \cdot [20 + \log 10^4] \times 10^{-3} \rightarrow T = 1500^{\circ}R = 1040^{\circ}F \simeq 560^{\circ}C \quad (7.50)$$

This value could be obtained by means of the figure enclosed to this exercise (Fig. 7.7).

Exercise 7.8. A bar of ductile cast iron with dimensions of 1 in. $\times$ 2 in. should work for 9 years at 650 $^{\circ}C$. Which would be the maximum stress that can be applied?

Question

The operation time of the bar is

$$9 \text{ years} \cdot \frac{365 \text{ days}}{1 \text{ year}} \cdot \frac{24 \text{ h}}{1 \text{ day}} = 78840 \text{ h} \quad (7.51)$$

Working temperature ($T(^{\circ}R)$) is

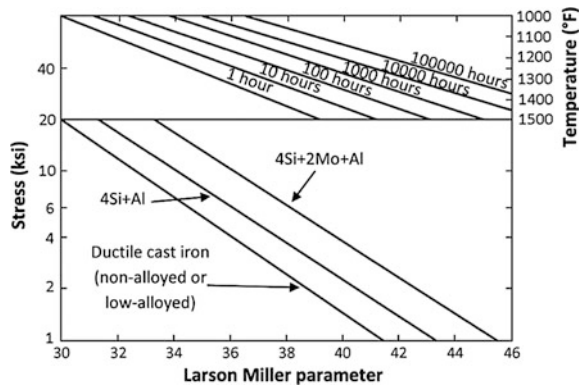
$$T(^{\circ}R) = \frac{9}{5} \cdot T(^{\circ}C) + 492 = \frac{9}{5} \cdot 650 + 492 = 1662 \quad (7.52)$$

Larson–Miller parameter (LMP) according to the equation that appears in Exercise 7.7 is

$$\text{LMP} = 1662 \cdot [20 + \log 78840] \times 10^{-3} = 41.4 \quad (7.53)$$

In the figure enclosed (Fig. 7.7) to Exercise 7.7 with the Larson–Miller parameter, the value of the stress can be read in y-axis. This value should not be higher than 1.3 ksi (1 ksi = 6.9 MPa). In this context, the load is

Fig. 7.7 Graphic to be used in the determination of the Larson–Miller parameter (ASM 1978)



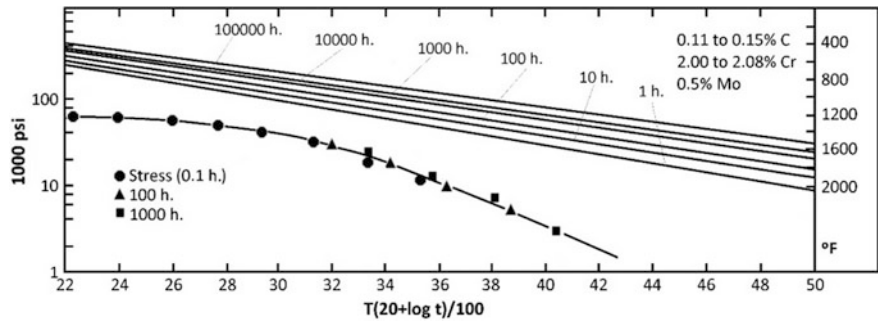


Fig. 7.8 Graph that correlates de LMP, stress and temperature

$$\sigma = 9 \text{ MPa} \tag{7.54}$$

$$F = 9 \times 10^6 \frac{\text{N}}{\text{m}^2} \cdot 2 \cdot (25.4 \times 10^{-3} \text{ m})^2 \cdot \frac{1 \text{ kg}}{9.81 \text{ N}} = 1180 \text{ kg} (\simeq 1.2 \text{ tonnes}) \tag{7.55}$$

Exercise 7.9. A bar of ductile iron works under 6 ksi for 1 year (8760 hours). Which would be the maximum permissible temperature under those conditions? Use Fig. 7.7.

Question

The operation time of the bar is of 8760 hours.
The Larson–Miller parameter (LMP) (under stress of 6 ksi) is 36 according to Fig. 7.7:

$$36 = 10^{-3} T \cdot (20 + \log 8760) \tag{7.56}$$

$$T = 1504 \text{ }^\circ\text{R} = 836 \text{ K} = 562 \text{ }^\circ\text{C} \tag{7.57}$$

Exercise 7.10. Compare Fig. 7.7 with one of the steels used in overheated steam pipes (Fig. 7.8). Calculate for the steel the maximum permissible stress at 540 °C (1000 K) and 100000 h of operating time.

Question

With the value of LMP = 36.5, the stress is around 10 ksi. That is to say, about 3 times higher than in the case of ductile cast irons.

7.3 Heat Treatments with Continuous Cooling

The properties of grey cast irons, either lamellar or spheroidal, depend on both the matrix constituent and the graphite morphology. It should be remembered that the structure of the matrix constituent, for growing cooling rates from the austenitic state, can be ferritic, ferritic-pearlitic, pearlitic, bainitic or martensitic. In the same order, hardness, tensile strength and wear resistance improve. On the other hand, ductility, toughness and machinability diminish.

Spheroidal graphite grey cast irons can be subjected to *heat treatments* with the purpose of modifying the structure of the metallic matrix. We recall those grey irons as metal matrix composites.

However, lamellar graphite cast irons present noticeable disadvantages for being heat treated, mainly because of two reasons: cracking risks due to the notch effect of the flake graphite during the dimensional changes derived from the heating and the cooling; and the inherent difficulties—common to all kind of cast irons, independently from the morphology of graphite—to the high carbon content in the matrix.

From all the heat treatments that is possible to apply to spheroidal graphite cast irons of medium and low alloy, some of them require a heating up to the austenization temperature. And for that reason, the use of molten salts furnaces or controlled atmosphere furnaces is necessary, with the purpose of avoiding—at those temperatures—the inherent risk of austenitic matrix decarburization due to the high carbon content.

For equal carbon content in the ferrous alloy and the same *activity in carbon* (relation $P_{CO}^2/(P_{CO_2} \cdot K)$ in the case of gaseous atmospheres) of the protector agent to the decarburization, decarburization risks are higher when the minimum the maximum carbon content (C_S) permitted by austenite, in solid solution, at that temperature (T_A).

Silicon of the cast iron, dissolved in the austenite, diminishes the C_S down to the value of $-0.95 - 0.17 \cdot \%Si + T_A/420$ °C. For that reason, silicon increases the decarburization risks for the same protecting atmosphere.

Exercise 7.11. At 900 °C, calculate the percentage CO/CO₂ in the protective atmosphere used in the heat treatment of a cast iron: Fe–3.5% C

(a) without silicon, (b) with 2.5% Si (spheroidal). Suppose that the superficial carbon content should be higher than 0.77%.

Question

Standard enthalpy of formation according to the Boudouard equation is

$$\begin{aligned} \text{CO}_2 + \text{C} &\rightleftharpoons 2\text{CO} \\ \Delta G_T^0 &= 40800 - 41.7 \cdot T \text{ cal/mol} \end{aligned} \quad (7.58)$$

The diffusion coefficient is

$$D_C^j \text{ (cm}^2/\text{s)} = 0.25 \cdot \exp\left(\frac{-35000 \text{ cal}}{RT}\right) \quad (7.59)$$

(a) In Fe–3.5% C, the maximum carbon content that saturates the austenite is

$$C_s = -0.95 + \frac{900}{420} = 1.19 \quad (7.60)$$

$$a_C^{\text{steel}} \simeq 0.77/1.19 \simeq 0.65 \quad (7.61)$$

In the equilibrium, $a_C^{\text{steel}} = a_C^{\text{atmosphere}} \simeq 0.65$

$$\Delta G^0 + RT \ln K = 0 \quad (7.62)$$

$$K = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2} \cdot a_C^{\text{atmosphere}}} = \exp\left(-\frac{\Delta G^0}{RT}\right) \quad (7.63)$$

$$\frac{P_{\text{CO}}^2}{P_{\text{CO}_2} \cdot a_C^{\text{atmosphere}}} = \exp\left[\frac{-40800 + 41.7 \cdot (900 + 273)}{2(900 + 273)}\right] \quad (7.64)$$

$$\frac{P_{\text{CO}}^2}{P_{\text{CO}_2} \cdot a_C^{\text{atmosphere}}} = 31.78 \rightarrow \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = 20.65 \quad (7.65)$$

Supposing that $P_{\text{CO}} + P_{\text{CO}_2} = 1$, we obtain a system of equations:

$$P_{\text{CO}} + \frac{P_{\text{CO}}^2}{20.65} = 1 \rightarrow P_{\text{CO}}^2 + 20.65 \cdot P_{\text{CO}} - 20.65 = 0 \rightarrow \quad (7.66)$$

$$P_{\text{CO}} = 0.956 \text{ atm} \quad (7.67)$$

$$P_{\text{CO}_2} = 0.044 \text{ atm} \quad (7.68)$$

- (b) In Fe–3.5% C–2.5% Si, the maximum carbon content that saturates the austenite is

$$C_s = -0.95 - 0.17 \cdot 2.5 + \frac{900}{420} \simeq 0.77 \quad (7.69)$$

$$a_{\text{C}}^{\text{steel}} \simeq 0.77/0.77 \simeq 1 \quad (7.70)$$

In the equilibrium, $a_{\text{C}}^{\text{steel}} = a_{\text{C}}^{\text{atmosphere}} \simeq 1$

$$\Delta G^0 + RT \ln K = 0 \quad (7.71)$$

$$K = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2} \cdot a_{\text{C}}^{\text{atmosphere}}} = \exp\left(-\frac{\Delta G^0}{RT}\right) \quad (7.72)$$

$$\frac{P_{\text{CO}}^2}{P_{\text{CO}_2} \cdot a_{\text{C}}^{\text{atmosphere}}} = \exp\left[\frac{-40800 + 41.7 \cdot (900 + 273)}{2(900 + 273)}\right] \quad (7.73)$$

$$\frac{P_{\text{CO}}^2}{P_{\text{CO}_2} \cdot a_{\text{C}}^{\text{atmosphere}}} = 31.78 \rightarrow \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = 31.78 \quad (7.74)$$

And as $P_{\text{CO}} + P_{\text{CO}_2} = 1$, we obtain a system of equations:

$$P_{\text{CO}} + \frac{P_{\text{CO}}^2}{31.78} = 1 \rightarrow P_{\text{CO}}^2 + 31.78 \cdot P_{\text{CO}} - 31.78 = 0 \rightarrow \quad (7.75)$$

$$P_{\text{CO}} = 0.97 \text{ atm} \quad (7.76)$$

$$P_{\text{CO}_2} = 0.03 \text{ atm} \quad (7.77)$$

The presence of reductant gas (CO) should be higher in presence of Si (spheroidal graphite cast iron).

If the activity $a_{\text{C}}^{\text{atmosphere}} \simeq 1$, coal dust (carbon black) can deposit over the part. If the carbon activity in the atmosphere and the carbon activity in the steel is diminished down to the value indicated for the Fe–3.5% C–2.5% Si situation, $a_{\text{C}}^{\text{atmosphere}} \simeq 0.65 = C_s/0.77 \rightarrow C_s \simeq 0.5$: the outer part would be of ferritic–

pearlitic structure in the cooling: some decarburization would be evident (unavoidable).

7.3.1 Ferritizing Treatments

To achieve a ferritic matrix from a structure (as-cast) ferritic–pearlitic (Fig. 4.5), two kinds of *indirect ferritization* (whose fundamentals were explained in Sects. 4.5.1 and 4.5.2) heat treatments can be used. Treatments are called supercritical annealing—by the English literature *full ferritizing annealing*—and subcritical annealing.

The spheroidal graphite cast iron is heated up to a temperature that allowed for the full austenization of the matrix. The purpose is carrying out the supercritical annealing, Fig. 7.9a. Generally, the treatment is performed at 900 °C. After holding the part at this temperature until the austenization is achieved, a slow cooling is carried out—at 15 °C per hour—down to a temperature that is almost always of 700 °C, lower and near to the metastable eutectoid. Like that, austenite is transformed into ferrite and

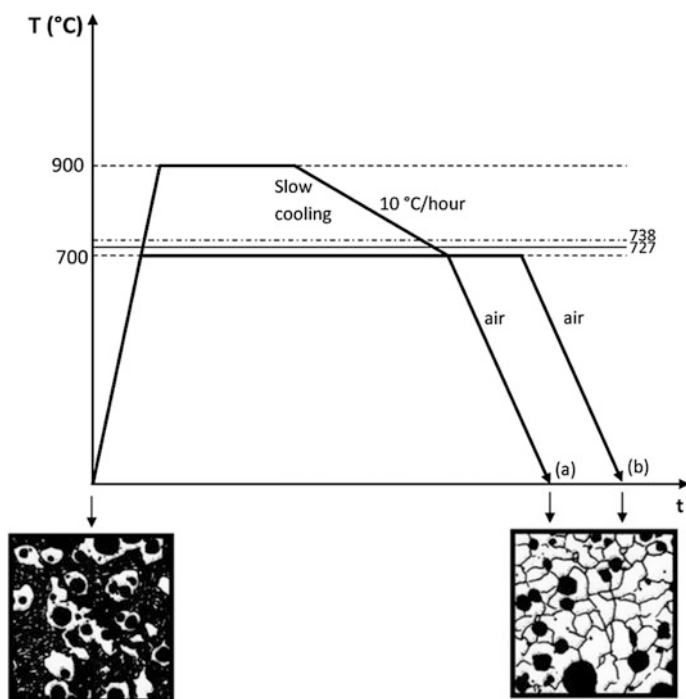


Fig. 7.9 Two ways of obtaining ferritic ductile iron from a ferritic–pearlitic as-cast ductile iron. **a** Supercritical annealing and **b** subcritical annealing

graphite (stable diagram), and the risk of pearlite appearance is avoided (metastable diagram). Finally, from this temperature (700 °C), the cast iron is air cooled. The *degree* obtained is usually 60–40–18.

It is also possible to achieve a *degree* 60–40–18 by means of the subcritical annealing (Fig. 7.9b), without austenization, by heating up to the temperature of 700 °C, which is lower but near to the eutectoid temperature. Then, the part is held at that temperature until achieving ferritization, and then the part is air cooled.

7.3.2 Heat Treatments for Pearlitic Matrix

To achieve a thoroughly pearlitic matrix, the cast iron is usually treated by means of a normalizing heat treatment. The normalizing is carried out by austenizing at 900 °C and then oil cooling with the purpose of transforming the austenite into pearlite (cooling I of Fig. 7.10).

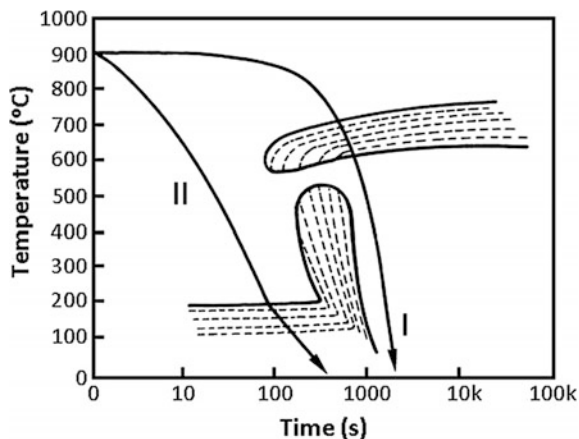
It can be surprising the low hardenability of the austenite as it is observed when the austenite is transformed into pearlite with a relatively fast cooling as happens in the oil cooling. But it should be remembered that—as also happens in the hyper-eutectic steels—the pro-eutectoid cementite favours the heterogeneous nucleation of the pearlitic cementite. That supposes a shift to the left in the corresponding TTT curve of the cast iron, and in this way, a lower hardenability of the cast iron if compared with that of the hypoeutectoid steel.

This structure can be globulized afterwards by tempering at 540–675 °C. At this temperature, the harmful ferritization of the matrix does not happen, because higher times than in the globulization treatment would be necessities. This *annealing for the pearlite globulization* is called *tempering*, in the same way that the treatment used in the martensite tempering (but the resulting structures are not the same).

After the normalizing treatment and the globulization, *degree* 100–70–03 can be obtained. This degree is suitable for machine components and automotive parts

Fig. 7.10 Ductile cast irons.

I. Normalizing thermal treatment. II. Quenching



(such as steering knuckles, brake shoes, camshafts, certain crankshafts, etc.). However, as-cast, lower elongations would be obtained, although enough for less critical applications such as, for instance, machine frames.

7.3.3 Treatments for Achieving a Matrix of Tempered Martensite

Martensite can be obtained by quenching of the austenite if the cooling severity is high. It would be enough with the use of oil, but the bath should be shaken (cooling II of Fig. 7.10).

Quenching is performed from 900 °C, and the subsequent tempering is carried out at 510–565 °C. In this way, structures of tempered martensite can be achieved (Fig. 7.11)—and the best wear resistance of all the spheroidal graphite cast irons is obtained—*degree* 120–90–02. This cast iron is employed in drawing dies, gears, gearwheels, rolling mill rolls, etc.

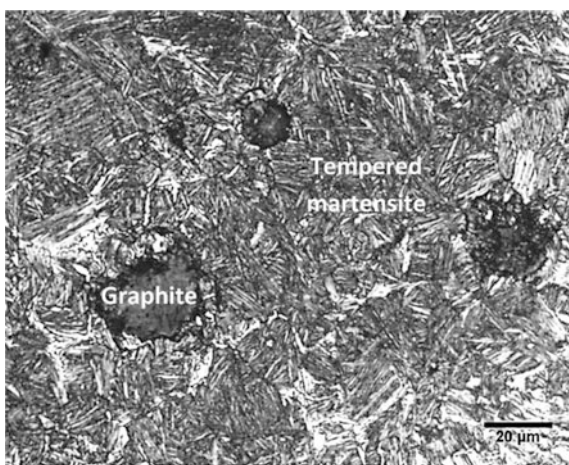
Exercise 7.12. From a grey cast iron of spheroidal graphite, how can be achieved the following structures?

Question

Spheroidal graphite in pearlitic matrix: austenization followed by cooling according to the metastable diagram.

Spheroidal graphite embedded in ferrite in a pearlitic matrix: as-cast structure with direct ferritization (slow cooling), or austenization with indirect partial ferritization followed by cooling according to the metastable diagram.

Fig. 7.11 Spheroidal graphite dispersed in tempered martensite matrix (in the graphite's periphery can be seen regions with lower carbon content than in the matrix because of the direct ferritization)



Spheroidal graphite embedded in pearlite in a ferritic matrix: austenization of the as-cast cast iron with ferritic matrix. Metastable cooling (air cooling).

Spheroidal graphite in martensitic matrix: austenization with fast cooling and tempering.

Lamellar graphite in pearlitic matrix: re-melting of the cast iron and cooling according to the metastable diagram.

7.3.4 Other Treatments for Austenitic Cast Irons: Stress Relieving and Hyperquenching

Ductile cast irons of austenitic matrix are usually subjected to heat treatment with the purpose of relieving stresses or solubilizing second phases.

The first of these treatments, which is given to parts of great size or with zones of different massivities, has as objective *relieving stresses of thermal origin* produced during the solidification process. The relief of these stresses can be achieved by heating the parts up to the temperature of 650 °C. Afterwards, the part is held at that temperature and finally is slowly cooled. This treatment does not produce structural modifications.

The other treatment consists in heating the parts up to 950 °C, with the purpose of dissolving secondary carbides followed by hyperquenching from this temperature. In this way, second phases, even though in unstable equilibrium, continue in solid solution at room temperature.

Exercise 7.13. Relief time (arbitrarily defined as the time necessary for relieving the stress down to a half of the initial value) can be calculated from the creep equation as follows. Total internal deformation of the part (ε_t) should remain constant. And the creep deformation (ε_{Cr}) begins to progressively replace elastic deformation (ε_{el}), and therefore, initial stress is reduced. For a time t ,

$$\varepsilon_t = \varepsilon_{el} + \varepsilon_{Cr} = \frac{\sigma}{E} + \int_0^t B \cdot \sigma^m \quad (7.78)$$

B is thermally activated:

$$B = B_0 \cdot \exp\left(-\frac{Q}{RT}\right) \quad (7.79)$$

As ε_t is constant, if the last equation is differentiated facing to the time, the following equation is obtained:

$$0 = \frac{1}{E} \cdot \frac{d\sigma}{dt} + B \cdot \sigma^m \quad (7.80)$$

If we integrate from $\sigma = \sigma_i$, at $t = 0$, until σ , at time t , we obtain

$$\frac{1}{\sigma^{m-1}} - \frac{1}{\sigma_i^{m-1}} = (m-1) \cdot B \cdot E \cdot t \quad (7.81)$$

When $\sigma = \sigma_i/2$ and reordering, it is obtained:

$$t_r = (2^{m-1} - 1)/(m-1) \cdot B \cdot E \cdot \sigma_i^{m-1} \quad (7.82)$$

When $\sigma = \sigma_i/4$:

$$t_r = (4^{m-1} - 1)/(m-1) \cdot B \cdot E \cdot \sigma_i^{m-1} \quad (7.83)$$

When $\sigma = \sigma_i/10$:

$$t_r = (10^{m-1} - 1)/(m-1) \cdot B \cdot E \cdot \sigma_i^{m-1} \quad (7.84)$$

In the cast iron: 3.5% C, 2.2% Si, 0.7% Mn, 0.14% P, 0.11% S, 0.25% Cr, internal stresses are of around 8 ksi, at 600 °C. The required time for the relief of those stresses down to a half of their initial value is of around 15 min. Calculate the time required for the relief of the stresses down to a value 4 and 10 times, respectively, of the initial value (Fig. 7.12).

Data: $m = 5$ (exponent of the creep equation in stationary regime).

Question

If relaxation times are compared when $\sigma_i/2$ and $\sigma_i/4$:

$$\frac{t_{\sigma/4}}{t_{\sigma/2}} = \frac{x}{15} = \frac{4^{m-1} - 1}{2^{m-1} - 1} \simeq 2^{m-1} \quad (7.85)$$

$$t_{\sigma/4} = 15 \cdot 2^4 = 240 \text{ min (4 h)} \quad (7.86)$$

In the same way, if the relaxation times are compared when $\sigma_i/10$ and $\sigma_i/2$,

$$\frac{t_{\sigma/10}}{t_{\sigma/2}} = \frac{x}{15} = \frac{10^{m-1} - 1}{2^{m-1} - 1} \simeq 5^{m-1} \quad (7.87)$$

$$t_{\sigma/10} = 15 \cdot 5^4 = 9375 \text{ min } (\simeq 156 \text{ h}) \quad (7.88)$$

Calculate the relieving process activation energy, when the relaxing time at 565 °C is known for $\sigma_i/2$. This time is around 60 min.

Question

At 565 °C,

$$t_{\sigma_i/2} = 60 = \frac{(2^{m-1} - 1)}{(m - 1) \cdot B_{565} \cdot E \cdot \sigma_i^{m-1}} \quad (7.89)$$

At 600 °C,

$$t_{\sigma_i/2} = 15 = \frac{(2^{m-1} - 1)}{(m - 1) \cdot B_{600} \cdot E \cdot \sigma_i^{m-1}} \quad (7.90)$$

If we divide the last two equations,

$$\frac{t_{565}}{t_{600}} = \frac{60}{15} = \frac{B_{600}}{B_{565}} = \frac{B_0 \cdot \exp(-Q/R \cdot 873)}{B_0 \cdot \exp(-Q/R \cdot 838)} \quad (7.91)$$

$$4 = \exp \left[\frac{Q}{R} \cdot \left(\frac{1}{838} - \frac{1}{873} \right) \right] \quad (7.92)$$

If we use Napierian logarithms,

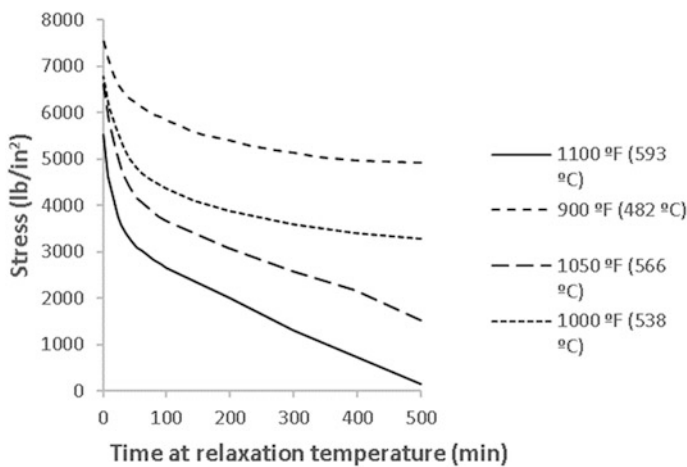


Fig. 7.12 Stress as a function of the time at relaxation temperature (3.51% C–2.15% Si–0.69% Mn–0.113% S–0.138% P–0.25% Cr) (elaborated with data from Flinn 1963)

$$Q = \frac{\ln 4 \cdot 8.31 \frac{\text{J}}{\text{mol K}} \cdot 838 \cdot 873 \cdot \text{K}^2}{35 \text{ K}} \simeq 241 \text{ KJ/mol} \quad (7.93)$$

This value is like that one of activation energies for the Fe_z diffusion in volume ($\simeq 250 \text{ KJ/mol}$), necessary in the cast iron creep processes.

Demonstrate that at 538 °C, relaxation times are around 200 min.

Question

$$\frac{t_{538}}{t_{600}} = \frac{x}{15} = \exp \left[\frac{Q}{R} \cdot \left(\frac{1}{811} - \frac{1}{873} \right) \right] = \exp \left[\frac{241000}{8.31} \cdot \left(\frac{1}{811} - \frac{1}{873} \right) \right] = 12.7 \quad (7.94)$$

$$t_{538} = 12.7 \cdot 15 = 190 \text{ min} \quad (7.95)$$

Demonstrate that at 500 °C, relaxation times can be excessively long (unfeasible). And, at 450 °C?

Question

$$\frac{t_{500}}{t_{600}} = \frac{x}{15} = \exp \left[\frac{Q}{R} \cdot \left(\frac{1}{773} - \frac{1}{873} \right) \right] = \exp \left[\frac{241000}{8.31} \cdot \left(\frac{1}{773} - \frac{1}{873} \right) \right] = 73.5 \quad (7.96)$$

$$t_{538} = 73.5 \cdot 15 = 1100 \text{ min } (\simeq 18 \text{ h}) \quad (7.97)$$

$$\frac{t_{450}}{t_{600}} = \frac{x}{15} = \exp \left[\frac{Q}{R} \cdot \left(\frac{1}{723} - \frac{1}{873} \right) \right] = \exp \left[\frac{241000}{8.31} \cdot \left(\frac{1}{723} - \frac{1}{873} \right) \right] = 984.5 \quad (7.98)$$

$$t_{450} = 984.5 \cdot 15 = 14768 \text{ min } (\simeq 10 \text{ days}) \quad (7.99)$$

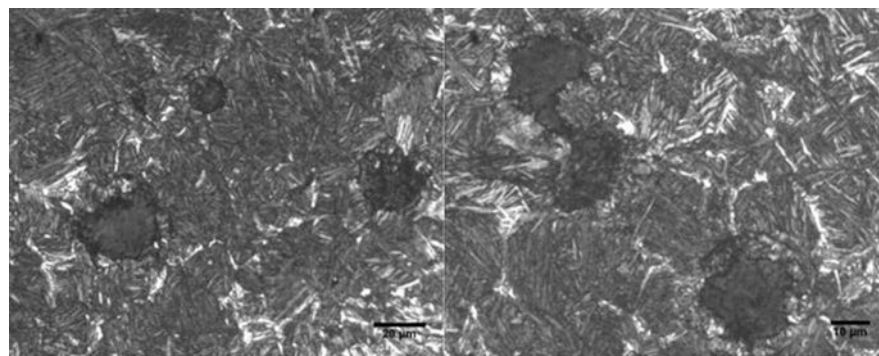


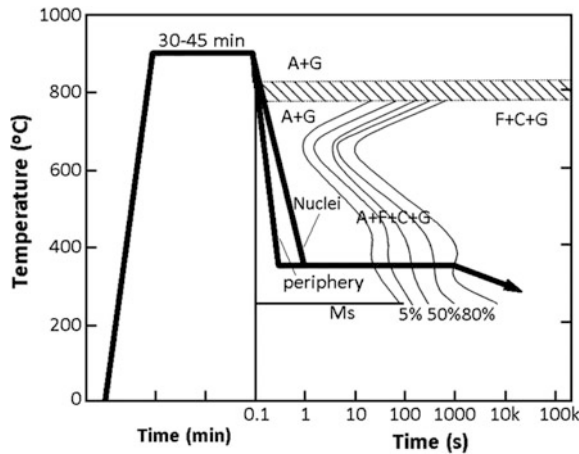
Fig. 7.13 Austempered ductile iron

7.4 Isothermal Treatments. Austempered Cast Irons, ADI (Austempered Ductile Iron)

Austempered ductile iron (ADI) (Fig. 7.13) is a spheroidal graphite cast iron of bainitic matrix that is competitive with steels, because of its low cost and good properties. The hardness of the matrix constituent as well as the advantageous mechanical properties justify the growing use of these cast irons. Austempered ductile irons are commonly used in guides and gears, as an alternative to the case-hardened steels, but are also used in the manufacture of crankshafts instead of using quenched and tempered steels.

In these spheroidal graphite bainitic cast irons, average levels of 1000 MPa for tensile strength can be achieved without difficulty, with yield strength of 750 MPa and toughness (in V notch test) of 15 Jules at room temperature. The use of those

Fig. 7.14 Austempering treatment for a ductile cast iron



materials took importance in the 80s, although their use started in the decade of the fifties. In 1990, 25000 tonnes of this kind of spheroidal cast irons were manufactured, while in the 2010s the production reached 300000 tonnes.

To achieve a bainitic structure (uniformly through the thickness of the part), an isothermal treatment of *austempering* is used whose cycle of temperature–time is schematized in Fig. 7.14.

Austenization temperatures do not usually exceed 900 °C. Cast iron austenitic grain size grows little with temperature, and austenite would stabilize with the holding time. Austenite so stabilized becomes more refractory to the transformation by cooling. Austenization should be done in salt baths or in controlled atmosphere furnaces because of the decarburization risks inherent to all cast irons.

Parts are heated at around 900 °C and are held at this temperature for around 30–45 min. For that reason, the full austenization of the typical thicknesses, which parts commonly used have, are achieved with this treatment. On the other hand, longer holding times could cause the precipitation of silicarbides. Cooling is performed at constant temperature, in the range of 250–400 °C, in salt bath furnace, habitually for 45 min.

It is convenient that this isothermal temperature for bainitic transformation should not exceed the temperature of 450 °C, to inhibit the appearance of pearlitic structures. Although to achieve acceptable toughness—in parts such as crankshafts, steering knuckles, cranks, etc.—is preferable that the isothermal temperature should be as high as 370 °C with the purpose of obtaining *upper bainite*, as it seems

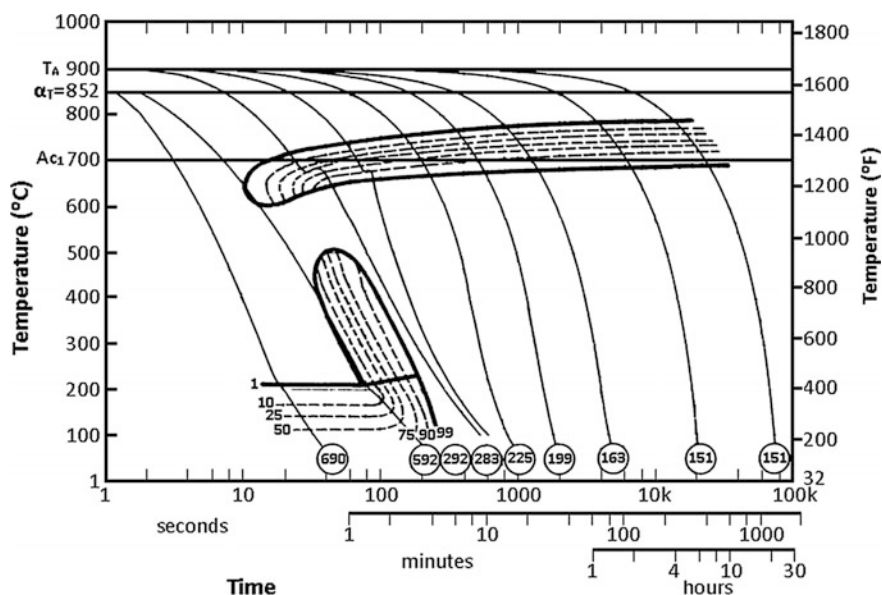
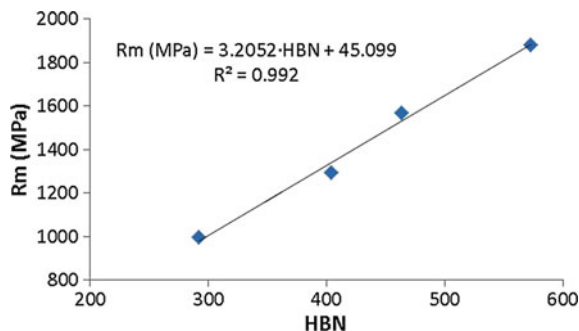


Fig. 7.15 Temperature–time curve (McArdle 1980)

Fig. 7.16 Representation
 R_m -HBN



checked that the upper bainite confers better ductility (although the hardness and the strength would be worse than in lower bainite).

When austempered, some of the carbon atoms (which are expelled by the alpha phase needles) precipitate as carbides when the formation of ferrite needles takes place (constitutive, together with the carbides, of the upper bainite). This precipitation happens in the surroundings of these needles as nanocarbides. Other part of the carbon atoms does not precipitate because of that their high activity hinders the carbides precipitation in the presence of silicon. In this case, carbon atoms diffuse out to the contiguous austenite, stabilizing austenite. This ensures that the increase in retained austenite improves toughness and elongation at room temperature, although the strength slightly diminishes.

By means of austempering treatments with isothermal cooling at temperatures around 370 °C, it is possible to reach a tensile strength of 1000 MPa, yield strength of 800 MPa and an elongation between 10 and 15%.

By contrast, it is possible to achieve through austempering at temperatures around 250 °C, a tensile strength of 1500 MPa, yield strength of 1300 MPa and elongation of 5–8%. These properties are interesting in applications where the toughness should be put ahead of the wear resistance, for instance, in gears.

In any case, obtained structures, logically (and because of the properties), depend on the shape and position of the cast iron TTT curve. It should be remembered that the nearer the TTT curve to the time's origin, the lower the hardenability.

Hardenability of the cast iron should be high enough to avoid austenitic transformation on cooling from the periphery to the nucleus of the part, in the time elapsed between the exit of the part from the austenization furnace and its put into the austempering furnace.

High hardenability is not desirable to avoid long times of austenite isothermal transformation. For that reason, nickel contents are usually below 2.5%. In short, the spheroidal graphite cast iron employed in austempering should be of medium alloy and equivalent carbon slightly hypereutectoid. It is recommended between 3.6 and 3.8% of carbon. Silicon content should be between 2.5 and 3% because higher contents would favour the austenitic matrix ferritization. On the other hand, needles

of bainitic ferrite with more than 3% of silicon in solid solution favour the brittle fracture.

As magnesium content is concerned, it should be around 0.04% after the spheroidization practice.

To obstacle the direct ferritization, other γ -forming elements in solid solution (apart from nickel) are convenient. Manganese is a carburigen element; for that reason, it should be limited to 0.3%. On this point, copper, which is γ -forming element and non-carburigen, is interesting in percentages around 0.6%. This copper content is such effective against ferritization as 1.5% of manganese or 1.5% of nickel. Copper percentages higher than 0.8% are not interesting because of the possible copper precipitation in the matrix, and this situation is unfavourable.

Finally, as recommended compositions, a maximum of 0.04% of phosphorus (maximum) and 0.04% of sulphur (maximum) are accepted.

Exercise 7.14. A grey cast iron of spheroidal graphite with a chemical composition of 3.5% C, 3% Si and 0.21% Mn has been austempered (with a previous heat treatment of austenization at 900 °C) at 225, 275, 350 and 400 °C, respectively, for 30 min. In the enclosed table (Table 7.6), the results obtained in the tensile test, hardness values and volume fraction of retained austenite measured by means of X-ray diffraction are collected. Besides, the continuous cooling time (CCT) curve of a spheroidal graphite cast iron with a similar chemical composition is included (Fig. 7.15). Calculate:

- Possible structures of the cast iron after the isothermal treatment. Is effective the continuous cooling of this cast iron?
- The degree (tensile strength/yield strength/elongation) of the austempered cast irons.
- The relationship between tensile strength and hardness.

Question

- If the transformations in the bainitic–martensitic region are analysed, it would be possible to say that
 - At 225 °C, the structure can be mainly constituted by lower bainite and 16% of retained austenite.

Table 7.6 Parameters obtained with the treatments

Temperature (°C)	R_m (MPa)	$Re_{0.2}$ (MPa)	A ($l_0 = 5d$)	HBN	(fv) _{austenite} (%)
225	1880	–	–	573	16
275	1565	1170	2.88	464	23
325	1294	901	5.96	404	26
400	996	682	18.60	292	39

Table 7.7 Class of the cast iron after the treatment

Temperature (°C)	R_m (MPa)	R_m (ksi)	Class
225	1880	273	270
275	1565	227	225
325	1294	188	185
400	996	144	140

- At 275 °C, the structure can be mainly formed by lower bainite and 23% of retained austenite.
- At 325 °C, the structure will be constituted by lower bainite and 26% of retained austenite.
- At 400 °C, the structure will be formed by upper bainite and 39% of retained austenite.

The continuous cooling from the austenitic range has several problems:

- (1) Risks of indirect ferritization above A_1 .
- (2) Risks of partial transformation into pearlite.
- (3) Risks of bainite (upper and lower) and martensite complex microstructures.
- (4) And lower percentage of retained austenite that negatively affects ductility and toughness.

(b) Class of the austempered ductile irons.

The class according to the American Society for Testing Materials (worldwide admitted) can be defined as the tensile strength divided by 0.69 when this strength has been calculated in MPa, or directly the tensile strength in ksi (Table 7.7).

(c) Correlation between the HBN– R_m :

The correlation HBN– R_m is like that one of the steels (Fig. 7.16). R_m (MPa) $\simeq 3.3 \cdot \text{HBN}$; $\text{HBN} \simeq 3 \cdot R_m$ (kg/mm²).

The austempering is a treatment that favours the formation of simple structures (lower and upper bainite), avoids the ferritization and pearlitic transformation, and improves (because of the proportion of retained austenite) the ductility, which is one of the main problems in cast irons when cast irons are considered as structural materials (considerable improvement in the fracture toughness).

Exercise 7.15. Austempered ductile irons, are white or grey irons? Indicate the main advantages of using these cast irons.

Question

Austempered ductile irons are spheroidal graphite cast irons of bainitic matrix.

These cast irons have lower cost than steels and have good mechanical properties (tensile strength: average 1000 MPa; yield strength: 750 MPa; toughness: 15 J at room temperature).

Abstract

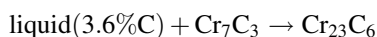
Chromium has been hardly mentioned in previous chapters, and it has only pointed out its carburigen and antigraphitizing character. It is the moment of considering the influence of chromium in the microstructures derived from the Fe–C–Cr system. That is because chromium is an essential element in some high-alloy cast irons. Fe–C–Cr system is also basic when the physical metallurgy of stainless steels is studied.

8.1 Binary Diagrams

Figure 8.1 represents the chromium–carbon equilibrium diagram. In this binary system, there are three carbides of 20, 30 and 40 at.% C. Their chemical formulas are respectively Cr_4C —or more exactly, Cr_{23}C_6 of 20.69 at.% C— Cr_7C_3 and Cr_3C_2 of 5.6, 8.9 and 13 wt% C, respectively.

Cr_{23}C_6 and Cr_7C_3 —and particularly Cr_7C_3 —frequently appear in alloys of the Fe–C–Cr system. Cr_7C_3 can partially solidify from melts whose carbon content is comprised in the range 8.9–5.6%, at temperatures between 1765 and 1510 °C.

The diagram in Fig. 8.1 marks the existence of three peritectic reactions in the C–Cr binary system. Cr_{23}C_6 , for instance, solidifies by peritectic reaction at 1510 °C:



Reciprocally, Cr_{23}C_6 would melt by heating at 1510 °C—if it was not previously dissolved—and for that reason it is said that this is the melting point of Cr_{23}C_6 . The diagram also shows the existence of a eutectic reaction at 1498 °C,

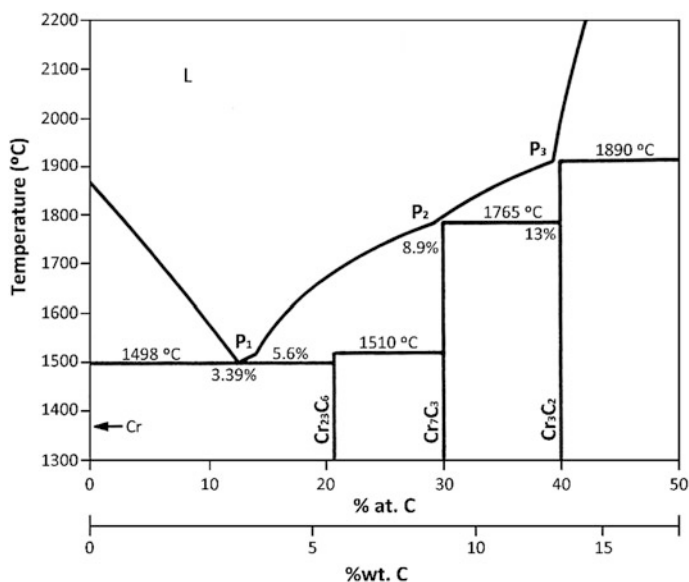


Fig. 8.1 Cr–C equilibrium diagram

when liquid of 3.39% of carbon solidifies and gives an aggregate of Cr_{23}C_6 and alpha solid solution of carbon in chromium. It should be warned that carbon solubility in chromium is nearly zero: 0.32 wt% at 1498 °C and 0.006 wt% at 900 °C.

Figure 8.2 illustrates the iron–chromium binary diagram. This diagram shows that all possible alloys of iron and chromium solidify giving alpha solid solution. The combination of the diagrams shown in Fig. 1.1, Figs. 8.1 and 8.2 gives the ternary Fe–C–Cr diagram (Fig. 8.3).

8.2 Solidification Reactions in the Fe–C–Cr System

In the Fe–C–Cr system, eutectic and peritectic reactions take place at temperatures and compositions that are shown in Fig. 8.3. As it is a ternary system, binary eutectics would have one degree of freedom, and consequently do not solidify at constant temperature.

With the purpose of achieving the 3D representation shown in Fig. 8.3, all reactions published by some authors until W. D. Forgens in 1973 and our experience have been considered. Later works of Warren R. Thorpe (1985) seem to confirm that the area of primary crystallization of M_{23}C_6 only appears with percentages of the order of those shown in our figure.

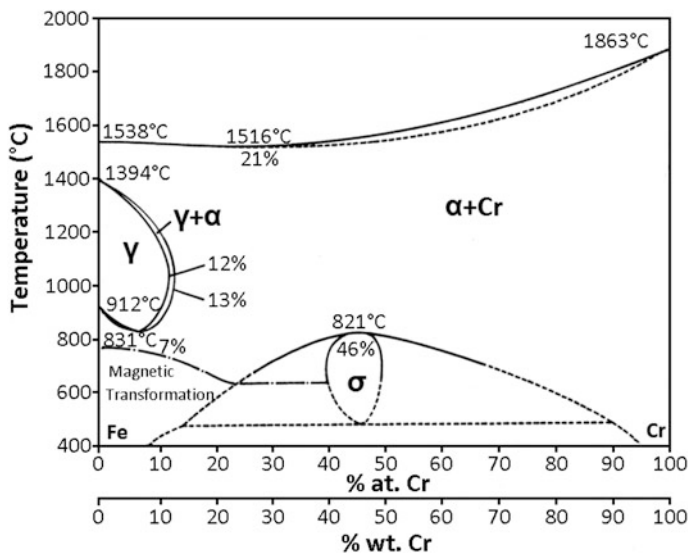
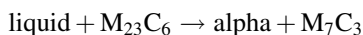


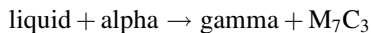
Fig. 8.2 Fe–Cr equilibrium diagram

Regarding the *invariant reactions*, it should be noticed that at 1415 °C, for around 60 wt% Cr—G point in Fig. 8.3—there is a second-class invariant peritectic reaction whose phases in equilibrium are:

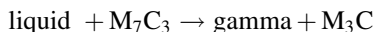


Furthermore, in the cooling from the molten state that temperature of the G point remains constant until the disappearance of the M_{23}C_6 .

At 1275 °C, for 35 wt% Cr—H point in Fig. 8.3—there is also an invariant reaction that is the second-class ternary peritexy:



Finally, at 1160 °C, for 15 wt% Cr—K point in Fig. 8.3—another invariant reaction can be observed, which is also second-class ternary peritectic:



Besides, the binary eutectic, which can solidify between 1160 and 1154 °C, should be analysed. Gamma and carbide of cementitic-type $(\text{Fe Cr})_3\text{C}$ compose this eutectic, where chromium atoms (15 wt% Cr maximum limit) substitute some iron atoms of the cementite. This carbide $(\text{Fe Cr})_3\text{C}$ is usually called K_C or M_3C .

Furthermore, in the other carbides previously mentioned, iron atoms can substitute chromium atoms in the corresponding crystalline structure— $(\text{Cr, Fe})_{23}\text{C}_6$ or $(\text{Cr, Fe})_7\text{C}_3$. These carbides are called K_1 or K_2 , respectively. *The maximum*

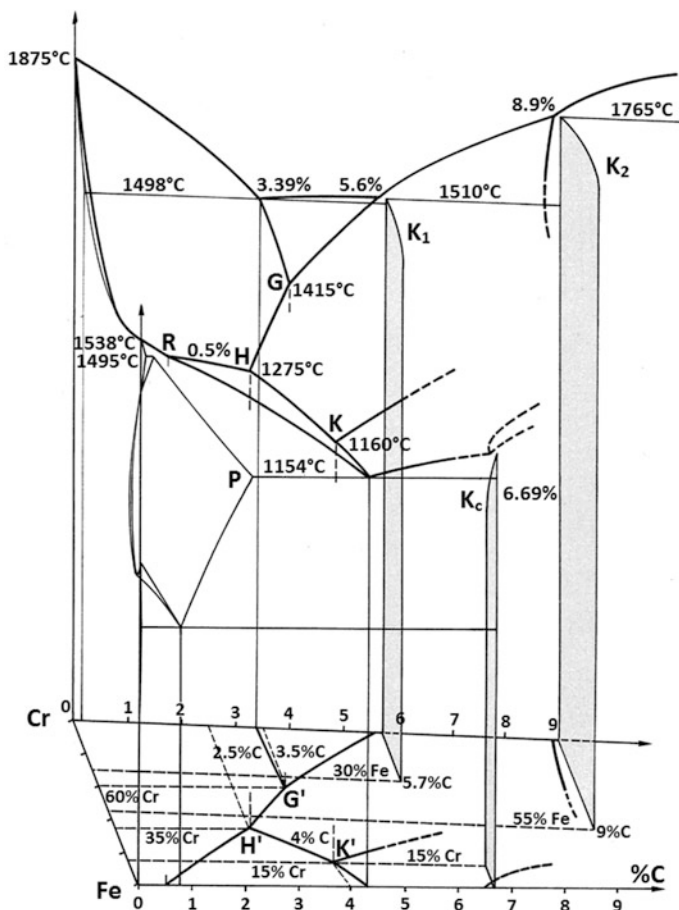


Fig. 8.3 Fe–C–Cr ternary system. Surfaces of liquidus

percentage of Fe is 30% in the carbide K_1 and 55% in the carbide K_2 . K_2 carbides are harder (1500–1800 HV) than K_C carbides (1000–1250 HV).

With the purpose of representing in a ternary diagram the position of K_1 and K_2 carbides, and as the carbon atomic percentage is kept constant in each one of these carbides, tracing parallels to the Fe–Cr side of the Roozeboom equilateral triangle should be done: on the one hand, the parallel should be traced from the representative point of the Cr_{23}C_6 in the Cr–C binary diagram for K_1 carbides; on the other hand, from the Cr_7C_3 point in the case of K_2 carbides, the parallel should be traced. In both situations, the scale in the equilateral triangle sides should be indicated in atomic percentage. Afterwards, above the corresponding straight line to each carbide, a segment limited by 0% Fe composition (point Cr_{23}C_6 or Cr_7C_3 placed in the Cr–C scale) and the representative point of Fe maximum content that can replace chromium in both of these carbides (Fig. 8.4) is calculated.

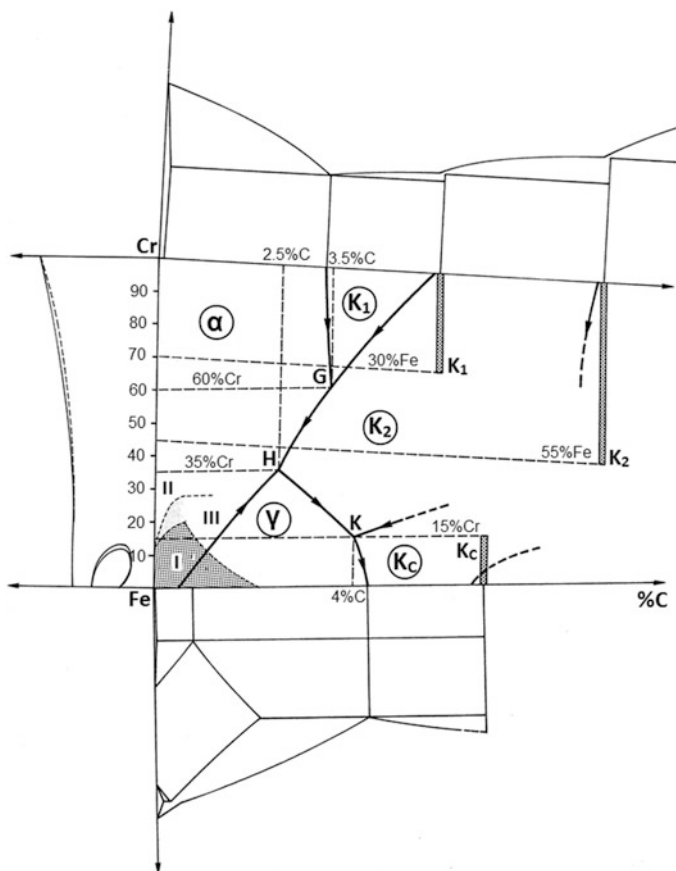


Fig. 8.4 Top view projection of the peritectic and eutectic binary lines—and of G, H, K points of the ternary peritexy—belonging to the Fe–C–Cr equilibrium diagram

In a ternary system composed of chromium, carbon and another metal, if the sides of the equilateral triangle were only set in weight percentages, double carbides—of chromium and another metal—could not be placed above parallel lines traced from the points corresponding to the weight percentages of binary chromium carbides. However, this ternary system can be done because the metal that replaces chromium in the carbide is iron, which has an atomic weight (55.847 g/mol) like that of the chromium (51.996 g/mol).

With the purpose of placing carbides of cementitic-type (K_C), the corresponding straight line will be also the parallel that was traced to the Fe–Cr side from the Fe_3C point situated in the Fe–C side.

Figure 8.3 specifies the liquidus surfaces of the Fe–C–Cr system, and the formation of K_1 , K_2 and K_C carbides involved in the solidification process.

It is convenient to mention that carbides are not necessarily formed during the solidification by primary crystallization, but they can appear by solid-state precipitation. It should be remembered, for example, the formation of vermicular Fe_3C during the cooling of mild carbon steels (C% lower than 0.021%), the formation of pro-eutectoid and eutectoid cementites during the annealing of hypereutectoid steels or the precipitation of cementite during tempering of hardened steels. For none of these cases, by contrast, cementite appears during the steel solidification.

8.3 Austenite with Chromium: Composition Limits and Temperature

It seems necessary to know the composition and temperature limits for austenite composed of iron, carbon and chromium because of its influence in the structure and properties of high chromium alloyed cast irons.

Fe–C–Cr alloys of industrial interest have chromium and carbon levels lower than 40 and 4%, respectively.

Ternary gamma austenite crystalizes in the face-centred cubic system. Saturation limits in carbon, as well as allotropic transformation temperatures or/and the precipitation of carbides, logically change with carbon and chromium contents. To follow those variations, it should be considered, first, the limits of the gamma iron constituent in the Fe–Cr binary system.

8.3.1 Gamma Iron Constituents in the Fe–Cr System

It should be remembered that iron has three different allotropic varieties: delta, gamma and alpha. Pure iron solidifies at 1538 °C as delta iron. Its unit cell is body-centred cubic. At 1394 °C, delta iron transforms into gamma iron, which is faced centred cubic. At 912 °C, another allotropic change takes place: gamma iron transforms into alpha iron. This one crystalizes in the body-centred cubic system, as happens with delta iron, but with a lower cell parameter.

Chromium influence in the transformation points of delta iron into gamma iron—temperature that is called A_4 —and of gamma iron into alpha iron (critical temperature A_3) can be seen in Fig. 8.2, which belongs to the Fe–Cr binary alloys.

Chromium increases stability of delta iron, body-centred cubic. This means that the transformation of delta phase—substitutional solid solution of chromium in delta iron—during the cooling to give gamma phase takes place at the lower temperatures, the higher the chromium content. In this respect, *chromium is always an α -forming element as δ - γ transformation is concerned*. On another note, regarding the gamma–alpha transformation that happens during the cooling, *chromium acts as γ -forming element for contents lower than 7% because it diminishes A_3 temperature, as it is possible to see in Fig. 8.2. When chromium*

content is higher than 7%, then it increases A_3 temperature and acts as α -forming element.

Therefore, when chromium content (percentage) in a Fe–Cr binary alloy is higher than 13%, then the α -forming behaviour of chromium is such enough to suppress the $\delta \rightarrow \gamma \rightarrow \alpha$ transformations. These ferrochromiums keep the primary structure of solidification—ferritic, body-centred cubic—without allotropic transformation down to the room temperature. It is not possible, for instance, to achieve a grain refining simply through heat treatment.

The gamma loop of Fig. 8.2 defines three singular composition domains in the Fe–Cr binary diagram: more than 13%, less than 12% and between 12 and 13%. Percentages of chromium lower than 12% mean that the ferrochromium can be thoroughly austenitized. Percentages between 12 and 13% imply that it is not possible—as shown in Fig. 8.2—to achieve a full austenization of these alloys. For instance, austenization at 1000 °C is incomplete and gives an $\alpha + \gamma$ mixed structure.

Transformation lines that can be seen in Fig. 8.2 for temperatures lower than 821 °C do not have relation with chromium's α -forming character. They belong to the formation during the cooling, after thousands of hours, of a tetragonal complex intermetallic constituent (called *sigma phase*) that can precipitate by spinodal reaction in the ferrite. This constituent gives brittleness to the ferrite. Sigma's phase appears when the alloys have high chromium content (around 45%), although the upper and lower limits of chromium content in sigma's phases have not been completely defined. In steels with more than 20% of chromium after long exposures at 550 °C, thousands of hours, sigma phase precipitates and impairs mechanical properties. Sigma phases can be redissolved in short times by means of heating at temperatures higher than 900 °C.

8.3.2 Limits of the Gamma Iron Constituent in the Fe–C–Cr Diagram

In Fe–Cr–C ternary alloys, carbon's γ -forming character and its ability to form carbides should be considered, apart from the chromium effects that were previously mentioned. Some consequences are defined because of it.

For instance, in Fe–Cr binary alloys, the limit of the gamma loop in Fig. 8.2 is 12% of chromium and the $\alpha + \gamma$ loop limit is 13%. However, in the case of Fe–C–Cr alloys, both limits are displaced towards higher chromium percentages when the carbon content grows. At the same time, as it is possible to see in top view in Fig. 8.5, when carbon content is increased, the region of duplex structures $\alpha + \gamma$ is widened. The higher broadening takes place for a 0.6% of carbon. The gamma loop, that is to say, the limit curve of the alloys that can be full austenitized during the heating, presents the vertical maximum when the chromium content is 18% (points N and N', Fig. 8.5). Analogously, when the carbon percentage is 0.6%, the maximum vertical in the region $\alpha + \gamma$ corresponds

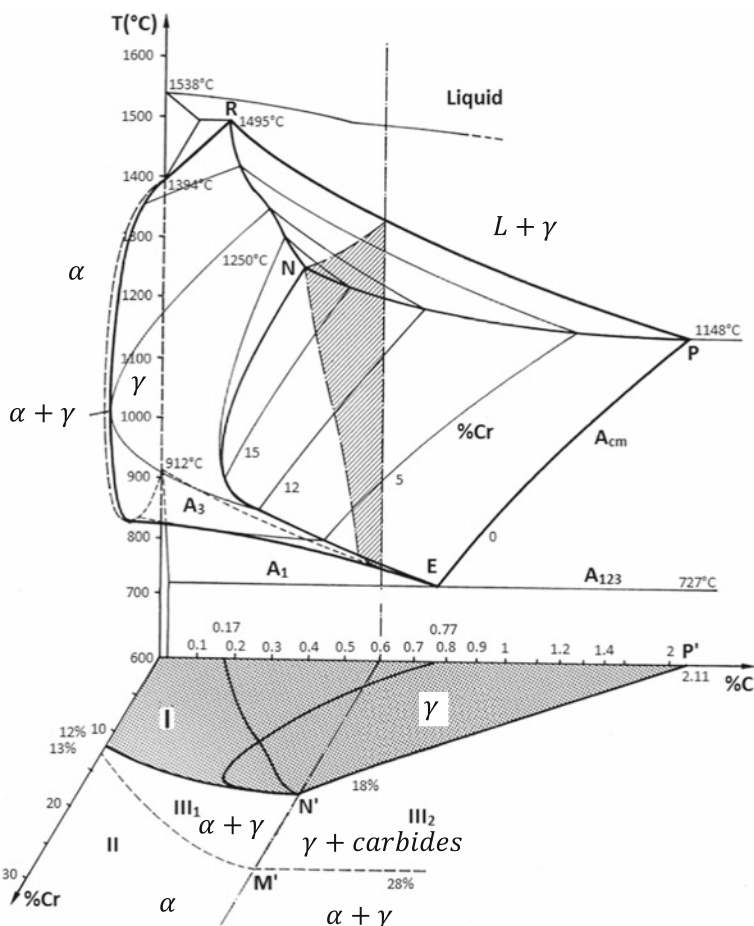


Fig. 8.5 3D representation of gamma field of Fe–C–Cr alloys. In top view: I—Projections of the gamma field; II—Ferritic compositions; III₁—Projections of the gamma + alpha field; III₂—Projections of the gamma + carbides field

with 28% Cr (M' point, in projection, Fig. 8.5). If chromium content is higher than 28%, the alloy is thoroughly ferritic, whatever the carbon percentage.

When the carbon content is higher than 0.6%, it can be observed the triple influence of chromium: in the saturation limits of the carbon in the austenite, in the A_{cm} of pro-eutectoid carbides of cementitic-type K_C precipitation, and in the composition and temperature of the pearlitic eutectoid transformation as well.

According to the first effect, in gamma iron–chromium substitutional alloys—apart from interstitial carbon in octahedral sites—the maximum carbon content admitted by that austenite would be lower than 2.11% and would decrease when chromium content rises.

In Fe–C binary alloys without chromium, carbon saturation in austenite happens—as it is known—when carbon percentage is of 2.11% at 1148 °C.

In Fe–C–Cr ternary alloys, it is possible to see that the carbon saturation limit in austenite—P point in Fig. 8.5—shifted towards higher temperatures and lower carbon contents: from 2.11% C at 1148 °C and 0% Cr to 0.6% C at 1250 °C and 18% Cr. It seems reasonable this tendency because chromium, because of its solidification in a different system compared with gamma iron distorts this structure, reduces the maximum amount of carbon that can enter into solid solution in that austenite and requires temperatures higher than 1148 °C to reach the solubility limit.

Regarding the carbon contents of eutectoid austenite and their pearlitic transformation temperatures, the evolution for rising chromium percentages can be observed in the EN curve of Fig. 8.5: the eutectoid point is found at higher temperatures and lower carbon contents when increasing chromium contents up to 15% Cr. In fact, for 12% Cr, the eutectoid has only 0.35% C.

It is not surprising that the eutectoid temperature changes in this way if it is considered that the eutectoid point is the intersection of the geometrical lines A_{cm} and A_3 . On the one hand, K_C carbides, $(Fe, Cr)_3C$, are more stables than cementite and, as a consequence, they will precipitate from the austenite at higher A_{cm} temperatures than cementite. On the other hand, chromium, for contents higher than 7%, because of its α -forming character, rises (as it is well known) the A_3 temperatures.

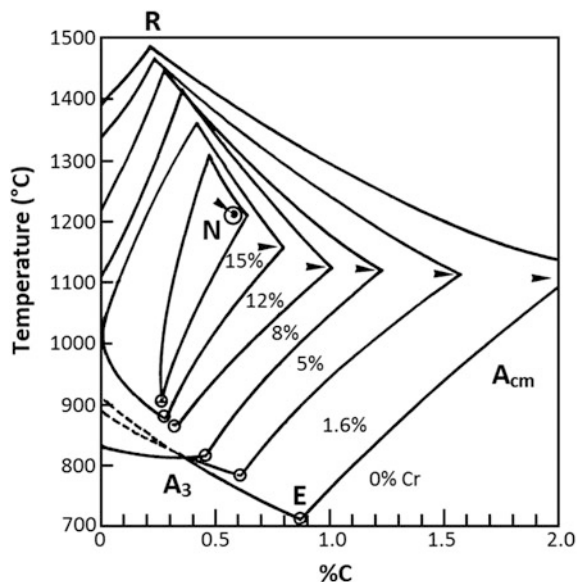
Different sections of the γ -loop in Fig. 8.5—for different chromium contents, constants—can be observed, projected in the plane temperature–carbon percentage, in Fig. 8.6. In Fig. 8.6, the carbon saturation limits in austenite are detailed, for different chromium percentages; the *pearlitic eutectoid* is also detailed in that graph. The gamma field, which closes when chromium content is increased, becomes in a point, N, when the Cr and C percentages are, respectively, 18 and 0.6%.

Shifting of the austenite saturation limit when carbon contents are lower than 2.11%—for instance, for 12% Cr the saturation is near to 0.8% C—justify that some steels, with less than 2.11% C, were called *ledeburitic steels*. In fact, their solidification ends with the formation of a eutectic and consequently they could be considered as *alloyed white cast irons*, with low carbon content. This is the case, for instance, of the steel with the following composition: 1.5% C, 12% Cr and 1% Mo. Other tool steels are also ledeburitic, for instance, high-speed tool steels, either of Taylor 18-4-1 type or W–Mo type (for instance, 0.82% C, 4% Cr, 6.5% W, 5% Mo and 2% V).

Eutectoid point displacement also motivates that a tool steel of carbon content lower than 0.77% is sometimes hypereutectoid. This happens with some tool stainless steels, for instance, the steel of composition: 0.5% C, 14% Cr, 1% Si, 1% Mn and < 1% Ni.

For making conclusion about microstructures and properties of the Fe–C–Cr ternary alloys at room temperature, not only the solidification equilibrium diagram of these alloys is necessary. However, we need to consider both the equilibrium and

Fig. 8.6 Sections of the gamma loop projected on a 0% Cr plane for different—constant—chromium percentages. ► Carbon saturation limits in the austenite (%C, T (°C)); ○ Pearlitic eutectoids (%C, T (°C))



non-equilibrium solid-state transformations. And, these transformations—for instance, the appearance of bainite or martensite from bearing chromium austenite—cannot be collected from equilibrium diagrams.

Those diagrams collect temperatures and equilibrium phases. Nevertheless, they do not indicate the time required for transformations, that is to say, *kinetics factors*. It is convenient to consider the aspects above mentioned when the relationship between microstructure and properties of a high-alloy cast iron (high-chromium) is intended to be predicted—as a function of the equilibrium diagrams.

For instance, high chromium contents improve the austenite hardenability. They make austenite more stable to the transformations during continuous cooling and drop the martensite start transformation temperature M_s . For that reason, when chromium proportions are high and slow cooling rates are applied, the pearlitic transformation of the austenite could not happen—as shown by the equilibrium diagram. The requirement of even slower cooling rates must be assessed. In contrast, by merely air cooling, austenite *will partially transform into martensite* and—because of the low M_s value—will also remain at room temperature a certain proportion of *retained austenite*.

Consequently, martensite appearance is quite common in as-cast structures of high-chromium cast irons (air cooled). Afterwards, a high hardening is possible to be achieved through subsequent heat treatment. For example, a tempering—with the purpose of making unstable the retained austenite—followed by air cooling, which allows for the transformation of the unstabilised austenite into martensite.

That hardening above mentioned should not be confused with the hardening that can be observed in some Fe–C–Cr alloys, for instance, of 35% Cr, after a long holding at temperatures between 500 and 700 °C. This hardening is not a

consequence of non-equilibrium transformations—martensite does not appear. It is due to the formation of sigma phases that were previously described. Fe–C–Cr alloys of high chromium content, all of them of the region II in Fig. 8.5, are always ferritic for any carbon content, and as a result, they have neither critical transformation points nor hardening possibilities through bainitic or martensitic reactions.

Composition, Structure and Properties of High-Alloy Cast Irons

9

Abstract

In previous chapters, low and medium alloy cast irons were considered. In those cast irons, silicon was the main alloying element, although others in small quantities were considered. However, in this chapter, cast irons with more than 10% in alloying elements will be presented, having as objective improving abrasion, corrosion and heat resistances in cast irons, as specific purposes.

9.1 Introduction to High-Alloy Cast Irons

In previous pages, the requirement of an alloying element—silicon—with the purpose of manufacturing grey cast irons was presented. The necessity of adjusting carbon and silicon contents to the different applications of lamellar graphite cast irons was also considered. Some aspects about composition of malleable (nodular) and spheroidal graphite cast irons were also indicated. The reader has available some criteria for being able to establish relationships between composition, structure, properties and applications. In this way, for instance (see Table 9.1), diminishing the equivalent carbon content seems logical when mechanical strength and tightness are pursued in lamellar graphite cast irons. A good castability requires high equivalent carbon contents. Silicon content should be increased if the parts are thin. It is also convenient a certain phosphorus content for achieving good wear resistance. However, in all these considerations, the sum of weight percentages of the different elements—excepting carbon because this element is always present in cast irons—is lower than 10%. Nevertheless, in this section, cast irons with an alloying percentage higher than 10% will be studied. These cast irons are known as high-alloy cast irons. High-alloy cast irons are used when looking for other additional properties such as *abrasion, corrosion and heat resistances*.

Table 9.1 Composition of some cast iron parts of common uses

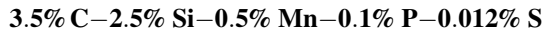
Type of part		Composition (wt%)				
		C	Si	P	S	Mn
High resistance		2.75	2.25	0.10	0.10	0.80
Ornamental		3.50	2.50	1.00	0.10	0.50
Machine equipment	Small thickness	3.25	2.25	0.25	0.10	0.50
	Average thickness	3.25	1.75	0.25	0.10	0.50
	High thickness	3.25	1.25	0.25	0.10	0.50
Ingot moulds		3.50	1.50	0.25	0.07	0.90
Mine waggon wheels		3.35	0.65	0.35	0.12	0.60
White heart malleable cast iron		3.00	0.75	<0.15	<0.20	0.50
Blackheart malleable cast iron		2.75	1.00	<0.15	<0.20	0.50
Ductile cast iron		3.50	2.50	<0.04	0.01	0.03–0.05 Mg

It seems logical to question about the advantages of employing these high-alloy cast irons (more expensive than the cast irons previously studied) instead of unalloyed or low-alloy cast irons. In relation to low and medium alloy grey cast irons, it was said that they have a good *corrosion resistance* (Chap. 5). Moreover, it was also mentioned that cast irons with martensitic matrix are used when a good *wear resistance* is pursued (Sect. 4.3). And some indications regarding the refractoriness were given in previous sections.

However, it should be considered that all above mentioned is referred to some ferrous materials whose primary requirements are the general properties of grey cast irons, and that secondarily it would be interesting that they have another property of the three previously listed. On the contrary, in the case of high-alloy cast irons, the required properties—abrasive wear resistance, corrosion resistance to the chemical attack or inalterability at high temperature—are pursued no matter they have grey or white structures.

On another note, the same high-alloy cast iron usually behaves satisfactorily faced to more than one of the requirements previously mentioned. In this way, high chromium alloy cast iron is almost always used because of its good abrasive wear resistance in the presence of very hard minerals (for instance, quartz), although has a good corrosion and heat resistances as well. High silicon alloy cast iron has good corrosion resistance but also has good wear resistance. High nickel alloy cast iron is stable to heat and behaves well in front of corrosive conditions. As it will be seen, chromium, silicon and nickel are usually present—one or more than one of them—in high proportion in all high-alloy cast irons.

Exercise 9.1. What is the use of the alloy that has the chemical composition mentioned below?



Question

First, the equivalent carbon should be calculated:

$$EC = C + \frac{\text{Si}}{3} + \frac{\text{P}}{3} = 3.5 + \frac{2.5}{3} + \frac{0.1}{3} = 4.37\% > 4.25 = EC_{\text{Grayiron}} \quad (9.1)$$

$EC = 4.37\%$, so, this cast iron is hypereutectic. As applications, it is possible to mention low resistance ornamental parts (sculptures, lampposts, manhole covers, etc.) because of the low solidification interval and excellent castability.

In ornamental applications, eutectic grey irons are usually employed because of the nearly zero solidification interval. With the same finality, hypereutectic grey irons are used in ornamental parts because the hypereutectic graphite does not impair the castability and increases the thermal conductivity.

Exercise 9.2. Reason what of the following chemical compositions would you choose for manufacturing grey cast irons with applications in *thin parts with tensile strength, ingot moulds and elements with resistance to wear and thermal growth?*

(A) 3.8% C–1.5% Si–0.9% Mn–0.2% P–0.07% S

(B) 2.75% C–2.25% Si–0.9% Mn–0.1% P–0.07% S

(C) 1% C–16% Si–0.4% Mn–0.1% P–0.012% S

Question

First, the equivalent carbon of the cast irons is calculated:

$$EC^A = C + \frac{\text{Si}}{3} + \frac{\text{P}}{3} = 3.8 + \frac{1.5}{3} + \frac{0.2}{3} = 4.37\% \quad (9.2)$$

$$EC^B = C + \frac{\text{Si}}{3} + \frac{\text{P}}{3} = 2.75 + \frac{2.25}{3} + \frac{0.1}{3} = 3.53\% \quad (9.3)$$

$$EC^C = C + \frac{\text{Si}}{3} + \frac{\text{P}}{3} = 1 + \frac{16}{3} + \frac{0.1}{3} = 6.3\% \quad (9.4)$$

The manufacture of *elements with growth and wear resistances* requires a grey iron with high silicon content. For that reason, *Cast Iron C* has the suitable chemical composition. This cast iron is commercially known as Duriron. The high silicon percentage (16%) impedes the growth that cementite suffers when splits into iron and graphite at temperatures higher than 450 °C, and also improves the scaling resistance as a consequence of that reduces the propensity of ferrite to oxidation. Duriron is a grey cast iron of matrix thoroughly ferritic (stable cooling). Moreover, this cast iron has wear resistance due to the hardness conferred by the silicon (vid. Sect. 9.3.1).

The manufacture of *ingot moulds* requires a grey iron with high carbon content because the graphite is a good heat conductor. The main feature of the ingot moulds is its ability for heat dissipation, which is achieved by means of graphite, especially lamellar graphite. For that reason, *Cast Iron A* has the suitable chemical composition.

The manufacture of *thin parts with tensile strength* requires cast irons of low carbon content, because the lower the carbon contents, the lower the graphite presence. In this way, the notch effect is reduced, and the resistant cross section is increased (higher toughness), and consequently the tensile strength is improved. That is to say, low carbon content is required. *Cast Iron B* has the suitable chemical composition.

9.1.1 Non-alloyed White Cast Irons

Except for the former reference to the metastable solidification, it was not mentioned in previous sections neither the structure of white cast irons *nor their most typical property, the abrasive wear resistance*. Before talking about the categories of high-alloy cast irons whose abrasion resistance is the main feature, it is noteworthy to refer to non-alloyed white cast irons. Non-alloyed white cast irons are cheap materials with an excellent abrasion resistance and with a better wear resistance in comparison with grey irons and steels. On the contrary, white cast irons have a worse toughness. Even though the components of the alloy are essentially iron and carbon, their excellent wear resistance comes from the microstructure inherited from the metastable solidification.

For instance, it should be considered the evolution from the molten state down to the room temperature of a sand-moulded binary hypoeutectic white cast iron of 3% C balance iron. Its solidification begins at the temperature T_1 of around 1280 °C (see Fig. 1.1). The primary constituent that solidifies (between T_1 and 1148 °C) is austenite. In equilibrium cooling conditions, the solidification ends at 1148 °C. The structure is constituted by primary austenite (2.11% C), and the ledeburitic eutectic matrix (52 wt% austenite (2.11% C) and, 48 wt% cementite, called ledeburite, where cementite is, in turn, the matrix constituent of this ledeburite).

During solid-state cooling, carbon solubility in austenite diminishes both in the primary austenite and in the austenite of the ledeburite. The carbon excess, which was rejected from the austenite cells, precipitates as cementite in either the boundaries of the dendrites or inside of the austenite.

When the temperature of 727 °C is reached, the carbon content in the austenite is 0.77% C (see Fig. 1.1). At this temperature, 0.77% C austenite transforms into pearlite (a lamellar eutectoid made of ferrite and cementite). This transformation affects the primary austenite and the eutectic austenite as well.

In Fig. 9.1, it is possible to see the morphology of the disperse constituent, which was austenite formed before reaching 1148 °C and that has already been transformed into pearlite. It is also possible to see the eutectic matrix that is formed by cementite (white constituent) and dark points that belong to the eutectic austenite, which has also been transformed into pearlite. The same considerations can be made in the case of the hypereutectic white cast irons (Fig. 9.2), but as distinct to

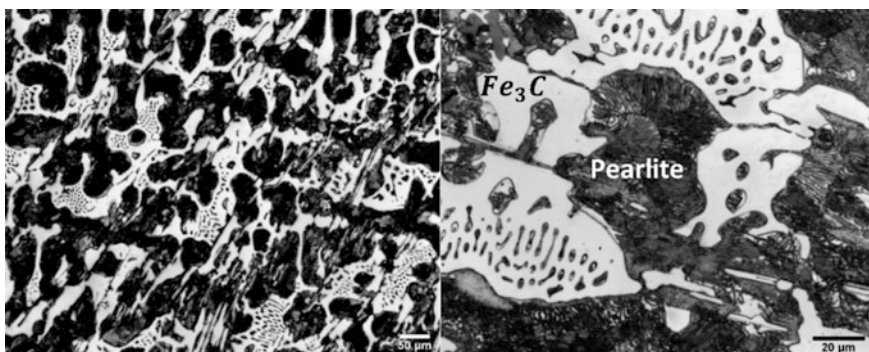


Fig. 9.1 Hypoeutectic white cast iron. The matrix constituent is ledeburite (ledeburitic austenite—and also primary austenite—is transformed into pearlite)

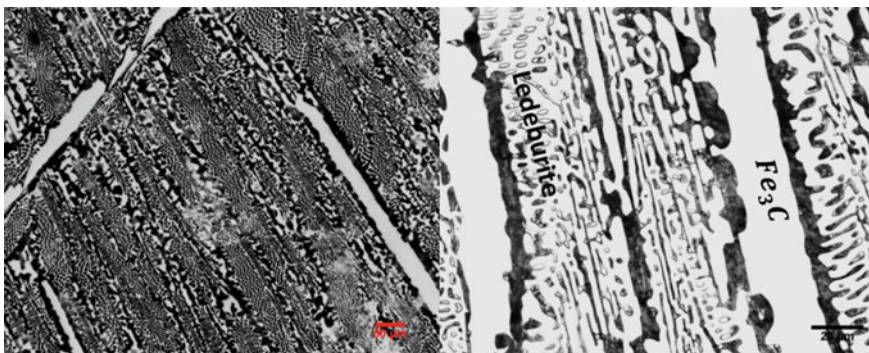


Fig. 9.2 Hypereutectic white cast iron

the hypoeutectic white cast irons, they have as primary constituent needles of Fe_3C that were formed previously to the eutectic solidification.

The microstructure of non-alloyed white cast irons, whose disperse constituent is pearlite, justifies their typical properties: all of them, both hypoeutectic and hypereutectic white cast irons, have *ledeburite as matrix constituent (and the matrix of the ledeburite is cementite)*.

According to the microstructure, a good model to explain the white irons' behaviour could be the *sponge of cementite* with hollows filled in by pearlite. These unalloyed white cast irons are ceramic matrix composites. Strictly speaking about hollows is not adequate because there are no void areas in white cast irons. In white cast irons, a coherency between the primary constituent and the ledeburitic matrix, which is obtained at the end of the solidification (just like between the eutectic cementite and the pearlite), exists. Apart from the above comment, the *sponge's model* is suitable for explaining white cast irons origin: discloses the history of the non-alloyed white cast iron since the liquid state and explains its excellent *abrasion resistance*, at least against abrasive materials, whose hardness in the Mohs scale is lower than the pearlite hardness. The *sponge of cementite* will suffer the most part of the fretting, although the pearlite that fills the hollows results also affected, and because of that pearlite has lower hardness than cementite, it will suffer, in comparison, more wear.

The hardness of an abrasive material has marked influence in the abrasion speed of the material that frets with it. In any case, with the aim of calculating the superiority of one material with respect to other, both materials should be subjected to the same kind of abrasive effort. And their behaviour also depends on the way by which the abrasion is produced and the mode of application of this abrasion as well: wet, dry, by erosion, with grinding wheel, with gouge, etc.

The degree of abrasion resistance of a white cast iron can also change for the same composition depending on the solidification technology that was used. In this way, for instance, a *white iron chill moulded*, or in a graphite mould, which is better heat transfer, usually results in *more resistant to wear than the same cast iron sand moulded*. Chill moulding confers columnar structure, a finer eutectic, and because of the non-equilibrium solidification, a major proportion of ledeburite.

If the white cast iron had 6.67% C, and therefore cementite was its only constituent, without pearlite, the cast iron would have a higher abrasion resistance in comparison with the hypereutectic white cast irons and, obviously, than all hypoeutectic white cast irons. On the contrary, toughness would be very low. Because of the low toughness of white cast irons, logically the higher the carbon content, the lower the toughness, explains that the hypereutectic white cast irons are hardly used.

The *sponge* model also justifies the lack of elongation in these cast irons during the tensile test: the cementite matrix breaks without elongation, as corresponds to the ceramic nature of the Fe_3C intermetallic compound.

The compromise between abrasion resistance, which grows with the carbon content, and toughness, which diminishes with the carbon content, advises the use of hypoeutectic white cast irons, and also justifies—as it will be seen afterwards—the utility of high-alloy cast irons. However, unalloyed white cast irons have

limitations that make necessary the use of high-alloy cast irons. This happens, for example, when the abrasive mineral has hardness higher than that one of the pearlites.

With all that, because of the large number of mining uses, such as mill balls, jaws, wearing plates, etc., unalloyed, or lowly alloyed white cast irons offer their possibilities in the abrasion resistance field. Behaviour of white cast irons that, as can be easily justified if we compare their microstructures, is better than in hypereutectoid steels and in grey cast irons. Reciprocally, due to the excellent abrasion resistance, white cast irons cannot be machined with common tools.

9.2 High-Alloy Cast Irons for Wear Resistance Applications

When it is intended to prevent that an abrasive could cause the pulling out of material, the main feature of this one should be that its hardness should be higher than the hardness of the abrasive. The ten materials of the Mohs scale are well known. They are ordered as growing hardness, in such a way that each one can plough the material that is placed in a previous position in the Mohs scale: talc, gypsum, calcite, fluorite, apatite, orthose, topaz, corundum and diamond. From the materials point of view, they can also be ordered according to their Vickers hardness (HV). Other kind of hardness value would not be adequate because—apart from the difficulty for individualizing the hardness of each micro-constituent—the print of the corresponding indenter would go accompanied with cracking in hard and brittle materials.

Regarding the abrasion behaviour in the field that is being studied, it seems useful the next growing series of Vickers hardness: pearlite of high carbon content (240–425 HV), austenite highly alloyed with chromium (350–400 HV), orthose (6 Mohs, 500–600 HV), martensite of high carbon content (770–800 HV), quartz (7 Mohs, 800–1000 HV), K_C cementitic carbides (1060–1240 HV), topaz (8 Mohs, 1300 HV), K_2 carbides (1500–1800 HV), corundum (9 Mohs, 2000 HV), tungsten carbide (2400 HV), silicon carbide (2500 HV) and diamond (10 Mohs, 8000 HV).

This list of hardnesses offers the first idea of some materials abrasive character. However, it is necessary to consider that a lot of materials that are used because of their abrasion resistance are composites whose structure is formed by various constituents with hardnesses and affinities that are different from those ones of the abrasive. At the same time, the abrasive in its natural form (mineral) is usually formed by more than one constituent. However, the material's abrasive behaviour is more difficult to be understood than the only comparison between the wear resistant material and the abrasive.

On another note, the election of the optimal material for the abrasion resistance usually depends on the economical and not on the technical aspects, except for complementary properties such as corrosion resistance, heat stability, etc. In this way, for instance, the abrasive wear requires the periodical change of the damaged material. Nevertheless, if the replacement of the material is not excessively

expensive, then the use of non-alloyed white cast irons (cheap) is preferable than the high-alloy cast irons (expensive), even when changing the first kind of material is more habitual than the second one.

9.2.1 Ni-Hard Cast Irons

In this section, a low-alloyed white cast iron type, which is normally utilized when the abrasive has hardness intermediate between pearlite and cementite, is considered.

In this case, and despite not being technically the most suitable material, cementite–pearlitic non-alloyed white cast irons could be also employed. From them, at first sight, white cast irons with minimum pearlite content might be used, that is, hypereutectic white cast irons. Nevertheless, the inappropriateness of using neither white cast irons of 6.67% C (thoroughly cementitic) nor hypereutectic white cast irons has been seen in previous paragraphs. For that reason, in the case of using non-alloyed white cast irons, they should be hypoeutectic.

The possibility of transforming the austenite into martensite provides a technical solution to the above-outlined question. In this way, by means of a hypoeutectic white cast iron quenching, it is possible to achieve martensite as disperse constituent, which has higher hardness than pearlite. This way, apart from having a good wear resistance (like that of hypereutectic white cast irons), the cast iron would be more tough than hypereutectic white cast irons because of having a lower cementite content, although transforming the austenite of a white cast iron into martensite (by water quenching) could cause material quenching cracks due to the low martensite start temperature transformation (M_s) attached to the high carbon content of the cast iron. However, the transformation into martensite by simply air cooling could be achieved without cracking risks, if a cast iron of higher hardenability was used (austenite enrichment with alloying elements in low-alloy white irons). This is the case of the trademark registered by the Mond Nickel Company: *Ni-hard cast irons*.

The hardenability of the Ni-hard cast irons is due to the presence of alloying elements such as nickel, chromium and molybdenum. With the purpose of avoiding the solidification as grey cast iron, silicon percentages should lower than 1%. However, a certain amount of silicon is advantageous because (for the same carbon content) it increases the equivalent carbon of the cast iron and, for this reason, its castability. The carbon percentage is usually between 2.5 and 3.5% C, because the lower the ledeburite, content the higher the toughness.

The chromium content in Ni-hard cast irons is favourable because it is an antigraphitizing element and also tends to form K_C carbides, whereas, because of its tendency to precipitate carbides instead of remaining in solid solution in the austenite, chromium results are less effective than nickel for increasing the hardenability. The proportions of chromium are normally between 1.5 and 4 wt%.

In Fig. 9.3, the Ni-hard alloy is represented (point 1). It should be observed that the eutectic of this cast iron (as opposed to the classical eutectic of the unalloyed

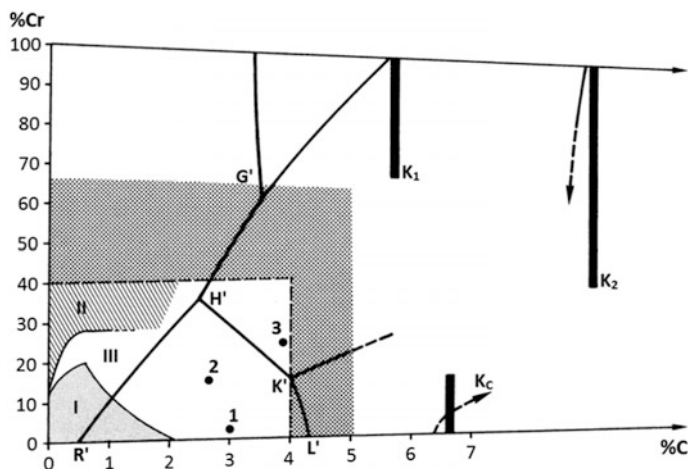


Fig. 9.3 Top view projection of the Fe–C–Cr equilibrium diagram (see Figs. 8.3 and 8.4). Some representative compositions are 1. 4% chromium, 3% carbon, balance iron; 2. 15% chromium, 2.67% carbon, balance iron; 3. 24% chromium, 3.9% carbon, balance iron

white cast irons that comprises Fe_3C and austenite) is a *ledeburite* constituted by K_C carbides and austenite. On the other hand, and analogously to unalloyed white cast irons, the matrix constituent of *Ni-hard ledeburite* is K_C carbide. K_C carbides—duplex of Fe and Cr, of cementitic type—are slightly harder than cementite, and from this point of view Ni-hard cast irons are better than unalloyed white cast irons as wear resistance is concerned.

Nickel, because of being a graphitizing element, favours grey solidification. However, this effect, which is unfavourable in this situation, is not relevant for the common percentages used in Ni-hard cast alloys: between 3.5 and 5% Ni. Nevertheless, these percentages are suitable for increasing the austenite hardenability and allow its transformation into martensite by means of simple air cooling.

Regarding the molybdenum addition, which is a strong carburigen element, the same conclusions than for chromium could be deduced. However, in percentages lower than 1% molybdenum, it remains in solid solution in the austenite, and efficiently increases the hardenability. Besides, molybdenum has the advantage of diminishing the martensite start temperature transformation (M_s) less than nickel. For that reason, the presence of molybdenum increases the hardenability without increasing the retained austenite content.

In Ni-hard cast irons, a large amount of retained austenite will be present after the air cooling. That is due to both the stabilizing effect conferred by the low severity of air cooling, and the high amount of carbon and alloying elements dissolved in the austenite, which brought about a low martensite start temperature transformation (M_s). The microstructure of the Ni-hard cast irons can be observed in Fig. 9.4. Needles of martensite in the grey background of retained austenite can

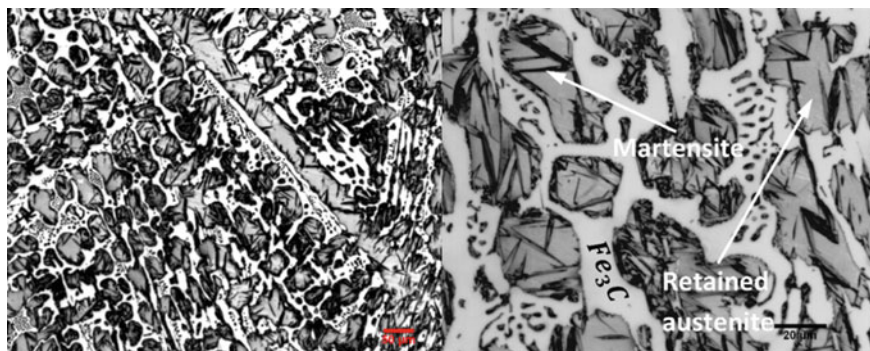


Fig. 9.4 Ni-hard cast iron (point 1 in Fig. 9.3). Inside of the austenite (both primary and ledeburitic), the needles of martensite appear (highlighted in the background of retained austenite)

be seen inside the primary austenite as well as in the eutectic austenite that forms part of the eutectic matrix.

It should be remembered that austenite is a soft constituent and, therefore, results unfavourable for wear and abrasion resistances. With the purpose of diminishing the amount of retained austenite, whether it is economically feasible, a sub-zero quenching (between -55 and -75 °C) can be performed. By means of this procedure, the amount of transformed martensite can be increased.

Other treatment that could be used with the purpose of reducing the amount of retained austenite and increasing the quantity of martensite is the tempering. The tempering destabilizes the austenite during the heating—by means of carbides partial precipitation—and achieves that carbon-depleted austenite transforms during the cooling in martensite.

If the working conditions imply crashes and the aggregate size is suitable, a certain amount of retained austenite could transform into martensite through mechanical deformation during the service. That is because the M_d temperature (temperature above which martensite cannot form under deformation) of the austenite (for the compositions above mentioned) is higher than the room temperature.

It is possible to manufacture cast irons cheaper than Ni-hard cast irons, but with higher amount of retained austenite and therefore, with lower abrasion resistance, if 3–5% of manganese is used instead of nickel.

With the same percentages, manganese reduces more the M_s temperature than nickel. The M_s drop can be balanced with a reduction of the carbon content down to 2.1%. The diminishing in castability would be compensated with silicon, which increases the equivalent carbon. Silicon content is commonly around 3%. This percentage could seem high for a white cast iron, but in fact, there are not graphitizing risks during the solidification because the carbon percentage is very low and manganese, the same as chromium, is carburigen. As it is logical, the composition of these cast irons, alternatives to the Ni-Hard cast irons, can change in

relation with the values that were mentioned. The compositions should be adjusted according to the massivity modulus, which has influence in the solidification and in the case hardening.

Exercise 9.3. The micrographic structure of a Ni-hard cast iron (chemical composition: 3.2% C, 3.5% Ni, 1.2% Cr, 0.4% Mn, 0.5% Si) has a great proportion of retained austenite. Explain the reasons. Data:

$$M_S(^{\circ}\text{C}) = 500 - 350 \cdot (\% \text{ C}) - 40 \cdot (\% \text{ Mn}) - 20 \cdot (\% \text{ Cr}) - 17 \cdot (\% \text{ Ni}) - 10 \cdot (\% \text{ Mo}) \quad (9.5)$$

$$\text{Koistinen and Marburger equation} \rightarrow f_A = \exp[-0.011 \cdot (M_S - T_A)] \quad (9.6)$$

where f_A is the fraction of retained austenite and T_A is the room temperature (quenching temperature).

Question

M_S temperature is calculated:

$$M_S = 500 - 350 \cdot 0.77 - 40 \cdot 0.4 - 20 \cdot 1.2 - 17 \cdot 3.5 = 131^{\circ}\text{C} \quad (9.7)$$

The fraction of retained austenite is calculated with the Koistinen and Marburger equation (25 °C is supposed as the room temperature):

$$f_A = \exp[-0.011 \cdot (131 - 25)] \simeq 0.31(31\%) \quad (9.8)$$

Ni-hard cast irons (cementite sponge) are alloyed white cast irons with a hardness intermediate between that one of the pearlites and the Fe_3C .

To increase the hardness (wear resistance) of the white cast iron, this one is air quenched with the idea of transforming the austenite into martensite. After this quenching treatment, it is common a huge amount of retained austenite. That is because of the stabilizing effect caused by the air-quenching low severity, and the high carbon and dissolved alloying elements that diminish the M_S . Austenite is a soft constituent, and for that reason it is unfavourable in wear and abrasion resistance applications. Retained austenite can be eliminated either through heat treatment as it was previously mentioned, or sub-zero quenching. In this way, in a quenching performed at -60°C , the fraction of retained austenite would be (according to the Koistinen and Marburger equations)

$$f_A = \exp[-0.011 \cdot (131 + 60)] \simeq 0.12(12\%) \quad (9.9)$$

Exercise 9.4. In the cast iron A: 2.65% C–13% Cr, the percentage of eutectic carbides calculated by quantitative metallography is 25%, and its chromium content is 40%. It is requested:

1. Represent the alloy and its phases in the Fe–C–Cr ternary diagram.
2. It was performed, initially, a treatment for 20 min. at 1000 °C with the finality of destabilizing the austenite (carbides precipitation). Afterwards, isothermal treatments were carried out for 24 h at the following temperatures: 250, 500, 600 and 700 °C; the hardness (HV50) was measured: 579, 784, 489 and 351, respectively. With the TTT curve of this alloy, calculate the microstructures that it will have at the mentioned temperatures.
3. Calculate the fraction of retained austenite that has this composition after the heat treatment ($M_S = 197$ °C).

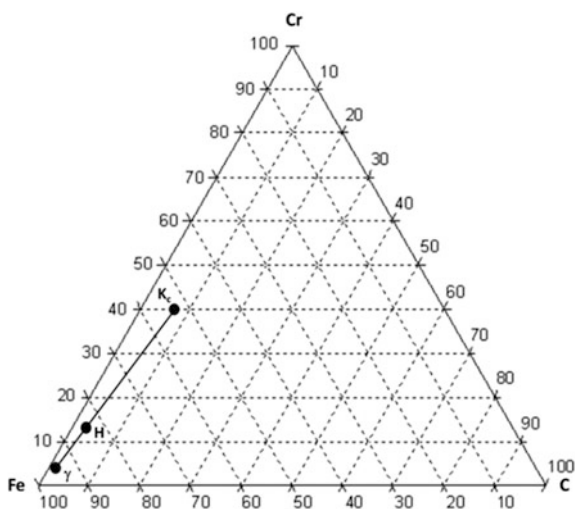
Question

1. Representation in the Fe–C–Cr diagram of the cast iron A and its phases (Fig. 9.5):

Fractions of austenite and K_C carbides calculated from the mass balance:
According to the enunciation information,

$$f_{\text{Carbides}} = 0.25 \text{ (25\%)} \quad (9.10)$$

Fig. 9.5 Cast Iron A: 2.65% C–13% Cr



$$f_{\gamma} + f_{\text{Carbides}} = 1 \rightarrow f_{\gamma} = 1 - f_{\text{Carbides}} = 1 - 0.25 = 0.75 \text{ (75\%)} \quad (9.11)$$

Austenite chromium content:

$$13 = 0.75 \cdot x + 0.25 \cdot 40 = 0.75 \cdot x + 10 \rightarrow x = 4\% \text{ Cr} \quad (9.12)$$

Fraction of austenite in the matrix according to the Fe–C diagram:

$$\frac{f_{\gamma}}{f_{\text{Carbides}}} = \frac{(6.67 - 4.3)/(6.67 - 2.11)}{(4.3 - 2.11)/(6.67 - 2.11)} = \frac{52}{48} \rightarrow f_{\gamma} = 25 \cdot \frac{52}{48} = 27\% \quad (9.13)$$

Constituents or phases in the alloy:

$$\gamma \text{ disperse} = (75 - 27) = 48\% \quad (9.14)$$

$$\gamma \text{ eutectic} = 27\% \quad (9.15)$$

$$K_C \text{ carbides} = 25\% \quad (9.16)$$

Austenite carbon content (carbon content in the K_C carbide is 6.67%):

$$2.65 = x \cdot f_{\gamma} + 6.67 \cdot f_{\text{Carbides}} \quad (9.17)$$

$$2.65 = 0.75 \cdot x + 6.67 \cdot 0.25 \rightarrow x = \frac{0.98}{0.75} = 1.31\% \text{ C} \quad (9.18)$$

2. TTT curve of the alloy (Fig. 9.6):

Microstructures (Fig. 9.7):

24 h/250 °C → 5% Bainite + Martensite + Retained austenite (579 HV)

24 h/500 °C → 50% Pearlite + Martensite + Retained austenite (782 HV)

24 h/600 °C → 100% Pearlite (489 HV)

24 h/700 °C → 100% Pearlite (351 HV)

3. Retained austenite:

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (M_s - T_a)] \quad (9.19)$$

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (197 - 25)] = \exp[-1.89] \simeq 15\% \quad (9.20)$$

9.2.2 Martensitic Cast Irons and K_C Carbides Eutectic (15–28% Cr)

Ni-hard cast irons are the most commonly used cast irons for mining applications: breaking/crushing, classification and transport operations. However, their characteristics are insufficient if the abrasive material has hardness equal to or slightly higher than quartz. That is because the abrasive will plough, and therefore will cause abrasion not only in the pearlite and the martensite constituents but also in the cementite and in the K_C carbides (duplex iron–chromium carbides, M_3C type). Against this kind of abrasive with hardness like quartz, any cast iron of *ledeburitic matrix* will experience a severe wear in service. Cast irons, as Ni-hard type, whose abrasion resistance is higher than that of unalloyed white cast irons, will experience too severe wear because of having K_C carbides as matrix constituent of the ledeburite.

When the hardness of the abrasive is higher than that of the K_C carbides, it seems reasonable to utilize other alloys of the Fe–C–Cr system that provide eutectic matrix of harder K_2 carbides and austenite instead of *ledeburite* (K_C carbides and austenite). These alloys are those that have chromium contents between 15 and 28%.

In the case of abrasives with hardness higher than 9 in the Mohs scale, such as corundum, there are small differences in the abrasion rate, whatever of white cast iron was used.

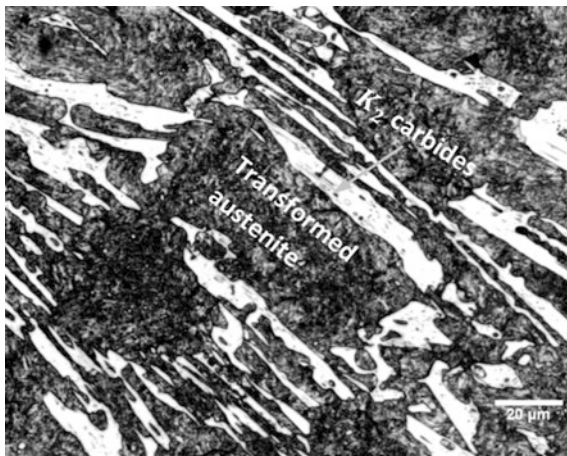
In the range of compositions between 15 and 28% Cr, there are two prototypes of high chromium alloy white cast irons: one hypoeutectic and the other hyper-eutectic. They are represented in Fig. 9.3 with points 2 and 3, respectively.

In Fig. 9.3, it was possible to see a projection in top view of liquidus surfaces that were previously represented in Figs. 8.3 and 8.4 as well. In Fig. 9.3, the limits for Fe–C–Cr cast alloys with industrial interest were also enclosed: no more than 40% Cr and no more than 4% C.

Apart from the alloys 2 and 3, the Ni-hard alloy is in the point 1, Fig. 9.3. As said, austenite and—as opposed to the eutectic of the alloys 2 and 3—cementitic carbides of K_C type (analogously to the ledeburite) form the eutectic of Ni-hard cast irons.

The alloy 2, hypoeutectic, solidifies as rich-chromium primary austenite (as disperse constituent) and non-ledeburitic eutectic (matrix constituent); the eutectic constituents are austenite and K_2 carbides. Austenite surrounds the carbides. This austenite, because of its higher proportion and lower melting point than the carbide, is the eutectic *matrix constituent*. As a consequence of the previously mentioned, this cast iron has a higher toughness than the Ni-hard cast iron and the non-alloyed white cast irons (because the matrix constituent is carbide and not austenite in Ni-hard and non-alloyed white cast irons). In Fig. 9.8, the microstructure of an alloy of chemical composition 2.67% C and 15% Cr (type 2) is represented.

Fig. 9.8 Alloy number 2 of
Fig. 9.3



Exercise 9.5. In the Cast Iron B: 2.7% C–21% Cr, the percentage of eutectic carbides calculated by quantitative metallography is 27.6%, and its chromium content is 55.3%. In this way, an analysis of the matrix austenite indicates that the chromium content is 12.5%. It is requested:

1. Represent the alloy and its phases in the Fe–C–Cr ternary diagram.
2. It was performed, initially, a treatment for 20 min. at 1000 °C with the finality of destabilizing the austenite. Afterwards, isothermal treatments were carried out for 24 h at the following temperatures: 500, 600 and 700 °C; the hardness (HV50) was measured: 860, 441 and 354, respectively. With the TTT curve of this cast iron, calculate the microstructures that this cast iron will have at the mentioned temperatures.
3. Calculate the fraction of retained austenite that has this composition after the heat treatment ($M_S = 270$ °C).

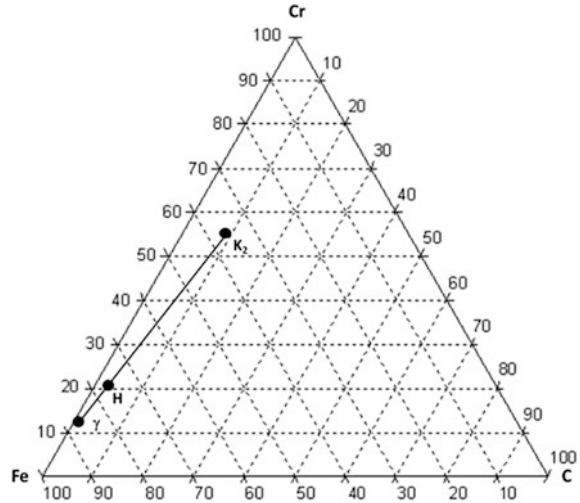
Question

1. Representation in the Fe–C–Cr diagram of the Cast Iron B and the phases: (Fig. 9.9)

Fractions of austenite and K₂ carbides calculated by means of the chromium mass balance:

$$21 = 12.5 \cdot f_\gamma + 55.3 \cdot (1 - f_\gamma) \rightarrow 21 = -42.8 \cdot f_\gamma + 55.3 \rightarrow f_\gamma = 0.8 \text{ (80\%)} \quad (9.21)$$

Fig. 9.9 Cast Iron B: 2.7%
C–21% Cr



$$f_{\gamma} + f_{\text{Carbides}} = 1 \rightarrow f_{\text{Carbides}} = (1 - f_{\gamma}) = (1 - 0.8) = 0.2 \text{ (20\%)} \quad (9.22)$$

Fraction of austenite in the matrix:

$$\frac{0.2}{(0.2 + \gamma_M)} = 0.276 \rightarrow \gamma_M = \frac{0.145}{0.276} = 0.525 \text{ (52.5\%)} \quad (9.23)$$

Constituents and phases in the cast iron:

$$\gamma \text{ disperse} = (80 - 52.5) = 27.5\% \quad (9.24)$$

$$\gamma \text{ eutectic} = 52.5\% \quad (9.25)$$

$$\text{K}_2 \text{ carbides} = 20\% \quad (9.26)$$

Austenite carbon content (carbon content in the carbide K_2 is 9%):

$$2.7 = x \cdot f_{\gamma} + 9 \cdot f_{\text{Carbides}} \quad (9.27)$$

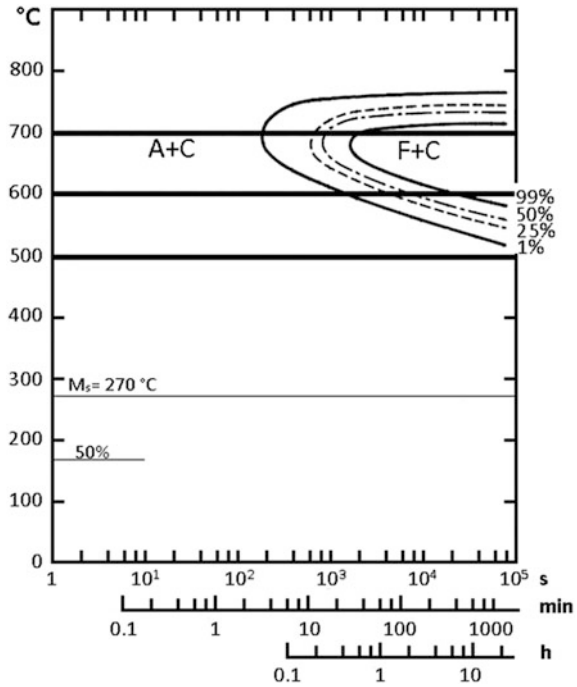
$$0.89 = 0.8 \cdot x + 0.2 \cdot 9 = 0.8 \cdot x + 1.8 \rightarrow x = \frac{0.9}{0.8} = 1.13\% \text{ C} \quad (9.28)$$

2. TTT curve of the cast iron (Fig. 9.10):

Microstructures (Fig. 9.11):

24 h/500 °C → Martensite + Retained austenite (860 HV)

Fig. 9.10 TTT curve of the alloy (adapted from Maratray and Usseglio-Nanot 1970)



24 h/600 °C → 100% Pearlite (441 HV)

24 h/700 °C → 100% Pearlite (354 HV)

3. Retained austenite:

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (M_s - T_a)] \quad (9.29)$$

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (270 - 25)] = \exp[-2.695] \simeq 7\% \quad (9.30)$$

When the chromium and carbon contents in a high chromium white cast iron are enough for being hypereutectic (see alloy 3 in Fig. 9.3), the abrasion resistance is higher than that of the hypoeutectic alloy number 2. This better behaviour is due to the presence of pro-eutectic carbides of K₂ type. In effect, the alloy begins its solidification with the formation of the pro-eutectic K₂ carbides that afterwards remain embedded in the eutectic matrix. As in the case of the alloy type 2, austenite and carbides of K₂ type compose the eutectic matrix. Figure 9.12 shows the microstructure of an alloy of chemical composition 3.9% C and 24% Cr (Type 3). As in alloy type 2, the matrix constituent is also austenite.

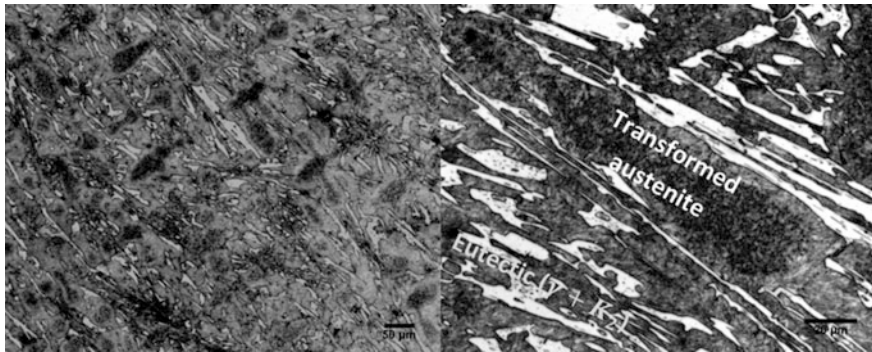
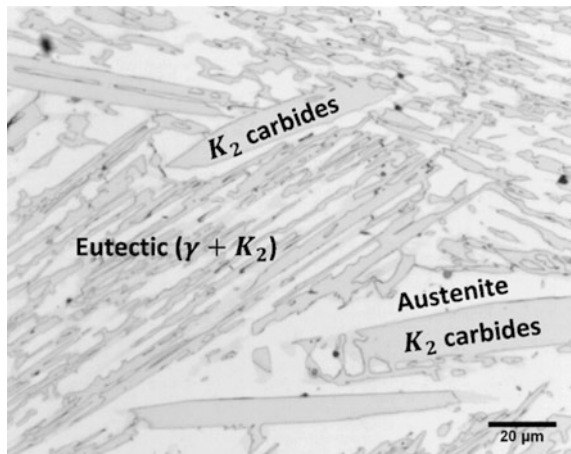


Fig. 9.11 Micrographs of the Cast Iron B

Fig. 9.12 Alloy number 3 of Fig. 9.3



Microstructurally talking, these cast irons, both the hypoeutectic and the hypereutectic, are (apart from being white cast irons because of the metastable nature of the eutectic) *martensitic*. The great hardenability of the pro-eutectic and/or eutectic austenite of these cast alloys, which is given by carbon and chromium dissolved in austenite, justifies that a merely air cooling—*air hardening*—can give martensite. For that reason, due to the presence of martensite, the as-cast parts are hard. If the as-cast part requires to be mechanized, they can be softened through an austenization annealing, followed by *isothermal cooling* in the pearlitic region, because otherwise a continuous cooling after austenization would give martensite once again.

It could seem surprising that the unalloyed white cast irons, which were previously classified as unmachinable, are now machinable if the chromium content is found to be in the range 15 and 28%. It should not be forgotten that the *sponge of cementite* (K_C carbide in the case of Ni-hard cast irons), which is responsible for the

non-machinability of the unalloyed white cast irons, does not appear in the high chromium alloy cast irons. In the last ones, as it is now well known, the *sponge* (the matrix constituent of the eutectic) is austenite instead of cementite; and if this austenite is isothermally transformed into pearlite, then the cast iron can be machinable. Summarizing, as a consequence of the austenitic matrix nature, these cast irons of high chromium content generally tend to be *more tough, and at the same time, more resistant to the abrasion and more machinable* than the cast irons with eutectic matrix of Fe_3C . White irons are ceramic matrix composites. High chromium white irons are metal matrix composites like steels and grey irons.

However, the simple air cooling of the as-cast parts commonly implies a non-negligible amount of retained austenite because of the slow cooling and the low value of the martensite start transformation temperature (M_S). And a faster cooling from the solidification temperatures is not exempt from quench cracks (just for the low value of M_S).

High-chromium cast irons in the as-cast state are subjected to quenching to increase the amount of martensite and improve the hardness in parts. To do this, parts must be austenitized again at 950–1050 °C. Afterwards, they must be held at these temperatures for around 4 h with the purpose of allowing the austenite destabilization through carbides precipitation. And finally, a cooling must be performed with the aim of achieving the transformation of the impoverished austenite (in carbon and chromium) into martensite.

Air cooling is usually employed with the objective of minimizing the cracking risks. Nevertheless, if the quenching is performed in oil or salts baths, the amount of retained austenite would be lower (and consequently the amount of martensite would be higher) and the hardness of the part would be higher.

It should be observed that, from the austenization temperatures that are required for the quenching, the cracking risks because of a fast cooling are lower than in the case of quenching from the solidification temperatures. On the one hand, quenching temperatures (950–1050 °C) are lower than the solidification temperatures. On the other hand, the destabilized austenite M_S value is higher than the solidification austenite M_S value. It should be remembered that the M_S temperature (the more alloyed the austenite, the lower the M_S temperature) is a logical index of the susceptibility to the cracking in the quenching if the parts have a certain thickness and the quenching severity is high. The lower the martensite start transformation temperature (M_S), the more probable the cracking appearance.

After the quenching, a tempering at 200–250 °C is usually performed with the purpose of relieving stresses. This treatment hardly diminishes the martensite hardness, which logically is more stable to the heating than the unalloyed martensite.

In Table 9.2—classes II and III according to the ASTM A532 standard—the common compositions of the high chromium alloy cast irons (15–28% Cr) are summarized. The hardness in different alloying states is also represented in this table. As final summary, it can be said that these cast irons are hardenable, although after the quenching some percentage of retained austenite remains. These alloys are susceptible to be softened by isothermal annealing with the purpose of making

Table 9.2 Class I shows different types of Ni-hard cast irons (white and martensitic)

Alloy		Chemical composition (wt%)							Hardness in different states (HB) ^a						
Class	Type	Name	C	Mn	Si	Ni	Cr	Mo	Cu	P	S	As-cast (sand)	As-cast (chill)	Hardening	Annealing (for machining)
I	A	Ni-Cr-HC	3.0–3.6	<1.3	<0.8	3.3–5.0	1.4–4.0	<1.0	–	<0.3	<0.15	550	600	–	–
	B	Ni-Cr-LC	2.5–3.0	<1.3	<0.8	3.3–5.0	1.4–4.0	<1.0	–	<0.3	<0.15	550	600	–	–
	C	Ni-Cr-GB	2.9–3.7	<1.3	<0.8	2.7–4.0	1.1–1.5	<1.0	–	<0.3	<0.15	550	600	–	–
	D	Ni-Hi-Cr	2.5–3.6	<1.3	1.0–2.2	5.0–7.0	7.0–11.0	<1.0	<1.2	<0.1	<0.15	550	500	600	400
II	A	12% Cr	2.4–2.8	0.5–1.5	<1.0	<0.5	11.0–14.0	0.5–1.0	<1.2	<0.1	<0.06	550	–	600	400
	B	15% Cr-Mo-LC	2.4–2.8	0.5–1.5	<1.0	<0.5	14.0–18.0	1.0–3.0	<1.2	<0.1	<0.06	450	–	600	400
	C	15% Cr-Mo-HC	2.8–3.6	0.5–1.5	<1.0	<0.5	14.0–18.0	2.3–3.5	<1.2	<0.1	<0.06	550	–	600	400
	D	20% Cr-Mo-LC	2.0–2.6	0.5–1.5	<1.0	<1.5	18.0–23.0	<1.5	<1.2	<0.1	<0.06	450	–	600	400
	E	20% Cr-Mo-HC	2.3–3.0	0.5–1.5	<1.0	<1.5	18.0–23.0	1.0–2.0	<1.2	<0.1	<0.06	450	–	600	400
III	A	25% Cr	2.3–3.0	0.5–1.5	<1.0	<1.5	23.0–28.0	<1.5	<1.2	<0.1	<0.06	450	–	600	400

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^aCalculated with tungsten carbide 10 mm and 3000 kg. of load

possible the mechanizing. They have a good abrasion resistance (more abrasion resistance in the case of hypereutectic than in the hypoeutectic cast irons). They have an acceptable toughness because of the eutectic austenite matrix. And these cast irons have an excellent corrosion resistance because of the high chromium content (this is the most appreciated property after the abrasion resistance) as will be demonstrated in the next section.

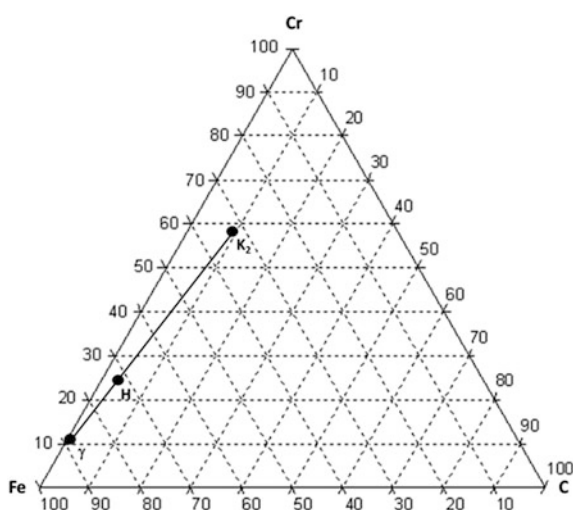
Exercise 9.6. In the Cast Iron C: 3.7% C–25% Cr, the percentage of eutectic carbides calculated by quantitative metallography is 39.4%, and its chromium content is 57%. In this way, an analysis on the austenite of the matrix indicates that the chromium content is 11.6%. It is requested:

1. Represent the alloy and its phases in the Fe–C–Cr ternary diagram.
2. It was performed, initially, a treatment for 20 min. at 1000 °C with the finality of destabilizing the austenite. Afterwards, isothermal treatments were carried out for 24 h at the following temperatures: 280, 500, 600 and 700 °C; the hardness (HV50) was measured: 864, 799, 502 and 408, respectively. With the TTT curve of this alloy, calculate the microstructures that this alloy will have at the mentioned temperatures.
3. Calculate the fraction of retained austenite that has this composition after the heat treatment ($M_S = 279$ °C).

Question

1. Representation in the Fe–C–Cr diagram of the Cast Iron C and its phases (Fig. 9.13):

Fig. 9.13 Cast Iron C: 3.7% C–25% Cr



Proportions of matrix constituent, f_m , and disperse constituent, f_d , deduced from the chromium mass balance:

$$25 = 11.6 \cdot f_m + 57 \cdot (1 - f_m) = -45.4 \cdot f_m + 57 \quad (9.31)$$

$$f_m = \frac{32}{45.4} = 0.7(70\%); \quad f_d = 0.3(30\%) \quad (9.32)$$

The fraction of carbides in the matrix (f_{cm}) and the fraction of austenite in the matrix ($f_{\gamma m}$) are

$$f_{cm} = 39.4 - 30 \rightarrow f_{cm} = 9.4\%; \quad f_{\gamma m} = 60.6\% \quad (9.33)$$

In the eutectic, there are $9.4/70 \simeq 13.4\%$ of K_2 carbides and 86.6% of γ . Chromium percentage in the austenite, x :

$$11.6 = 0.134 \cdot 57 + 0.866 \cdot x \rightarrow x = 4.6\% \text{ chromium} \quad (9.34)$$

Carbon percentage in the austenite, x :

$$3.7 = 0.606 \cdot x + 0.394 \cdot 9 \rightarrow x = 0.25\% \text{ carbon} \quad (9.35)$$

Constituents or phases in the cast iron:

$$K_2 \text{ disperse} = 30\% \quad (9.36)$$

$$\gamma \text{ eutectic} = 60.6\% \quad (9.37)$$

$$K_2 \text{ eutectic} = 9.4\% \quad (9.38)$$

2. TTT curve of the cast iron (Fig. 9.14):

Microstructures (Fig. 9.15):

24 h/280 °C → 1% Bainite + Martensite + Retained austenite (864 HV)

24 h/500 °C → 1% Pearlite + Martensite + Retained austenite (799 HV)

24 h/600 °C → 100% Pearlite (502 HV)

24 h/700 °C → 100% Pearlite (408 HV)

3. Retained austenite:

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (M_s - T_a)] \quad (9.39)$$

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (279 - 25)] = \exp[-2.794] \simeq 6\% \quad (9.40)$$

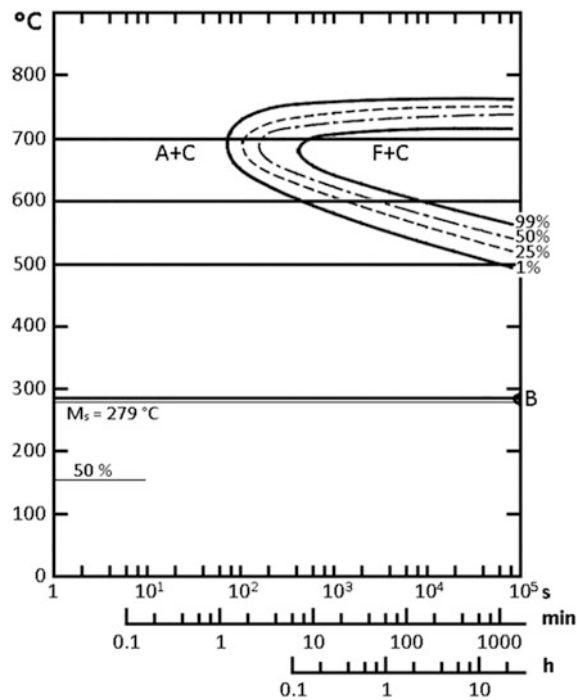


Fig. 9.14 TTT curve of the alloy (adapted from Maratray and Usseglio-Nanot 1970)

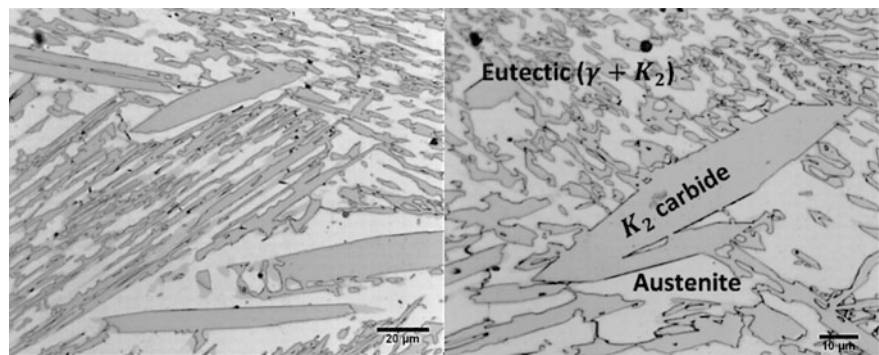


Fig. 9.15 Micrographs of the cast iron C

Conclusions to the analysis of the Cast Iron A (Exercise 9.4), Cast Iron B (Exercise 9.5) and Cast Iron C (Exercise 9.6):

1. Cast Iron A has cementitic matrix, formed by K_C carbides.
2. Cast Irons B and C have austenitic matrix, with K₂ carbides disperse.

3. The cast irons hardness (wear resistance) grows with the chromium and carbon content. The change from K_C carbides to K_2 carbides affects positively this parameter.
4. Austenite carbon content diminishes with the chromium content, and for that reason the M_S value rises, and the percentage of retained austenite is reduced.
5. Cast irons usually get softer for mechanizing after an isothermal treatment at 700 °C. The structure that would be obtained is mainly globulized pearlite.

9.3 Corrosion-Resistant Cast Irons

The selection and design of a material is solved through the compromise between the different properties (sometimes opposed), with the price as decisive factor. On another note, with the purpose of selecting (technically) a metallic material, whose service behaviour facing to the environmental corrosion would be satisfactory, is necessary to establish a certain number of boundary conditions, such as pH of the solution, degree of aeration, temperature, concentration of the corrosive element, circulation speed, etc. This section will not be focused in this way. With general character, it was mentioned in Chap. 5 that grey cast irons are appropriate for water piping, subterranean pipes and outdoors pipes, and interesting for remaining outdoors. Mainly for that reason it is said that grey cast irons are resistant to the corrosion. When this statement is made, it implicitly supposes an environmental corrosion in water presence.

In this section, cast irons that are resistant to the generalized chemical attack (is a kind of corrosion) produced by chemical agents such as sulphuric acid, nitric acid, organic acids, etc. are considered. However, the diverse materials' behaviour facing to different corrosive agents will not be detailed (in case of requiring more information related to this behaviour, the reader should be remitted to the specialized literature in chemical corrosion). In this section, the chemical composition, microstructure and main properties of cast irons that are used because of their corrosion resistance will be explained.

There are three different high-alloy cast irons that are resistant to corrosion: high-silicon, high-chromium and high-nickel cast irons, depending on the alloying elements incorporated to the iron in substitutional solid solution. The graphitizing or carburigen nature of those elements determines the grey or white structure.

9.3.1 High-Silicon Cast Irons

It would be more appropriated talking about *high-silicon cast iron* than high-silicon cast irons. This is because the family of these cast irons can be reduced (in practice) to one cast iron with 16% of silicon, although cast irons with silicon contents between 12 and 16% can be found. This cast iron is one of the most commonly used

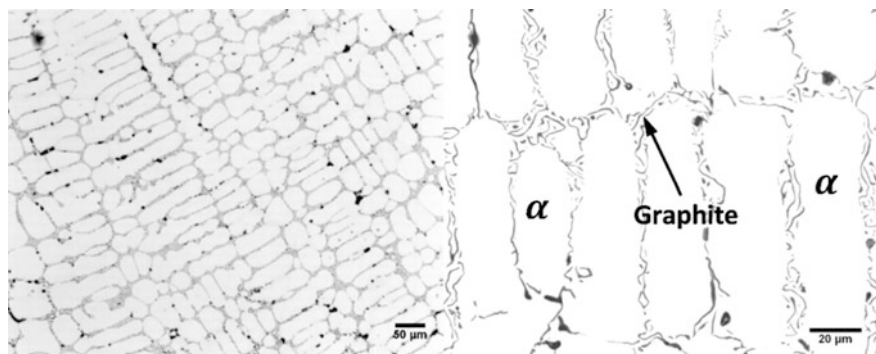


Fig. 9.16 *Duriron* cast iron (16% Si, 0.8% C)

because of its low cost (it would be possible to manufacture this cast iron with the beach sand addition to a molten pig iron). It is usually employed in the drainage system pipes in chemical factories, laboratories, hospitals, etc. Due to the excellent resistance to the sulphuric, nitric and other acids, this cast iron is highly employed in the fertilizer and explosives industries, in paper factories, in the pigments and colourants industries, in electrochemistry, etc. This cast iron is commercially known as *Duriron* and its structure corresponds to a *grey cast iron of matrix thoroughly ferritic* (Fig. 9.16).

Because of its high-silicon content, this cast iron will not present metastable eutectic, but it will present stable eutectic with the formation of graphite instead of carbides. For that reason, it would be a *grey cast iron*. On the other hand, due to the silicon α -forming character, the austenite appearance both in the solidification and during the cooling is avoided. In this way, the eutectics are of *stable* type and are constituted by delta ferrite (with silicon in solid solution) and graphite. The carbon content in the *Duriron* cast iron is between 0.4 and 1%.

In the absence of allotropic transformations during the iron cooling, the grey cast iron will be *ferritic*: dendrites of siliceous ferrite as primary constituent and eutectic of ferrite and graphite that occupies the interdendritic areas.

In *oxidizing* mediums—for instance, in the presence of sulphuric and nitric acids—silicon contributes to the formation of a strongly *protective* superficial film of oxide. This explains that the cast iron results very resistant to sulphuric and nitric acids even at boiling point. This cast iron is also resistant to the solutions of organic acids at any concentration or temperature. However, the behaviour in front of the caustic solutions, mainly at high temperatures, is not good. At low temperatures and low concentrations, its behaviour is not better than that of the non-alloyed grey cast irons facing to caustic solutions.

Silicon, dissolved in substitutional solid solution inside the ferrite, confers high hardness to this constituent, and definitely, to the cast iron: 480–520 HB. *Duriron* cast iron is resistant to wear and almost *unmachinable*. The cast iron is also brittle:

its impact toughness is between 2.5 and 5.5 Joules. The tensile strength is low, 90–180 MPa and has very low thermal shock resistance.

The mechanical features of the Duriron cast iron could be improved by means of decreasing the silicon content, although the corrosion resistance would be reduced. For that reason, silicon contents lower than 12% are only justified (the corrosion resistance would noticeably fall) when the behaviour facing to the chemical attack was a secondary factor in the material choice.

9.3.2 Ferritic Cast Irons with More Than 28% Chromium

In Chap. 8, and in Sect. 9.2, some microstructural consequences derived from certain alloys in the Fe–Cr–C system were studied. Nevertheless, it was made none reference to the chemical behaviour that chromium confers to the cast iron.

Chromium, from 4 wt%, increases the iron resistance to the oxidation in dry atmosphere. And, for a satisfactory behaviour under oxidizing atmospheres, at temperatures up to 750 °C, steels and cast irons are usually of high chromium.

Moreover, chromium, because of forming a film of its oxide, modifies the iron position in the electromotive series. In this way, iron, which without chromium in substitutional solid solution is anodic, changes its behaviour to cathodic in aqueous mediums when the chromium percentage is higher than 12% wt. For that reason, *steels with more than 12% Cr are called ‘stainless steels’*. This corrosion resistance will be worse with increasing K₁ chromium carbides, because the precipitation of these carbides causes chromium depletion at the boundaries of those carbides. These dechromed regions with less than 12% Cr become anodic and are attacked.

Stainless steels with no other components than Fe, Cr and C in their microstructure, at room temperature, will be ferritic if their composition is situated in the region II of Fig. 8.5. Or they will be martensitic if their composition is situated in the region I of Fig. 8.5 (due to the hardenability conferred by the chromium). Martensitic stainless steels, whose mechanical strength is much higher than that of the ferritic stainless steels, behave worse than ferritic stainless steels against corrosion in aqueous solutions.

High-chromium cast irons (some alloys were mentioned in Sect. 9.2 because of their abrasion resistance) are also corrosion resistant. The chromium that did not precipitate as carbide, that is, the one that is in solid solution, favours the formation of an oxide protective film resistant to oxidizing acids, to numerous saline solutions and to the industrial atmospheres. However, its resistance in front of the reducing acids is not good.

With the aim of achieving the highest amount of chromium in solid solution (after the precipitation as carbides of all the carbon of the cast iron), the iron crystalline structure must be body-centred cubic because the chromium solubility in the gamma iron (face-centred cubic) is noticeably lower. For that reason, faced to oxidizing acids, the best corrosion resistance is achieved with alloys whose composition is placed in the ferritic region II of Fig. 8.5, for instance, the *alloy 35% Cr and <1.2% C*. Considering Figs. 8.3, 8.5 and 9.3, it is obvious that the structure of

the primary constituent of that cast iron is delta ferrite. It is also observed that, at the end of the solidification, the allotropic variety delta remains stable down to the room temperature and the carbides will appear located in the interdendritic areas of the delta ferrite. For that reason, it is possible to talk about a *stainless ferritic white cast iron*. Decreasing carbon content, we shall obtain superferritic stainless steels, as well.

The alloy 35% Cr and < 1.2% C resists: any concentration of sulphurous acid up to temperatures of 80 °C; sulphite liquors of the paper industry; phosphoric acid (of concentration up to 60%) until the boiling temperatures; nitric acid in 95% concentrations at room temperature; nitric acid in 50% concentration at 100 °C (at higher concentrations the *Duriron* cast iron has a better behaviour); hypochlorite at room temperature; sea water and the greater part of the mine waters (including acidic type).

Alloys of 35% Cr and low carbon also resist the presence of molten metals such as Pb, Zn and Al, and because of the lack of nickel, they are resistant to sulphurous atmospheres at high temperatures, and, in general, to environmental corrosion.

The maximum temperature in service of the high-chromium cast irons is between 800 and 1100 °C. Up to this temperature limit, they could be considered as *refractories ferrous alloys*: the high chromium content noticeably diminishes the iron thermal conductivity.

If the high-chromium alloys are held for a long time—thousands of hours—in the interval of temperatures between 600 and 900 °C, high-chromium ferrites could give sigma phases (Fig. 8.2). The sigma's phase appearance enhances hardness and brittleness.

Regarding the mechanical properties of high-chromium cast irons, their features are better than the ones of the *Duriron* cast iron. They have higher tensile strength (between 200 and 480 MPa), lower hardness (between 290 and 340 HB) and higher toughness. As opposed to the *Duriron* cast iron, they can be mechanized if carbon percentage is lower than 3% (in high-chromium cast irons, higher carbon percentages are only used when the mechanization is not necessary).

9.3.3 High-Nickel Cast Irons (15–35% Ni)

Other characteristic group of materials that are resistant to the corrosion is that of high-nickel cast irons (15–35% Ni). They are usually called *Ni-Resist*.

In a grey cast iron (these ones are grey cast irons), the addition of nickel improves its resistance to the reducing acids and provides a high increase of the resistance in front of the alkaline bases.

If these cast irons are compared with the high-chromium and high-silicon ones, the main difference is its *excellent* toughness and better mechanical properties (machinability is one of them). As corrosion resistance is concerned, high-nickel cast irons only overtake the high-chromium and high-silicon families in basic

mediums and under stress corrosion they also resist better to the caustic mediums. However, high-silicon and high-chromium cast irons work better against oxidizing mediums, for instance, against sulphuric acid.

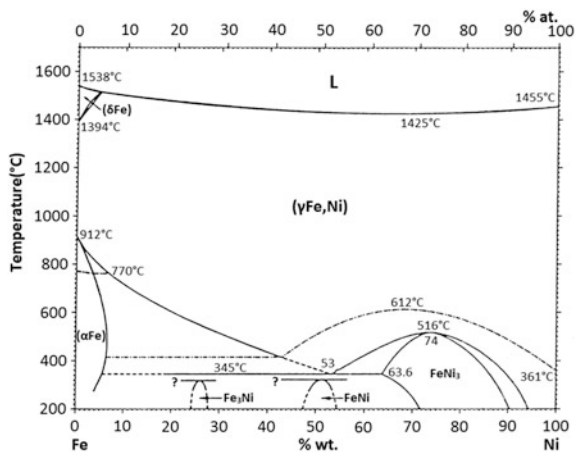
Ni-Resist cast irons can be even used at 950 °C when they do not contain phosphorus (phosphorus eutectics would ruin the material because they melt at 950 °C). In oxidizing atmospheres, Ni-Resist can be used until 700–800 °C. Above these temperatures high-chromium cast irons are preferable. In sulphurous atmospheres, Ni-Resist maximum temperature in service is 550 °C to prevent the eutectic reaction of nickel sulphide and nickel that melts at 630 °C.

Ni-Resist alloys are *grey cast irons*. The high nickel contents, which is graphitizing, favour the solidification of the eutectics according to the stable diagram with the formation of austenite and graphite instead of carbides. On another note, the nickel γ -forming nature should be considered (see the Fe–Ni binary diagram in Fig. 9.17). In Fe–C–Ni alloys with nickel percentages higher than 15%, the enlargement of the austenite stability field (because of the rising of A_4 and the drop of A_3) implies not allotropic transformations during the cooling down to room temperature. Ni-Resist cast irons are *austenitic* and consequently *nonmagnetic*.

The structure can be also austenitic, although the A_3 temperature was higher than the room temperature, when the nickel content is lower than 15%. That is the case of steels with 8% Ni: 18–8 stainless steel and cryogenic steels. In those ones, the alpha–gamma transformation kinetics is very slow, and the M_s temperature is lower than 25 °C. A slow air cooling produces neither the gamma–alpha nor the martensitic transformations. Consequently, the microstructure of these steels is austenitic at room temperature and the same occurs when high-nickel cast irons are concerned.

Ni-Resist cast irons (Fig. 9.18), apart from nickel, usually have a certain chromium content due to the advantages derived from the protection that provides its oxide film. They normally contain between 2 and 6% of chromium, and also γ -forming elements in small amounts: 0.5–2% of manganese (although it is a

Fig. 9.17 Fe–Ni equilibrium diagram (Kubaschewski 1982)—Magnetic transformation



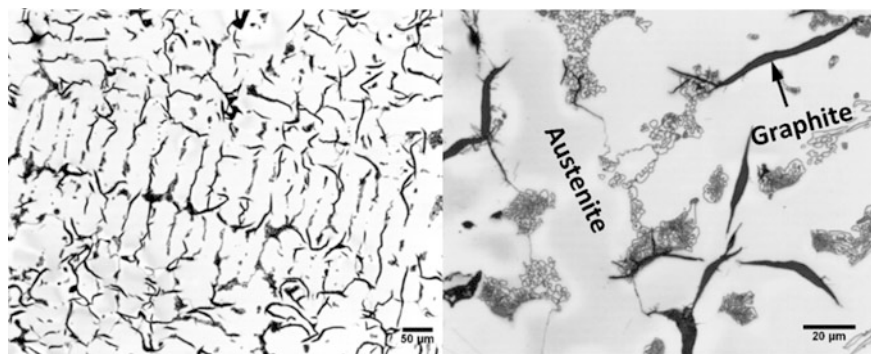


Fig. 9.18 Ni-Resist cast iron of 2.2% C, 2% Si, 29% Ni, 2.6% Cr

carburigen element) and 0.5–7% of copper that stabilizes the austenite without increasing the nickel content. The chilling effect because of the chromium and manganese contents can be counteracted with silicon (also its oxide film is advantageous). The silicon proportions are between 1 and 2.75%. The carbon percentage is usually 3%.

Austenitic alloys of Ni-Resist type, but with 6% Cr (30% Ni and 2.6% C maximum) with the purpose of improving the oxidation resistance at high temperatures, also have 6% Si. The presence of silicon neutralises the possibility of *chilling* of the cast iron due to the chromium increase, apart from the favourable effect of its oxide. These austenitic grey cast irons are called *Nicrosilal* (Ni–Cr–Si alloys).

Ni-Resist cast irons are softer (120–180 HB), because of the abundant proportion of austenite matrix constituent, than the 35% Cr cast irons (290–340 HB) and also than the *Duriron* cast irons (480–520 HB). For the same reason, they are more deformable and noticeably tougher. In transverse bending test, they resist similar loads than high-chromium cast irons (both have a better modulus of rupture than *Duriron* cast irons), but the austenitic cast irons have the highest deflection in this test.

If the graphite is spheroidal, the austenitic cast irons are the toughest of all the grey cast irons. They have a yield strength of around 250 MPa, a tensile strength that can reach 500 MPa, and elongations between 10 and 40%. The tensile strength in the case of austenitic cast irons of flake graphite is relatively low, between 150 MPa and 300 MPa, that is, lower than the tensile strength of cast irons with 35% Cr (around 480 MPa), but higher than the resistance of the *Duriron* cast irons, between 90 and 180 MPa (the mechanical properties assessment, logically approximate, the values established by the Committee of Alloyed Cast Irons of the American Society for Materials, are considered). Figure 9.19 shows the resistance to generalized corrosion for different families of high-alloy cast irons.

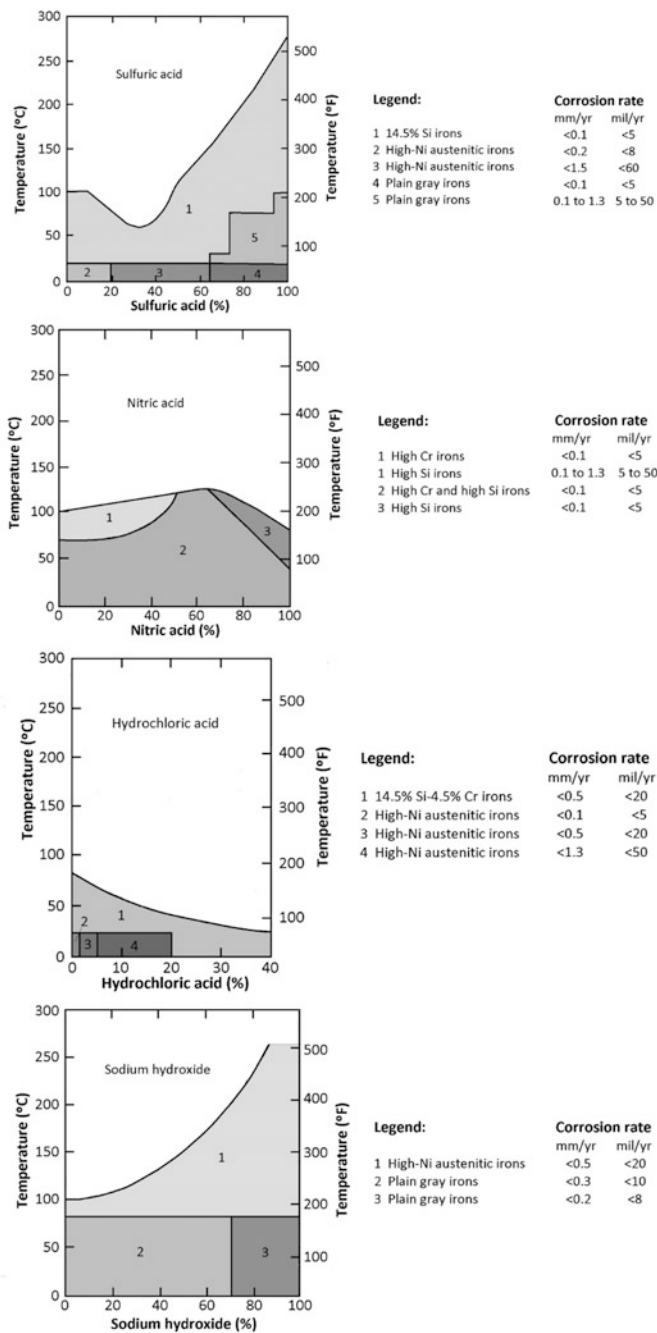


Fig. 9.19 Corrosion resistance of high-alloy and unalloyed cast irons in alkali or acid mediums as a function of the concentration and the temperature (adapted from ASM 1978)

Exercise 9.7. From Fig. 9.19, it should be deduced which and which not of the alloyed grey cast irons are suitable for corrosion resistance.

Question

In sulphuric medium:

The best behaviour is achieved with Duriron cast irons, for whatever sulphuric concentration and up to 250 °C. Austenitic cast irons have a good resistance at room temperature except when concentrations are higher than 60% when conventional grey irons have a better behaviour.

In nitric medium:

High-chromium and high-silicon cast irons have a good resistance up to 100 °C. For intermediate concentrations (60%) and temperatures up to 100 °C, cromosilal cast irons are the most effective.

In hydrochloric medium:

Whatever concentration and temperatures lower than 100 °C, cromosilal cast irons are the most effective. In low hydrochloric acid concentrations and at room temperature, austenitic grey irons can be used.

In alkali medium:

Whatever concentration and temperatures lower than 250 °C, austenitic cast irons would be the best ones. At room temperature, conventional grey irons are the best option (cheaper).

Using high-chromium and high-silicon cast irons in caustic mediums is totally non-recommended—as it was mentioned in the text.

9.4 Heat-Resistant Cast Irons

Regarding the transformations that take place in the cooling of the grey cast irons, the effect of silicon in the matrix structure (the matrix can be thoroughly ferritic because of the silicon α -forming nature) was mentioned in Sect. 4.4. It was also mentioned that the nickel γ -forming effect in high nickel alloy grey cast irons alloyed with this element brings about an austenitic matrix in the cast irons.

In relation with the transformations that can happen in grey cast irons because of the heating above the temperature of 450 °C, two possible failures, the *growth* and the *scaling*, were mentioned in Chap. 4. The improvement that for a grey cast iron is derived from the ferritic or austenitic matrix was commented in Sect. 4.5.2.

To avoid *scaling*, or at least achieving a better behaviour than in the case of common unalloyed cast irons, the silicon content must be increased, and the cast iron must be alloyed with chromium (whose effect is strengthened with the nickel or aluminium addition).

A good scaling resistance up to 900 °C is achieved with 7% of aluminium. Cast irons are free of scaling with 16–25% of aluminium even at 1100 °C. Nevertheless, because of brittleness and moulding difficulties, these alloys are of little interest from the commercial point of view.

Growth does not appear if the *graphitization* did not previously happen. The graphitization does not take place when there are not carbides (mainly cementite) that can be dissociated in iron and graphite. Thus, *growth* appears neither in ferritic matrix grey cast irons (*Duriron* type) nor in austenitic matrix grey cast irons (*Ni-Resist* type). Cast irons, because of the high silicon or nickel contents, exhibit a good behaviour against oxidizing atmospheres up to around 800 °C and do not present *scaling* problems. One or other type of cast irons (with austenitic or ferritic matrix) has another advantage as high-temperature behaviour is concerned: they do not undergo allotropic transformation, and therefore they are not prone to dimensional changes.

Regarding the *growth* of the unalloyed grey cast irons, it is possible to say that they behave rightly below 400–450 °C, unless in the presence of superheated steam. In this case, temperatures must be lower than 300 °C.

There is a kind of high-silicon cast iron with 6% Si that is called *Silal*. This cast iron is heat resistant and ferritic, and it keeps an acceptable equilibrium between heat resistance and toughness, as opposed to the cast irons with 16% Si (*Duriron* type) that behave well under heat conditions against to both *growth* and *scaling* but have a low toughness (Sect. 9.3.1). If the silicon content is diminished with respect to the *Duriron* cast irons, the corrosion resistance is a little lower, but the toughness is improved. This is the case of the *Silal* cast irons. They solidify giving eutectic of austenite and graphite, and after the solidification, through a stable solid-state transformation that was conferred by silicon, they are ferritic at room temperature (see Fig. 9.20). In other words, *Silal* is a *ferritic matrix grey cast iron* (it should be remembered Sect. 4.2), and as opposed to the *Duriron*, it is machinable and tougher, because the ferrite has less silicon in solid solution than the *Duriron* (being less hard and tougher).

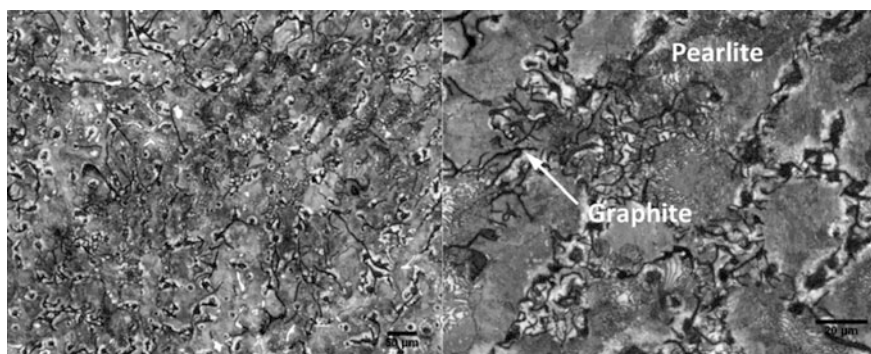


Fig. 9.20 *Silal* cast iron of 6% Si, 2.35% C

Despite the above mentioned, *Silal* cast irons have little toughness and also have low thermal shock resistance, although that resistance results higher than in the case of the conventional grey cast irons when the temperature of service exceeds 250 °C.

Exercise 9.8. A mild steel, unalloyed, at 500 °C, in the open air, for a year of exposition has an oxidized layer of 0.33 mm, and at 600 °C, of 1.13 mm. If a parabolic oxidation law is supposed, calculate the activation energy required for the iron oxidation.

Question

For mild steel:

$$\langle x \rangle^2 = k \cdot t \text{ (parabolic law)} \quad (9.41)$$

where $\langle x \rangle$ is the thickness of the oxidized layer, k is the constant of the equation, thermodynamically activated, and t is the time.

$$k = k_0 \cdot \exp\left(-\frac{Q}{RT}\right) \quad (9.42)$$

Q is the activation energy for the oxidation.

If the oxidized layer at both temperatures is compared,

$$\left(\frac{1.13}{0.33}\right)^2 = \exp\left[\frac{Q}{R} \cdot \left(\frac{1}{773} - \frac{1}{873}\right)\right] \quad (9.43)$$

If Naiperian logarithms are considered,

$$2.46 = \frac{Q}{R} \cdot \frac{100}{773 \cdot 873} \rightarrow Q \simeq 138 \text{ KJ/mol} \quad (9.44)$$

Thickness of the oxidized layer after a day of exposition at $0.7 \cdot T_M$ ($T_M = 1809 \text{ K}$):

Question

$$\langle 1.13 \rangle^2 = \text{cte} \cdot \exp\left(-\frac{138000}{8.31 \cdot 873}\right) \cdot 365 \quad (9.45)$$

$$\langle x \rangle_{0.7 \cdot T_M}^2 = \text{cte} \cdot \exp\left(-\frac{138000}{8.31 \cdot 0.7 \cdot 1809}\right) \cdot 1 \quad (9.46)$$

$$\left(\frac{\langle 1.13 \rangle}{\langle x \rangle}\right)^2 = 365 \cdot \exp\left[\frac{138000}{8.31} \cdot \left(\frac{1}{873} - \frac{1}{0.7 \cdot 1809}\right)\right] = 0.99 \quad (9.47)$$

$\langle x \rangle \simeq 1.13$ mm. The thickness of oxidized layer after a day at 993 °C ($0.7 \cdot T_M$) is equivalent to an exposition of 1 year at 600 °C. Oxidation is exponentially activated with the temperature.

Compare the iron oxidation rate (mm/year) at 700 °C, with the following cast irons:

Pearlitic ductile iron (2.5% Si): 1.4 mm/year

Ferritic ductile iron (4.0% Si): 1.1 mm/year

Grey iron (2.5% Si): 4.8 mm/year

Pearlitic malleable iron: 3.3 mm/year

Question

$$\left(\frac{\langle 1.13 \rangle}{\langle x \rangle_{700}}\right)^2 = \exp\left[\frac{138000}{8.31} \cdot \left(\frac{1}{873} - \frac{1}{973}\right)\right] = 0.14 \quad (9.48)$$

$$\langle x \rangle_{700} \simeq 3 \text{ mm/year} \quad (9.49)$$

Oxidation kinetics is equivalent to the grey and malleable irons' ones, but higher than that belonging to ductile irons, mainly in the case of the ferritic matrix, that is because of having higher silicon content (>3%) that the oxidation resistance is increased.

Compare the iron oxidation rate (mm/year) at 760 °C, with one of the following cast irons:

Ferritic grey iron (1% Cr–1.6% Ni): overheated

Austenitic grey iron (2% Cr–20% Ni): 6.9 mm/year

Austenitic grey iron (5% Cr–20% Ni): 0.2 mm/year

Austenitic grey iron (3% Cr–31% Ni): 2.0 mm/year

Austenitic grey iron (5% Cr–30% Ni): <0.1 mm/year

Question

$$\left(\frac{\langle 1.13 \rangle}{\langle x \rangle_{760}}\right)^2 = \exp \left[\frac{138000}{8.31} \cdot \left(\frac{1}{873} - \frac{1}{1033} \right) \right] \simeq 0.05 \quad (9.50)$$

$$\langle x \rangle_{760} \simeq 5 \text{ mm/year} \quad (9.51)$$

Oxidation–corrosion rate is very high in the case of the alloyed ferritic grey iron. Oxidation–corrosion rate in the case of the austenitic grey irons (30% Ni) is 2.5 times (3% Cr) and 25 times (5% Cr) lower, respectively. Austenitic grey irons, highly alloyed with nickel (30%), do not have oxidation, scaling or growth signs at mentioned temperature.

Exercise 9.9. Analyse the micrographic structure, properties and applications of the following cast irons:

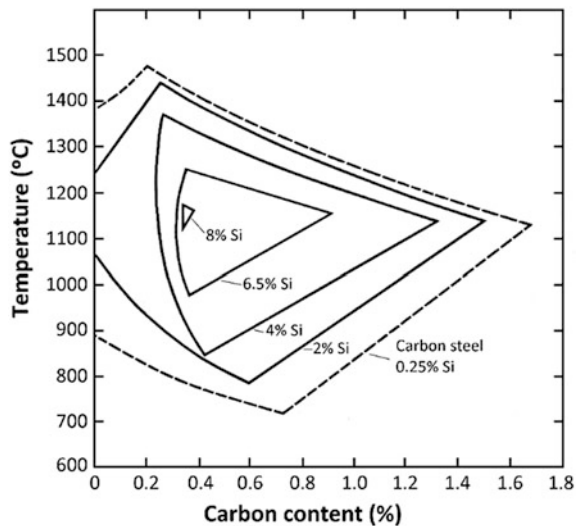
A: 3.5% C–2.5% Si

B: 2.35% C–6% Si

C: 0.8% C–16% Si

In Fig. 9.21, the Fe–C–Si diagram appears (it is recommended considering: Figs. 2.5, 9.16 and 9.20).

Fig. 9.21 Simplified section of the Fe–C–Si diagram



Question

Cast Iron A: Equivalent carbon $\simeq 4.3$. Cast Iron A presents eutectic grey iron whose matrix is commonly pearlitic. Graphite type A or B appears depending on the cooling rate. This cast iron has an excellent castability and a low mechanical strength (class 20 or 25), good machinability and wear resistance and good thermal conductivity. Ornamental parts and ingot mould manufacture are their applications. Temperature $A_{13} \simeq 780$ °C.

Cast Iron B: Silal type. Hypoeutectic cast iron. Eutectic temperature higher than 1160 °C. Carbon content that saturates the austenite $\simeq 0.9\%$. Austenite transforms into pearlite at $A_{13} \simeq 950$ °C, unless in the equilibrium cooling where the matrix of the cast iron would be ferritic. Silicon, in solid solution in the iron, makes noticeably harder the ferrite and increases the wear resistance and the oxidation–corrosion resistance. Cast Iron B has low mechanical strength and poor toughness. This cast iron has acceptable resistance to growth if the matrix is pearlitic.

Cast Iron C: Duriron type. For 16% Si, there is not γ -loop. The cast iron solidifies as hypoeutectic grey iron with ferritic matrix. There are not allotropic transformations $\delta \rightarrow \gamma \rightarrow \alpha$ in solid state. Cast Iron C has high hardness ($\simeq 500$ HB), low mechanical strength and toughness (embrittlement behaviour of silicon). Non-machinable. This cast iron has excellent resistance to growth and corrosion resistance in very oxidizing mediums. The applications of this cast iron are pumping systems and pipes under very corrosive liquid (no caustic bleach).

This cast iron can be replaced by the Cast Iron B (Silal) when the oxidation–corrosion resistance requirements were not excessively severe, with improvement in the toughness (that is low).

The toughness and the thermal shock resistance of *Silal* cast irons can be significantly improved by means of using nickel. The objective of employing nickel is achieving an austenitic matrix. For instance, the *Nicrosilal* grey cast iron of chemical composition 4–5% Si, 20–22% Ni, 2–4% Cr and 1.8–2% C is austenitic and thus tough. The *Nicrosilal* has an excellent resistance to air scaling up to 815 °C, with a limit temperature of 950 °C.

Despite the above mentioned, austenitic cast irons with nickel content lower than 20% do not have a good thermal shock resistance (but superior as compared with other heat-resistant cast irons) due to the high-austenite thermal expansion coefficient. With the purpose of improving the behaviour in front of abrupt changes of temperature, and against the *thermal fatigue*, the use of higher nickel contents is a common practice (higher than 30%), because increasing the nickel proportion diminishes the austenite thermal expansion coefficient. In this way, for instance, the austenitic alloy *Invar* of 35% Ni (2.5% max C, 1–2% Si, 0.5% max Cu, 0.4–0.8% Mn and 0.8% max Cr) because of its thermal stability in front of the temperature changes is used in precision mechanics, in moulds for the glass and polymer industries, measure instrumentation, etc.

Regarding *high-alloy white cast irons*, due to the lack of graphitizing risks because of the stability that provides the presence of chromium in K_C carbides, there is neither growth nor scaling (because of the adherent nature of the chromium oxides). In this way, for example, *ferritic cast irons with more than 28% Cr* do not present growth even at 1100 °C. These cast irons, whose thermal shock resistance is good and the resistance against oxidizing atmospheres and some chemical agents is excellent, are commonly used at those temperatures. Especially, the full ferritic cast irons are 33% Cr and 1.2% C. It should be remembered that these cast irons, because of not having allotropic transformations, are immune to the dimensional changes.

Growth, scaling, oxidation, thermal shock resistance, and refractoriness are not the only factors that should be considered for a good service at high temperature. Other high-temperature failures can be caused by factors like *transformations of the constituents* (pearlitic, bainitic, martensitic, etc.) both in grey and white cast irons, which cause changes in hardness, wear resistance and other mechanical properties; superficial *decarburization and corrosion*; *melting of eutectics* that are inherent to the chemical composition of the cast iron, such as the case of the *steadite* that melts at 950 °C if the phosphorus content is higher than 0.2%, or the eutectic's melting that appear during the service, as happens in the case of high-nickel cast irons when exposed to sulphurous gases at temperatures higher than 635 °C; dimensional changes as a consequence of a high thermal expansion coefficient, *creep* problems, etc.

As opposed to the previously mentioned in relation to the abrasion resistance, the high-temperature behaviour (that sometimes implies corrosion problems) bring with some technical limitations (it should be enough to remember the melting of eutectics or the structural transformations that happens with temperature changes). The choice of the suitable material will require knowledge about fundamentals of the Physical Metallurgy, the transformations carried out by heat treatments, the basic principles of the gaseous carburization and decarburization, the mechanisms and oxidation kinetics, the physical–chemical theory of the corrosion processes and the boundary conditions where the heat instability takes place as well.

10.1 Introduction

This chapter is focused on exercises, problems and case studies that complement the theoretical information described in previous chapters. For a better understanding of the exercises, problems and case studies of this chapter, we recommend reading the book *Solidification and Solid-state Transformations of Metals and Alloys* (Pero-Sanz et al., Elsevier, 2017), apart from the previous chapters of this book. This chapter is structured into 13 blocks of problems and exercises and three case studies:

- 10.1. Thermal analysis. Carbon solubility in the metastable and stable systems.
- 10.2. Thermodynamics of the Fe–C–Si ternary system. Interaction coefficients. Carburizing and graphitizing elements.
- 10.3. Magnesium effect. Pig iron desulphurization.
- 10.4. Solidification times. Chvorinov equation.
- 10.5. Riser design. Equations of Caine and Adams–Taylor. Exothermic isolation. Solidification defects.
- 10.6. Mould filling times. Gating design. Downhill casting and bottom casting.
- 10.7. Superheating. Fluidity. Castability.
- 10.8. Mechanical properties. Reliability (Weibull statistics).
- 10.9. Creep. Stress relieving.
- 10.10. Thermal shock resistance. Damping capacity.
- 10.11. Fatigue.
- 10.12. Heat treatments.
- 10.13. Fe–C–Cr system.

Case study 1: CAM-CAD methods applied to the feeding system of Ni-hard cast iron parts.

Case study 2: Relation structure–mechanical properties in camshafts manufactured in cast iron.

Case study 3: Relation structure–properties in crankshafts manufactured in forged steel and spheroidal cast iron.

10.2 Thermal Analysis. Carbon Solubility in the Metastable and Stable System

Exercise 10.1. Represent the maximum solubility of the carbon in the stable and metastable diagrams (θ = Temperature in Celsius; T = Absolute temperature).

According to Stefanescu (ref. *Metals Handbook* 1990), the following equations are defined:

Stable diagram:

—

$$\text{Liquid : \% C} = 1.3 + 2.57 \times 10^{-3} \cdot \theta \quad (10.1)$$

—

$$\% \text{ C} - \gamma : -0.435 + 0.355 \times 10^{-3} \cdot \theta + 1.61 \times 10^{-6} \cdot \theta^2 \quad (10.2)$$

—

$$\% \text{ C} - \alpha : 2.46 \times 10^3 \cdot \exp(-11460/\theta) \quad (10.3)$$

Metastable diagram:

—

$$\text{Liquid : \% C} = 4.34 + 0.1874 \cdot (\theta - 1150) - 200 \cdot \ln(\theta/1150) \quad (10.4)$$

$$\%C - \gamma : -0.628 + 1.222 \times 10^{-3} \cdot \theta + 1.045 \times 10^{-6} \cdot \theta^2 \quad (10.5)$$

$$\%C - \alpha : 1.8 \times 10^3 \cdot \exp(-10908/\theta) \quad (10.6)$$

Question

By using an Excel sheet, the representation in Fig. 10.1 is obtained.

At 900 °C:

Stable (*E*):

$$\begin{aligned} \%C &= -0.435 + 0.355 \times 10^{-3} \cdot 900 + 1.61 \times 10^{-6} \cdot 900^2 \\ &= -0.435 + 0.3195 + 1.3041 = 1.19 \end{aligned} \quad (10.7)$$

Metastable (*M*):

$$\begin{aligned} \%C &= -0.628 + 1.222 \times 10^{-3} \cdot 900 + 1.045 \times 10^{-6} \cdot 900^2 \\ &= -0.628 + 1.0998 + 0.84645 = 1.32 \end{aligned} \quad (10.8)$$

Difference = 0.13

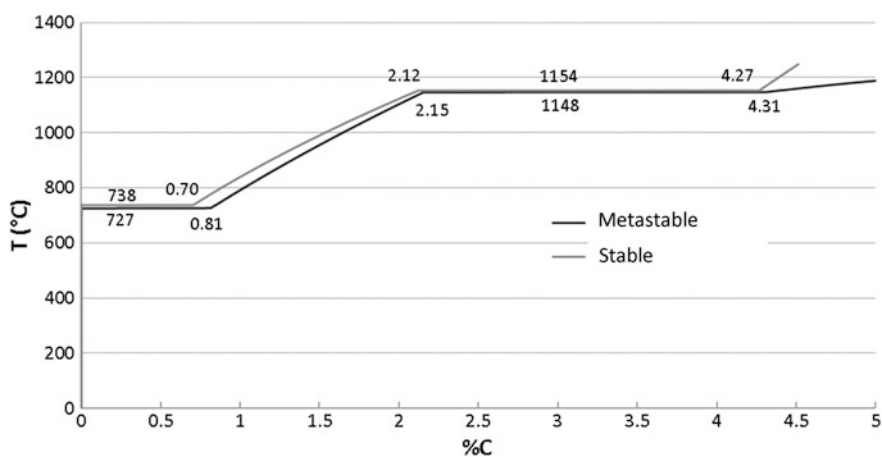
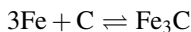


Fig. 10.1 Representation of the carbon percentage as a function of the temperature

Exercise 10.2. Demonstrate that the driving force for the decomposition of Fe_3C into C is very low at 900°C (to effectuate, for instance, either a malleabilization annealing or ferritization of a ductile iron).

Question

For the reaction:



Between 840 and 1537°C (Ellingham diagram for the carbides formation):

$$\Delta G (\text{kJ/mol}) = 9.8 - 0.010 \cdot T \quad (10.9)$$

At 900°C (1173 K) $\rightarrow \Delta G = 9.8 - 11.73 = -1.93\text{ kJ/mol}$ (slightly exothermic, at least if it is compared with standard enthalpy of the aluminothermic reaction, see the corresponding exercise, 290 kJ/mol). The times for the indirect ferritizing annealing are long, they depend on the carbon diffusion in solid state in the austenite.

At 738°C , calculate $\%C$ in γ (stable diagram):

$$\begin{aligned} \%C &= -0.435 + 0.355 \times 10^{-3} \cdot 738 + 1.61 \times 10^{-6} \cdot 738^2 \\ &= -0.435 + 0.262 + 0.877 \simeq 0.704 \text{ (0.68 stable diagram)} \end{aligned} \quad (10.10)$$

At 727°C , calculate $\%C$ in γ (metastable diagram):

$$\begin{aligned} \%C &= -0.628 + 1.222 \times 10^{-3} \times 727 + 1.045 \times 10^{-6} \times 727^2 \\ &= -0.628 + 0.89 + 0.552 = 0.81 \text{ (0.77 metastable diagram)} \end{aligned} \quad (10.11)$$

Slightly different from the *theoretical* diagrams.

Exercise 10.3. The specific heat of liquid iron is $0.146\text{ cal/(g }^\circ\text{C)}$, that of solid iron is $0.179\text{ cal/(g }^\circ\text{C)}$ and the latent heat of solidification is 63.7 cal/g . Heat is extracted at a constant rate per unit mass of $10\text{ calories per minute}$ as casting cools from 1621°C , through the freezing point (1538°C), to 1454°C . Draw to scale a graph of the cooling curve between 1621 and 1454°C .

Question

The graphic representation is shown in Fig. 10.2.

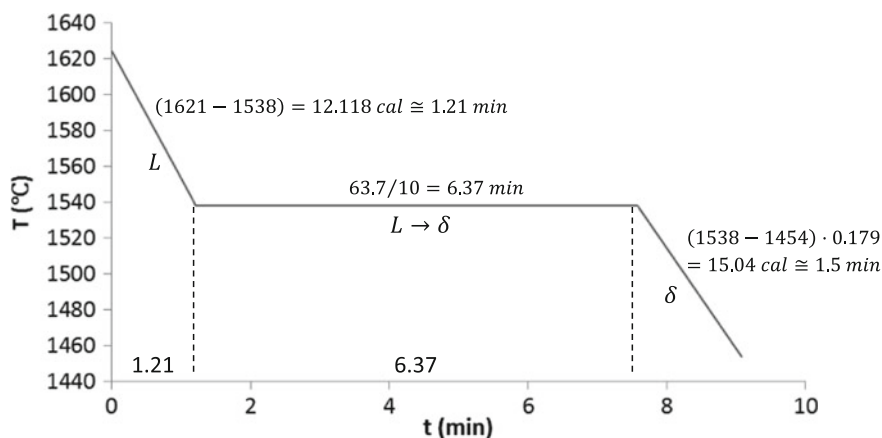


Fig. 10.2 Representation of the cooling curve

10.3 Thermodynamics of the Fe–C–Si Ternary System. Interaction Coefficients. Carburizing and Graphitizing Elements

Exercise 10.4. According to the Japan Society for Promotion of Science, 1988, p. 294, the variation of the autointeraction parameter in the solid solution of the carbon in the austenite (Henry's law) is

$$e_C^C = \frac{197.5}{T(K)} + 0.025 \quad 1173 < T(K) < 1673 \quad (10.12)$$

Apart from that, the maximum carbon solubility in the austenite (Fe–C stable equilibrium diagram) is, according to Stefanescu (1988: 67) (Table 10.1).

Calculate, at the temperatures of 1100, 1000, 900 and 800 °C, the value of the activity coefficient at infinite dilution (Raoult's law) of the solid solutions of insertion of the carbon in the Fe- γ (austenite). In the same way, calculate at the mentioned temperatures, the standard free energy associated to the reaction:



Table 10.1 Carbon solubility as a function of the temperature

T (°C)	1100	1000	900	800
%C	1.90	1.53	1.19	0.88

Table 10.2 Raoult values as a function of the temperature

T (°C)	1100	1000	900	800
ε_C^C	8.50	9.01	9.60	10.31

$a_{H,C}$ is the Henry's activity of the carbon in the austenite.

Question

First, the interaction parameter (Raoult's law) of the carbon in the austenite is calculated. According to Ballester et al. (2000, p. 494), the relation between e_C^C (Henry) and ε_C^C (Raoult) is

$$\varepsilon_C^C = \frac{230.3}{55.85} \cdot 12.01 \cdot e_C^C + \frac{55.85 - 12.01}{55.85} \quad (10.13)$$

The following values are represented in Table 10.2.

Apart from that, as we have seen, the relation between the activity coefficient of Raoult, the carbon concentration (in the austenite) and the temperature is

$$\ln \gamma_C = \ln \gamma_C^* + \varepsilon_C^C \cdot x_C \quad (10.14)$$

where γ_C^* , activity coefficient at infinite dilution; x_C , mole fraction of carbon. When the carbon at a temperature T , saturates the austenite:

$$\gamma_C = \frac{1}{(x_C)_{\max}} \quad (10.15)$$

For instance, at 1100 °C:

$$\gamma_C = \frac{1}{0.0828} = 12.08 \quad (10.16)$$

At the chosen temperatures, the value of γ_C^* , infinite dilution of the carbon in the austenite are shown in Table 10.3.

The value of the standard free energy associated to the change in the reference thermodynamic system (Raoult $\rightarrow$ Henry) will be, according to Ballester et al. (2000, p. 495):

$$\Delta G^0(a_C/a_{H,C}) = R \cdot T \cdot \ln (55.85 \cdot \gamma_C^*/12.01 \cdot 100) \quad (10.17)$$

Table 10.3 γ_C^* , infinite dilution of the carbon as a function of the temperature

T (°C)	1100	1000	900	800
γ_C^*	5.98	8.09	11.35	16.78

Table 10.4 ΔG^0 as a function of the temperature

$T\ (^{\circ}\text{C})$	1100	1000	900	800
$\Delta G^0(\text{J/at} \cdot \text{g C})$	-14,611.2	-10,349.4	-6231.5	-2215.3

a_{C} is the activity of Raoult; $a_{\text{H,C}}$ is the activity of Henry of the carbon. The obtained data are in Table 10.4.

NOTE: it is necessary to mention that the interaction coefficient $\varepsilon_{\text{C}}^{\text{C}}$ and γ_{C} rise when the temperature diminishes. For instance, at 800 °C:

$$\ln \gamma_{\text{C}} \simeq \ln \gamma_{\text{C}}^* + 10.31 \cdot x_{\text{C}} = \ln 18.14 + 10.31 x_{\text{C}} = \ln \frac{1}{(x_{\text{C}})_{\text{max}}} \tag{10.18}$$

When:

$$x_{\text{C}} = \frac{0.88/12.01}{0.88/12.01 + 99.12/55.85} = \frac{0.06911}{0.06911 + 1.77565} = 0.0396 \tag{10.19}$$

$$\ln \frac{1}{0.0396} = 3.23; \gamma_{\text{C}} = 25.84 \tag{10.20}$$

From the Fe–C diagram, it is possible to deduce the activity coefficients and the thermodynamic interaction parameters, and vice versa.

Exercise 10.5. According to Pero-Sanz et al. (2017) (Elsevier), page 283, the maximum solubility of the carbon in the austenite, with 0.25 and 2% Si, respectively, are those mentioned in Table 10.5.

Calculate, in these ternary Fe–C–Si alloys, the activity coefficients at infinite dilution $\gamma_{\text{C–Si}}^*$ and the interaction parameter $\varepsilon_{\text{C}}^{\text{Si}}$, at the mentioned temperatures.

Question

The equation of the last exercise is, when the silicon effect is incorporated, the following one:

Table 10.5 Maximum solubility of the carbon in the austenite with 0.25 and 2% Si

0.5% Si	$T\ (^{\circ}\text{C})$	1100	1000	900	800
	$C_{\text{max}}(\%)$	1.62	1.38	1.15	0.91
2% Si	$T\ (^{\circ}\text{C})$	1100	1000	900	800
	$C_{\text{max}}(\%)$	1.40	1.15	0.90	0.64

Table 10.6 $\gamma_{\text{C-Si}}^*$ and $\varepsilon_{\text{C}}^{\text{Si}}$ as a function of the temperature

T (°C)	1100	1000	900	800
$\gamma_{\text{C}} - \text{Si}^*$	4.41	5.12	5.80	7.01
$\varepsilon_{\text{C}}^{\text{Si}}$	7.55	9.25	11.62	15.53

Table 10.7 D_{C}^{γ} as a function of the temperature

T (°C)	1100	1000	900	800
D_{C}^{γ} (cm ² /s)	9.5×10^{-7}	3.6×10^{-7}	1.16×10^{-7}	3.03×10^{-8}

$$\ln \gamma_{\text{C}} = \ln \gamma_{\text{C-Si}}^* + \varepsilon_{\text{C}}^{\text{C}} \cdot x_{\text{C}} + \varepsilon_{\text{C}}^{\text{Si}} \cdot x_{\text{Si}} \quad (10.21)$$

The value of the interaction coefficient $\varepsilon_{\text{C}}^{\text{C}}$ is known (see last exercise), the same as the activity coefficient of the carbon: $\gamma = 1/(x_{\text{C}})_{\text{max}}$. Two equations are necessary to calculate $\gamma_{\text{C-Si}}^*$ and the C–Si interaction coefficient, $\varepsilon_{\text{C}}^{\text{Si}}$. The weight fractions (w_{C} , w_{Si}) are expressed in atomic fractions, and the results are shown in Table 10.6.

In the ternary Fe–C–Si system, $\gamma_{\text{C-Si}}^*$ and $\varepsilon_{\text{C}}^{\text{Si}}$ only depend on the temperature. Both rise when the temperature diminishes. The positive values of the interaction C–Si ($\varepsilon_{\text{C}}^{\text{Si}}$) contributes to diminish the carbon solubility in the austenite, favouring the precipitation/segregation of the C-graphite. It is also necessary considering that the diffusivity of the carbon in the austenite diminishes exponentially with the temperature (equation of Arrhenius type): $D_{\text{C}}^{\gamma} = 0.21 \cdot \exp(-33800/R \cdot T)$ cm²/s (see enclosed Table 10.7). It is divided by 30 when passing from 1100 to 800 °C, and the square-root mean diffusion distances $x \simeq (D \cdot t)^{0.5}$ by 5 ($t = \text{cte}$).

Exercise 10.6. According to Pero-Sanz et al. (2017) (Elsevier), page 283, the solubility of the carbon in the austenite at 1100 °C, as a function of the silicon percentage in the ternary Fe–C–Si system, is presented in Table 10.8.

Demonstrate that whether the interaction parameter $\varepsilon_{\text{C}}^{\text{Si}}$ is or not function of the silicon content.

Table 10.8 Carbon solubility in the austenite as a function of the silicon percentage

% Si	0.25	2.00	4.00	6.50
% C _{max}	1.62	1.40	1.21	0.75

Question

From the general equation that relates the activity coefficients and the interaction parameters (see Exercise 10.5):

$$\ln \gamma_C = \ln \gamma_{C-Si}^* + \varepsilon_C^C \cdot x_C + \varepsilon_C^{Si} \cdot x_{Si} \quad (10.22)$$

The value of ε_C^C is taken from the Exercise 10.4, ε_C^{Si} is calculated with the data obtained at 1100 °C (Exercise 10.5). Thus, when $w_{Si} = 0.25$ and 2% Si, respectively:

$$\ln \frac{1}{0.0710} = \ln \gamma^* + 8.50 \cdot 0.0710 + \varepsilon_C^{Si} \cdot 0.00468 \quad (10.23)$$

$$\ln \frac{1}{0.0608} = \ln \gamma^* + 8.50 \cdot 0.0608 + \varepsilon_C^{Si} \cdot 0.0371 \quad (10.24)$$

This will mean a value of ε_C^{Si} of 4.41 (lower than that calculated previously, 7.55).

With silicon contents of 4 and 6.5%, the corresponding equations would be:

$$\ln \frac{1}{0.0519} = \ln \gamma^* + 8.50 \cdot 0.0519 + \varepsilon_C^{Si} \cdot 0.0734 \quad (10.25)$$

$$\ln \frac{1}{0.0320} = \ln \gamma^* + 8.50 \cdot 0.0320 + \varepsilon_C^{Si} \cdot 0.1184 \quad (10.26)$$

It results in $\varepsilon_C^{Si} = 7.15$. Concluding that the C–Si interaction coefficient depends not only on the temperature but also on the silicon content. Everything seems indicating that the C–Si interaction increases when the carbon content diminishes, and the silicon content rises (T constant).

The knowledge of the maximum solubility of the carbon in the austenite, function of the temperature and of the silicon content has a large interest for calculating the malleablizing and graphitizing (ferritizing) times for the ductile irons.

Exercise 10.7. A few years ago, the General Motors developed a new kind of cast iron (also known graphitic steel), which in as-cast state has graphite nodules, seeming those of the malleable iron. Its composition is as follows: C: 1.75%; Si: 2.25%; Mn: 0.40%; S: 0.10%; P: 0.05%; B: 0.01%; $EC = \%C + \%Si/3 \simeq 2.5$. Can be justified, considering the Fe–C and Fe–Fe₃C diagrams, that, after an isothermal annealing for several hours at 750 °C, it has a ferritic structure with an ultimate tensile strength equivalent to 45 kg/mm²(60 ksi)? Note: These cast irons are characterized by

their high yield strength ($E = 190$ GPa), higher than that of the grey irons ($E < 160$ GPa), very similar to that of the steels ($E = 210$ GPa).

Question

By using Stefanescu's equations previously mentioned (between the eutectic and eutectoid temperatures):

$$\%C(E, 750^\circ\text{C}) = -0.435 + 0.355 \times 10^{-3} \cdot 750 + 1.61 \times 10^{-6} \cdot (750)^2 = 0.74 \quad (10.27)$$

$$\%C(M, 750^\circ\text{C}) = -0.628 + 1.222 \times 10^{-3} \cdot 750 + 1.045 \times 10^{-6} \cdot (750)^2 = 1.16 \quad (10.28)$$

The time required for the malleablizing annealing would be (see exercise in the book):

$$t = f_v^{\text{Fe}_3\text{C}} \cdot c_{\text{Fe}_3\text{C}} \cdot l_0^2 / (c_m - c_0) \cdot 0.21 \cdot \exp(-33800 \text{ cal}/2 \cdot (750 + 273)) \\ \simeq 1.25 \times 10^8 \cdot \frac{\text{s}}{\text{cm}^2} \cdot l_0^2 \quad (10.29)$$

l_0 is the distance between plates of Fe_3C and nodules of graphite.

$$f_v^{\text{Fe}_3\text{C}} \simeq (1.75 - 1.16)/(6.67 - 1.16) \simeq 0.11 \quad (10.30)$$

When $l_0 \simeq 100 \mu\text{m} = 10^{-2} \text{ cm} \rightarrow t \simeq 1.25 \times 10^4 \text{ s} \simeq 3.5 \text{ h}$

Regarding R_m , in ferritic steels (Pickering 1983) $\text{TS (MPa)} \simeq 295 + 83 \cdot (\% \text{Si}) = 481.75 \text{ MPa} \simeq 49 \text{ kg/mm}^2$, which justifies the mechanical strength of the graphitic steel. Its microstructure would comprise grains of ferrite with dispersed graphite cells.

NOTE: Phosphorus and silicon, in this order, are the elements that harden the ferrite more; 1% P rises the yield strength 670 MPa; 1% Si, 85 MPa. However, they are also responsible of making brittle the material, specially the phosphorus.

These *steels* are known in Europe with the generic name of *graphitic steels*. They are usually employed after malleablizing and machining in the hardened state (quenched and tempered). They are typically used in the manufacture of calibres, cutting matrices and dies (tool steels).

Exercise 10.8. What effect has the presence of 2% Si in the temperature and composition of the eutectic in the Fe–C diagram? And over the eutectoid? What other important effect has the silicon?

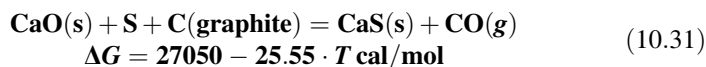
Question

See Fig. 4.2:

- + Maintains, or slightly reduces the eutectic temperature.
- + Raises the eutectoid temperature.
- + Facilitates the stable solidification (Fe–graphite diagram).

10.4 Magnesium Effect. Pig Iron Desulphurization

Exercise 10.9. Liquid pig iron produced in the blast furnace often contains concentrations of sulphur that are too high (>0.1%) to produce a low sulphur product in the cupola furnace to which the pig iron will be charged (i.e. in the production of ductile cast iron). External desulphurization, i.e. intermediate treatment of molten pig iron with a desulphurization agent, is sometimes employed to lower the sulphur content (<0.01%) in the pig iron. Liquid basic slags and some alkalis, or a solid desulphurization agent, can be used. For example, powdered lime injected into the bath in a gas stream is a very effective desulphurization agent. Consider a pig iron saturated with graphite at 1200 °C. Estimate the equilibrium sulphur content when lime is injected in a nitrogen stream into the pig iron bath and desulphurization takes place according to the reaction:

**Question**

The activity of S is 5 at infinite dilution (Henry's law).

$$\log k = \frac{\log a_{\text{CaS}} \cdot P_{\text{CO}}}{a_{\text{CaO}} \cdot a_{\text{C}}} = -\frac{27050}{4.6 \cdot 1523} + \frac{27.55}{4.6} = 2.0 \quad (10.32)$$

The activity of the pure solids CaS, CaO and graphite saturated iron can be taken as unity. The pressure of carbon monoxide can be assumed to be 1 atm, although the presence of nitrogen would markedly reduce this pressure, enhancing desulphurization. Thus:

$$\frac{1}{a_S} = \frac{1}{(\%S) \cdot f_S} = 100 \rightarrow (\%S) = \frac{1}{100} \cdot \frac{1}{5} = 0.002\% (< 0.01\%) \quad (10.33)$$

Exercise 10.10. A cast irons book says: ‘The amount of residual magnesium, Mg_{res} , required to produce spheroidal graphite is generally from 0.03 to 0.05%. The amount of magnesium to be added in the iron is a function of the initial sulphur level, S_{in} , and the recovery of magnesium, η in the process used: $Mg_{ad} = (0.75 \cdot S_{in} + Mg_{res})/\eta$. A residual magnesium level that is too low results in insufficient nodularity. If the magnesium content is too high, carbides are promoted’. Explain the formula and comment this paragraph.

Question

The coefficient 0.75 in the previous equation results from the required Mg to catch all the S, in the form of MgS. That is to say:

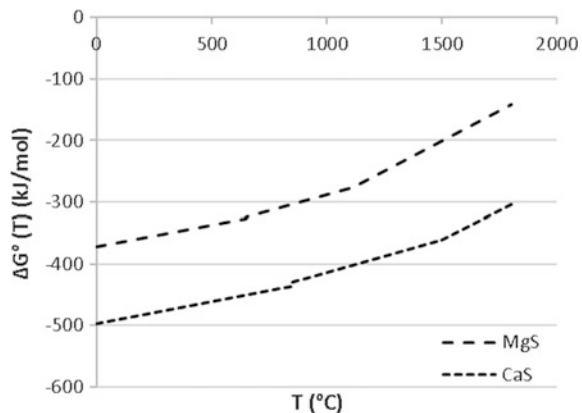
$$Mg/S = Mg \text{ atomic weight}/S \text{ atomic weight} = 24/32 = 0.75 \quad (10.34)$$

Thus, for an amount of S of 0.1% in weight and unit yield $Mg_{ad} = 0.75 \cdot 0.1 + 0.04 \simeq 0.115\%$; for $S = 0.02\%$; $Mg_{ad} \simeq 0.055$ ($\eta = 1$).

If the Mg content is too high, the presence of carbides is possible: metastable solidification (chilling).

See Ellingham’s diagram in Fig. 10.3. Magnesium is first used in catching sulphur and then used in nodulizing the cast iron.

Fig. 10.3 Ellingham’s diagram for sulphides



10.5 Solidification Times. Chvorinov Equation

Exercise 10.11. Sand castings A and B are geometrically similar. B weights three times as much as A; A freezes in 10 min. How long it takes B to freeze?

Question

Geometrical similarity:

$$V = k \cdot l^3; A = k \cdot l^2; l \text{ is the intersected average length} \rightarrow (V/A) = l \quad (10.35)$$

Using Chvorinov, which allows calculating the time required for solidification (see Exercise 2.32 in Pero Sanz et al. 2017, Elsevier), then:

$$t_A = C \cdot (V/A)^2 = C \cdot l_A^2 \quad (10.36)$$

$$\begin{aligned} t_B &= C \cdot (V/A)^2 = C \cdot l_B^2 = C \cdot (3 \cdot V_A/V_B)^2 = C \cdot 9 \cdot l_A^6/l_B^2 \\ &= 9 \cdot \frac{10}{(l_A)^2} \cdot \frac{(l_A)^6}{(l_B)^2} = 90 \cdot \left(\frac{l_A}{l_B}\right)^4 = 90 \cdot \left[\left(\frac{l_A}{l_B}\right)^2\right]^2 \\ &= 90 \cdot \left(\frac{10}{t_B}\right)^2 \rightarrow t_B^3 = 90 \cdot 100 = 9000 \rightarrow t_B = 20.8 \text{ min} \end{aligned} \quad (10.37)$$

Exercise 10.12. A 6-in cast iron cube freezes in a sand mould in 5 min. How long will a cast iron sphere 6-in diameter require to solidify completely?

Question

By using Chvorinov equation, we determine the constant in the equation in the case of the cube:

$$t_S = C \cdot \left(\frac{V}{A}\right)^2 \quad (10.38)$$

$$5 = C \cdot \left(\frac{V}{A}\right)^2 = C \cdot \left(\frac{6 \cdot 6 \cdot 6}{6 \cdot 6 \cdot 6}\right)^2 \rightarrow C = 5 \quad (10.39)$$

In the case of the sphere, the value of the constant C is the same that in the cube:

$$t_S = 5 \cdot \left(\frac{V}{A}\right)^2 = 5 \cdot \left(\frac{4/3 \cdot \pi \cdot r^3}{4 \cdot \pi \cdot r^2}\right)^2 = 5 \cdot \left(\frac{r}{3}\right)^2 = 20 \text{ min} \quad (10.40)$$

The volume of molten metal in the casting is proportional to the heat energy to be dissipated. The surface area of the casting is the exposed area from which the heat must be dissipated. Therefore, the cooling rate is directly related to the ratio of the volume to surface area V/A .

Exercise 10.13. Why do you think ingot moulds have been traditionally manufactured in cast iron? Why sand moulds, for example, are not used?

Question

First of all, the constant of Chvorinov is calculated for both the sand and the copper moulds.

Data:

Sand mould: $k_m = 0.61 \text{ J/m}^\circ\text{C s}$, $\rho_m = 1500 \text{ kg/m}^3$, $c_m = 1128.6 \text{ J/kg}^\circ\text{C}$

Metallic mould (copper): $k_m = 392.92 \text{ J/m}^\circ\text{C s}$, $\rho_m = 9000 \text{ kg/m}^3$, $c_m = 376.2 \text{ J/kg}^\circ\text{C}$

Steel: $T_M = 1538^\circ\text{C}$, $\Delta H_f = 15290.44 \text{ J/mol}$, $\rho = 8000 \text{ kg/m}^3$, atomic weight = $5.58 \times 10^{-2} \text{ kg/mol}$

The first step to calculate the solidification times is to obtain the values of the constant C for both moulds, supposing that the mould is at room temperature:

$$\begin{aligned}
 C_{\text{sand}} &= \frac{\pi}{4} \left(\frac{\rho_s \Delta H_f}{T_M - T_0} \right)^2 \frac{1}{k_m \rho_m c_m} \\
 &= \frac{\pi}{4} \left[\frac{\left(8000 \frac{\text{kg}}{\text{m}^3} \right) \left(15290.44 \frac{\text{J}}{\text{mol}} \right) \left(\frac{1}{5.58 \times 10^{-2}} \frac{\text{mol}}{\text{kg}} \right)}{1538^\circ\text{C} - 23^\circ\text{C}} \right]^2 \frac{1}{\left(0.61 \frac{\text{J}}{\text{m}^\circ\text{C s}} \right) \left(1500 \frac{\text{kg}}{\text{m}^3} \right) \left(1128.6 \frac{\text{J}}{\text{kg}^\circ\text{C}} \right)} \\
 C_{\text{sand}} &= 1.60 \times 10^6 \frac{\text{s}}{\text{m}^2}
 \end{aligned} \tag{10.41}$$

$$\begin{aligned}
 C_{\text{copper}} &= \frac{\pi}{4} \left(\frac{\rho_s \Delta H_f}{T_M - T_0} \right)^2 \frac{1}{k_m \rho_m c_m} \\
 &= \frac{\pi}{4} \left[\frac{\left(8000 \frac{\text{kg}}{\text{m}^3} \right) \left(15290.44 \frac{\text{J}}{\text{mol}} \right) \left(\frac{1}{5.58 \times 10^{-2}} \frac{\text{mol}}{\text{kg}} \right)}{1538^\circ\text{C} - 23^\circ\text{C}} \right]^2 \\
 &\quad \times \frac{1}{\left(392.92 \frac{\text{J}}{\text{m}^\circ\text{C s}} \right) \left(9000 \frac{\text{kg}}{\text{m}^3} \right) \left(376.2 \frac{\text{J}}{\text{kg}^\circ\text{C}} \right)} \\
 C_{\text{copper}} &= 1236.09 \frac{\text{s}}{\text{m}^2}
 \end{aligned} \tag{10.42}$$

Summarizing, the constants of Chvorinov for sand and Cu are

$$(C)_{\text{sand}} \simeq 160 \text{ s/cm}^2; (C)_{\text{copper}} \simeq 0.12 \text{ s/cm}^2 \quad (10.43)$$

In eutectic grey irons:

$$C = \frac{\pi}{4} \cdot \left(\frac{\rho \cdot \Delta H_f}{T_m - T_0} \right)^2 \cdot \frac{1}{k \cdot c_p \cdot \rho} \quad (10.44)$$

From the data:

$$\begin{aligned} \rho &= 7.3 \text{ g/cm}^3; \Delta H_f(L) = 44.4 \text{ cal/g}; T_m = 1154 \text{ }^\circ\text{C}; \\ T_0 &= 20 \text{ }^\circ\text{C}; k = 0.07 \text{ cal/cm}^\circ\text{C} \cdot \text{s}; c_p = 0.16 \text{ cal/g}^\circ\text{C} \end{aligned}$$

It results:

$C_{\text{iron}} = 0.78 \text{ s/cm}^2$, that is to say, 200 times lower to that of the sand and around 6 times higher than that of the Cu.

Comparing, the solidification times for a thin slab of 1 cm in thickness (cooled, refrigerated for both sides) would be:

$$(t)_{\text{sand}} \simeq 40 \text{ s}; (t)_{\text{iron}} \simeq 0.20 \text{ s}; (t)_{\text{Cu}} \simeq 0.03 \text{ s} \quad (10.45)$$

This explains that in the manufacture of steel ingots, cast iron moulds are preferred facing to sand moulds. And copper ingots strongly refrigerated with water are preferred in continuous casting.

Hypereutectic grey cast irons (with primary graphite, pearlitic structure) are the selected material as the graphite notably increases the thermal conductivity of the cast iron, the thermal conductivity of the cast iron is around $0.18 \text{ cal/(cm }^\circ\text{C s)}$, while the thermal conductivity of the iron is around, $0.07 \text{ cal/(cm }^\circ\text{C s)}$. However, the melting point is notably lower in the cast iron than in the steel ($1538 \text{ }^\circ\text{C}$ in the iron, $1154 \text{ }^\circ\text{C}$ in the cast iron). Cast iron ingot moulds are least expensive, compact and resist better the heating cycles than that of steel.

10.6 Riser. Equations of Caine and Adams–Taylor. Exothermic Isolation. Solidification Defects

10.6.1 Introduction to Caine's Equation

As the shrinkage characteristics of a metal during solidification are due to a phase change, they are very precise and do not vary appreciably within composition range encountered for any particular alloys. This should make a scientific approach to the dimensioning of risers amenable to precise mathematical study. All that need take

into consideration is the rate of heat evolution by the metal until it has solidified and the rate of heat transfer across the sand–metal interface, as the two controlling factors in the relative rate to complete solidification of the casting and riser.

Only two factors are required for the study of this phase of risering: volume, and a factor denoting the relative rate of solidification of the casting and riser. Some limits are also known. If the solidification rate of the riser is infinitely small in relation to that of the casting, the riser volume required would be equivalent to the contraction in volume during solidification, in some instances, the amount of liquid contraction occurring between the pouring temperature and the beginning of the solidification.

In steels, this would be equivalent to a riser of about 5.0% of casting volume. This value is made up of 3.0% solidification contraction and 2.0% liquid contraction from an average pouring temperature of 1620 °C and is much smaller than that required in production. This is because solidification in both riser and casting is progressing at the same time. For efficient scientific risering, the problem is to determine the smallest riser that will solidify at a slower rate than the casting it is to feed, delivering sufficient feed metal to fill all the voids opening up within the feeding range of the riser until the casting is completely solidified.

Another limit has been established. It has been proved for metals that a riser of a section equal to the casting section will not feed efficiently; in fact, it will not feed at all, regardless of its height, unless some type of insulation is placed around the riser to lower its freezing range, or some addition be made (exothermic, shielding) to accomplish the same purpose. This limit should also be applied to cast irons even if expand during solidification (4% liquid contraction –2% solid expansion $\simeq$ 2% shrinkage). As two equal sections must solidify at the same rate, it is concluded that if the riser freezes at the same rate as the casting, the riser volume required is infinite.

Both limits are now established. If the riser freezes infinitely slowly in relation to the casting, the riser volume required is equal to the liquid contraction, plus the volume contraction on solidification. If the riser freezes at the same rate as the casting, the riser volume required is infinite. The problem now is to establish the shape of the curve designating this relation between the two extremes. The freezing times of the casting and riser between these two extremes must be in relation to the amount of heat evolved by the metal as it cools from the pouring temperature through the solidification range, and the amount of heat dissipated into the sand in contact with the casting and riser.

As a riser is a casting differing only in shape from the casting to be fed, the established relations can be used to bypass all the difficulties associated with determining and handling absolute values such as specific heat, latent heat of fusion, the quantitative rate of heat flow across the sand–metal interface (thermal diffusivity). The amount of heat evolved must be in relation to the volume; the amount of heat dissipated to the surface area of the casting and riser, according to the Chvorinov rule:

$$t_f = C \cdot \left(\frac{V}{A}\right)^2 \quad (10.46)$$

where t_f is the total time of solidification of the casting, V the volume, A the cross section area and C a constant for a given metal–mould material and mould temperature T_0 , calculated with:

$$C = \frac{\pi}{4} \cdot \left(\frac{\rho_s \cdot \Delta H_f}{T_M - T_0}\right)^2 \cdot \frac{1}{k_m \cdot \rho_m \cdot c_m} \quad (10.47)$$

where ρ_s is the density of the metal, ΔH_f the latent heat of the melting, T_M the melting point of the metal, k_m the thermal conductivity of the mould, ρ_m the density of the mould and c_m the specific heat of the mould. Furthermore, the $k_m \cdot \rho_m \cdot c_m$ product, known as heat diffusivity, is a measure of the rate at which the mould can absorb heat.

From the standpoint of scientific riser dimensioning, the riser should be proportioned for maximum riser efficiency so that the minimum riser freezes at slower rate than the casting or section it is to feed. At the same time, it should contain a sufficient volume to satisfy the feed requirements of the casting.

It is therefore possible to use absolute values such as specific heat, latent heat and thermal diffusivity and solve the problems of scientific riser dimensioning with relations. Only two relations are required, one for relative volume, one for relative freezing times to complete solidification, as follows:

$$Y = \frac{\text{riser volume as poured}}{\text{casting volume}} = \frac{V_r}{V_c} \quad (10.48)$$

$$X = \frac{\text{casting surface area/casting volume}}{\text{riser surface area/riser volume}} = \frac{(A/V)_c}{(A/V)_r} = \frac{(V/A)_r}{(V/A)_c} \propto (t_r/t_c)^{1/2} \text{ (Chvorinov rule)} \quad (10.49)$$

As discussed previously, Y for volume approaches infinity as X approaches the unity. And Y approaches the amount of liquid and solidification contraction when X approaches infinite. Such a relation indicates a hyperbolic function, most simply expressed through the equation:

$$X = \frac{a}{Y - b} + c \quad (10.50)$$

Whose asymptotes for steel are unity relative freezing time and 0.05 relative volume. Therefore, the Caine's equation can be written:

For steels:

$$X = \frac{0.12}{Y - 0.05} + 1 \quad (10.51)$$

For grey castings:

$$X = \frac{0.08}{Y - 0.02} + 1 \quad (10.52)$$

For ductile castings:

$$X = \frac{0.04}{Y - 0.02} + 1 \quad (10.53)$$

For aluminium casting:

$$X = \frac{0.18}{Y - 0.07} + 1 \quad (10.54)$$

Constant a has been assigned from experiments, constant b is the sum of the liquid and solidification contraction and this value varies according to the metal and pouring temperature, and finally constant c is a measure of any change in the relative freezing rate of the casting and riser. If both casting and riser are in contact with sand and are dissipating heat into the sand at the same rate, constant c is 1.0. Mathematically the inclusion of constant c merely shifts one asymptote from $X = 0$ to $X = 1$ (Fig. 10.4).

If insulators or liquidizers (exothermic suppliers) are used on shielding or padding around the riser, constant c will be decreased from $1 \rightarrow 0$, depending on the efficiency of them. It has been determined empirically that the liquidizer and pipe eliminators commonly used decrease constant c from 1 to 0.8. This change shifts the curves to the left (see Fig. 10.4), changing the vertical asymptote from 1 to 0.8. Using gypsum (plaster of paris) insulator constant c can decrease the freezing rate of the riser in relation to the casting is quite useful in increasing riser efficiency of low surface area, resulting in freezing ratios, X , below about 1.4. If the freezing ratio of the casting-riser combination is below $X = 1.1$ some method of decreasing the relative freezing rate of the riser is almost imperative.

Finally, the values given in Fig. 10.4 are the yields when the weight of the gate (pouring cup, downsprue) equals the weight of metal equivalent to the volume of the shrinkage cavity in the solidified riser. In production, the actual yield will vary according to the weight of the gate, being lower if a long weighty gate is used, higher if an exceptionally small or no gate is used. See the examples treated below.

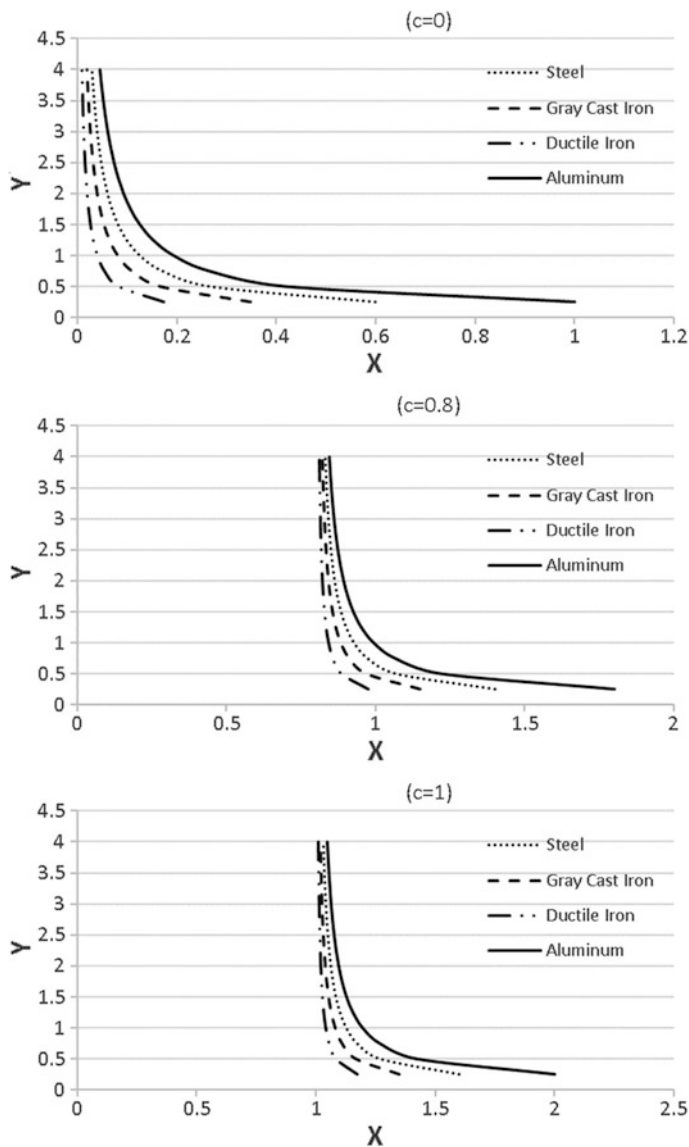


Fig. 10.4 Representation of Caine’s equation

Exercise 10.14. Demonstrate the equation of Adams and Taylor used in the calculation of the volume of a blind riser that should feed a sound part:

Data: V_C , volume of the part; V_r , volume of the riser; A_C , surface of cooling of the part; A_r , surface of cooling of the riser; ρ_L , density of the liquid; ρ_S ,

density of the solid; β , contraction in the transformation liquid $\rightarrow$ solid; V_{rf} , final volume of the solid in the riser.

Question

Conditions:

- (a) the riser should cold more slowly than the part.
- (b) the macro-shrinkage should be placed completely in the riser, it should not cross the interphase riser-cast part.

For a mould of the same nature (riser and casting), Chvorinov's equation establishes that

$$\frac{V_{rf}}{V_C} \geq \frac{A_r}{A_C} \quad (10.55)$$

Or:

$$\frac{V_{rf}}{A_r} \geq \frac{V_C}{A_C} \quad (10.56)$$

In the limit:

$$\frac{V_{rf}}{V_C} = \frac{A_r}{A_C} \quad (10.57)$$

Shrinkage:

$$\beta = \frac{(V_L - V_S)}{V_L} = \frac{\{(V_C + V_r) - (V_C + V_{rf})\}}{(V_C + V_r)} = \frac{(V_r - V_{rf})}{(V_C + V_r)} \quad (10.58)$$

$$(V_r - V_{rf}) = \beta \cdot (V_C + V_r) \rightarrow \frac{V_r}{V_C} - \frac{V_{rf}}{V_C} = \beta \cdot \left(1 + \frac{V_r}{V_C}\right) \quad (10.59)$$

$$\frac{V_r}{V_C} \cdot (1 - \beta) = \frac{A_r}{A_C} + \beta \quad (10.60)$$

Known as Adams and Taylor equation.

Exercise 10.15. A ductile iron of $5 \times 5 \times 5$ sand moulded is fed from a blind top riser of 5 in. in diameter. What should be the height required to obtain a sound part? Data: $\beta = 0.02$

Question

$$V_r = \pi \cdot \frac{D^2}{4} \cdot H = 19.64 \cdot H \quad (10.61)$$

$$V_C = 5 \cdot 5 \cdot 5 = 125 \text{ in.}^3 \quad (10.62)$$

$$A_r = \pi \cdot D \cdot H + \pi \cdot \frac{D^2}{4} = 15.70 \cdot H + 19.64 \quad (10.63)$$

$$A_C = 5 \cdot 5 \cdot 6 = 150 \quad (10.64)$$

By applying Adams and Taylor:

$$(1 - 0.02) \cdot \frac{19.64 \cdot H}{125} = \frac{15.70 \cdot H + 19.64}{150} + 0.02 \rightarrow H = 3.06 \text{ in. } (H/D \simeq 0.6) \quad (10.65)$$

What would be the height of the riser if the top of the riser would be exothermically isolated?

Question

The equation of Taylor and Adams would be:

$$(1 - 0.02) \cdot \frac{19.64 \cdot H}{125} = \frac{15.70 \cdot H}{150} + 0.02 \rightarrow H = 0.4 \text{ in. } (H/D \simeq 0.08) \quad (10.66)$$

The height of the riser results around 13 times lower. The top cooling surface of the riser ($\pi \cdot D^2/4$) would disappear.

Or, by applying Caine in the case of ductile irons:

$$X = \frac{0.04}{Y - 0.02} + 1 \quad (10.67)$$

$$X = \frac{V_r/V_C}{A_r/A_C} = \frac{19.6}{15.7} = 1.25 \quad (10.68)$$

When:

$$X = 1.25 \rightarrow Y = 0.18 < \frac{V_r}{V_C} = \frac{25 \cdot \pi \cdot 0.7}{125} = 0.44 \text{ (blind riser)} \quad (10.69)$$

The new design would be correct.

10.6.2 Riser in Grey Irons

The risering of grey irons has been reserved for special attention, since it is a complex problem having some features in common with steel, whereas others are completely different. For example, the solidification of a 3% carbon grey iron takes place through two distinct mechanisms:

- (1) liquidus to eutectic; separation of austenite dendrites (primary austenite);
- (2) eutectic, concurrent precipitation of graphite and austenite.

Reaction (1) is like that for steels, i.e. the solidification of primary austenite involves the formation of a denser phase than that of the liquid, and therefore, feed metal is required from a riser at this time. On the other hand, reaction (2) involves an expansion, since the density of the solid eutectic mixture is less than that of the parent liquid. During this reaction, metals flow back into the riser, a process known as *purging*. If the riser is small and has frozen over at the top, great pressure will be generated within the casting and the walls will be bowed outward. However, if the riser is open to the atmosphere, the pressure is relieved by metal flow. This can be of major importance in determining dimensional accuracy.

Exercise 10.16. A 5-in. cube of grey cast iron is casted in dry sand with a 5-in. diameter cylindrical top riser. How high must the riser be to produce a sound casting? Assume the Caine's relationship:

$$X = \frac{0.04}{Y - 0.02} + 1 \quad (10.70)$$

Question

First of all, the volume and area of both the riser and the casting are calculated:

$$V_{\text{riser}} = \pi \cdot \frac{D^2}{4} \cdot H = 19.63 \cdot H \quad (10.71)$$

$$A_{\text{riser}} = \pi \cdot D \cdot H + \pi \cdot \frac{D^2}{4} = 15.7 \cdot H + 19.63 \quad (10.72)$$

$$A_{\text{casting}} = 125 \text{ in.}^2 \quad (10.73)$$

$$V_{\text{casting}} = 5 \cdot 5 \cdot 5 = 125 \text{ in.}^3 \quad (10.74)$$

Assuming $H = 1.5 \cdot D \rightarrow$

$$V_{\text{riser}}/A_{\text{riser}} = 19.63 \cdot H / 15.7 \cdot H + 19.63 = 1.07 \quad (10.75)$$

$$V_{\text{casting}}/A_{\text{casting}} = 1 \rightarrow X = 1.07 \quad (10.76)$$

By using Caine:

$$Y = 0.59 < V_{\text{riser}}/V_{\text{casting}} = 147.23/125 = 1.18 \text{ (ensures sound casting)} \quad (10.77)$$

If both casting and riser are completely enclosed in sand, how must the riser be to produce a sand casting?

Question

By using Adams and Taylor equation (demonstrated in Exercise 10.14):

$$(1 - \beta) \cdot \frac{V_{\text{riser}}}{V_{\text{casting}}} = \frac{A_{\text{riser}}}{A_{\text{casting}}} + \beta; \quad \beta = 0.02 \quad (10.78)$$

$$V_{\text{riser}} = \frac{\pi \cdot D^2}{4} \cdot H = 19.6 \cdot H \quad (10.79)$$

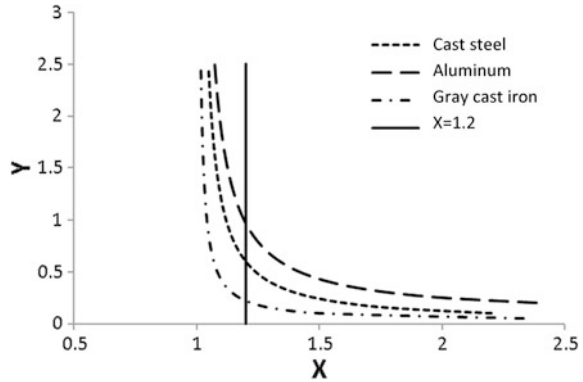
$$V_{\text{casting}} = 125 \text{ in.}^3 \quad (10.80)$$

$$A_{\text{riser}} = \pi \cdot D \cdot H = 15.7 \cdot H \quad (10.81)$$

$$A_{\text{casting}} = 125 \text{ in.}^2 \quad (10.82)$$

$$(1 - 0.02) \cdot \frac{19.6 \cdot H}{125} = \frac{15.7 \cdot H}{125} + 0.02 \rightarrow H = 0.67 \text{ in.} \rightarrow \frac{V_{\text{riser}}}{V_{\text{casting}}} = \frac{19.6 \cdot H}{125} = 0.11 \quad (10.83)$$

Fig. 10.5 Representation of Caine's equation



The relation $V_{\text{riser}}/V_{\text{casting}}$ is significantly lower (0.11) if compared with the result in the last exercise as heat loss by radiation through the surface was higher in the open riser than in the blind riser.

Assuming that Caine's equations are:

For grey cast irons: $X = 0.04/(Y - 0.02) + 1$.

For cast steel: $X = 0.12/(Y - 0.05) + 1$.

For aluminium: $X = 0.18/(Y - 0.07) + 1$.

Represent the functions $Y(X)$ of Caine and compare the values $V_{\text{riser}}/V_{\text{casting}}$ when $X = 1.2$ in parts of cast iron, cast steel and aluminium (Fig. 10.5). What are the consequences that can be deduced?

Question

Low values of the ratio $V_{\text{riser}}/V_{\text{casting}}$ lead to work in the side of the positive yielding of the process, as the required riser would be smaller. The yielding in each situation is

$$\text{yielding} = \frac{V_{\text{casting}}}{V_{\text{casting}} + V_{\text{riser}}} \cdot 100 \quad (\text{without considering the feeding system}) \quad (10.84)$$

Cast steel:

$$X = 1.2 \rightarrow X = 0.12/(Y - 0.05) + 1 \rightarrow Y = 0.65 \quad (10.85)$$

$$Y = \frac{V_{\text{riser}}}{V_{\text{casting}}}; V_{\text{casting}} = 125 \rightarrow V_{\text{riser}} = 81.25 \text{ in.}^3 \quad (10.86)$$

$$\text{yielding}_{\text{Cast steel}} = \frac{125}{125 + 81.25} \cdot 100 = 60.61\% \quad (10.87)$$

Aluminium:

$$X = 1.2 \rightarrow X = 0.18/(Y - 0.07) + 1 \rightarrow Y = 0.97 \quad (10.88)$$

$$Y = \frac{V_{\text{riser}}}{V_{\text{casting}}}; V_{\text{casting}} = 125 \rightarrow V_{\text{riser}} = 121.25 \text{ in.}^3 \quad (10.89)$$

$$\text{yielding}_{\text{Aluminium}} = \frac{125}{125 + 121.25} \cdot 100 = 50.76\% \quad (10.90)$$

Grey cast iron (ductile):

$$X = 1.2 \rightarrow X = 0.04/(Y - 0.02) + 1 \rightarrow Y = 0.22 \quad (10.91)$$

$$Y = \frac{V_{\text{riser}}}{V_{\text{casting}}}; V_{\text{casting}} = 125 \rightarrow V_{\text{riser}} = 27.5 \text{ in.}^3 \quad (10.92)$$

$$\text{yielding}_{\text{Grey Cast Iron}} = \frac{125}{125 + 27.5} \cdot 100 = 81.97\% \quad (10.93)$$

And then:

Riser Grey Cast Iron < Riser-Cast Steel < Riser Aluminium.

Exercise 10.17. Repeat the calculation of the last problem for a grey cast iron plate of the same weight as the 5-in. diameter cube ($10 \times 12.5 \times 1 \text{ in}^3$). Would you recommend using a 3-in. diameter open riser on this casting? Assuming $H = D$

Question

$$V_{\text{riser}} = \frac{\pi \cdot D^3}{4} = 21.2 \text{ in.}^3 \quad (10.94)$$

$$V_{\text{casting}} = 2 \cdot (10 \cdot 12.5) + 2 \cdot (10 \cdot 1) + 2 \cdot (12.5 \cdot 1) = 490 \text{ in.}^3 \quad (10.95)$$

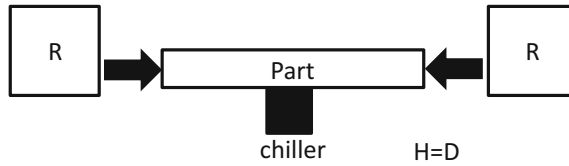


Fig. 10.6 Risering scheme

$$A_{\text{riser}} = \frac{9 \cdot \pi}{4} + 9 \cdot \pi = 31.8 \text{ in.}^2 \quad (10.96)$$

$$A_{\text{casting}} = 490 \text{ in.}^2 \quad (10.97)$$

$$Y = \frac{V_{\text{riser}}}{V_{\text{casting}}} = 0.17 \quad (10.98)$$

$$X = \frac{V_{\text{riser}}/V_{\text{casting}}}{A_{\text{riser}}/A_{\text{casting}}} = 1.58 \quad (10.99)$$

By using Caine's equation:

$$X = \frac{0.1}{Y - 0.02} + 1 \quad (10.100)$$

When $X = 1.58 \rightarrow Y = 0.19 > V_{\text{riser}}/V_{\text{casting}} = 0.17$ (the difference is small)

The exothermic isolating of the riser (upper face) would be enough to obtain a sound part, without defects, the same as the feeding distance (demonstrate). Another safer solution could be provided: feeding with two lateral risers and placing an external chiller in the centre (Fig. 10.6).

When: $H = D = 2.5$, $Y = V_{\text{riser}}/V_{\text{casting}} = (\pi \cdot D^3/4)/62.5 = 0.20$

Each riser could feed a distance equivalent to $4.5 t$ (thickness) + 2 (chiller) = $6.5 > 6.25$ (semilength of the plate). Both two risers would have a total volume of 24.5 in.^3 , slightly higher than that of the previous case (riser of 3 in, $V_{\text{riser}} = 21.2 \text{ in.}^3$). The design would be safe.

Exercise 10.18. Optimum riser geometry is one which has the least surface area for a given size. Demonstrate that for a cylindrical top riser, this would be one whose height is half its diameter, $H = D/2$.

Question

$$V_{\text{riser}} = \pi \cdot (D^2/4) \cdot H \quad (10.101)$$

$$A_{\text{riser}} = \pi \cdot D \cdot H + \pi \cdot D^2/4 \quad (10.102)$$

Blind riser: no heat evolved through the interphase riser/part:

$$V/A = \pi(D^2/4) \cdot H / \pi \cdot D \cdot H + \pi \cdot D^2/4 = 4 \cdot D \cdot H / 4 \cdot H + D \quad (10.103)$$

Deriving:

$$\partial(V/A)/\partial D = 0; \partial(V/A)/\partial H = 0 \quad (10.104)$$

We have

$$\frac{H \cdot (4 \cdot H + D) - D \cdot H}{(4 \cdot H + D)^2} = 0 \quad (10.105)$$

$$\frac{D \cdot (4 \cdot H + D) - 4 \cdot D \cdot H}{(4 \cdot H + D)^2} = 0 \quad (10.106)$$

That is,

$$4 \cdot H^2 + D \cdot H - DH = 4 \cdot D \cdot H + D^2 - 4 \cdot D \cdot H \rightarrow 4 \cdot H^2 = D^2 \rightarrow H = D/2 \quad (10.107)$$

From the relation:

$$\frac{V}{A} = \frac{D \cdot H}{4 \cdot H + D} = \frac{D}{4 + (D/H)} \quad (10.108)$$

The lower the relation D/H , the ratio V/A rises up to a value $V/A = D/4$ for $H \rightarrow \infty$ (blind risers). In normal open risers $H/D = 1.5$ ($V/A = 0.67 \cdot D$), in compact risers $H = D$ ($V/A = 0.20 \cdot D$), and in ‘optimum’ risers $H = D/2$ ($V/A = 0.17 \cdot D$).

Exercise 10.19. A shaft of 5 cm in diameter and 50 cm in length is manufactured in ductile iron 65-45-12 with a nitriding surface treatment with the purpose of increasing its hardness and resistance to fatigue. Calculate the dimensions of the riser considering $H = 1.5 \cdot D$. Caine's equation is verified:

$$X = \frac{0.04}{Y} - 0.02 + 0.8 \quad (10.109)$$

Question

As in previous exercises, the volumes and areas for both the riser and the casting are calculated:

$$V_{\text{riser}} = 1.5 \cdot \pi \cdot D^3 / 4 \quad (10.110)$$

$$A_{\text{riser}} = 1.5 \cdot \pi \cdot D^2 \quad (10.111)$$

$$\left(\frac{V}{A}\right)_{\text{riser}} = D/4 \quad (10.112)$$

$$V_{\text{casting}} = \pi \cdot 25 \cdot 20 / 4 = 981.7 \text{ cm}^3 \quad (10.113)$$

$$A_{\text{casting}} = \pi \cdot \frac{25}{4} + \pi \cdot 5 \cdot 50 = 805 \text{ cm}^2 \quad (10.114)$$

By applying the Adams and Taylor equation:

$$(1 - \beta) \cdot (V_r / V_C) \geq (A_r / A_C) + \beta \quad (10.115)$$

$$\begin{aligned} 0.98 \cdot \frac{1.5 \cdot \pi \cdot D^3}{4 \cdot 981.7} &\geq \frac{1.5 \cdot \pi \cdot D^2}{805} + 0.02 \rightarrow 1.18 \times 10^{-3} \cdot D^3 \\ &\geq 5.85 \times 10^{-3} \cdot D^2 + 0.02 \end{aligned} \quad (10.116)$$

The above inequation is verified from $D \simeq 5 \rightarrow H = 7.5$

$$V_r / V_C = 1.5 \cdot \pi \cdot 5^3 / 4 \cdot 981.7 = 0.15 \quad (10.117)$$

By applying Caine's equation:

$$X = \frac{0.04}{0.15 - 0.02} + 0.8 = 1.1 \quad (10.118)$$

which coincides approximately with the value:

$$X = (V_r/A_r)/(V_C/A_C) = 1.25/(981.7/805) \simeq 1.03 \quad (10.119)$$

Note: The appearance of a value of $\beta \simeq 0.02$ (contraction) means that the cast iron was casted with an superheating of around 200 °C above the melting point.

Exercise 10.20. A shaft of 8 in. in length and 3.75 in. in diameter is manufactured in ductile iron, quality 60-40-18 annealed. Calculate the diameter of the riser when $H = 2 \cdot D$. Apply the equation of Adams and Taylor:

$$(1 - \beta) \cdot (V_{\text{riser}}/V_{\text{casting}}) \cdot 0.6 \geq (A_{\text{riser}}/A_{\text{casting}}) + \beta \quad (10.120)$$

The correction coefficient $k = 0.6$ comes from the fact that the upper base of the cylindrical riser is isolated, impeding the heat losses by radiation, which are the most important. Suppose that $\beta \simeq 0.02$.

Question

$$V_{\text{riser}} = 2 \cdot \pi \cdot D^3/4 \quad (10.121)$$

$$A_{\text{riser}} = 2 \cdot \pi \cdot D^2 \quad (10.122)$$

$$\left(\frac{V}{A}\right)_{\text{riser}} = D/4 \quad (10.123)$$

$$V_{\text{casting}} = \pi \cdot 3.75^2 \cdot 8/4 = 88.36 \text{ in.}^3 \quad (10.124)$$

$$A_{\text{casting}} = \pi \cdot \frac{3.75^2}{4} + \pi \cdot 3.75 \cdot 8 = 105.3 \text{ in.}^2 \quad (10.125)$$

By applying Adams and Taylor:

$$\frac{(1 - 0.02) \cdot 2 \cdot \pi \cdot D^3}{4 \cdot 88.36} = \frac{0.6 \cdot 2 \cdot \pi \cdot D^2}{105.3} + 0.02 \quad (10.126)$$

Solving by successive approximations (Newton–Raphson) results:

$$D \simeq 2.4 \text{ in.} \rightarrow H = 4.8 \text{ in.} \quad (10.127)$$

The $V_{\text{riser}}/V_{\text{casting}}$ ratio is equal to:

$$\frac{2 \cdot \pi \cdot 2.4^3}{4 \cdot 88.36} \simeq 25\% \quad (10.128)$$

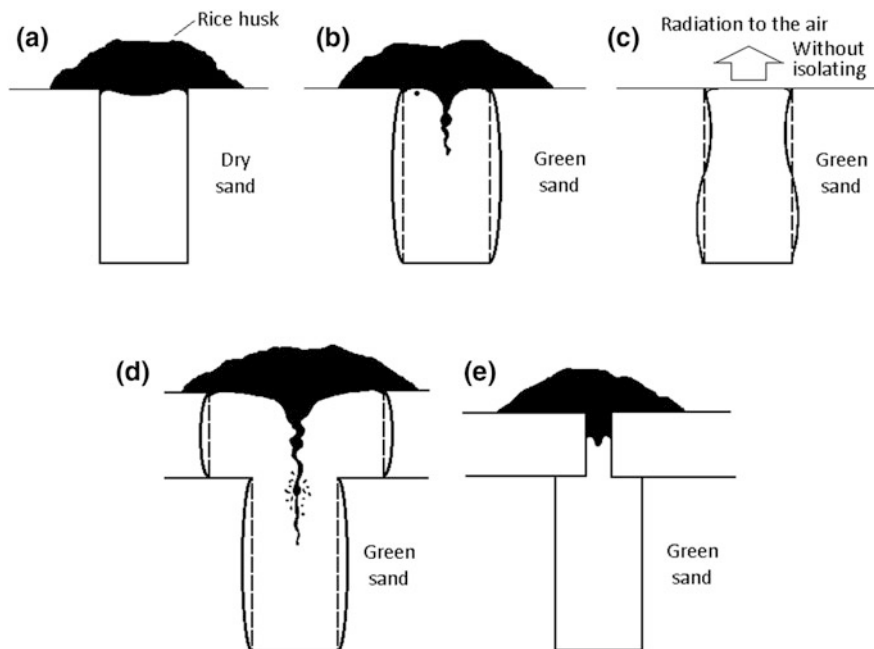


Fig. 10.7 **a** Right moulding, small contraction; **b** growth and macro-shrinkage; **c** deformed part; **d** excessive risering, macro-shrinkage; and **e** suitable risering, sound part

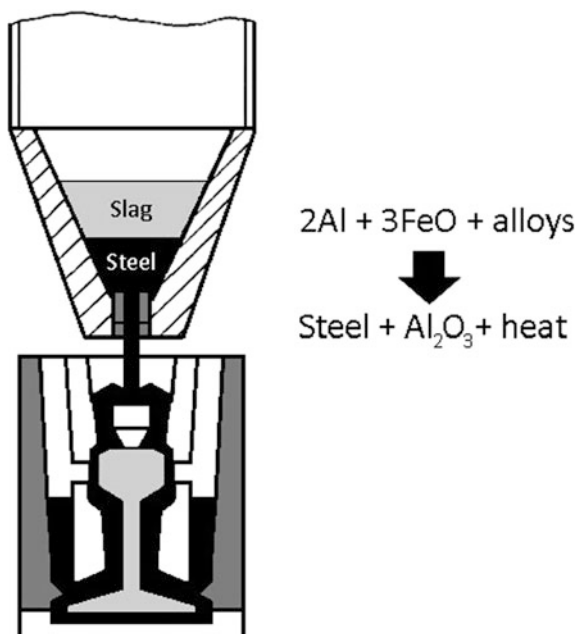
The graphite expansion in cast irons can in large measure counterbalance solidification shrinkage, and it is possible to feed the alloys with much more smaller risers than those needed for other metals. In fact, $\beta \leq 0.02$, but positive due to the contraction operated in the liquid between pouring liquid temperature (to improve fluidity) and solidification temperature (see Figs. 3.5 and 10.7).

Exercise 10.21. What type of exothermic materials would you use for making iron castings?

Question

Exothermic riser compounds are loose material sprinkled on the top of risers in place of insulating powders. They may be used not only to prevent heat loss from the top of the riser but also to add some heat, and even to add some metal to the riser. Exothermic riser compounds are essentially mixtures of a metal oxide and aluminium. When placed on the metal in an open riser, the mixtures react to

Fig. 10.8 Rail
aluminothermic welding
(cross section)



give molten metal, heat and slag insulator. With iron oxide and aluminium, the reaction is



The molten metal produced through the reaction is an effective transfer medium for the very high heat, the sand around the riser is preheated, and the slag layer insulates the riser against heat loss to the atmosphere. Accordingly, feeding efficiency is improved by about 70%, and risers can be made about a third size of a normal riser. In fact, it is necessary to use short risers to concentrate the heat at the casting-riser neck where it is needed to prolong feeding and develop desirable thermal gradients in the casting. See Fig. 10.8.

10.6.3 Rail Aluminothermic Welding (Applicable to Exothermic Risers)

Exercise 10.22. The FeO aluminothermic reduction makes up an alternative in the welding of steel parts when electric power is not available. Calculate:

1. The heat released by the reaction in kJ/kg of Fe.
2. The maximum temperature that is possible to reach assuming that the process is completely adiabatic and does not dissipate heat to the environment.

3. If the temperature that is really reached in the weld bead is 2100 °C, calculate the percentage of energy dissipated by radiation, convection and conduction.

Data:

Al (27 g/mol); Fe (55.85 g/mol); O (16 g/mol); ρ – alumina (l)
 $\simeq 3.5 \text{ g/cm}^3$; – iron (l) $\simeq 7 \text{ g/cm}^3$

Average specific heat of the Fe (solid) = 38.80 J/atom – g · K.

Average specific heat of the Fe (liquid) = 46.02 J/atom – g · K.

Average specific heat of the Al (solid) = 28.33 J/atom – g · K.

Average specific heat of the Al (liquid) = 31.75 J/atom – g · K.

Average specific heat of the Al_2O_3 (solid) = 125.75 J/mol Al_2O_3 · K.

Average specific heat of the Al_2O_3 (liquid) = 144.0 J/mol Al_2O_3 · K.

Average specific heat of the FeO (solid) = 56.33 J/mol FeO · K.

Heat of fusion of the Fe at 1536 °C = 13807 J/atom – g.

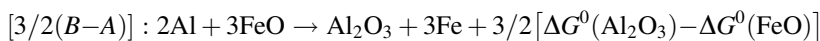
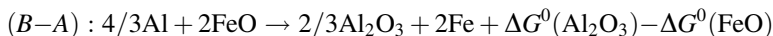
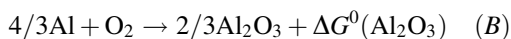
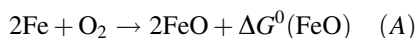
Heat of fusion of the Al at 600 °C = 10711 J/atom – g.

Heat of fusion of the Al_2O_3 at 2054 °C = 25551 J/mol Al_2O_3 .

Enthalpy of formation of the FeO at 25 °C = –268.6 kJ/mol FeO.

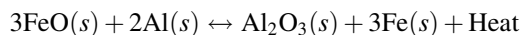
Enthalpy of formation of the Al_2O_3 at 25 °C = –1675.5 kJ/mol Al_2O_3 .

Question



That constitutes the starting reaction.

Aluminothermic process:



Data (from the Ellingham diagrams for the oxides formation):

$$\Delta G^0_{\text{FeO}}(25^\circ\text{C}) = -268.6 \text{ kJ/mol FeO} \quad (10.129)$$

$$(\Delta G^0_{\text{Al}_2\text{O}_3}(25) = -1675.5 \text{ kJ/mol Al}_2\text{O}_3) \quad (10.130)$$

Heat released by kg of Fe:

$$\Delta G^0(25^\circ\text{C}) = 1675.5 - 3.268.6 \simeq 869.7 \text{ kJ/3 moles Fe} \quad (10.131)$$

$$\frac{869.7 \text{ kJ}}{3 \text{ moles Fe}} \cdot \frac{\text{mol Fe}}{56 \text{ g}} \cdot \frac{1000 \text{ g}}{1 \text{ kg}} \simeq 5177 \text{ kJ/kg Fe} \quad (10.132)$$

Maximum temperature that the reaction products can reach (adiabatic conditions; it does not exist heat losses).

Fe:

Specific heat Fe (s): $3 \cdot 38.80 \cdot (1536 - 25) = 175880 \text{ J}$.

Latent heat Fe (s $\rightarrow$ l): $3 \cdot 13807 = 41421 \text{ J}$.

Latent heat Fe (l): $3 \cdot (T - 1536) \cdot 46.02 = (138 T - 212060) \text{ J}$.

TOTAL (Fe): $(138 T + 5241) \text{ J}$.

Al₂O₃:

Specific heat Al₂O₃ (s): $125.75 \cdot (2054 - 25) = 255147 \text{ J}$.

Latent heat Al₂O₃ (s $\rightarrow$ l): $25551 = 25551 \text{ J}$.

Latent heat Al₂O₃ (l): $144 \cdot (T - 2054) = (144T - 295776) \text{ J}$.

TOTAL (Al₂O₃): $(144T - 15078) \text{ J}$.

TOTAL PRODUCTS: $(282T - 9837) \text{ J}$.

All heat of the reaction is used in heating the products Al₂O₃ and Fe.

$$869700 = 282T - 9837 \quad (10.133)$$

$$T(^{\circ}\text{C}) = \frac{869700 + 9837}{282} = 3119^{\circ}\text{C} \quad (10.134)$$

If the temperature reached would be 2100 °C, what are the heat losses of the aluminothermic process?

$$869700 \text{ J} = 282 \cdot 2100 - 9837 + Q (\text{losses}) \quad (10.135)$$

$$Q = 869700 + 9837 - 592200 = 287337 \text{ J} \quad (10.136)$$

$$\text{Losses} = \frac{287337}{869700} = 0.33 (33\%) \quad (10.137)$$

In the industrial practice, molten iron (aluminothermic metal makes possible the welding of the extremes of the rail) is found at a temperature higher than 2100 °C; for that reason, it is feasible the separation by gravity of the molten alumina (3.5 g/cm^3) and liquid iron (7 g/cm^3) in the crucible.

10.6.4 Gases in Cast Metals

Gases are almost universally more soluble in liquid metals than in solid metals. As the metal cools and particularly as it freezes, dissolved gases tend to be expelled from the solution to form *gas holes*. The gas holes may be in the form of large *blowholes*, finer *pinholes*, or still finer *microporosity*, depending on the amount of gas present and on the way the metal or alloy freezes. These gas holes in their various forms can be quite detrimental for the mechanical properties, for pressure tightness and for the surface finish of machined or cast surfaces. Every effort should be made in the foundry to assure that molten metal is free of all dissolved gases before it is casted.

Blowholes: a rimmed ingot is one made from *under-deoxidized* steel, i.e. steel which continues to evolve carbon monoxide gas in the mould after pouring. Blowholes develop near the ingot surface. A skin of relatively pure iron (very low in carbon) solidifies quickly at the mould–metal interface, and oxygen is rejected from the solution, as oxygen concentrates ahead of the solid wall, and the carbon–oxygen concentration product increases after gas bubbles form. Many bubbles rise from the bath, but some will be trapped by the advancing wall of solidifying metal. At a certain critical value of freezing rate, ferrostatic head and carbon–oxygen content, the primary blowholes form; the size, shape, distribution and depth of *primary blowholes* beneath the ingot skin determine ingot quality, and much work has been done to develop a scientific explanation of the process to make closer control of ingot structure (see Fig. 10.9).

Pinholes: Surface reactions sometimes cause subsurface porosity or pinholes. In aluminium alloys containing more than about 1 percent magnesium, a reaction tends to occur between the magnesium of the alloy and the water vapour of the mould; $\text{Mg} + \text{H}_2\text{O} = \text{MgO} + \text{H}_2\uparrow$. Hydrogen-filled pinholes at the surface are the result. Some copper base and other alloys are subjected to similar defects unless proper precaution is observed. In steel casting, subsurface pinholes can result from incomplete deoxidation of the molten metal.

Micro-shrinkage: are micro-cavities that appear in the grain boundaries of between colonies because of the contraction that the metal or alloy suffers in the transformation of liquid into solid, which cannot be fed with other liquid (for instance, coming from the riser). They usually have the shape of spherical triangles, with concave morphologies or ‘diabolo’ when are connected between them (Figs. 10.10 and 10.11).

Micro-shrinkage is abundant in alloys with long interval of solidification ($\Delta T = T_L - T_S$): high-carbon steels, aluminium alloys, bronzes and cast irons with steadite ($\%P > 1\%$)*. Such defects diminish, if they are interconnected, the

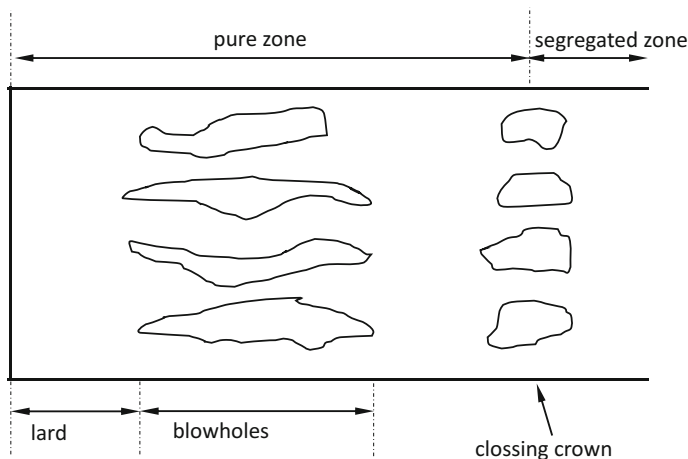


Fig. 10.9 Deoxidized steels

tightness of the parts, giving the leakage of the liquids and gases that flow inside the parts.

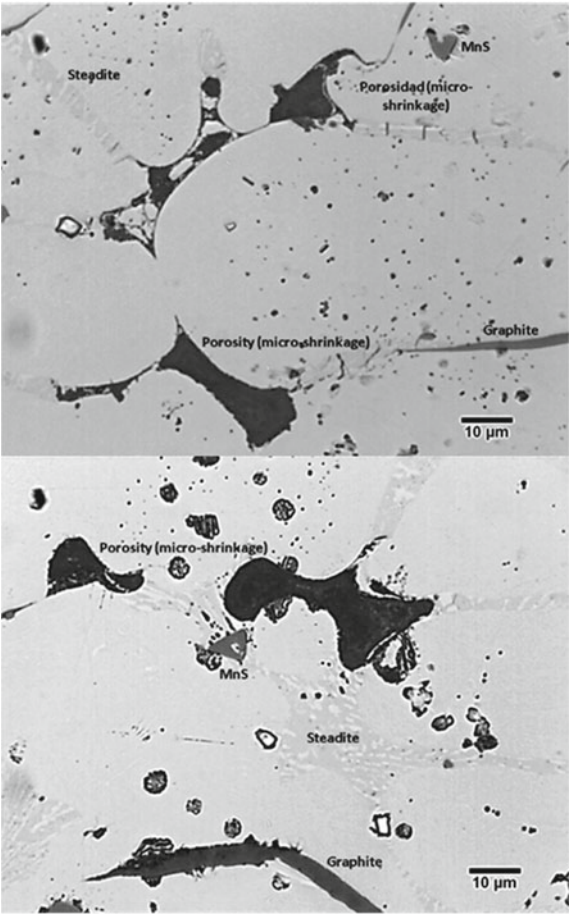
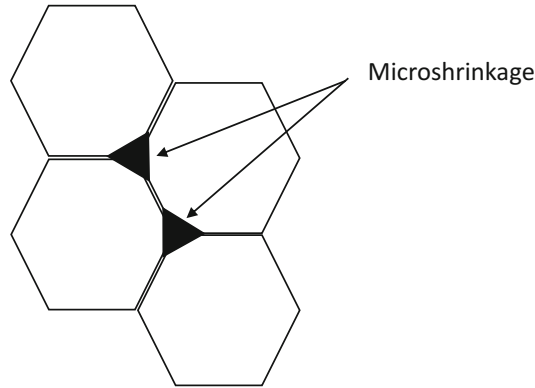
*Appear in alloys with a high CFR (Central Feed Resistance): alloys that freeze over a wide temperature interval tend to exhibit interdendritic shrinkage (microporosity) improperly fed. Microporosity also results from dissolved gas, an adequate degassing as well as directional solidification is necessary to produce a sound casting.

10.6.5 Pressure Tightness

Grey iron castings are widely used in pressure applications such as cylinder blocks, manifolds, pipe and pipe fittings, compressors and pumps. An important design factor for pressure tightness is uniformity of section. Most trouble with leaking casting is encountered when there are unavoidable abrupt changes in section. Shrinkage, internal porosity, stress cracking and other defects are most likely to occur at junctions between heavy and light sections. A slight sponginess or internal porosity at heavy sections will not usually leak water, and even if there is slight seepage, internal rusting will soon plug the passages permanently. For gas tightness, however, the cast must be quite sound.

Lack of pressure tightness in grey iron can usually be traced to internal porosity, in the form of micro-shrinkage. Internal porosity or micro-shrinkage is usually associated with poor feeding (high centre line feeding resistance) and lack of directional solidification (dendritic equiaxed microstructure). It is better to have high eutectic cell size (such as obtained with strontium-bearing inoculants) than high graphite cell count (promoted with heavy inoculation with calcium).

Fig. 10.10 Location of the micro-shrinkage (above). Cast iron: 3.35% C; 2.5% Si; 1% P



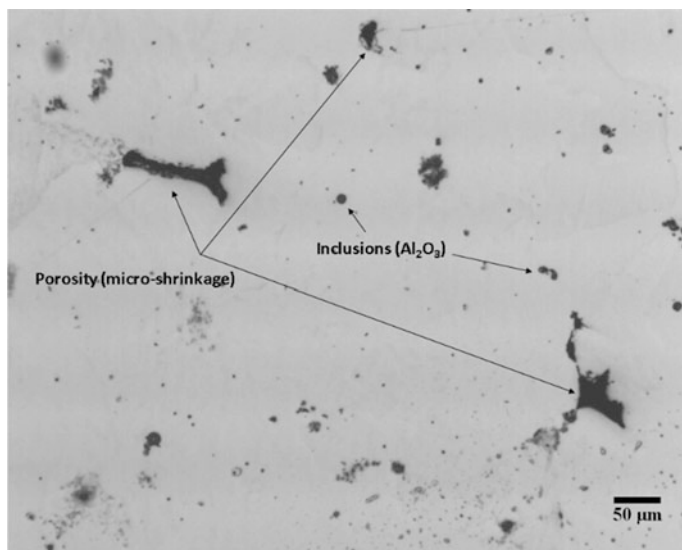


Fig. 10.11 Micro-shrinkage in an aluminothermic steel

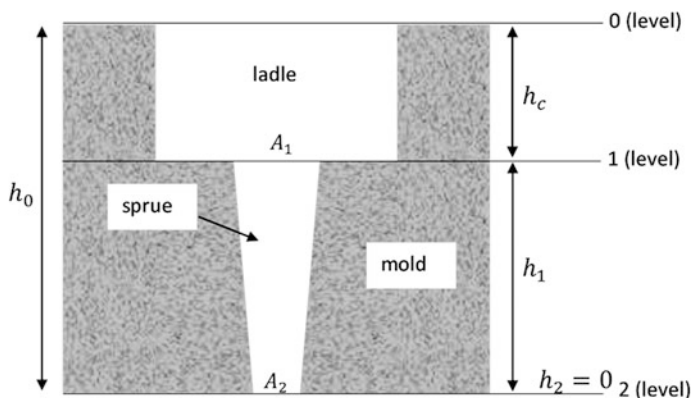


Fig. 10.12 Relations area-speed in a simple impermeable mould

Visible internal porosity may appear at centre of mass when the phosphorus content exceeds 0.25%. But lowering phosphorus content also lowers the effective carbon content (castability). Lowering carbon equivalent by reducing carbon or silicon contents may also create other foundry problems (such as increasing amounts of normal shrinkage). ASTM A278 for pressure castings requires a carbon equivalent of 3.8% (max), a phosphorus content of 0.12% (max) for castings to be used above 230 °C (450 °F).

In addition to composition control, good overall foundry practice is required for consistently producing the pressure-tight casting. More precisely, sand properties and gating must be controlled to avoid sand inclusions.

Exercise 10.23. Problem of pressure tightness. How can be this problem eliminated in grey cast irons?

Question

With a few exceptions, alloys freeze with such a wide *mushy* zone that they are not prone to the centre line shrinkage defects commonly found in improperly risered pure metals or steel castings. Rather, they are subjected to microporosity (micro-shrinkage). In improperly risered castings, the microporosity can be so concentrated that is readily visible on machined surfaces; *leaky* castings with low mechanical properties result and if the micropores are interconnected the cast iron can *leak* (see pressure tightness in Chap. 5). It is lower in grey irons with equivalent carbon lower than 3.8%. The reduction of the micro-shrinkage (microporosity) must be considered both from the compositional (low equivalent carbon, $P < 0.25\%$, $S < 0.12\%$, type of inoculant) point of view and the moulding practice, diminishing the amount of dissolved gases, and favouring the solidification towards the risers.

10.7 Mould Filling Times. Gating Design. Downhill Casting and Bottom Casting

Gating systems are used on all types of shaped castings. Many types of modern ingot casting now also employ a sort of gating system. As an example, in continuous casting of aluminium alloys, modern plants filter the liquid metal and then introduce it to the continuous caster through channels that provide minimum exposure of the metal to air. Many steel continuous-casting plants do the same, with filtering increasingly employed. Most large static cast steel are still filled (top and bottom pouring) from the ladle without an intermediate gating system. Typical gating system ratio (area of the runner to that of the sprue base to that of the sum of the cross-sectional areas of all gates) vary from about 1:1.5:1.5 to 1:5:5, the higher ratios been used for alloys which easily form oxides, or from which is difficult to remove entrained slag or oxides, e.g. ductile irons.

Exercise 10.24. In the system ladle sprue that is shown enclosed (Fig. 10.12), calculate through two different methods the relation A_2/A_1 that would avoid

the adsorption of gases of the mould by de-pressure of the stream, (a) by applying the theorem of Bernoulli and (b) by calculating the mould profile that better adjust to the liquid stream.

Question

(a) The equation of Bernoulli is deduced from the principle of energy conservation: the sum of the potential energy, kinetic energy and pressure energy (internal) in each point of the system must be constant (losses apart). If g is the gravitational acceleration and ρ is the density:

$$p \cdot V + \frac{1}{2}m \cdot v^2 + m \cdot g \cdot h = \text{cte} \quad (10.138)$$

Dividing by $m \cdot g$:

$$h + \frac{1}{2} \cdot \frac{v^2}{g} + \frac{p}{\rho} = \text{cte} \quad (10.139)$$

In the proposed system (law of continuity):

$$p_0 = p_1 = p_2 \quad (10.140)$$

When $v_0 = 0$ and $h_2 = 0$ it is checked that:

$$h_0 = h_1 + \frac{v_1^2}{2g} = \frac{v_2^2}{2g} \quad (10.141)$$

$$v_1 = \sqrt{2g(h_0 - h_1)} \quad (10.142)$$

$$v_2 = \sqrt{2gh_0} \quad (10.143)$$

As the flow is constant:

$$A_1 \cdot v_1 = A_2 \cdot v_2 = Q \quad (10.144)$$

Then:

$$\frac{A_2}{A_1} = \sqrt{\frac{h_0 - h_1}{h_0}} \quad (10.145)$$

From the *constants* h_0 and A_1 it is possible to calculate $A_2 = f(h_1)$, that is to say, the *impermeable* mould profile, which would avoid losses by turbulence and *de-pressures* (*pressure drops*).

(b) By applying the law of continuity (flow), previously mentioned:

$$Q = A_1 \cdot v_1 = A_2 \cdot v_2 \rightarrow \frac{A_2}{A_1} = \frac{v_1}{v_2} \quad (10.146)$$

where v_1 is known and equal to $\sqrt{2\rho(h_0 - h_1)}$. That is to say:

Knowing Q and v_1 , A_1 is calculated.

Knowing Q and v_2 , A_2 is calculated.

Exercise 10.25. Application of the results of the previous exercise to a system where $h_0 = 25$ cm and $h_0 - h_1 = 2$ cm. A grey cast iron ($\rho \simeq 7$ g/cm³) is casted in the quantity of 10.5 kg/s. See Fig. 10.8. $A_1 = 1.5$ cm² (squared section).

Question

Flow:

$$\frac{10.5 \text{ kg/s}}{7 \times 10^{-3} \text{ kg/cm}^3} = 1500 \frac{\text{cm}^3}{\text{s}} \quad (10.147)$$

If the orifice has squared section $A = l^2$:

$$A_1 \cdot v_1 = 1500 \frac{\text{cm}^3}{\text{s}} = 1.5 \text{ cm}^2 \cdot v_1 \rightarrow v_1 = 1000 \text{ cm/s} \quad (10.148)$$

Then:

$$A_2 = A_1 \cdot \sqrt{\frac{h_c}{h_0}} = 1.5 \cdot \sqrt{\frac{2}{h_0}}; h_c = h_0 - h_1 \quad (10.149)$$

By giving values to h_0 , the A_2 values are obtained (sprue profile, Fig. 10.13).

Exercise 10.26. Application to the system of vertical casting without aspiration (pressurized) shown in Fig. 10.14. American units are employed in this exercise. Vertical casting.

Data: $g = 386$ in./s²

Question

Stream speed:

$$v = \sqrt{2 \cdot g \cdot h} = 27.7 \cdot \sqrt{h} \text{ in./s} \quad (10.150)$$

Fig. 10.13 Representation of h_0 facing to A_2/A_1

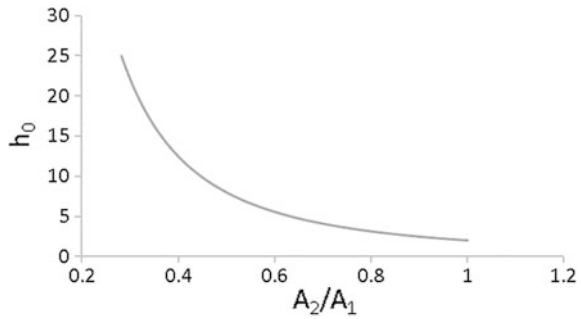
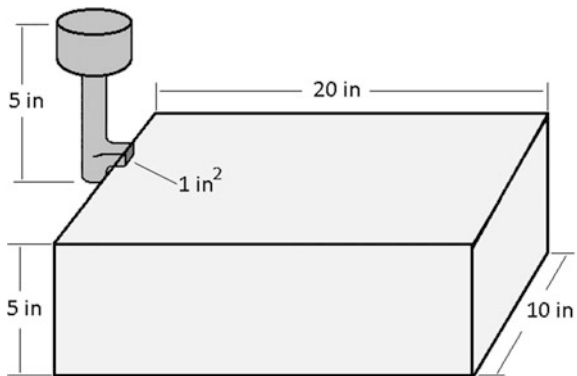


Fig. 10.14 Illustration of the feeding system used in the calculations



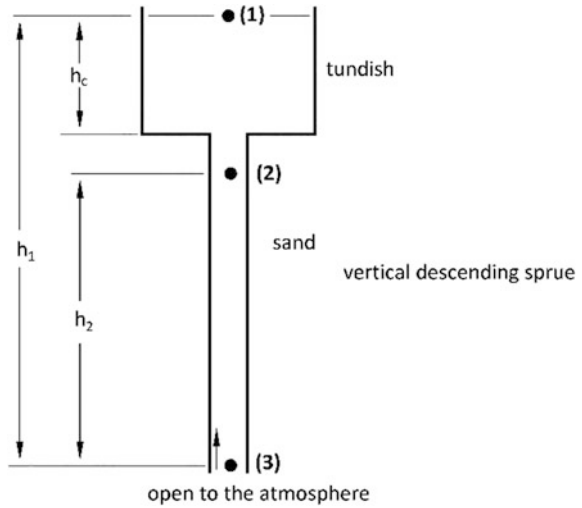
$$\text{Casting time} = \frac{\text{volume}}{\text{flow}} = \frac{5 \times 10 \cdot 20 \text{ in.}^3}{1 \text{ in.}^2 \cdot 27.7 \cdot \sqrt{5}} = 16.1 \text{ s} \quad (10.151)$$

10.7.1 Aspiration of Gases

Sand moulds are usually permeable, and the liquid can aspirate gases from the moulds: air, water vapour, products coming from the decomposition of sand organic binders, etc. We suppose that the casting equipment is that described in Fig. 10.15. A grey cast iron ($\rho = 7 \text{ g/cm}^3$) is casted. We consider two situations:

- *Permanent mould*: By applying Bernoulli's principle to the points 1 and 3:

Fig. 10.15 Simple vertical feeding system in permanent mould



$$h_1 + 0 + \frac{1 \text{ kg/cm}^2}{7 \times 10^{-3} \text{ kg/cm}^3} = 0 + \frac{v_3^2}{2g} + \frac{1 \text{ kg/cm}^2}{7 \times 10^{-3} \text{ kg/cm}^3} \quad (10.152)$$

$$v_3 = \sqrt{2 \cdot g \cdot h_1} \text{ cm/s} = 44.3 \sqrt{h_1} \text{ cm/s} \quad (10.153)$$

By applying the law of continuity, the speed in the points 2 and 3 should be the same, but this question disagrees the principle of energy conservation if $p_2 = 1 \text{ atm}$; (p_3) should be lower than (p_2) in such a way that:

$$h_2 + \frac{v_2^2}{2g} + \frac{p_2}{\rho} = 0 + \frac{v_3^2}{2g} + \frac{1 \text{ kg/cm}^2}{\rho} \quad (10.154)$$

As: $v_2 = v_3$

$$p_2 = 1 - \rho \cdot h_2 = 1 - 7 \times 10^{-3} \frac{\text{kg}}{\text{cm}^3} \cdot h_2(\text{cm}) \quad (10.155)$$

For instance, if: $h_1 = 20 \text{ cm}$, $h_c = 5 \text{ cm}$ and $h_2 = 15 \text{ cm}$.

$$p_2 = 1 - 7 \times 10^{-3} \cdot 15 = 0.895 \text{ atm (when } h \simeq 143 \text{ cm} \rightarrow p_2 = 0) \quad (10.156)$$

That is to say, the stream from 2 can absorb gases coming from the mould that either can react with the liquid (oxides and films), can dissolve in the liquid or can generate porosity. Thus, in the cast iron that we are considering, the trapped air in

the liquid and coming from the mould, can either form oxides (O), dissolve or form bubbles of H_2 . In aluminium castings, the problem is more important because the alumina films formed both reduce the castability, impurify the metal (presence of oxide) and the H_2 can remain trapped as bubbles (the tension $\gamma_{Al(l)/Al_2O_3(s)}$ is too high).

Exercise 10.27. How can be eliminated (minimized) the gas trapped in the metal: designing a sprue profile with the suitable shape, in such a way that inside $p = 1$ atm. Under these conditions:

Question

$$\frac{v_3^2}{2g} = h_2 + \frac{v_2^2}{2g} \text{ (Bernoulli). Conservation} \quad (10.157)$$

$$A_2 \cdot v_2 = A_3 \cdot v_3 \text{ (Law of continuity)} \quad (10.158)$$

$$v_2 = (A_3/A_2) \cdot v_3 \rightarrow \left(\frac{A_3}{A_2}\right)^2 = 1 - \frac{2gh_2}{v_3^2} \quad (10.159)$$

As

$$v_3^2 = 2gh_1 \rightarrow \left(\frac{A_3}{A_2}\right)^2 = \frac{(h_1 - h_2)}{h_1} \rightarrow \frac{A_3}{A_2} = \sqrt{\frac{h_c}{h_1}} \quad (10.160)$$

$$\text{If } h_1 = 20 \text{ cm, } h_c = 5 \text{ cm, } h_2 = 15 \text{ cm, } \frac{A_3}{A_2} = \sqrt{\frac{5}{20}} = 0.5 \quad (10.161)$$

In a more general way:

$$A_h = A_2 \sqrt{\frac{h_c}{h_1}} \quad (10.162)$$

Being $A_2 = \text{flow}/v_2$. For a flow of $1500 \text{ cm}^3/\text{s}$ and $v_2 = \sqrt{2 \cdot \rho \cdot 15} = 171.6 \text{ cm/s} \rightarrow A_2 = 8.74 \text{ cm}^2 (l \simeq 3 \text{ cm})$

- *Permanent mould (free gravity fall of stream)*: It was previously detailed. In a model of free gravity fall of stream:

$$v_2 = \sqrt{2 \cdot g \cdot h_c}; v_3 = \sqrt{2 \cdot g \cdot h_1} \quad (10.163)$$

From the law of continuity principle:

$$A_2 \cdot v_2 = A_3 \cdot v_3 \quad (p = 1 \text{ atm}) \quad (10.164)$$

Then:

$$A_3/A_2 = v_2/v_3 = \sqrt{h_c/h_1} \quad (10.165)$$

This is the same answer that was obtained in the previous case: in this second case, the sprue of hyperbolic shape is *outlined* with the purpose of that the stream conserve $p = 1 \text{ atm}$, impeding the trapping of gases from the mould. The solution is simplified in the case of linking the points 2 and 3 with a straight line (tapered downsprue), which also solves the problem of gases aspiration.

Exercise 10.28. Bottom casting: the entrances to the part are in the bottom of the mould, reducing splatter and liquid oxidation. Considering the model (system) proposed in Fig. 10.16, we calculate the required time for casting. We suppose a casting equipment with a suitable tundish-sprue system of height h_t . During the casting, the metalostatic pressure diminishes. Naming h_t , total height; t , casting time; h , height of the liquid in the mould; A_m , cross section of the mould; A_g , section of the gates. The entry speed of the liquid in the mould v_2 .

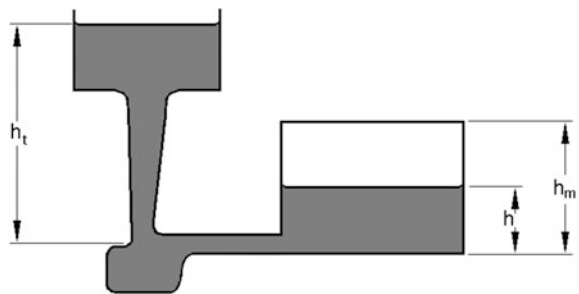
Question

$v_2 = \sqrt{2 \cdot g \cdot (h_t - h)}$, variable with h (height of the liquid in the mould).

According to the flow conservation law:

$$A_m dh = A_g \sqrt{2 \cdot g \cdot (h_t - h)} \cdot dt \quad (10.166)$$

Fig. 10.16 Non-aspirating downsprue for permeable mould



Separating variables and integrating:

$$\frac{dh}{\sqrt{2 \cdot g \cdot (h_t - h)}} = \frac{A_g}{A_m} \cdot dt \rightarrow \int_0^{h_m} \frac{1}{\sqrt{2 \cdot g}} \cdot \frac{dh}{\sqrt{(h_t - h)}} = \frac{A_g}{A_m} \int_0^{t_f} dt \quad (10.167)$$

Then:

$$t_f = \frac{2 \cdot A_m}{A_g \cdot \sqrt{2 \cdot g}} \cdot \left(\sqrt{h_t} - \sqrt{h_t - h_m} \right) \quad (10.168)$$

The casting time rises. We are going to compare this time with the previous one.

Vertical feeding: $h_t = 5, A_g = 1 \text{ in.}^2, \text{part } 5 \cdot 10 \cdot 20 \text{ in.}^3$

$$v_2 = \sqrt{2 \cdot g \cdot h} = 27.7 \cdot \sqrt{5} \text{ in./s} = 62 \text{ in./s} \Rightarrow t_{\text{filling}} = \frac{5 \times 10 \cdot 20 \text{ in.}^3}{62 \text{ in./s} \cdot 1 \text{ in.}^2} = 16.1 \text{ s} \quad (10.169)$$

Bottom casting:

$$t_f = \frac{2 \cdot (20 \cdot 10)}{1 \text{ in.}^2 \cdot \sqrt{2 \cdot g}} \cdot \left(\sqrt{5} - \sqrt{5 - 5} \right) = 32.2 \text{ s (twice)} \quad (10.170)$$

By using an *Excel sheet* demonstrate that bottom casting times can be twice the simple vertical feeding casting times ($h_t = h_m$).

Exercise 10.29. A cylinder of aluminium alloy of 10 cm Ø 20 cm height is fed by head through a system tundish-troncoconic sprue, as shown in the enclosed figure (Fig. 10.17). The cross section of the sprue on its basis has 3 cm². The height of the tundish h_c is 8 cm. The total height h_0 is 30 cm. Disregarding energy/friction losses, what should be the cross section of the sprue on its head to avoid the aspiration of gases? What is the casting time?

Question

NOTE: In a matchplate pattern for casting the cope part (upper) of a pattern is mounted on one side of a wood or metal plate, and the drag part (lower) is mounted in accurate register on the opposite side. Runner is mounted on drag side of plate and gates on cope side.

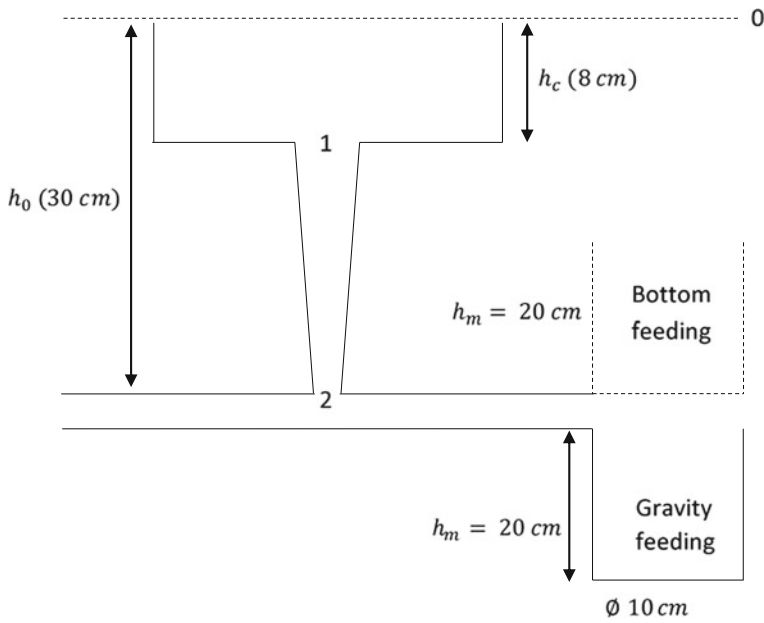


Fig. 10.17 Feeding scheme

By applying Bernoulli, considering $v = 0$ in the level 0.

$$\frac{v_1^2}{2 \cdot g} + (h_0 - h_c) = h_0 \quad (p = 1 \text{ atm}) \quad (10.171)$$

$$\frac{v_2^2}{2 \cdot g} = h_0 \quad (10.172)$$

$$v_1 = \sqrt{2 \cdot g \cdot h_c} \quad (10.173)$$

$$v_2 = \sqrt{2 \cdot g \cdot h_0} \quad (10.174)$$

$$A_1 \cdot v_1 = A_2 \cdot v_2 \quad (\text{constant flow}) \quad (10.175)$$

$$\frac{A_1}{A_2} = \sqrt{\frac{h_0}{h_c}} = \sqrt{\frac{30}{8}} = 1.94 \quad (10.176)$$

$$A_1 = 3 \cdot 1.94 = 5.82 \text{ cm}^2 \quad (10.177)$$

$$v = \text{flow} \cdot t = \pi \cdot 20 \cdot \left(\frac{10}{2}\right)^2 = 3 \cdot \sqrt{2 \cdot 981 \frac{\text{cm}}{\text{s}^2} \cdot 30 \text{ cm} \cdot t} \quad (10.178)$$

$$t = \frac{1571}{728} \simeq 2.16 \text{ s (vertical casting)} \quad (10.179)$$

If it is a bottom casting, as can be seen in Fig. 10.17, the position of the part is represented in dotted lines.

With the solution provided in the previous example:

$$t_f = \frac{2 \cdot A_m}{A_g \cdot \sqrt{2 \cdot g}} \cdot \left\{ \sqrt{h_0} - \sqrt{(h_0 - h_m)} \right\} \quad (10.180)$$

$$h_0 = 30 \text{ cm}; h_m = 20 \text{ cm}; A_m = \pi \left(\frac{10}{2}\right)^2 \text{ cm}^2; A_g = 3 \text{ cm}^2$$

$$t_f = \frac{\sqrt{2} \cdot 25 \cdot \pi}{3 \cdot \sqrt{981}} \cdot \left\{ \sqrt{30} - \sqrt{(30 - 20)} \right\} = 2.74 \text{ s} \quad (10.181)$$

$$t_c = 2.74 \text{ (bottom)} > 2.16 \text{ (stream)} \quad (10.182)$$

$$\text{Si } h_0 = h_m \rightarrow t_c = 6.48 \text{ s (bottom)} \text{ y } t = 3.24 \text{ (stream)}$$

Exercise 10.30. A cylinder of 4 in. in diameter and $H = 8$ in. wants to be moulded. The mould is totally situated in the drag. The part is fed on its upper zone and it does not have riser. The cope has 10 in. in height (sprue) and the tundish has a height of 2 in. above the cope. The sprue (troncoconic

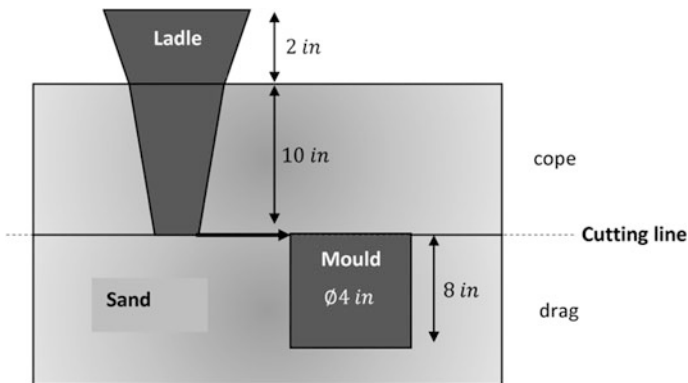


Fig. 10.18 System mould feeding

to avoid gas suction) has on its base a section of 1 in^2 . The feeding system (sprue section: runner section: gates section) has a relation of 1:3:3. Discounting the energy losses, calculate the time required for filling the mould (Fig. 10.18).

Question

$$v_1 = \sqrt{2 \cdot g \cdot h} = \sqrt{2 \cdot 32.2 \cdot 12/12} \simeq 8 \text{ ft/s} (96 \text{ in./s}) \quad (10.183)$$

Considering the continuity equation:

$$Q = A_1 \cdot v_1 = 3 \cdot A_1 \cdot v_2 = 3 \cdot A_1 \cdot v_3 \quad (10.184)$$

$$v_1 = 3 \cdot v_2 = 3 \cdot v_3 \quad (10.185)$$

$$1 \cdot 96 \text{ in.}^3/\text{s} = 3 \cdot v_3 \rightarrow v_3 = 32 \text{ in./s} \quad (10.186)$$

$$V_{\text{casting}} = \pi \cdot 4^2 \cdot 8/4 = 100.5 \text{ in.}^3 \quad (10.187)$$

$$Q = 3 \text{ in.}^2 \cdot 32 \text{ in./s} = 96 \text{ in.}^3/\text{s} \rightarrow t = 100.5/96 \simeq 1.05 \text{ s} \quad (10.188)$$

What should be the section of the entrance to the sprue that would avoid the gas suction?

Question

According to the last exercise:

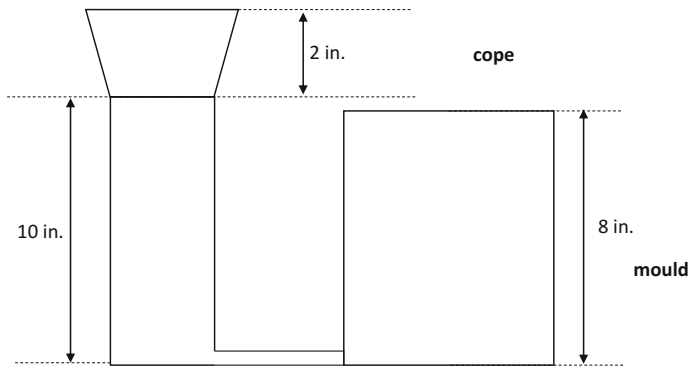
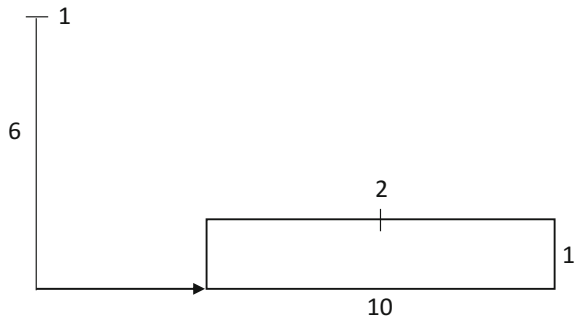
$$A_0/A_1 = \sqrt{12/2} = \sqrt{6} \quad (10.189)$$

$$A_0 = A_1 \cdot \sqrt{6} = 7.35 \text{ in.}^2 \quad (10.190)$$

Solve the same exercise for a cylinder entirely moulded in the cope, bottom fed, but keeping the rest of the conditions (Fig. 10.19).

In the resolution of this section of the exercise the previous exercises should be studied:

$$t_f = \frac{2 \cdot A_m}{A_g \cdot \sqrt{2 \cdot g}} \cdot \left[\sqrt{h_t} - \sqrt{h_t - h_m} \right] \quad (10.191)$$

**Fig. 10.19** Feeding system**Fig. 10.20** Feeding scheme

$$A_m = \pi \cdot 4^2 / 4 = 12.6 \text{ in.}^2 \quad (10.192)$$

$$g = 32.2 \text{ ft/s}^2 \quad (10.193)$$

$$\sqrt{2 \cdot g} = 27.8 \sqrt{\text{in.}}/\text{s} \quad (10.194)$$

$$A_g = 1 \text{ in.}^2 \quad (10.195)$$

$$h_t = 12 \text{ in.}; h_m = 8 \text{ in.} \quad (10.196)$$

$$t_f = \frac{2 \cdot 12.6 \text{ in.}^2}{1 \text{ in.}^2 \cdot \sqrt{2 \cdot 32.2 \cdot 12 \text{ in.}}/\text{s}^2} \cdot \left[\sqrt{12} - \sqrt{12 - 8} \right] \sqrt{\text{in.}} = 1.32 \text{ s} \quad (10.197)$$

Exercise 10.31. An iron plate of $12 \times 12 \times 1$ in. is casted from a sprue of 6 in. in height, that feeds the mould at its bottom. Calculate the stress that should support the cope. Study the same situation in the case of an aluminium plate (Fig. 10.20).

Data: $\rho_{\text{Fe}}^{\text{L}} = 0.26 \text{ lb/in.}^2$; $\rho_{\text{Al}}^{\text{L}} = 0.09 \text{ lb/in.}^2$; $P_{\text{atm}} = 14.7 \text{ lb/in.}^2$

Question

By applying the Bernoulli's equation to the points 1 and 2:

$$\frac{P_1}{\rho} + \frac{v_1^2}{2 \cdot g} + h_1 = \frac{P_2}{\rho} + \frac{v_2^2}{2 \cdot g} + h_2 \quad (10.198)$$

Assuming that:

$$v_1 = v_2 \simeq 0 \quad (10.199)$$

Then:

$$\frac{14.7}{0.26} + 0 + 6 = \frac{P_2}{0.26} + 0 + 1 \rightarrow P_2 = 14.7 + 5 + 0.26 = 16 \text{ lb/in.}^2 \quad (10.200)$$

$$F_{\text{rising}} = 16 \frac{\text{lb}}{\text{in.}^2} \cdot (12 \times 12) \text{ in.}^2 = 2304 \text{ lb} (\simeq 1037 \text{ kg} \simeq 1 \text{ tonne}) \quad (10.201)$$

The aluminium has a density of around 1/3 of that of the liquid iron:

$$P_2 = 14.7 + 5 + 0.09 = 15.15 \text{ lb/in.}^2 \quad (10.202)$$

$$F_{\text{rising}} = 15.15 \frac{\text{lb}}{\text{in.}^2} \cdot (12 \times 12) \text{ in.}^2 = 2182 \text{ lb} (\simeq 982 \text{ kg} \simeq 1 \text{ tonne}) \quad (10.203)$$

Nevertheless, the rising force over the cope is only slightly lower to that of the iron.

Exercise 10.32. Low carbon steel is vertical casted in the tundish of a continuous casting machine. Calculate the maximum amount of N_2 absorbed by the stream during the transferring process. **Data:** $D_{\text{N}} = 7.5 \times 10^{-4} \text{ cm}^2/\text{s}$; $\delta = 0.003 \text{ cm}$; diameter of the stream, 7.6 cm, stream height, 76 cm; average speed of the stream, 305 cm/s. Sievert's equation for the N_2 at 1600°C , $s(\text{cm}^3/100 \text{ gFe}) = 36 \cdot \sqrt{p_{\text{N}_2}}$

Question

The pressure of the stream at the exit of the ladle:

$$p = 1 - \rho \cdot h = 1 - 7.1 \times 10^{-3} \frac{\text{kg}}{\text{cm}^3} \cdot 76 \text{ cm} = 0.54 \text{ atm} \quad (10.204)$$

By a mass balance (boundary layer model, like that appears in a progressive solidification model by zones, Pero-Sanz et al. (2017) (Elsevier) p. 145:

$$V \cdot \frac{ds}{dt} = \frac{A}{\delta} \cdot D(s - s_0) \rightarrow \frac{dc}{c_0 - c} = \frac{D \cdot A}{V \cdot \delta}; s = c = g(\text{N}_2)/\text{cm}^3 \quad (10.205)$$

Separating variables and integrating:

$$[-\ln(s_0 - s)]_{c_e}^c = \frac{D \cdot A}{V \cdot \delta} \cdot t \rightarrow \ln \frac{(c_0 - c_e)}{(c_0 - c)} = \frac{D \cdot A}{V \cdot \delta} \cdot t; t = \frac{76}{305} = 0.25 \text{ s} \quad (10.206)$$

$$A = \pi \cdot d \cdot h; V = \frac{\pi d^2}{4} \cdot h; \frac{A}{V} = \frac{4}{d} = 0.53 \text{ cm}^{-1} \quad (10.207)$$

$$\log \frac{(s_0 - s_e)}{(s_0 - s)} = \frac{7.5 \times 10^{-4} \text{ cm}^2/\text{s} \cdot 0.53 \text{ cm}^{-1}}{3 \times 10^{-3} \text{ cm} \cdot 2.3} \cdot 0.25 \text{ s} = 1.44 \times 10^{-2} \quad (10.208)$$

$$\frac{c_0 - c_e}{c_0 - c} = 1.0337; s = 36 \cdot \sqrt{P_{\text{N}_2}} \rightarrow s_0 = 36; s_e = 26.45 \quad (10.209)$$

$$36 - c = \frac{36 - 26.45}{1.0337} = 9.24; s = 26.76 \quad (10.210)$$

$$c_e - c = 26.76 - 26.45 = 0.31 \text{ cm}^3/100 \text{ g} \quad (10.211)$$

From the ideal gases law:

$$0.31 = \frac{a}{28} \cdot 0.082 \cdot 1000 \cdot 273 \rightarrow a = 3.87 \times 10^{-4} \text{ gN}_2/100 \text{ gFe} \simeq 4 \text{ ppm} \quad (10.212)$$

T_L : temperature of the liquid (solidification); T_0 : room temperature.

If the liquid flows at a speed, v , it would solidify (would block the entrance to the spiral) when it has covered a distance of:

$$L_f \simeq t_f \cdot v \rightarrow L_f = \rho_S \cdot a \cdot v \cdot (L_m + c_e \cdot \Delta T) / 2 \cdot h \cdot (T_M - T_0) \quad (10.215)$$

Calculus of v :

The pouring basin, see Fig. 10.21, has a height of $2 \cdot 3/4$ in. ($\simeq 7$ cm), which implies a speed of entrance to the mould of:

$$v = \sqrt{2 \cdot g \cdot h} = \sqrt{2 \cdot 9.8 \text{ cm/s}^2 \cdot 7 \text{ cm}} \simeq 120 \text{ cm/s} \quad (10.216)$$

Replacing in the last equation:

$$L_f = \rho_S \cdot a \cdot v \cdot (L_m + c_e \cdot \Delta T) / 2 \cdot h \cdot (T_M - T_0) \quad (10.217)$$

With the values of $\rho_S, v, a, L_m, c_e, h, T_m$ above indicated results in, approximately:

$$\Delta T = 100^\circ \text{C} \quad (10.218)$$

$$L_f = \frac{7.3 \text{ g/cm}^3 \cdot 0.1 \text{ cm} \cdot 120 \text{ cm/s} \cdot (44.4 + 100 \cdot 0.16) \text{ cal/g}}{2 \cdot 0.04 \text{ cal/g} \cdot ^\circ\text{C} \cdot \text{s} \cdot (1154 - 20) \text{ K}} \simeq 58 \text{ cm} (\simeq 23 \text{ in.}) \quad (10.219)$$

Analogously:

$$\Delta T = 200^\circ \text{C} \rightarrow L_f = 73.8 \text{ cm} (29 \text{ in.}) \quad (10.220)$$

$$\Delta T = 300^\circ \text{C} \rightarrow L_f = 89.2 \text{ cm} (35 \text{ in.}) \quad (10.221)$$

It is possible to compare the results obtained with those experimentally obtained in four grey cast irons of different compositions, see Fig. 10.22. It is possible to see that fluidity tends to zero when approaching to the solidification temperature. The fluidity rises almost lineally with the superheating, ΔT . It should be remembered that the contraction in the transformation liquid $\rightarrow$ solid also increases with the value of that parameter (a superheating of 35°C is equivalent to around 1% of contraction).

In other words, the castability, defined by the foundrymen, refers to the fluidity of the liquid between the pouring temperature and the solidification temperature. The castability depends mainly on the superheating (also called overheating).

The fluidity of the cast irons is compared with the fluidity of other non-ferrous alloys (aluminium, red brass, pure lead) in Fig. 10.23. They are all of them situated in a relatively narrow scatter band. However, the characteristic

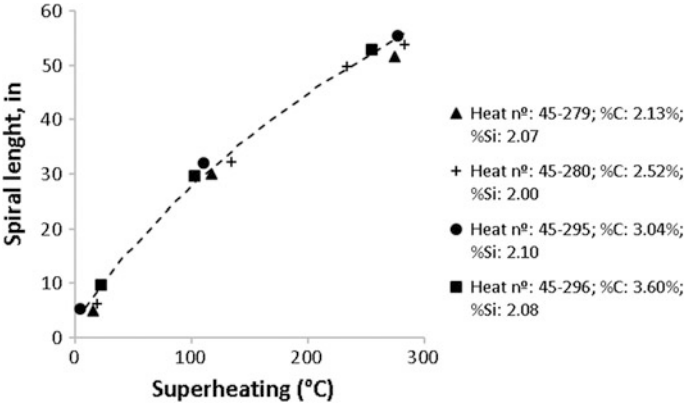


Fig. 10.22 Fluidity versus superheating (elaborated with data from Flinn 1963)

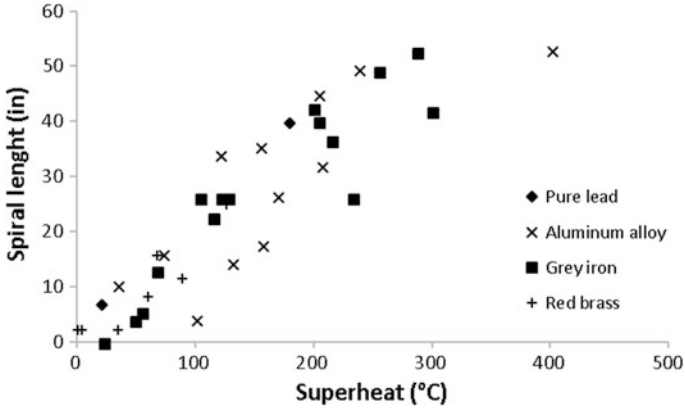


Fig. 10.23 Fluidity versus superheating (elaborated with data from Flinn 1963)

deviation has been noted in the alloys with pronounced film-forming tendencies, such as that caused by high aluminium contents: the fluidity of these alloys is lower than the general pattern.

In conclusion, it is evident the excellent castability of cast irons (black squares), as compared with other non-ferrous and ferrous alloys as well.

Exercise 10.34. Criticize the statement ‘A 3.5% carbon cast iron is more fluid than a 2.5% carbon malleable iron, and therefore lighter and more intricate sections can be casted’. If you do not agree, explain why cast irons are chosen for delicate artwork.

Question

Considering the simplified Fe–C stable diagram (Fig. 10.24), fluidity increases when the interval of solidification diminishes for the same superheating as showed in the previous exercise. That is to say, the amount of eutectic liquid that feeds the interdendritic spaces rises, although the cast iron expands during the solidification (lack of shrinkage).

$$(T_L)_{2,5} = 1314\text{ }^{\circ}\text{C}; (T_L)_{3,5} = 1225\text{ }^{\circ}\text{C} \rightarrow (T_L)_{2,5} - (T_L)_{3,5} = 1314 - 1225 = 89\text{ }^{\circ}\text{C}$$

(10.222)

Supposed the lines L and S straight, it is obtained by similarity of triangles that (Table 10.9):

The cast iron 3.5% C is lighter than that of 2.5% C because of having more graphite. It should be also considered that the cast iron 2.5% C is white, with a longer interval of solidification (lower fluidity). Because of being graphitized through a malleabilization annealing, which transforms the proeutectoid cementite and maybe the eutectoid cementite (depending on the cooling rate) into graphite, the cast iron can expand slightly.

Eutectic (or hypereutectic) cast irons have higher fluidity (for the same superheating) and they are materials of election in the elaboration of ornamental parts (see Fig. 5.15).

To conclude this exercise, Table 10.10 and Fig. 10.25 are enclosed, both adapted from R. A. Flinn *Fundamental of Metal Casting*, 1963. Verify using both that the equivalent carbon of the cast iron plays an important role on its

Fig. 10.24 Section of the Fe–C stable diagram

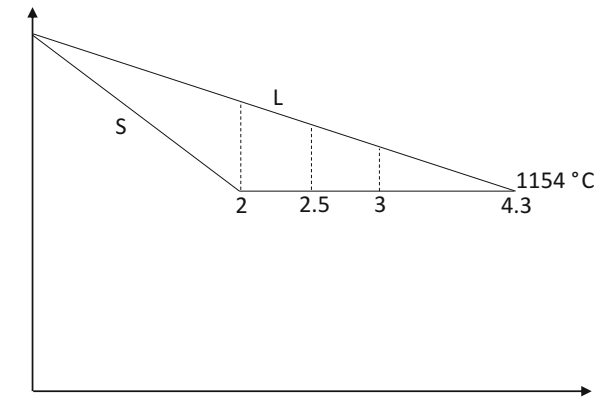


Table 10.9 Relation % C, T_L and ΔT

c (% C)	T_L ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)
2	1359	205
2.5	1314	160
3.5	1225	71

Table 10.10 Fluidity versus temperature of liquidus

Iron	Pouring temperature for 30-in. spiral		Difference above Iron 1		Liquidus		Liquidus, degrees above Iron 1	
	°F	°C	°F	°C	°F	°C	°F	°C
(1) 3.6% C, 2.08% Si	2370	1299	—	—	2150	1177	—	—
(2) 3.04% C, 2.10% Si	2480	1342	110	43	2270	1226	120	49
(3) 2.52% C, 2.00% Si	2610	1415	240	116	2360	1276	210	99
(4) 2.13% C, 2.07% Si	2660	1444	290	143	2425	1312	275	135

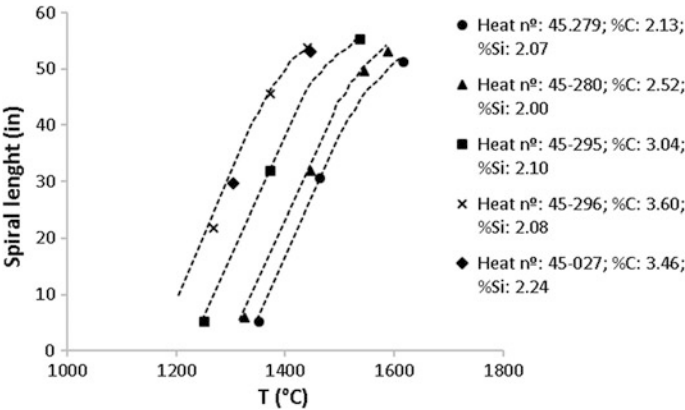


Fig. 10.25 Typical curves of temperature fluidity for several cast irons (elaborated with data from Flinn 1963)

fluidity (castability): the higher the equivalent carbon, the lower the required pouring temperature and lower the superheating to ensure the fluidity and the soundness of the cast iron.

Exercise 10.35. Comment the reasons for what, from the casting ability point of view, result in more (or less) favourable grey cast irons than aluminium alloys. Justify the reasons for what—from the same point of view —‘modified silumin’ is used for the moulding of light parts.

Question

Abnormal eutectics are those whose constituents differ notably regarding their melting point and ponderal proportions. These aspects notably conditionate the structure and properties of the eutectic.

Two examples of abnormal eutectic are found in:

- Silumin Al–12.6% Si ($T_E = 577^\circ\text{C}$). In this case, the melting point of the aluminium is 660°C while in the case of the silicon, it is 1414°C , and the ponderal proportions are 11.13% of silicon and 88.87% of aluminium. The structure obtained after the solidification presents cuboids or needles of silicon covered by aluminium, which cause notch effect, and for that reason the low toughness of the alloy of eutectic composition. See Fig. 10.26. It is metal matrix composites (MMC).
- Grey cast irons Fe–4.3% C ($T_E = 1154^\circ\text{C}$). They are also MMC, as silumin. In this case, the melting point of their constituents are 1350°C for the austenite and $\approx 3700^\circ\text{C}$ for the graphite, and the ponderal proportions are 2 and 98%, respectively. The structure obtained after the solidification present graphite embedded in austenite, which causes notch effect, and for that reason the low toughness of the alloy of eutectic composition. See Fig. 10.27.

Comparing the properties of both materials:

Diffusivity:

$$\alpha_{\text{Silumin}} = \frac{k}{c_p \cdot \rho} = \frac{121 \text{ W/m K}}{0.96 \text{ J/g} \cdot \text{K} \cdot 2.66 \text{ g/cm}^3} = 0.4 \text{ cm}^2/\text{s} \quad (10.223)$$

$$\alpha_{\text{Grey Iron}} = \frac{46 \text{ W/m} \cdot \text{K}}{0.59 \text{ J/g} \cdot \text{K} \cdot 7.15 \text{ g/cm}^3} = 0.11 \text{ cm}^2/\text{s} \quad (10.224)$$

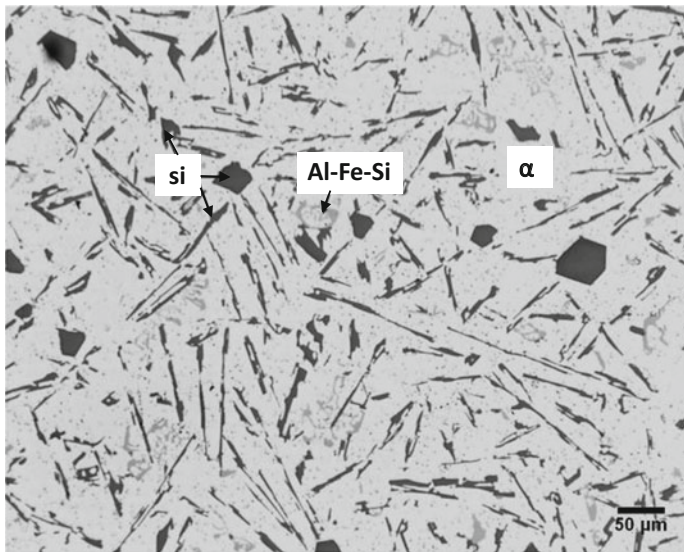


Fig. 10.26 Silumin as polished

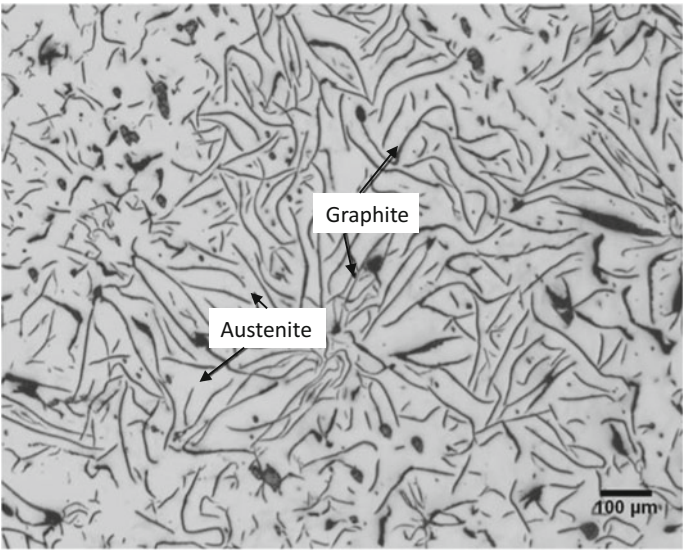


Fig. 10.27 Eutectic grey cast iron. As polished

The properties mentioned in Table 10.11 allow inferring that the grey cast irons would require much lower risering and higher metallic yield than the silumin. Theoretically, it would not be necessary risering in grey cast irons, although risers are used due to that the liquid expands during the solidification and if it does not reflow towards the riser, the part could deform.

Regarding the advantages and disadvantages of using one or other in the manufacture of engine blocks, it is possible to mention (apart from all that pointed out) that the silumin requires shorter solidification times (higher diffusivity), but its working temperatures are much lower than those of the grey cast irons.

Table 10.11 Properties of the silumin and the grey cast iron

Al–12.6% Si	Fe–4.3% C
$T_E = 577\text{ }^{\circ}\text{C}$	$T_E = 1154\text{ }^{\circ}\text{C}$
$\rho = 2.66\text{ g/cm}^3$	$\rho = 7.15\text{ g/cm}^3$
$L = 93\text{ cal/g}$	$L = 53\text{ cal/g}$
$c_e = 0.23\text{ cal/g }^{\circ}\text{C}$	$c_e = 0.14\text{ cal/g }^{\circ}\text{C}$
$k = 121\text{ W/m K}$	$k = 46\text{ W/m K}$
Contraction liquid $\rightarrow$ solid $\simeq 3.3\%$	Contraction liquid $\rightarrow$ solid < 0
$\alpha = 21.2 \times 10^{-6}\text{ }^{\circ}\text{C}^{-1}$	$\alpha = 13 \times 10^{-6}\text{ }^{\circ}\text{C}^{-1}$
Yield strength = 130 MPa (non-alloyed 1000 series)	Yield strength = 140 MPa (class 20)

10.9 Mechanical Properties. Reliability (Weibull Statistics)

Exercise 10.36. ASTM A278 standard correlates chemical composition and mechanical properties of grey iron castings for pressure containing parts. As it was previously mentioned, tight grey cast irons, working at temperatures higher than 450 °F (230 °C), are limited to classes 40, 45, 50, 55, 60, 70 and 80 (Equivalent Carbon, $EC < 3.8$). Demonstrate this assessment by applying Winte's equation:

$$R_m(\text{ksi}) \simeq 162.37 + 16.61/d - 54.03 \cdot (\text{Si}) + 14.16 \cdot (\text{Si})^2 - 21.78 \cdot EC \quad (10.225)$$

$$EC \simeq \text{TC (Total Carbon)} + 0.3 \cdot (\% \text{ Si} + \% \text{ P}) \quad (10.226)$$

Question

If we choose a EC of 3.2 and 3.5 for a silicon percentage of 2.4%, it is obtained that:

$$EC = 3.2 \rightarrow R_m(\text{ksi}) = 61.1 \text{ ksi} \quad (10.227)$$

$$EC = 3.5 \rightarrow R_m(\text{ksi}) = 54.6 \text{ ksi} \quad (10.228)$$

For $EC = 3.8$ ($\text{Si} = 2.1\%$) $\rightarrow R_m(\text{ksi}) = 45.2 \text{ ksi}$

With a EC higher than 3.8, for instance, $EC = 4$, it is possible to say that:

$$EC = 4; \text{Si} = 1.8\% \rightarrow R_m(\text{ksi}) \simeq 40 \text{ ksi} \quad (10.229)$$

$$EC = 4; \text{Si} = 1.9\% \rightarrow R_m(\text{ksi}) \simeq 40 \text{ ksi} \quad (10.230)$$

$$EC = 4; \text{Si} = 2\% \rightarrow R_m(\text{ksi}) \simeq 40 \text{ ksi} \quad (10.231)$$

That means that a class 40 is the minimal that ensures pressure tightness in grey cast irons.

ASTM A278 also indicates that sulphur content should be lower than 0.12%. In the generalized Winte's equation, it is possible to find the following term of the equation:

$$-10.59 \cdot (\% \text{ Mn} - 1.7 \cdot \% \text{ S}) \quad (10.232)$$

What would happen with the proposed sulphur content and a manganese content of 0.8?

Question

$$-10.59 \cdot (0.8 - 1.7 \cdot 0.12) = 6.3 \quad (10.233)$$

The class of the cast iron would diminish in around 6 ksi.

Exercise 10.37. Why in the Winte's equation the manganese appears with a corrector term of 1.7 %S?

Question

The amount of sulphur must be counterbalanced with the corresponding amount of manganese. The aim is to drag out sulphur from solid solution by forming MnS, that is to say:

$$\text{Mn/S} = \text{atomic weight of Mn/atomic weight of S} \simeq 55/32 = 1.7 \quad (10.234)$$

An excess of sulphur would give a eutectic of iron and iron sulphide that would melt at 998 °C, or that would solidify at that temperature in the interdendritic spaces (as a consequence of the high tendency to segregate of sulphur) reducing in a significant way the mechanical strength of the cast iron (see Chap. 1).

Exercise 10.38. Winte's equation, proposed in previous exercises in the calculation of the ultimate tensile strength of grey cast irons, as a function of massivity and chemical composition, has the following term:

$$-61.29 \cdot (\text{Si}) + 14.16 \cdot (\text{Si})^2 \quad (10.235)$$

Find a possible interpretation. Express R_m as a function of silicon content and EC. What massivity and chemical composition should have the cast iron to achieve a class 60?

Question

The term: $-61.29 \cdot (\text{Si}) + 14.16 \cdot (\text{Si})^2$ passes through a minimum.

Deriving: $-61.29 + 2 \cdot 14.16 \cdot (\text{Si}) = 0 \rightarrow (\text{Si}) = 2.2$

For values lower than 2.2, if the grey behaviour of the cast iron is wanted to be kept, the total carbon should be higher, increasing, consequently, the content

in graphite. For higher contents in silicon would happen exactly the opposite. The same conclusion is reached by replacing the total carbon in the Winte's equation by the EC:

$$R_m(\text{ksi}) \simeq 162.37 + 16.61/d - 21.78 \cdot C - 61.29 \cdot (\text{Si}) + 14.16 \cdot (\text{Si})^2 \quad (10.236)$$

or

$$R_m(\text{ksi}) \simeq 162.37 + 16.61/d - 54.03 \cdot (\text{Si}) + 14.16 \cdot (\text{Si})^2 - 21.78 \cdot \text{EC} \quad (10.237)$$

Increasing the class of the cast iron is equivalent to increase the silicon content (>1.9%) and diminishing the EC (keeping the value of the massivity).

For instance, in the cast iron 3% C–2.1% Si, it would be possible to obtain a class 60 cast iron in a sample with d equal to:

$$\begin{aligned} 60 &= 162.37 + 16.61/d - 54.03 \cdot (\text{Si}) + 14.16 \cdot (\text{Si})^2 - 21.78 \cdot (3 + 2.1/3) \\ &\rightarrow \frac{16.61}{d} = 26.23 \rightarrow d \simeq 0.6 \text{ in.} \end{aligned} \quad (10.238)$$

That is to say, at a cooling rate equivalent to that of a sheet of $12 \times 12 \times 0.25$ in. ($V/A = 0.120$). The appendix should have a length of approximately 21 in.

Exercise 10.39. By using the full equation of Winte, for what value of (V/A) a class 60 cast iron with $\text{EC} = 3.48$, $\text{TC} = 3.11$, $\text{Si} = 1.1\%$ could be obtained?

Question

By using the complete Winte's equation:

$$R_m = 162.37 - 54.03 \cdot (\text{Si}) + 14.16 \cdot (\text{Si})^2 - 21.78 \cdot \text{EC} + 16.61/d = 60 \quad (10.239)$$

Replacing, it is obtained that, with $d \simeq 1''$, a specimen with a length of 20 in. would have a cooling rate equivalent to that of a sheet of $10 \times 10 \times 0.5$ in. In fact:

- For the specimen:

$$(V/A) = (\pi \cdot D^2/4) \cdot H / (\pi \cdot D \cdot H + \pi \cdot D^2/2) \simeq 0.24 \quad (10.240)$$

- For the part:

$$(V/A) = (10 \cdot 10 \cdot 0.5) / (2 \cdot 100 + 4 \cdot 10 \cdot 0.5) \simeq 0.23 \quad (10.241)$$

Exercise 10.40. Compare a ductile iron with a grey iron of the same composition for (a) tensile strength, (b) yield strength, (c) elongation, (d) young modulus, and (e) thermal conductivity (Table 10.12). What single factor is primarily responsible for these differences?

Question

The morphology of the graphite (spheroidal in ductile irons and lamellar in grey irons) is the main responsible of the properties presented in Table 10.12. The single property that is deteriorated when the graphite nodules (ductile irons) are considered is the thermal conductivity, as the flakes conduct better the heat than the nodules, increasing the solidification time.

Exercise 10.41. Weibull statistics of a hypereutectic white cast iron (chill cast pig iron).

The manufacture of cast irons is carried out, in general, in cupola and electric furnaces, using as raw material mainly pig iron. Cast iron scraps and sometimes steel scraps are used in the feeding of the furnace. To adjust the chemical composition, ferrosilicon and ferromanganese are added, and when special cast irons are considered (Nihard, Niresist, etc.), ferrochromium, ferronickel, etc. are added.

The cast iron is chill casted to analyse its chemical composition, which is enclosed to this exercise. The cast iron is slightly hypereutectic and, in its micrograph, primary carbides in a ledeburitic matrix are observed, with austenite transformed partially into pearlite and other non-equilibrium constituents (bainite, martensite). Cast pig iron is the principal raw material for the obtaining of steels (conversion) and commercial cast irons: the cupola is the standard melting unit of iron foundry; cupola melting is generally considered the cheapest method for converting cold scrap metal or pig iron to usable molten iron (see Chap. 11).

A sample of pig iron is provided with the purpose of carrying out a certain number of Vickers hardness with a load of 100 kg. The chemical composition is that of a slightly hypereutectic cast iron. From the results obtained, the representation of the frequencies histogram for the measured hardnesses is required (from the minimum to the maximum), choosing the most adequate intervals.

In non-metallic materials (ceramics, as is the case, as a consequence of the cementitic matrix of white cast irons), the properties measured in the same part or batch of parts (hardness, for instance) usually have a notably dispersion in results consequence of the heterogeneity of the microstructure and defects produced in the manufacture of them (pores, cracks, segregations, inclusions, etc.). In the study of the reliability of these materials the Weibull's statistics are considered, according to:

$$P(\text{HV}) = \exp\left(-\left(\frac{\text{HV}}{\text{HV}_0}\right)^m\right) \quad (10.242)$$

- $P(\text{HV})$: probability of that the sample (or batch of them) had a hardness higher or equal to HV.
- HV_0 : probability of that the sample (or batch of them) was of 37% for a hardness higher or equal to HV_0 .
- m : reliability coefficient of the material. This coefficient is low in the cement, porous ceramics, engineering ceramics and metallic materials as-moulded (from 5 to 20, habitually). This coefficient is high in metallic materials thermally and mechanically treated (around 100). Effectuate the representation of the cumulated diagram of frequencies $P(\text{hardness} \geq \text{HV})$, of sigmoidal shape, and choosing the suitable measurement intervals. Taking double logarithms in Eq. (10.242), it is possible to demonstrate that:

$$\ln\left\{\ln\left(\frac{1}{P(\text{HV})}\right)\right\} = m \cdot \ln\left(\frac{\text{HV}}{\text{HV}_0}\right) \quad (10.243)$$

This allows performing a linear regression analysis, the calculus of m (reliability) and HV_0 (previously defined).

Note: In Table 10.13 (from Pero-Sanz 2006), the hardnesses of some abrasive materials are collected: the hardness of the cementitic carbides is in the range of 1060–1240 HV. And that of the undissolved pearlite ($\simeq 0.8\% \text{C}$) between 240 and 425 HV, depending on the interlamellar spacing, S_0 (Figs. 10.28, 10.29; Tables 10.14, 10.15, 10.16).

Table 10.12 Properties of ductile irons and grey irons

	Ductile iron	Grey iron
Tensile strength	400–1100 MPa	150–450 MPa
Yield strength	250–900 MPa	They do not have
Elongation	3–25%	<1%
Young modulus	160 GPa	Secant modulus
Thermal conductivity	Lower than in grey irons but depends on the size of the nodules	46 W/m K

Table 10.13 Hardness of some abrasive materials

Constituents	Vickers hardness
High-carbon content pearlite	240–425
High-chromium austenite	350–400
Orthose (6 in Mohs scale)	500–600
High-carbon martensite	770–800
Quartz (7 in Mohs scale)	800–1000
Cementitic carbides K_C	1060–1240
Topaz (8 in Mohs scale)	1300
Carbides K_2	1500–1800
Corundum (9 in the Mohs scale)	2000
Tungsten carbide	2400
Silicon carbide	2500
Diamond (10 in the Mohs scale)	8000

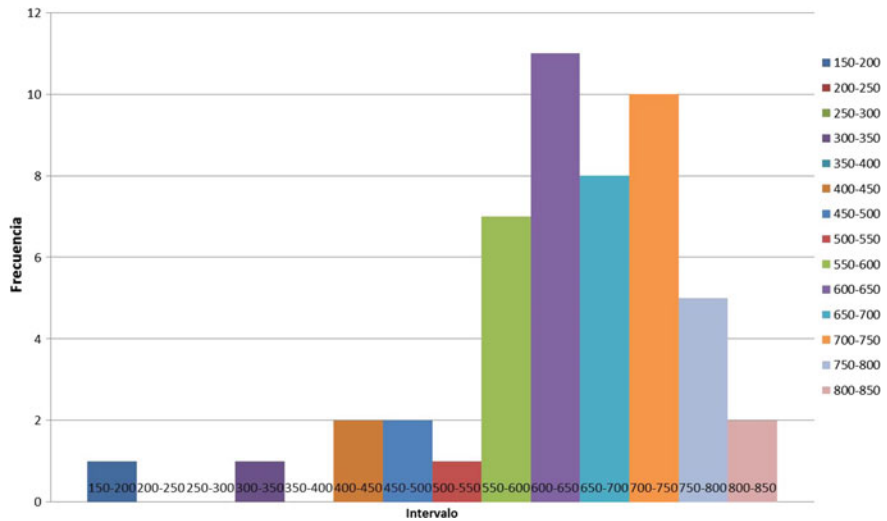


Fig. 10.28 Frequencies histogram

Table 10.14 Values of HV

Test	HV	Test	HV	Test	HV
1	550	18	742	35	727
2	425	19	805	36	760
3	592	20	772	37	698
4	742	21	401	38	541
5	742	22	772	39	636
6	592	23	570	40	178
7	636	24	660	41	313
8	614	25	592	42	592
9	712	26	499	43	660
10	742	27	636	44	698
11	712	28	636	45	660
12	754	29	614	46	648
13	727	30	742	47	660
14	614	31	685	48	636
15	685	32	636	49	592
16	754	33	840	50	636
17	483	34	727		

Table 10.15 Frequencies histogram

Interval	Frequency
150–200	1
200–250	0
250–300	0
300–350	1
350–400	0
400–450	2
450–500	2
500–550	1
550–600	7
600–650	11
650–700	8
700–750	10
750–800	5
800–850	2

Question

Values of Vickers hardness.
Indenter load = 100 kg

$$P(50\%) = 650$$

(10.244)

Table 10.16 Cumulated probability histogram

Interval	% Cumulated
150	100
200	98
250	98
300	98
350	96
400	96
450	92
500	88
550	86
600	72
650	50
700	34
750	14
800	4
850	0

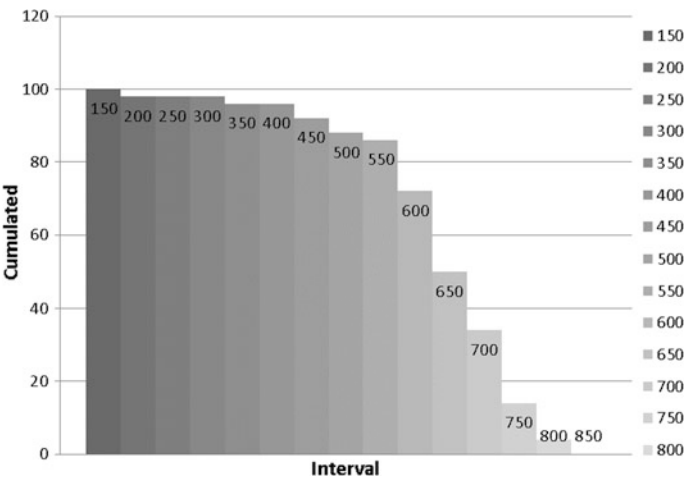


Fig. 10.29 Cumulated histogram

$$P(37\%) = 700 \tag{10.245}$$

$$m \simeq 5 \tag{10.246}$$

Chemical composition: Sample of pig iron, water cooled, for chemical analysis.

4.60% C; 0.62% Si; 0.51% Mn; 0.074% P; 0.023% S; 0.036% Ti

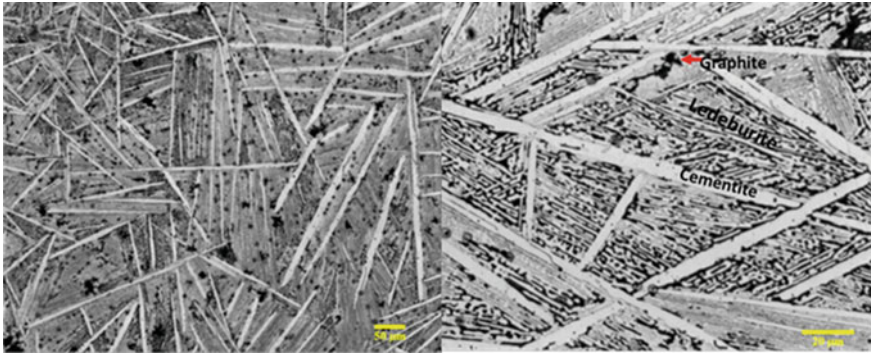


Fig. 10.30 Metallography of the cast iron

Metallography:

Hypereutectic white cast iron (Fig. 10.30). Cementite as needles as disperse constituent. Ledeburite as matrix constituent. Rests of stable solidification (graphite). As it is a material with ceramic matrix, its Weibull coefficient, $m \simeq 5$, is low. Moreover, its *reliability* as structural material is also low.

10.10 Creep: Stress Relieving

10.10.1 Measurement of Residual Stresses

Before analysing the development of residual stresses in an actual casting, we wish to review briefly various methods of measuring internal stresses, since such a review may help the reader to understand the nature of this phenomenon. When a cylindrical grey cast iron specimen (part) of $\varnothing 1$ cm is gripped at its ends in a tensile testing machine, it will, of course, elongate under tensile loading. If two reference marks are placed 10 cm apart on the surface of the bar before stressing and stress is applied, the distance separating the marks will change. Thus, for example, under a load of 100 MPa, the distance between the marks will increase to 10.0058 cm, since.

$$e = \frac{s}{E} \simeq \frac{100 \text{ MPa}}{1.7 \times 10^5 \text{ MPa}} \simeq 5.88 \times 10^{-4} (0.058\%) \quad (10.247)$$

Within the elastic range of the grey iron specimen. When the load is removed, the distance between marks returns to 10 cm. Similarly, if a cut is made to isolate the gage section from the remainder of the bar, instead of unloading the gage length by reversing the controls, the test length will revert to 10 cm.

Now imagine that the test bar under the same stress of 100 MPa is not clamped in the machine, but it is a light section of a huge casting composed of the testing

heads and frame of the machine (i.e. dumb bell-shaped casting or hot-tear test casting specimen). Let us suppose further than the stress (uniaxial in the direction of the gage marks) in the bar is unknown to the observer. To determine the stress, we could place reference marks at desired location under stress and then unload the section by cutting it away from the remainder. In our case, reference marks are placed 10 cm apart under the *unknown* stress of 100 MPa would be 9.9942 cm apart after unloading. Small holes are accurately drilled and the distance between them is measured, and then the section is cut away for measurement.

Nowadays *SR4* strain gages have found wide use. This method depends upon the change in electrical resistance with the change in the length of a wire. A fine wire is cemented to the casting, and the wire resistance is measured. Then, the section is cut free and the wire resistance is remeasured. The change in electrical resistance is related to the change in strain by a calibrated instrument. When the directions of principal stresses are not known, one must resort to the Mohr circle analysis which requires that gages be placed in three directions. Note that in both of these methods, the stress is experimentally determined without regard to section shape.

Exercise 10.42. Calculate the residual stresses developed in a part of squared section with two masses separated (see Fig. 10.31) casted in grey iron. Two extensometric gages are placed in the directions L and T (supposed principal directions of deformation) previous to the cut effectuated in the central part were measured the deformations: $\varepsilon_L = 1000 \times 10^{-6}$ and $\varepsilon_T = 100 \times 10^{-6}$ (a per one). Calculate the residual stresses (of tension) in both directions.

Question

Constitutive equations (elastic stress–strain relations) are:

$$\varepsilon_x = \frac{1}{E} \cdot [\sigma_x - \nu \cdot (\sigma_y + \sigma_z)] \quad (10.248)$$

$$\varepsilon_y = \frac{1}{E} \cdot [\sigma_y - \nu \cdot (\sigma_x + \sigma_z)] \quad (10.249)$$

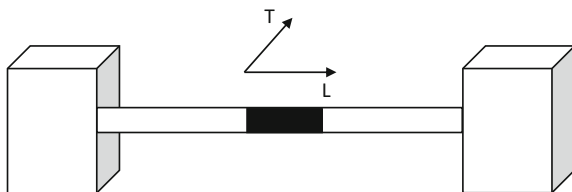


Fig. 10.31 Scheme to be used in the exercise

$$\varepsilon_z = \frac{1}{E} \cdot [\sigma_z - \nu \cdot (\sigma_x + \sigma_y)] \quad (10.250)$$

In our case:

$$\sigma_z = 0, \varepsilon_z = 0 \text{ (unknown)}, E = 1.7 \times 10^5 \text{ MPa}, \nu = 0.25$$

The relation strain–stress can be summarized in

$$1000 \times 10^{-6} = \frac{1}{1.7 \times 10^5} \cdot (\sigma_x - 0.25 \cdot \sigma_y) \quad (10.251)$$

$$100 \times 10^{-6} = \frac{1}{1.7 \times 10^5} \cdot (\sigma_y - 0.25 \cdot \sigma_x) \quad (10.252)$$

Then:

$$\sigma_x = 185.9 \text{ MPa (27.1 ksi)} \quad (10.253)$$

$$\sigma_y = 63.5 \text{ MPa (9.2 ksi)} \quad (10.254)$$

10.10.2 Stress Relieving

Stress relieving treatments may be required to remove stresses of three different origins: (a) as-cast stresses, (b) residual stresses resulting from a heat treatment such as quenching, malleablizing, fastening, etc., and (c) stresses produced by welding or weld repair. All three types may be discussed from the same point of view because in each case the basic requirement is to convert elastic strain in plastic strains by *creeping*. That is to say, for an initial deformation e_0 , after a certain time, t :

$$e_0 = e_e + e_p \text{ (elastic and plastic components of deformation)} \quad (10.255)$$

$$e_0 = \frac{\sigma}{E} + \int_0^t B \cdot \sigma^n \quad (10.256)$$

$$\dot{\varepsilon} = B \cdot \sigma^n \text{ (potential creep law, } 3 < n < 8) \quad (10.257)$$

Differentiating:

$$de_0 = 0 = \frac{1}{E} \cdot \frac{d\sigma}{dt} + B \cdot \sigma^n \quad (10.258)$$

Integrating between σ and σ_i (initial stress) we obtain:

$$\left\{ \frac{1}{\sigma^{n-1}} - \frac{1}{\sigma_i^{n-1}} \right\} = (n-1) \cdot B \cdot E \cdot t \quad (10.259)$$

Thus, the required time to achieve a reduction of σ_i down to a half is

$$t_{\sigma_i/2} = (2^{n-1} - 1) / (n-1) \cdot B \cdot E \cdot \sigma_i^{n-1} \quad (10.260)$$

The required time to achieve a reduction of σ_i down to the forth part is

$$t_{\sigma_i/4} = (4^{n-1} - 1) / (n-1) \cdot B \cdot E \cdot \sigma_i^{n-1} \quad (10.261)$$

Thus, the required time to achieve a reduction of σ_i down to tenth part is

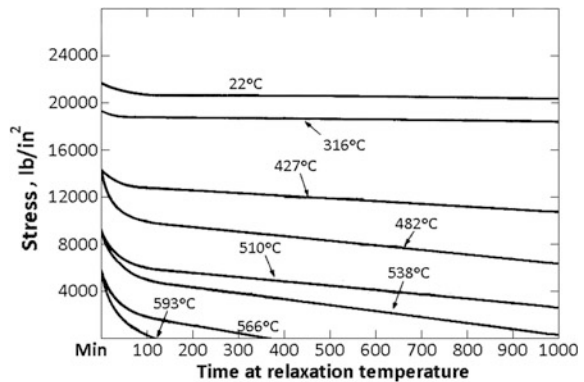
$$t_{\sigma_i/10} = (10^{n-1} - 1) / (n-1) \cdot B \cdot E \cdot \sigma_i^{n-1} \quad (10.262)$$

The false *constant* B , in the potential creep law, is thermally activated, $B \propto \exp(-Q/R \cdot T)$, being Q the activation energy for the diffusion of vacancies (iron atoms) in the specimen. Then, to achieve an effective relieving treatment, the temperature should be around or higher to:

$$\frac{T_M(K)}{2} \simeq (1154 + 273)/2 = 714 \text{ K} (\simeq 450^\circ \text{C}) \quad (10.263)$$

Data for the stress relief of a grey iron 2.7% C–2% Si–0.08% P are presented in Fig. 10.32. The specimens were loaded to reach a total strain of 0.3% at the start of the test, resulting in the various starting stresses shown at zero time. The data indicate that very little stress relief take below 900 °F (482 °C) and thus show that the old practice of achieving stress relief by allowing castings to age at room temperature has little merit.

Fig. 10.32 Stress relief of cast iron (2.72% C, 1.97% Si, 0.51% Mn, 0.08% S, 0.14% P) at various temperatures (elaborated with data from Flinn 1963)



Exercise 10.43. The mentioned cast iron with residual stresses of 6 ksi ($\simeq 41$ MPa) is subjected to stress relieving treatment at 1050 °F (566 °C). After 20 min, the stress has fallen to a half of the initial value; after 160 min to the forth part. How long would take the complete disappearance of the residual stresses ($\sigma \ll \sigma_i/10$)?

Question

According to the general equation:

$$t_{\sigma_i/2} = (2^{n-1} - 1)/B \cdot E \cdot n \cdot \sigma_i^{n-1} \quad (10.264)$$

$$t_{\sigma_i/4} = (4^{n-1} - 1)/B \cdot E \cdot n \cdot \sigma_i^{n-1} \quad (10.265)$$

That is,

$$\frac{t_{\sigma_i/4}}{t_{\sigma_i/2}} = \frac{(4^{n-1} - 1)}{(2^{n-1} - 1)} \simeq 2^{n-1} = \frac{160}{20} = 8 \quad (10.266)$$

As $n \simeq 4$ (exponent of the creep behaviour law), then:

$$\frac{t_{\sigma_i/10}}{t_{\sigma_i/2}} = \frac{(10^{n-1} - 1)}{(2^{n-1} - 1)} \simeq \left(\frac{10}{2}\right)^{4-1} \rightarrow t_{\sigma_i/10} \simeq 2500 \text{ min (42 h)} \quad (10.267)$$

A rough calculation of the activation energy for the self-diffusion of iron, Q , can be carried out as follows:

At 566 °C the relieving stresses can be divided by 10 after 400 min while at 593 °C are divided by 10 in 120 min. In the above equation of reference, all parameters with the exception of the temperature can be considered constant. That is to say:

$$\begin{aligned} \frac{t_{566}}{t_{593}} &\simeq \frac{400}{120} = \frac{B_{593}}{B_{560}} \propto \exp\left\{\frac{Q}{R} \cdot \left(\frac{1}{839} - \frac{1}{856}\right)\right\} \rightarrow Q = \frac{8.31 \cdot 839 \cdot 866}{(866 - 839)} \cdot \ln\left(\frac{400}{120}\right) \\ &= 269 \text{ kJ/mol} \end{aligned} \quad (10.268)$$

Approximately the activation energy for the self-diffusion in the Fe_α ($\simeq 250$ kJ/mol).

Exercise 10.44. If we consider the same cast iron than in the last exercise (2.7% C–2% Si–0.08% P) subjected to the residual stresses of the Exercise

10.42, calculate the relieving time necessary at 1050 °F (566 °C) to achieve the disappearance of the longitudinal and transverse stresses built up during the solidification process ($\sigma \ll \sigma_i/10$).

Data: $n = 4$; $t_{\sigma_i/4} = 20$ min; $\sigma_i = 6$ ksi

Question

Considering the equation:

$$t_{\sigma_i/10} = (10^{n-1} - 1)/B \cdot E \cdot n \cdot \sigma_i^{n-1} \quad (10.269)$$

Calculus of $B \cdot E$ (B associated to the creep law behaviour; E Young's modulus with a value of around 170 GPa).

When:

$\sigma = \sigma_i/2$ (from the last exercise)

$$20 = (2^3 - 1)/B \cdot E \cdot 4 \cdot 6^3 \rightarrow B \cdot E \simeq 4.05 \times 10^{-4} \quad (10.270)$$

To achieve the disappearance of the longitudinal stress ($\sigma \simeq \sigma_i/10$):

$$\sigma_i = 27.1 \text{ ksi} \rightarrow t_{\sigma_i/10} = (10^3 - 1)/4.05 \times 10^{-4} \cdot 4 \cdot 27.1^3 \simeq 31 \text{ min} \quad (10.271)$$

To achieve the disappearance of the transversal stress:

$$\sigma_i = 9.2 \text{ ksi} \rightarrow t_{\sigma_i/10} = (10^3 - 1)/4.05 \times 10^{-4} \cdot 4 \cdot 9.2^3 \simeq 792 \text{ min} \quad (10.272)$$

which is 25 times higher.

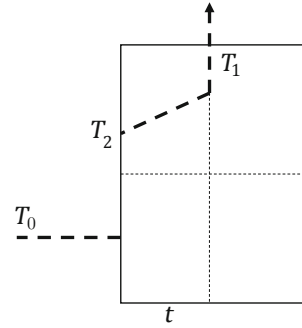
NOTE: It is interesting to mention that the relieving times are inversely proportional to σ_i^{n-1} , that is to say, the lower the relaxation time, the higher the initial internal stress. Furthermore, the rate of replacement of the elastic deformations by plastic deformations increases with the exponent n of σ_i ($\dot{\epsilon}_p \propto A \cdot \exp(-Q/R \cdot T) \cdot \sigma^n$) or potential law of stationary creep.

10.11 Thermal Shock Resistance. Damping Capacity

10.11.1 Thermal Shock Resistance

One way of measuring thermal shock resistance is to drop a part of material, heated progressively to high temperatures, into cold water. The maximum temperature drops ΔT which it can survive is a measure of its thermal shock resistance. If its coefficient of expansion is α then the quenched surface layer suffers a shrinkage

Fig. 10.33 Scheme to be used in the calculations



strain of $\alpha \cdot \Delta T$. But it is part of much larger body which is still hot, and this constrains it to its original dimensions; it then carries an elastic tensile stress $E \cdot \alpha \cdot \Delta T$. If this tensile strength exceeds that for tensile fracture, σ_{TS} , the surface of the component will crack and ultimately spall off. So, the maximum temperature drop ΔT is given $E \cdot \alpha \cdot \Delta T = \sigma_{TS}$. For most of the engineering metallic materials, α is small and σ_{TS} is large, so they can be quenched suddenly through several hundred degrees without fracturing.

In fact, $\Delta T/B = \sigma_{TS}/\alpha \cdot E$. We calculate the value of the constant B . Internal stresses generated in the part also depend on the coefficient of heat transfer h through the surface. In fact (Fig. 10.33), by applying the heat transmission laws to a part of $2 \cdot t$ in thickness:

$$h \cdot (T_2 - T_0) = K \cdot (T_1 - T_2)/t \quad (10.273)$$

$$t \cdot h/K = (T_1 - T_2)/(T_2 - T_0) = B \quad (10.274)$$

B is known as Biot number:

$$\Delta T = (T_1 - T_2) = B \cdot (T_1 - T_0) \quad (10.275)$$

That is to say:

$$\frac{\Delta T}{B} = \frac{\sigma_{TS}}{\alpha \cdot E} \quad (10.276)$$

Biot's coefficient for a metal ($T \simeq 1000^\circ\text{C}$; $E \simeq 100 \text{ GPa}$; $\alpha \simeq 10^{-5} \text{ K}^{-1}$; $K \simeq 100 \text{ W/m s } ^\circ\text{C}$ and $h(\text{water cooling}) \simeq 10^4 \text{ W/m}^2 \text{ K}$), when $t = 1 \text{ cm}$, $\sigma_{TS} \simeq 300 \text{ MPa}$ is

$$B = \frac{t \cdot h}{K} = \frac{0.01 \times 10^4}{100} \simeq 1 \rightarrow \Delta T = 300/10^5 \cdot \text{K}^{-1} \cdot 10^5 \text{ MPa} \simeq 300 \text{ K} \quad (10.277)$$

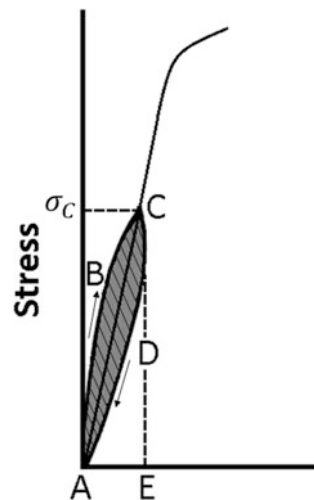
Cast irons have a lower thermal conductivity (45 W/m K) than steels (75 W/m K), and for that reason a lower thermal shock resistance, even though high.

10.11.2 Damping Effect

In, an actual material where a specimen is loaded and unloaded in continuous cycle ($\sigma_M = \sigma$, $\sigma_m = 0$), the elastic hysteresis loop resembles the next Fig. 10.34. The energy loss per cycle is represented by the area ABCDA. Although the area included within the hysteresis loop may be very small, it can be an important quantity for a material subjected to rapid vibration since the total energy dissipated in a given time is the product of the hysteresis area per cycle times the number of cycles. From an engineering point of view, this elastic hysteresis leads to the generation of heat and the damping of vibrations. It is one of the mechanisms by which vibrational energy is dissipated internally by the material. The various energy-dissipating effects can be grouped under the generic heading of internal friction.

Internal friction is usually expressed through the logarithmic decrement, δ . Internal friction frequently is measured through a system which is set into motion with a certain amplitude and then allowed to decay freely. The amplitude at any time A_t is given $A_t = A_0 \cdot \exp(-\beta \cdot t)$, where β is the attenuation coefficient. The logarithmic decrement is the logarithm of the ratio of successive amplitudes $\delta = \ln(A_n/A_{n+1})$.

Fig. 10.34 Hysteresis cycle for materials subjected to cyclic loads



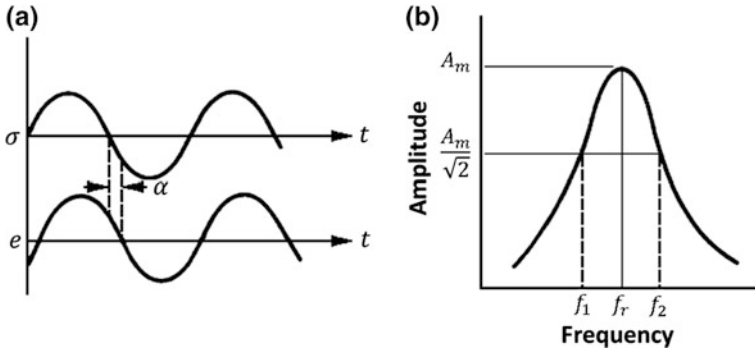


Fig. 10.35 **a** Lag between waves σ and ε ; **b** amplitude of the vibration

A plot of $\ln A$ versus the number of cycles of vibration will be linear and the slope of the curve is the decrement. With anelastic behaviour the stress and strain are not in phase (see Fig. 10.35). The phase angle by which the stress lags behind the strain in time is α . The logarithmic decrement is related to the lag angle by $\delta = \pi \cdot \alpha$. For a condition of forced vibration in which the specimen is driven at a constant amplitude, a measure of internal friction is the fractional decrease in vibrational energy per cycle $\delta = \Delta W/2W$ where ΔW is the energy lost per cycle (area ABCD in Fig. 10.34) and W the energy associated to the vibration per cycle, area ACE in Fig. 10.34. If a fixed amount of energy per cycle is supplied to the specimen, a maximum amplitude of vibration occurs at the resonant frequency (vid Fig. 10.35), a maximum amplitude of vibration occurs at the resonant frequency. The logarithmic decrement for a resonance curve is given approximately by:

$$\delta = \pi(\text{band width})/f_r \simeq \pi \cdot (f_2 - f_1)/f_r \quad (10.278)$$

A measure of internal friction that often is used is the Q parameter, where

$$Q = \frac{\pi}{\delta} \quad (10.279)$$

So:

$$\delta = \frac{\pi}{Q} = \frac{\pi \cdot \Delta f}{f_r} \quad (10.280)$$

That is to say:

$$Q^{-1} = \frac{f_2 - f_1}{f_r} \quad (10.281)$$

If Q^{-1} increases Δf increases (more internal energy dissipation). Internal energy dissipation at larger stresses and strains generally is called *damping*. High damping capacity is important in minimizing noises in machinery or in suppressing vibration in high-speed machinery. A high damping capacity is of practical engineering importance in limiting the amplitude of vibration at resonance conditions and thereby reducing the likelihood of fatigue failure. For example, the exceptionally high damping capacity of cast irons arises from the presence of graphite flakes which do not readily transmit elastic waves because their surfaces rub with the matrix dissipating energy. Remind that a grey cast iron is a metal matrix composite: a steel whose cracks (flaws) are filled with graphite.

Exercise 10.45. Compare the damping capacity of both a cast iron ($\delta \simeq 20$) and an austenitic stainless steel 18/8 ($\delta \simeq 0.5$):

Question

- In the case of the cast iron:

$$\delta = \ln\left(\frac{A_n}{A_{n+1}}\right) = 20 \rightarrow \frac{A_n}{A_{n+1}} = \exp(-20) = 2 \times 10^{-9} \text{ (extremely fast)} \quad (10.282)$$

- In the case of the steel:

$$\delta = \ln\left(\frac{A_n}{A_{n+1}}\right) = 0.5 \rightarrow \frac{A_n}{A_{n+1}} = \exp(-0.5) = 0.61 \text{ (slow)} \quad (10.283)$$

How long would be necessary to have 10^{-4} the initial vibration amplitude in the case of the steel?

Question

$$10^{-4} = \exp(-\delta \cdot t) \rightarrow t \simeq 18 \text{ s} \quad (10.284)$$

And in the cast iron?

Question

$$t \simeq 0 \quad (10.285)$$

10.12 Fatigue

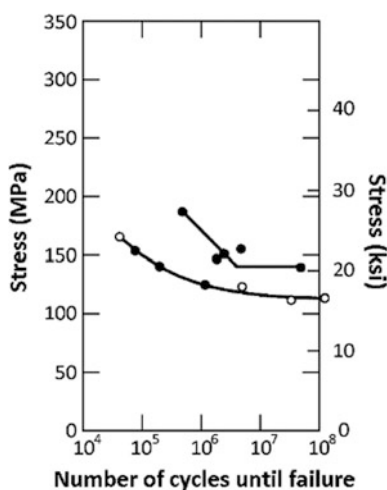
When a component or structure is subjected to repeated stress cycles (alternative, repeated, irregular), it may fail at stresses well below the tensile stress, TS, and often below the yield strength, YS, of the material. The fatigue failure is especially dangerous because the material subjected to alternative cycles, can break soon, after a certain number of cycles, without previous deformation and without being possible, for that reason, to foresee its reposition. It does not seem exaggerated the affirmation of that the 80% of the failures, in parts and components subjected to alternative stresses is due to the fatigue.

The called *fatigue limits* are determined with the curve of Wöhler S-N (stress–number of cycles). The specimens are subjected to rotative bending, in three points, for instance ($\sigma_{\max} = -\sigma_{\min}$), changing the amplitude of the cyclic loads. It is known as *endurance limit* to the maximum value of the cyclic stress that causes that at less 50% of the tested parts do not break after 10^7 cycles (10^8 – 10^9 in components of higher responsibility). Figure 10.36 represents the curves of Wöhler obtained in a class 60 cast iron: the fatigue limit is found between 100 and 150 MPa. Fatigue tests, as it is obvious, are expensive and long. Without data, it is possible to estimate the fatigue limit as around a third part of the ultimate tensile strength, $\sigma_f \simeq R_m/3$.

The phenomenon of fatigue happens due to nucleation and growing of cracks in the material, or from pre-existing cracks. When these cracks reach their critical value, the material breaks catastrophically. The growth rate is described by the Paris–Gómez and Anderson law, Fig. 10.37:

$$\frac{da}{dN} = A \cdot \Delta K^m \quad (10.286)$$

Fig. 10.36 Fatigue life curves at room temperature under stress cycles of reversible fatigue (2.84% C, 1.52% Si, 1.05% Mn, 0.07% P, 0.12% S, 0.31% Cr, 0.20% Ni, 0.37% Cu (ASM 1978)



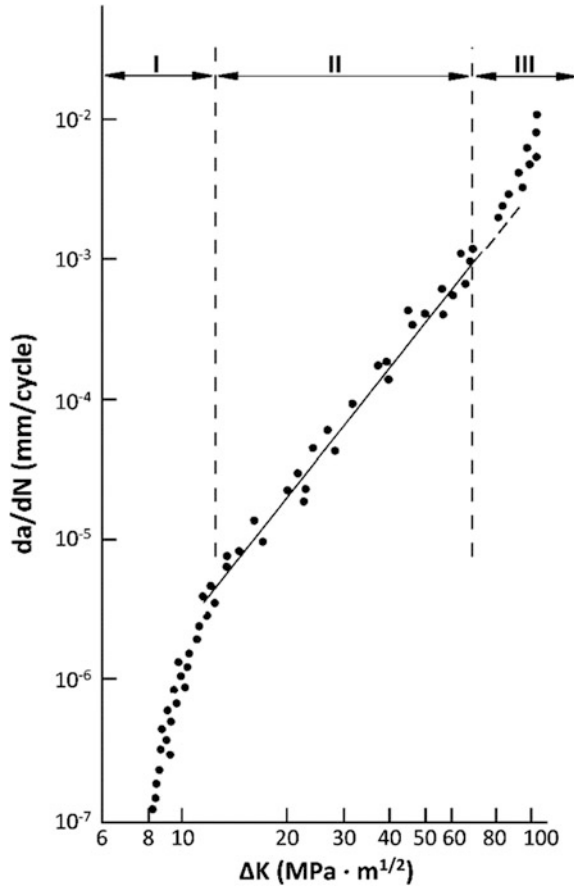


Fig. 10.37 Crack growing rate as a function of the increase of the stress intensity factor

a semilength of the currently (at present) crack

N number of cycles

ΔK variation of the critical stress intensity factor, $\Delta K = (\sigma_{\max} - \sigma_{\min}) \cdot \sqrt{\pi \cdot a}$

where A and m are constants of the material. Separating variables and integrating:

$$\begin{aligned}
 N_f &= \int_0^{N_f} dN = \int_{a_0}^{a_f} \frac{da}{A \cdot \Delta K^m} \\
 &= 2/(m-2) A \pi^{m/2} (\Delta \sigma)^m \left\{ 1/a_i^{(m-2)/2} - 1/a_f^{(m-2)/2} \right\}
 \end{aligned} \tag{10.287}$$

a_i : initial semilength of the crack considered or possible;
 a_f : final semilength of the crack, at failure.

Exercise 10.46. For a grey iron, whose S–N curves are provided (Fig. 10.36), 2.84% C, 1.52% Si, 1.05% Mn, 0.07% P, 0.12% S, 0.31% Cr, 0.20% Ni, and 0.37% Cu, calculate:

- (a) The class of the cast iron by applying Winte's equation:

Question

$$\begin{aligned} \text{TS (ksi)} = & 162.37 - 16.61/d - 54.03 \cdot \% \text{Si} + 14.16 \cdot \% \text{Si}^2 - 21.78 \cdot \text{EC} \\ & - 10.59 \cdot (\% \text{Mn} - 1.7 \cdot \% \text{S}) + 13.80 \cdot \% \text{Cr} \\ & + 2.05 \cdot (\% \text{Ni} + 30.66 \cdot \% \text{Cu}) - 26.25 \cdot \% \text{Cu}^2 \end{aligned} \quad (10.288)$$

$$\text{EC} = 2.84 + \frac{(1.52 + 0.07)}{3} = 3.37 \quad (10.289)$$

It results in:

$$\text{TS} \simeq 59.62 \text{ ksi} \quad (10.290)$$

Classes 55 or 60 ($d \simeq 1$ in.).

- (b) Calculate the value of N_f for the cast iron when it is subjected to cyclic stresses of 100 MPa. The length of the graphite flakes is approximately 20 μm , $K_C \simeq 6 \text{ MPa}\sqrt{\text{m}}$. The value of the constant A in the Paris equation is $10^{-11} (\text{MPa}\sqrt{\text{m}})^{-3} \cdot \text{m}$.

Question

Calculus of a_f :

$$6 \text{ MPa}\sqrt{\text{m}} = 100 \text{ MPa}\sqrt{\pi \cdot a} \rightarrow a = \frac{1}{\pi} \cdot \left(\frac{6}{100} \right)^2 = 1.15 \times 10^{-3} \text{ m (1.15 mm)} \quad (10.291)$$

$$a_i \simeq 20 \mu\text{m}/2 = 10^{-5} \text{ m} \quad (10.292)$$

Integrating the Paris equation, it results:

$$N_f = 2/1 \times 10^{-11} \cdot \pi^{1.5} 100^3 \left[\frac{1}{(10^{-5})^{\frac{1}{2}}} - \frac{1}{(1.15 \cdot 10^{-3})^{\frac{1}{2}}} \right] \simeq 1.03 \times 10^7 \text{ cycles} \quad (10.293)$$

REITERATIVE NOTE: Without experimental data, an estimation of the fatigue limit in regime of cyclic alternative loads in mechanized parts would be, approximately, a 30% of the minimum specified for the tensile strength for the particular class of the considered grey cast iron (in our case, between 16 and 20 ksi).

10.13 Heat Treatments

Exercise 10.47. What heat treatment can be used for ductile irons to increase the tensile and yield strength? How would this heat treatment alter the microstructure? Would the heat treatments alter the microstructure of grey cast irons in similar manner? Would the mechanical properties change in a similar manner?

Question

Many ductile irons are used in the as-cast conditions. By proper control of composition and cooling rate castings can be produced with an all-ferritic matrix (ferritic ductile iron, YS $\simeq$ 50 ksi; TS $\simeq$ 70 ksi; El $\simeq$ 20%) or with essentially all-pearlitic structure (pearlitic ductile iron, YS $\simeq$ 80 ksi; TS $\simeq$ 110 ksi; El $\simeq$ 6%). If carbides are present in the as-cast structure, ferritic ductile iron can be produced through an annealing treatment at 700 to 760 °C (see indirect ferritization treatments). Martensitic ductile iron, an iron with a tempered martensite matrix is obtained through quenching and tempering (YS $\simeq$ 110 ksi; TS $\simeq$ 140 ksi; El $\simeq$ 5%). A better compromise between strength and ductility can be obtained through austempering after normalizing and isothermal treatment between 200 and 400 °C (YS $\simeq$ 1300 ksi; TS $\simeq$ 1500 ksi; El $\simeq$ 8%). See exercise of austempering in the textbook.

Exercise 10.48. To obtain a ductile iron of ferritic matrix from a ductile iron of pearlitic matrix is suggested a heating (isothermal treatment) at 750 °C, slightly higher to the temperature of the transformation pearlite $\rightarrow$ austenite in the diagram Fe-Fe₃C. Calculate the duration of the treatment: (use the same data than in Exercise 4.2).

Question

$$g_{\alpha} = 2 \cdot \gamma \cdot \sqrt{D_{\text{C}}^{\alpha} \cdot t} / l_0 \quad (10.294)$$

$$F = \gamma \cdot e^{\gamma^2} \cdot \text{erf}(\gamma) = \frac{1}{\sqrt{\pi}} \cdot \frac{(0.021 - 0.020)}{(0.76 - 0.02)} = 7.6 \times 10^{-4} \quad (10.295)$$

With low values of γ , then:

$$e^{\gamma^2} \simeq 1 \quad (10.296)$$

$$\text{erf}(\gamma) \simeq \gamma \rightarrow F \simeq \gamma^2 = 7.6 \times 10^{-4} \rightarrow \gamma \simeq 0.028 \quad (10.297)$$

With a distance between nodules of $100 \mu\text{m}$ and $D_{\text{C}}^{\alpha} = 0.02 \cdot \exp(-20000/2 \cdot (750 + 273)) = 1.14 \times 10^{-6} \text{ cm}^2/\text{s}$, we have

$$t_{\text{r}} \simeq \left(\frac{0.01 \text{ cm}}{2 \cdot 0.028} \right)^2 \cdot \frac{1}{1.14 \times 10^{-6}} \simeq 28000 \text{ s (7.8 h)} \quad (10.298)$$

After holding at 750°C , the iron must be slowly cooled between 750 and 700°C , following the Fe–C stable diagram (to avoid pearlite). By the contrary, heat treatments do not greatly improve the mechanical properties of most grey irons, since no matter how strong the matrix may be, the flake graphite particles act as stress raiser to cause failure at relatively low loads. Heat treatments, especially quenching and tempering treatments do, however, improve hardness and wear resistance. Here the surface is hardened through heating and rapidly cooling (and subsequent tempering), while the centre of the casting is unheated and retains essentially their properties. Rapid surface heating is obtained through flame hardening or induction heating and cooling, although the surface chilling as cast (to obtain a white iron or a mottled iron) or the nitriding treatment after quenching and tempering (see the case study of the camshafts) are usually employed.

As example, Fig. 10.38 shows the stress concentration in the boundaries of a hole of spheroidal section and elliptical section, respectively. It is possible to demonstrate that:

$$\sigma_{\text{max}} = \sigma \cdot \left(1 + 2 \cdot \frac{a}{b} \right) \quad (10.299)$$

Round hole:

$$a = b \rightarrow \sigma_{\text{max}} = 3 \cdot \sigma \text{ (spheroidal)} \quad (10.300)$$

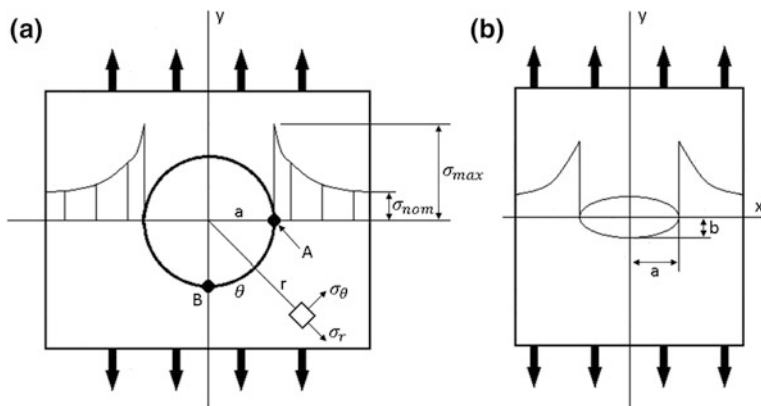


Fig. 10.38 Stress concentration in the boundaries of a round and an elliptic hole

Elliptic hole:

$$a = 10 \cdot b \rightarrow \sigma_{\max} = 11 \cdot \sigma \text{ (lamellar)} \quad (10.301)$$

That is to say, flakes concentrate the stresses in its surroundings, almost 4 times more than the nodules.

10.14 Fe–C–Cr System

Fe–C–Cr alloys of industrial interest—stainless steels, tool steels, refractory steels and high alloy white cast irons—have chromium contents lower than 40% wt., and carbon contents lower than 4%; lower than 40% wt. Cr due to their high solidification temperature; and, lower than 4% wt. C consequence of the low toughness of the alloys with carbon contents higher than this value. When chromium content is higher than 5%, this element confers refractoriness and resistance to the oxidation in dry atmosphere; when chromium content is higher than 12%, this element confers stainlessness due to the formation of a film of its oxide. The film is protective facing to oxidizing acids and numerous saline solutions, although its resistance facing to reducing acids is not good. On another note, in high alloy cast irons an excellent wear resistance, compatible with a suitable toughness, is pursued as they are usually employed in mining applications of crushing, classification and transportation of minerals with a hardness equal or higher to that one of the quartz, where common white irons or medium alloy cast irons, as for instance Ni-hard cast irons, would be unusable. A classification of the different families of possible alloys in the Fe–C–Cr system, and thus a selection of their potential applications (stainless steels for tools, ledeburitic cast irons, heat and thermal shock resistant cast irons), can be performed by studying the Fe–C–Cr diagram, in the Fe-rich side

(conditioned by the C and Cr contents) for the structures that could be obtained in equilibrium cooling, but also by studying the structures obtained as a consequence of non-equilibrium cooling conditions (due to the hardenability conferred to the Fe by the Cr and C).

The ensemble of the Fe–C metastable, Cr–C and Fe–Cr diagrams allows obtaining the Fe–C–Cr ternary diagram, as it is represented in Fig. 8.3. In the Cr–C diagram, there are three carbides, whose chemical formulas are Cr_{23}C_6 , Cr_7C_3 and Cr_3C_2 , being their carbon percentages 5.7, 9 and 13%, respectively. The carbide $(\text{Cr}, \text{Fe})_{23}\text{C}_6$ —with a maximum Fe content of 30%—is called K_1 carbide; the carbide $(\text{Cr}, \text{Fe})_7\text{C}_3$ —with a maximum Fe content of 55%—is called K_2 carbide. In the Fe–C diagram, the carbide $(\text{Fe}, \text{Cr})_3\text{C}$ —with a maximum Cr content of 15%—is called K_C carbide. Finally, in the Fe–Cr diagram, the alloys with less than 12% of Cr have a γ loop; the alphasenous behaviour of the chromium can suppress the transformations $\delta \rightarrow \gamma \rightarrow \alpha$ during the cooling, when chromium content is higher than 13%. It is not possible, for instance, a grain refinement by simple heat treatment. When we are talking about Fe–C–Cr alloys, both limits are moved towards higher chromium percentages, enlarging the region of mixed structures ($\alpha + \gamma$). The highest enlargement takes place when 0.6% C; the γ loop, that is to say, the limit curve of the alloys that can be fully austenitized during the heating, has the vertical maximum when 18% Cr; and the vertical maximum of the region ($\alpha + \gamma$) when 28% Cr. That way, when chromium content is higher than 28%, the ternary alloys are usually considered fully ferritic.

In the Fe–C–Cr ternary system, eutectic and peritectic reactions take place for the temperatures and compositions that are indicated in Fig. 8.3. These reactions are those shown below:

Point G (1415 °C, 3.5% C–60% Cr); liquid + $\text{K}_1 \rightarrow \alpha + \text{K}_2$.

Point H (1275 °C, 2.5% C–32% Cr); liquid + $\alpha \rightarrow \gamma + \text{K}_2$.

Point K (1160 °C, 4% C–15% Cr); liquid + $\text{K}_2 \rightarrow \gamma + \text{K}_\text{C}$.

Line HG: liquid $\rightarrow \alpha + \text{K}_2$.

Line HK: liquid $\rightarrow \gamma + \text{K}_2$.

Line LK: liquid $\rightarrow \gamma + \text{K}_\text{C}$.

Line RH: liquid + $\alpha \rightarrow \gamma$.

The top view projection of the binary peritectic RH and the binary eutectics HG and HK allows delimitating in Fig. 10.39 our map of materials selection; and from the solidification point of view, three fields of compositions can be defined:

- (A) Alloys whose solidification begins with the formation of pro-eutectic K_2 carbides.
- (B) Alloys that begin their solidification with the appearance of primary austenite.
- (C) Alloys that begin the solidification with δ ferrite as primary constituent.

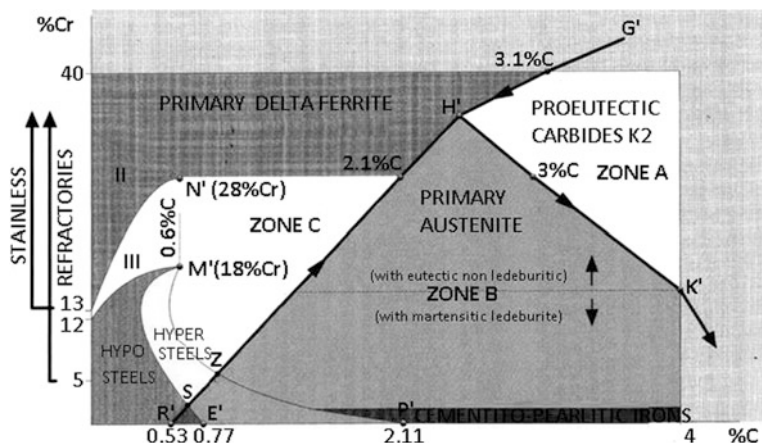


Fig. 10.39 Selection diagram of the Fe-C-Cr alloys

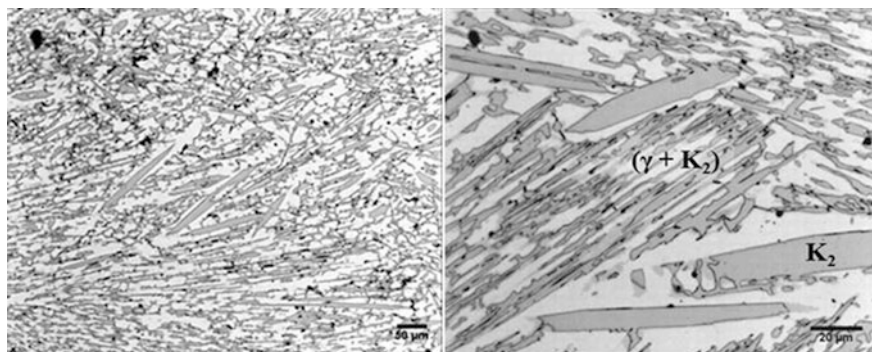


Fig. 10.40 Zone A: alloy Fe-3% C-29% Cr. As-cast condition. 426 HBS

The alloys located in the first of these three regions, A, delimited by the lines H'G' and H'K' in Fig. 10.39, are cast irons with eutectic matrix non-ledeburitic: of austenite and K_2 carbides. This is the case of the cast iron 3.1% C-29.3% Cr represented in Fig. 10.40. They are cast irons with eutectic matrix non-ledeburitic, being the austenite—partially transformed into martensite due to its high hardenability—the matrix constituent. The alloys in this region are refractory white cast irons, stainless, wear resistant and tough.

The region B, delimited by the lines H'K' and H'R', Fig. 10.39, includes several kinds of alloys: some of them are cast irons, and the others are hypo- and hypereutectoid steels. In this region, alloys with more than 15% of chromium are made up, at the end of the solidification, by primary austenite and eutectic matrix non-ledeburitic: this last one made up by austenite and K_2 carbides. The austenite, matrix constituent, with high hardenability, is transformed into martensite by air

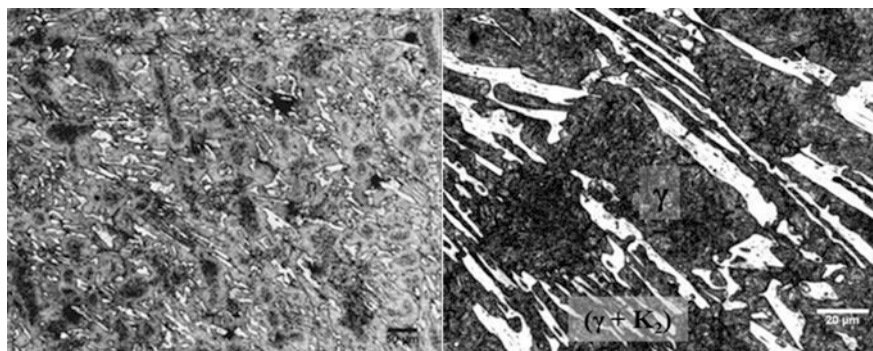


Fig. 10.41 Zone B: alloy Fe–2.75% C–17% Cr as-cast condition. 473 HBS

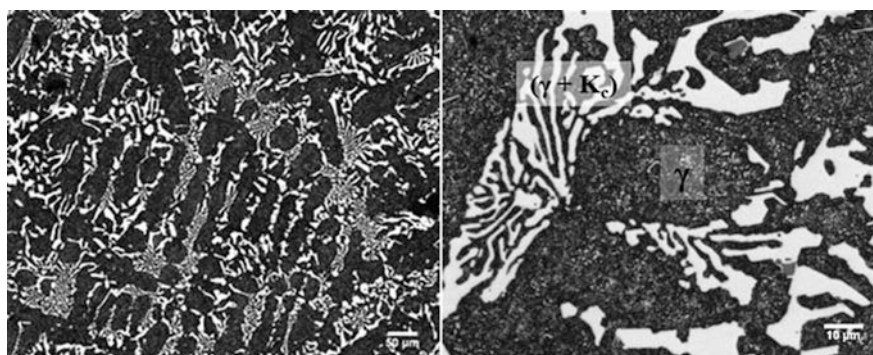
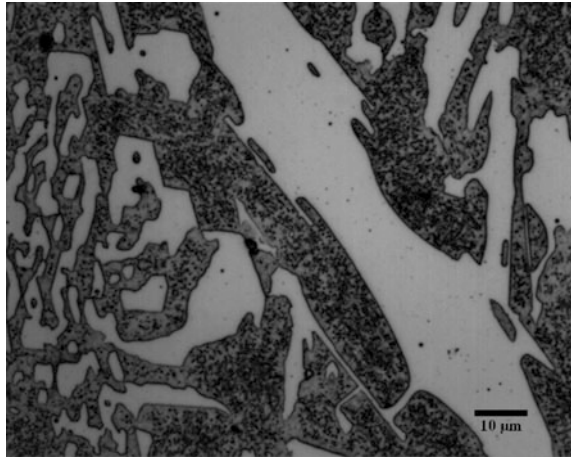


Fig. 10.42 Zone B: alloy Fe–3% C–10% Cr as-cast condition and hardened after heat treatment of quenching and tempering. 651 HBS

cooling, although a certain amount of residual austenite is found. This is the case of the 2.75% C–16.9% Cr cast iron represented in Fig. 10.41, characterized by its wear resistance and toughness.

In this same region, the alloys with less than 15% Cr, delimited in the lower part by the white cast irons, are also cast irons: the primary constituent is austenite; but, as opposed to the previous ones, the eutectic matrix is of ledeburitic type—made up by austenite and K_C carbides. This is the case of the 3.1% C–10.4% Cr cast iron, Fig. 10.42: the matrix constituent is the K_C carbide over background of martensite, adequate due to the wear resistance. The behaviour in service of this martensitic cast irons, as well as that one of those with more than 15% Cr, depending obviously on the relative proportions between the primary constituent and the eutectic; that, in first approximation can be determined by drawing the tie lines as in Fig. 8.3 (lever rule); or in the top view projection, Fig. 10.39.

Fig. 10.43 Micrograph of the alloy used in the exercise (as-cast)



Exercise 10.49. In the alloy: 3.25% C–11.80% Cr–2.60% Mo (Fig. 10.43), the percentage of primary and eutectic carbides calculated by means of quantitative metallurgy is 28.50%, and the chromium content is 33%. At the same time, an analysis effectuated in the austenite of the matrix indicates that the chromium content is 5%. It is requested:

1. Represent the alloy and its phases in the Fe–C–Cr ternary diagram.
2. It was performed, initially, a treatment for 20 min. at 1000 °C with the purpose of destabilizing the austenite. Then, isothermal treatments were carried out during 24 h at the following temperatures: 250, 500, 600 and 700 °C; the measured hardness HV50 values are 631, 925, 653 and 426, respectively. With the support of a TTT curve for this alloy, determine the microstructures that this alloy will have at the mentioned temperatures.
3. Determine the fraction of retained austenite that presents this alloy after the heat treatment ($M_S = 148$ °C).

Question

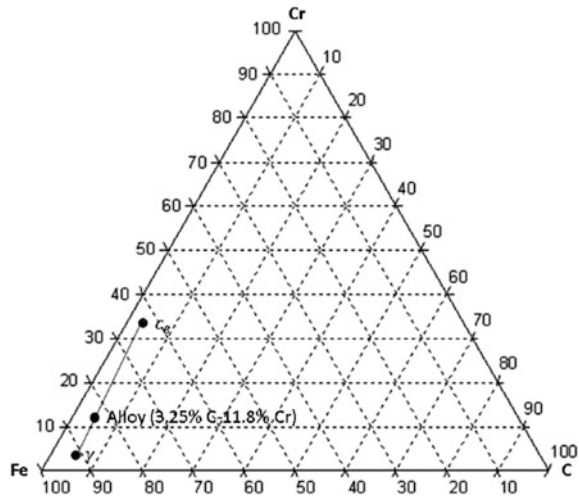
1. Representation in the Fe–C–Cr diagram of the alloy and the phases that is possible to find in the alloy (Fig. 10.44):

Fractions of austenite and carbides (primary, c_p ; and eutectic, c_e):

$$c_p + c_e = 28.5\% \quad (10.302)$$

$$f_\gamma = 100 - 28.5 = 71.5\% \quad (10.303)$$

Fig. 10.44 Alloy: 3.25% C–
11.8% Cr



Balance to chromium total (x chromium in the austenite):

$$11.8 = 71.5 \cdot x + 28.5 \cdot 0.33 \rightarrow x = 3.35 \% \text{ Cr} \quad (10.304)$$

Balance to chromium in the matrix:

$$71.5 \cdot 0.0335 + c_e \cdot 0.33 = (71.5 + c_e) \cdot 0.05 \rightarrow c_e = 4.21\% \quad (10.305)$$

$$c_p = 28.5 - 4.21 = 24.29\% \quad (10.306)$$

2. TTT curve of the cast iron: (Fig. 10.45)

Microstructures:

24 h/250 °C: 40–50% Bainite + martensite.

24 h/500 °C: 2–3% Pearlite + martensite.

24 h/600 °C: 100% Pearlite.

24 h/700 °C: 100% Pearlite.

3. Retained austenite:

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (M_s - T_a)] \quad (10.307)$$

$$\gamma_{\text{retained}} = \exp[-0.011 \cdot (148 - 25)] = \exp[-1.353] \simeq 25\% \quad (10.308)$$

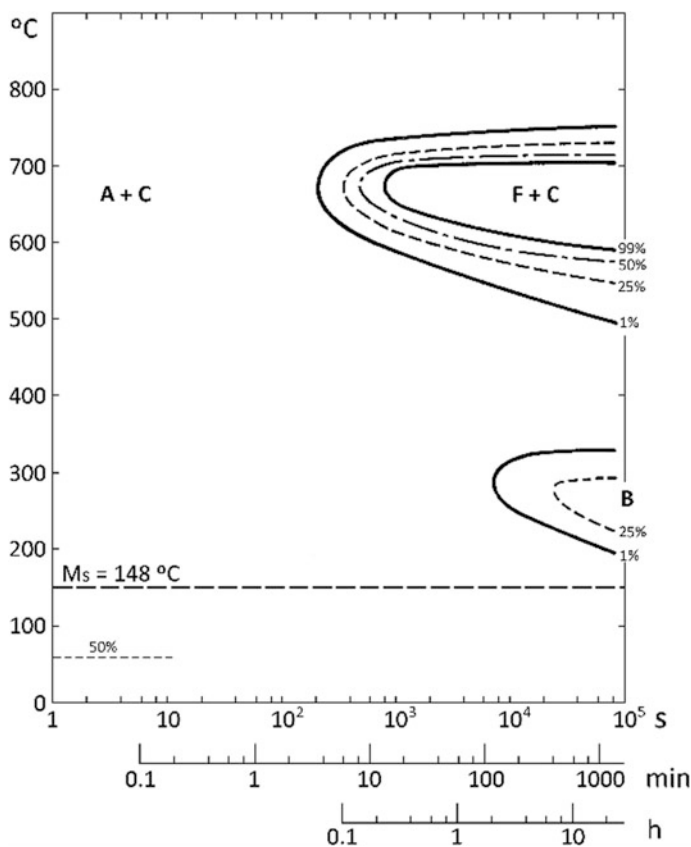


Fig. 10.45 TTT curve of the alloy (adapted from Maratray and Usseglio-Nanot 1970)

In the region C, that includes all alloys located at the left side of the lines G'H' and H'R', the alloys begin their solidification with the appearance of δ ferrite. When the carbon content is low-lower than 0.1% C, the solidification ends with the formation of only delta solid solution. On another note, for those alloys of low carbon and high chromium content located in II over Fig. 10.39, δ ferrite does not transform into γ during the cooling. They are, for that reason, ferritic steels that, because of having more than 12% of chromium, are stainless, with a thermal refractoriness that rises with the chromium content.

When increasing chromium contents (for instance with 36% Cr, carbon content lower than 1.2%, and Fe balance), the alloys in this region will have as primary constituent δ ferrite and eutectic matrix of δ ferrite (in high proportion) and K₂ carbides. They are ferritic refractory cast irons, as the δ constituent does not transform allotropically during the cooling. For lower chromium contents, the eutectic will be made up by austenite and K₂ carbides. This is the case of the 1% C–30% Cr cast iron, represented in Fig. 10.46: the disperse constituent is ferrite in a eutectic matrix

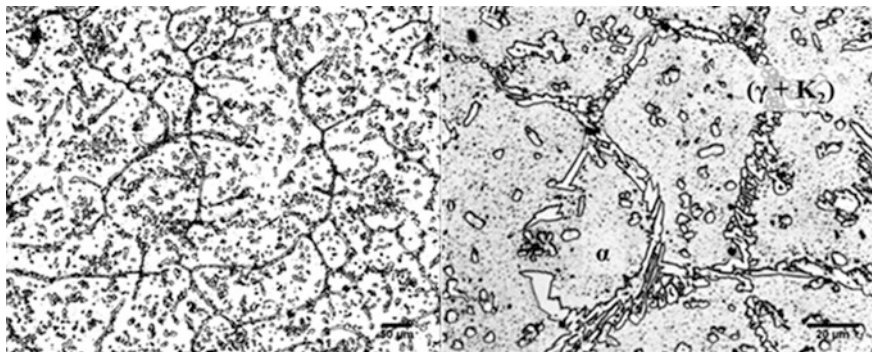


Fig. 10.46 Zone C: alloy Fe–1% C–30% Cr in as-cast condition. 239 HBS

of austenite and K_2 carbides, recommended due to its stainless, heat resistance and thermal shock resistance.

The alloys located in the region delimited by the line $M'P'$, the coordinate axes and the curve M' (0% C–12% Cr) are hypo and hypereutectoid steels. Steels located at the left side of the line $R'H'$ begin with the solidification of δ , although, during the cooling, they undergo the transformation $\delta \rightarrow \gamma$. On the contrary, those located at the right side of the peritectic line $R'H'$ solidify directly in γ . Both sets, if the cooling is of equilibrium, will have eutectoid transformation. The composition of the eutectoid austenite is located over the curve E' (0.77% C, 0% Cr); and for that reason, as it is mentioned in Fig. 10.39, ones are hypoeutectoids and the others hypereutectoids. Both of them, if have more than 12% Cr, are stainless and, due to the possibility of transforming their austenite into martensite, are called martensitic stainless steels. As a consequence, and for the same reason, steels with more than 5% Cr, which is indicated as the lower limit for *refractoriness*, are named martensitic steels slightly refractories.

In such a way, the map for the selection of the properties as a function of the structure, Fig. 10.39, presented for the Fe–C–Cr diagram, for all industrial alloys up to 4% C and 40% Cr indicates the regions where the typical structures of the refractory and stainless steels, ledeburitic steels, low, medium, half and high alloy cast irons are presented, with specification of their primary constituents— K_2 carbides, ferrite and austenite and eutectics—ledeburitic or non-ledeburitic. Obviously, the addition of other elements, for instance, gammagenous as nickel, in sufficient amount, partially modifies the critical points of the Fe–C–Cr ternary diagram, and for that reason, the structure and properties of the obtained alloys.

Case study 1: CAM-CAD methods applied to the feeding system of parts manufactured in Ni-hard cast iron.

Computer-aided design and manufacture (CAD-CAM) systems are becoming increasingly prevalent in industrial design, and their use offers both opportunities and problems for casting designers. One effective computer tool is available and uses CAD

designs to simulate the solidification of a casting through solidification modelling. The developed algorithms of such simulations can be divided into three basic types:

- Those based on classical heat transfer equations ($\partial T / \partial t = \alpha \cdot \partial^2 T / \partial x^2$, α is the thermal diffusivity).
- Those based on finite element methods (FEM or FDM), which are iterative techniques based on classical heat transfer.
- Those based on ratios of surface area to volume, as described in this book (Caine's method, Adams and Taylor equation).

Here you have the CAD design of a ball-miller liner of dimensions of $60 \times 5 \times 2 \text{ in.}^3$, manufactured in Ni-hard alloy (3.5% C, 4% Ni, 2% Cr, class 1, type A, 550 HBN as sand cast).

A drawing of the complete casting and dimensions of the feeding and risering systems calculated with CAD-CAM is enclosed (Fig. 10.47). We shall recalculate through traditional Caine's equation the obtained results. The Caine's equation for white cast irons with exothermically top insulated riser can be approached by $X = 0.08 / ((Y - 0.04) + 0.8)$, where X (freezing ratio) and Y (yield casting) are the meaning already cited above. Data for CAD design are the following (see the drawing, Fig. 10.47):

Case 1: flat sheet:

Data:

Part: $60 \times 50 \times 2 \text{ in.}$,

Sprue: 40 mm in diameter, 60 mm in height,

Runner: $40 \times 40 \text{ mm}$,

Riser: 200 mm in diameter, $H = 300 \text{ mm}$ ($1.5 \cdot D$) and

Riser: $200 \times 300 \text{ mm}$.

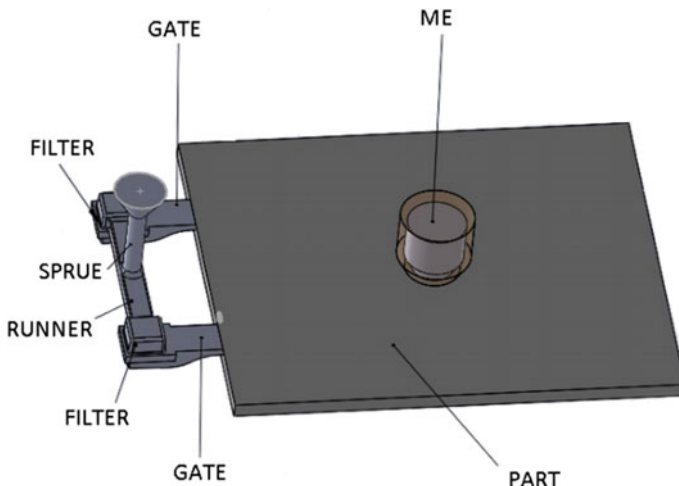


Fig. 10.47 CAM-CAD model of the flat sheet (Fundyser S. A.)

$$\left(\frac{V}{A}\right)_{\text{riser}} = \frac{\pi \cdot (20)^2 / 4 \cdot 30}{\pi \cdot 20 \cdot 30} = 5 \text{ cm} \quad (10.309)$$

$$\left(\frac{V}{A}\right)_{\text{part}} = \frac{60 \cdot 50 \cdot 2}{2 \cdot 3000 + 2 \cdot 100 + 2 \cdot 120} = \frac{6000}{6440} = 0.93 \text{ in. (2.37 cm)} \quad (10.310)$$

$$X = \left(\frac{V}{A}\right)_{\text{riser}} / \left(\frac{V}{A}\right)_{\text{part}} = 2.11 \quad (10.311)$$

By applying Caine's equation:

$$X = 2.11 \rightarrow Y = 0.10$$

Relation:

$$V_m/V_p = \pi \cdot ((20)^2/4) \cdot 30/6000 \cdot (2.54)^3 = 0.096 (\simeq 0.10) \quad (10.312)$$

Calculations seem correct (the riser is necked at the bottom to facilitate its removal by flogging or cutting from the casting; when items are very hard (550 BHN) as it is the case). Right riser to feed the part.

Feeding (Fig. 10.48):

$$\text{Sprue } \varnothing 40 \text{ mm} \rightarrow S = \pi \cdot d^2/4 \simeq 1257 \text{ mm}^2.$$

$$\text{Runner } 40 \times 40 \text{ mm} \rightarrow S = 1600 \text{ mm}^2.$$

$$\text{Gates } 2 \times 25 \times 122 \text{ mm} \rightarrow S = 6100 \text{ mm}^2.$$

Relation 1:1.27:4.85.

$$v = \sqrt{2 \cdot g \cdot h} = \sqrt{2 \cdot 981 \cdot 6} = 108.5 \text{ cm/s} \quad (10.313)$$

$$\text{Flow} = \frac{\pi \cdot 4^2}{4} \cdot 108.5 \text{ cm/s} = 1363.4 \text{ cm}^3/\text{s} \quad (10.314)$$

$$t_{\text{filling}} = \frac{6000 \cdot (2.54)^3}{1363.4} = 72 \text{ s} (\simeq 1.2 \text{ min}) \quad (10.315)$$

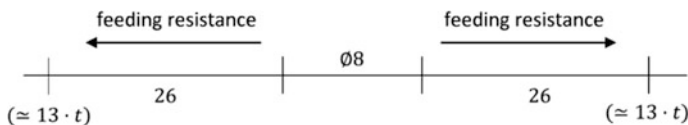


Fig. 10.48 Feeding distances

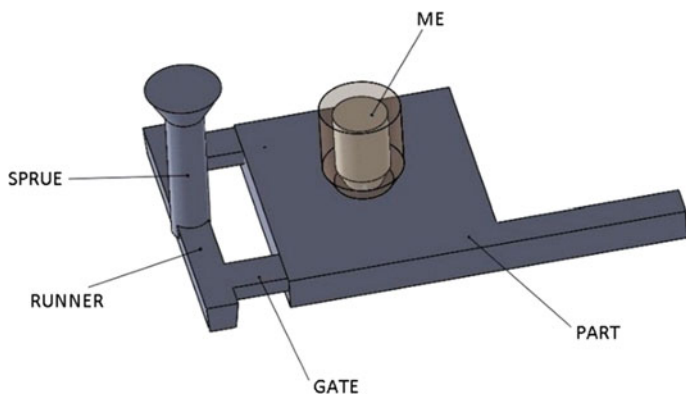


Fig. 10.49 CAM-CAD model of the flat sheet (Fundyser S. A.)

Case 2: part with appendix (Fig. 10.49):

Data:

Part: $15 \times 13 \times 2 + 11 \times 2 \times 2$ in.,

Riser: 3.4×4.5 in. ($H = 1.35 \cdot D$),

Sprue: $H = 9$ in.; $D = 3$ in.,

Runner: $2 \times 2 \times 15$ in. and

Gates: $2.4 \times 1 \times 5$ in.

$$V_{\text{riser}} = \pi \cdot 3.4^2 \cdot 4.5 / 4 = 40.9 \text{ in.}^3 \quad (10.316)$$

$$A_{\text{riser}} = \pi \cdot 3.4 \cdot 4.5 = 48.1 \text{ in.}^2 \quad (10.317)$$

$$\frac{V_{\text{riser}}}{A_{\text{riser}}} = 0.85 \text{ in.} \quad (10.318)$$

$$V_{\text{part}} = 434 \text{ in.}^3 \quad (10.319)$$

$$A_{\text{part}} = 556 \text{ in.}^2 \quad (10.320)$$

$$\frac{V_{\text{part}}}{A_{\text{part}}} = 0.78 \text{ in.} \quad (10.321)$$

$$X = \frac{\frac{V_{\text{riser}}}{A_{\text{riser}}}}{\frac{V_{\text{part}}}{A_{\text{part}}}} = 1.09 \quad (10.322)$$

By applying Caine's equation:

$$X = \frac{0.08}{Y - 0.04} + 0.8 \rightarrow Y = 0.32 > \frac{40.9}{434} = 0.09 \quad (10.323)$$

It would not be possible feeding the part only with the riser, it is necessary considering the sprue, runners and gates.

Sprue:

$$\pi \cdot 3^2 \cdot 9/4 = 63.6 \text{ in.}^3 \quad (10.324)$$

Runner:

$$2 \cdot 2 \cdot 15 = 60 \text{ in.}^3 \quad (10.325)$$

Gates:

$$2.4 \cdot 1 \cdot 5 \cdot 2 = 24 \text{ in.}^3 \quad (10.326)$$

$$\text{Total} = 147.6 \text{ in.}^3 \quad (10.327)$$

Total volume of the *riser* including the feeding system:

$$V_{\text{riser}} = 147.6 + 40.9 = 188.5 \text{ in.}^3 \quad (10.328)$$

$$Y = \frac{V_{\text{riser}}}{V_{\text{part}}} = \frac{188.5}{434} = 0.43 > 0.32 \quad (10.329)$$

We are on the side of the security.

The time required for feeding the part is

Sprue: 9 in. (*H*), 3 in. (*D*): $\pi \cdot D^2/4 = 7.07 \text{ in.}^2$ (cross section of the sprue).

Runners: $2 \cdot 2 = 4 \text{ in.}^2$ (cross section of the runners).

Gates: $2.4 \cdot 1 \cdot 2 = 4.8 \text{ in.}^2$ (cross section of the gates).

Relation of areas:

$$7.07:4:4.8$$

$$v = \sqrt{2 \cdot g \cdot h_{\text{sprue}}} = \sqrt{2 \cdot 32.2 \text{ ft/s}^2 \cdot 0.75 \text{ ft}} = 6.95 \text{ ft/s} = 83.4 \text{ in./s} \quad (10.330)$$

$$\text{flow (at the exit of the sprue)} = 83.4 \frac{\text{in.}}{\text{s}} \cdot 7.07 \text{ in.}^2 = 589.6 \text{ in.}^3/\text{s} \quad (10.331)$$

$$t_{\text{filling}} = \frac{V_{\text{part}}}{\text{flow}} = \frac{434}{589.6} = 0.7 \text{ s} \quad (10.332)$$

As in the other case, the riser is necked to facilitate its removal by impact.

Case study 2 and case study 3. Relationship structure–mechanical properties in camshafts and crankshafts manufactured in cast iron.

Introduction

Enclosed Figs. 10.50, 10.51 and 10.52 (adapted from Arias-Paz 1965) collect the elements of an engine with a single cylinder (cylinder, piston, admission and exhaust valves, spark plug, camshaft, crankshaft, flywheel, etc.). The crankshaft receives the impulse from explosions inside the cylinder, the impulse causes the rotation of the cylinder with the flywheel. The flywheel (in the engines with a single cylinder) causes the rotation of the crankshaft in the exhaust, admission and compression. The crankshaft must be strong, manufactured in a material resistant to fatigue (cyclic stresses) and properly balanced with the purpose of avoiding vibrations. For all the above mentioned, it is usually provided with the highest number of bearings as possible (if it is possible one at each two connecting rods). Selected materials are:

- Hardened and annealed steels: 0.3–0.5% C low alloyed with Ni, Cr, Mo. Structure of tempered martensite.

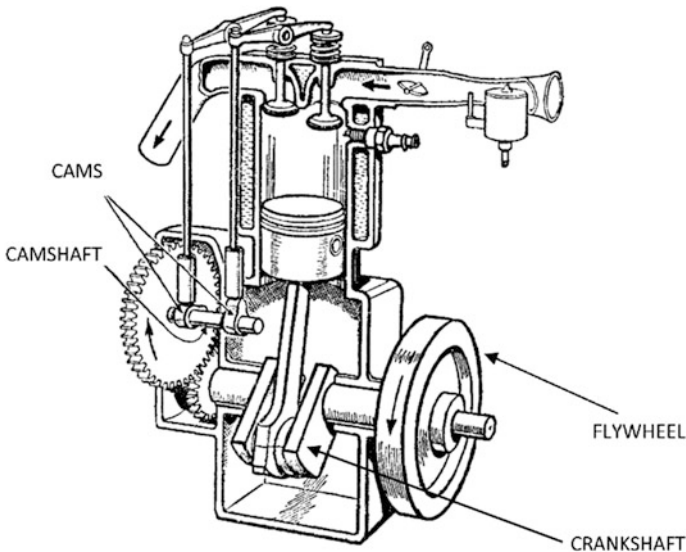
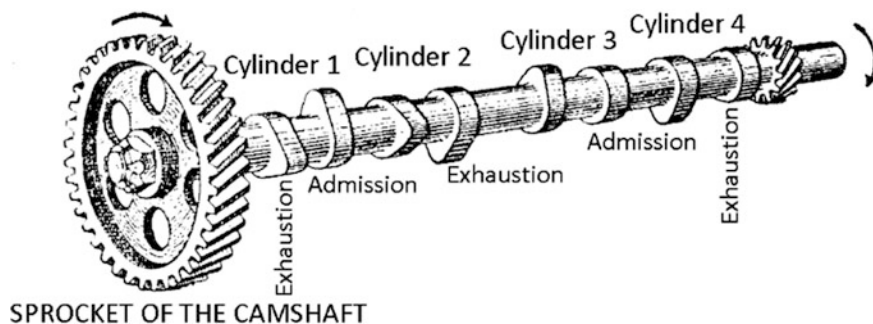
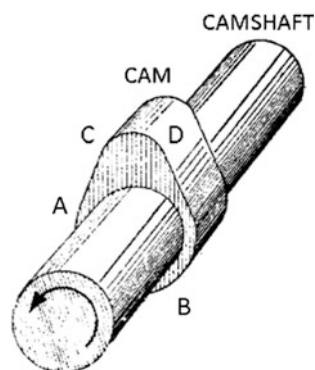


Fig. 10.50 Description of a single cylinder engine

**Fig. 10.51** Camshaft**Fig. 10.52** Scheme of a cam

- Forged steels, with continuous cooling: 0.4% C with surface treatment to achieve acceptable wear resistance and resistance to fatigue (induction hardening, nitridation).
- Ductile cast irons of spheroidal graphite manufactured in permanent mould. A surface hardening must be required.

Cams (camshaft, Figs. 10.51 and 10.52) are prominences of the camshaft, where they are placed, that lift the valves (of admission and exhaustion) from their sits when the prominence of the cam (C-D) moves the tappet. The valve is opened until the heel of the tappet rests in B (Fig. 10.52), when the valve is closed because of the action of its spring. The materials that are chosen for the manufacture of the camshaft are the grey irons of lamellar graphite in the nucleus, with white periphery with the objective of increasing the wear resistance, by friction with the tappets. They can be also manufactured with mottled cast iron as it is mentioned in the following case study.

Case study 2. Relation structure–mechanical properties of camshafts manufactured in cast iron.

In this case study, the structure–properties relationships of three camshafts are evaluated. They are used in cars and are called P, R and F, respectively.

Macrography of the parts (Figs. 10.53, 10.54 and 10.55):

Chemical analysis (Table 10.17):

Metallography of the shaft (Figs. 10.56, 10.57 and 10.58)

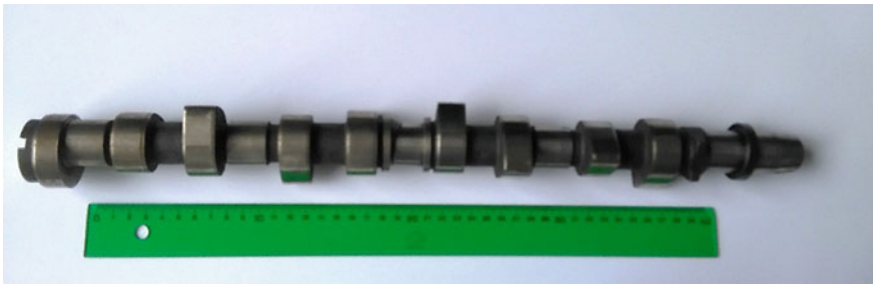


Fig. 10.53 Camshaft F

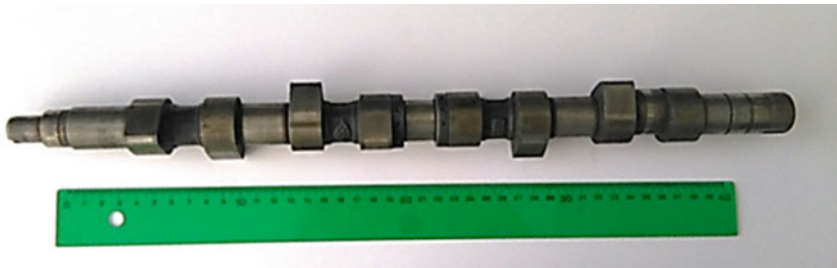


Fig. 10.54 Camshaft P



Fig. 10.55 Camshaft R

Table 10.17 Chemical analyses of the camshafts

Camshaft	TC (%)	Si (%)	Mn (%)	P (%)	S (%)	Cr (%)	EC (%)
F	3.72	2.31	0.84	0.02	0.034	0.82	4.5
P	3.36	1.71	1.02	0.078	0.216		3.96
R	3.59	2.04	1.05	0.109	0.218		4.31

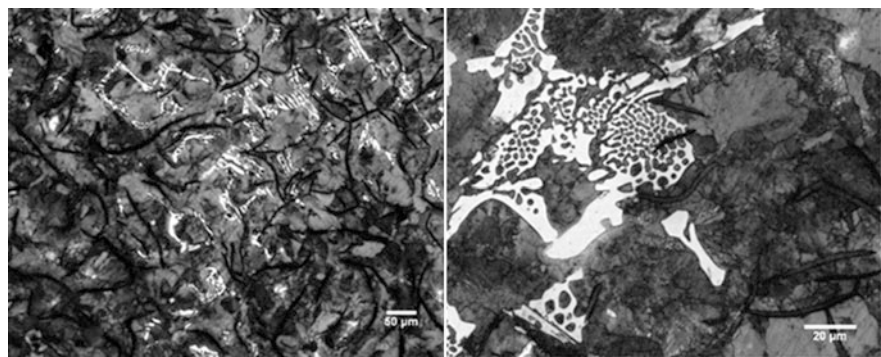


Fig. 10.56 Shaft F. Nital-2. Mottled cast iron

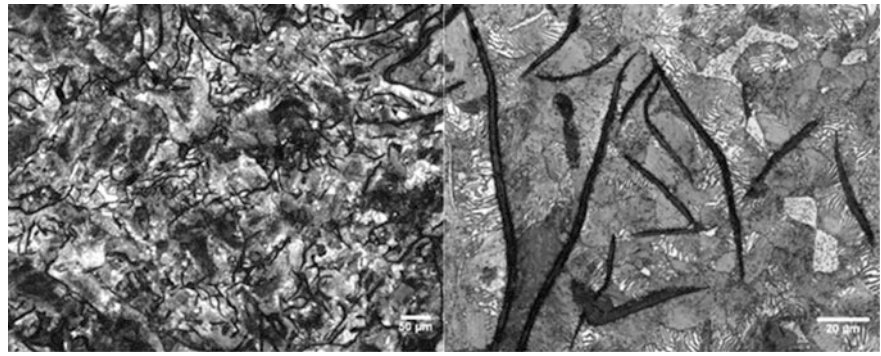


Fig. 10.57 Shaft P. Nital-2. Lamellar graphite cast iron

Mechanical properties:

1. Hardness test (shaft). Standard ASTM A 370-77 (Table 10.18).
2. Strain–stress test (shaft). Standard ASTM A 48-76 (Figs. 10.59 and 10.60; Table 10.19).

In all tests performed the reduction in area was lower than 1%.
Approximate calculation of the ultimate tensile strength for the shafts P and R (Winte’s equation):

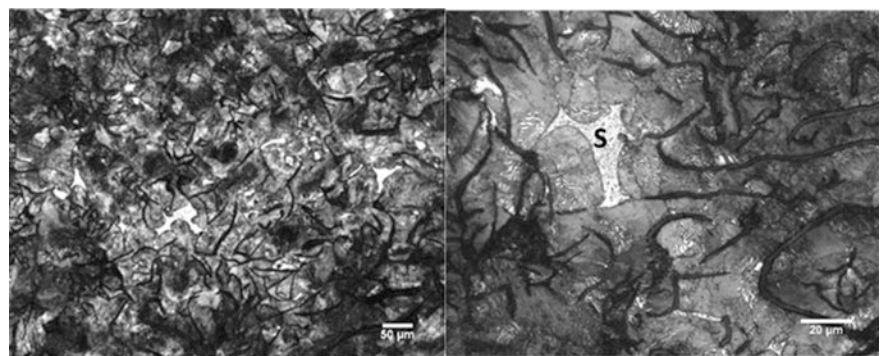


Fig. 10.58 Shaft R. Nital-2. Lamellar graphite cast iron. Areas of steadite

Table 10.18 Hardness of the shaft

Specimen shaft	HB
F	249 (24 HRC)
P	202 (93 HRB)
R	187 (90 HRB)



Fig. 10.59 Stress–strain specimens

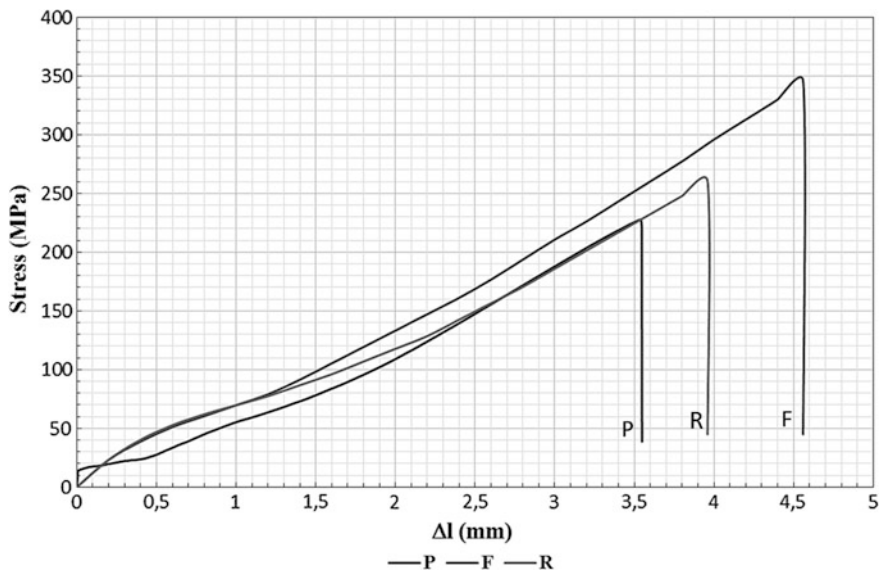


Fig. 10.60 Engineering stress–strain curves

Table 10.19 Ultimate tensile strength of the shafts

Specimen shaft	Ultimate tensile strength MPa (ksi)
F	345 (50.0)
P	228 (33.1)
R	260 (37.7)

$$\begin{aligned} R(\text{ksi}) &= 162.37 + 16.61/d(\text{in.}) - 21.78 \cdot (\% \text{C}) - 61.29 \cdot (\% \text{Si}) \\ &\quad + 14.16 \cdot (\% \text{Si})^2 \simeq 162.37 + 16.61/d(\text{in.}) - 54.03 \cdot (\% \text{Si}) \quad (10.333) \\ &\quad + 14.16 \cdot (\% \text{Si})^2 - 27.78 \cdot \text{EC}; (d \simeq 1 \text{ in.}) \end{aligned}$$

For the shaft *P*:

$$\begin{aligned} R &\simeq 162.37 + 16.61/d(\text{in.}) - 21.78 \cdot (3.36) \\ &\quad - 61.29 \cdot (1.71) + 14.16 \cdot (1.71)^2 \simeq 42.4 \text{ ksi (291 MPa)} \rightarrow \text{Class 40} \end{aligned} \quad (10.334)$$

For the shaft *R*:

$$\begin{aligned} R &\simeq 162.37 + 16.61/d(\text{in.}) - 21.78 \cdot (3.59) - 61.29 \cdot (2.04) \\ &\quad + 14.16 \cdot (2.04)^2 \simeq 34.7 \text{ ksi (238 MPa)} \rightarrow \text{Class 35} \end{aligned} \quad (10.335)$$

3. Microstructures of the cams (macrography, metallography) and hardness. ASTM A 367-78.

Cam F (Fig. 10.61):

Columnar structure, from periphery to nucleus. Mottled cast iron.

Metallography (Figs. 10.62 and 10.63):

Cam P (Fig. 10.64):

Metallography (Figs. 10.65 and 10.66):

Cam R (Fig. 10.67):

Metallography (Figs. 10.68 and 10.69):

Hardness profiles (Fig. 10.70):

Note 1: The hardness profile of the cam P is very similar to that shown in Fig. 3.4, with an evolution from periphery to the nucleus of white cast iron to grey cast iron.

Note 2: The camshafts P and R could be manufactured through *shell moulding* specially adapted to large productions. By this method, castings can be made with excellent finishing and good dimensional control. The mould in contact with the cams could be covered with zircon sand ($\text{ZrO}_2 \cdot \text{SiO}_2$) used as mouldable chill since it is able to extract heat from a casting somewhat more rapidly than silica sand.

The camshaft *F* could be manufactured in a *permanent mould casting* where higher production rates are obtained. The addition of chromium increases the chilling tendency.

Fig. 10.61 Macrography of the cam F



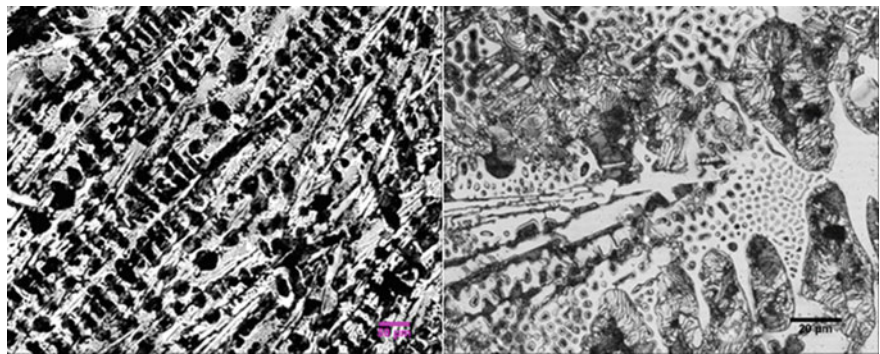


Fig. 10.62 Periphery. Nital-2. Structure of hypoeutectic white cast iron

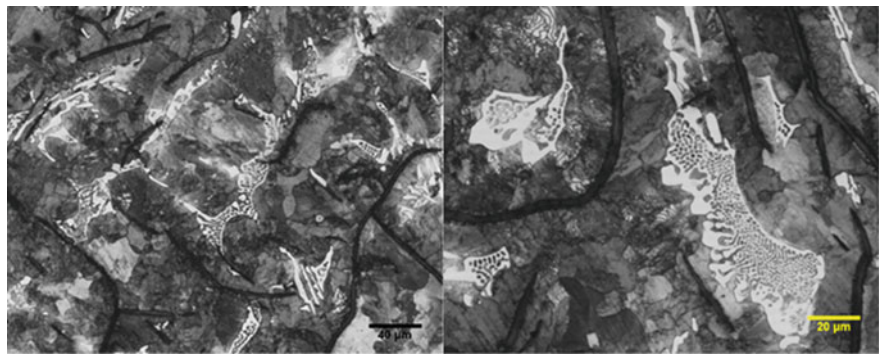


Fig. 10.63 Nucleus. Nital-2. Structure of mottled cast iron

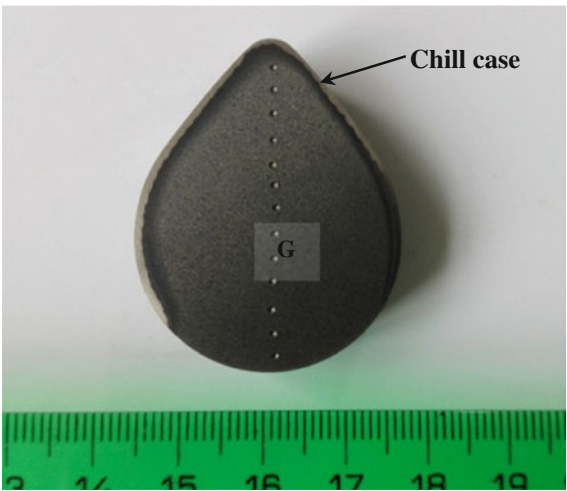


Fig. 10.64 Macrography of the cam P

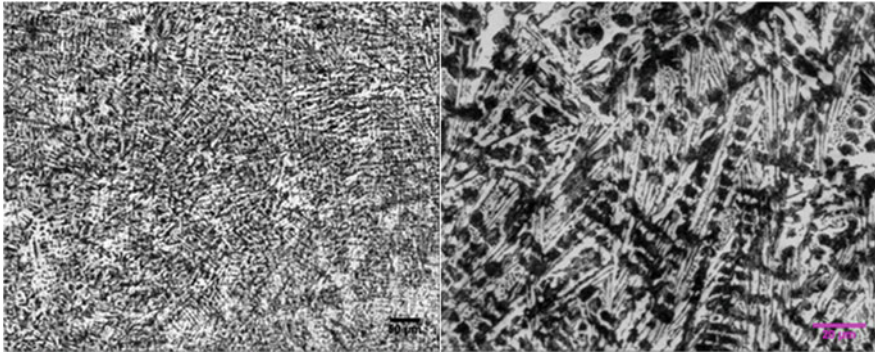


Fig. 10.65 Periphery. Etched with Nital-2. Structure of slightly hypoeutectic white cast iron

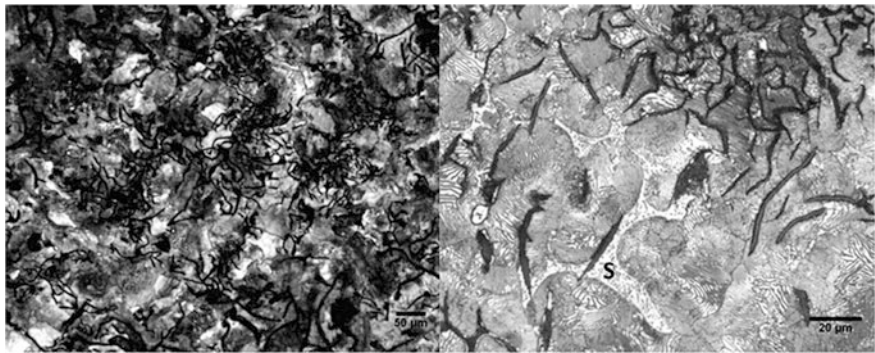


Fig. 10.66 Nucleus. Nital-2. Grey cast iron with pearlitic matrix (regions of steadite, S)

Case study 3. Relation structure–properties in crankshafts manufactured in forged steel and spheroidal cast iron.

Introduction

Crankshafts, as we have seen, have a complex shape, which does not impede their manufacture by moulding. Crankshafts have been traditionally manufactured in forged steel with the idea of keeping their functional integrity (Fig. 10.71). A few decades ago, crankshafts have begun to be manufactured by moulding, in spheroidal grey cast iron, for engines (Otto and Diesel) of small and medium sizes.

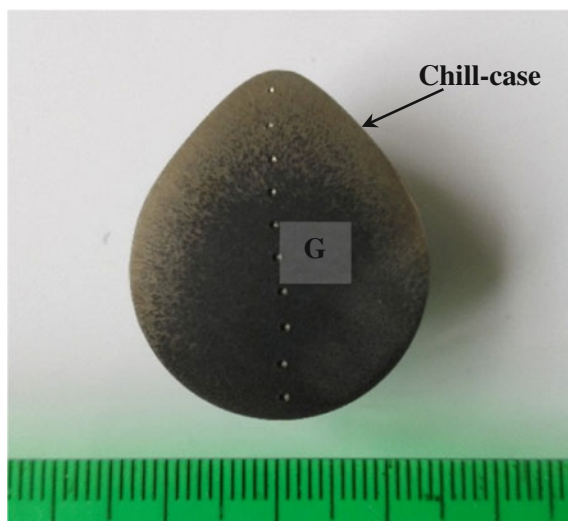


Fig. 10.67 Macrography of the cam R

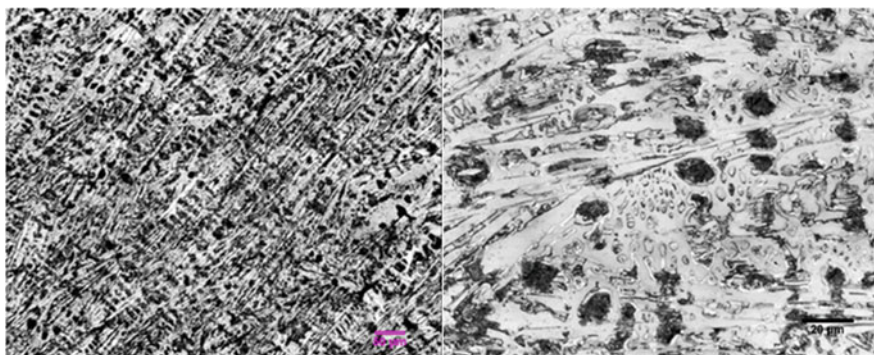


Fig. 10.68 Periphery. Etched with Nital-2. Structure of slightly hypoeutectic white cast iron

The work carried out by the crankshafts, subjected to torsion efforts of variable intensity, makes them vulnerable to fatigue failures. The manufacture and treatment depend on the requirements. Ductile iron crankshafts, for engines with capacities higher than 1000 cm^3 require a control, careful, of the microstructure and hardness. For instance, the microstructure should be necessarily pearlitic.

Crankshafts manufactured in forged steel are supplied, after forging, in normalizing or quenching–tempering state. The success of the spheroidal irons has limited today's use to engines used in demanding applications (competition

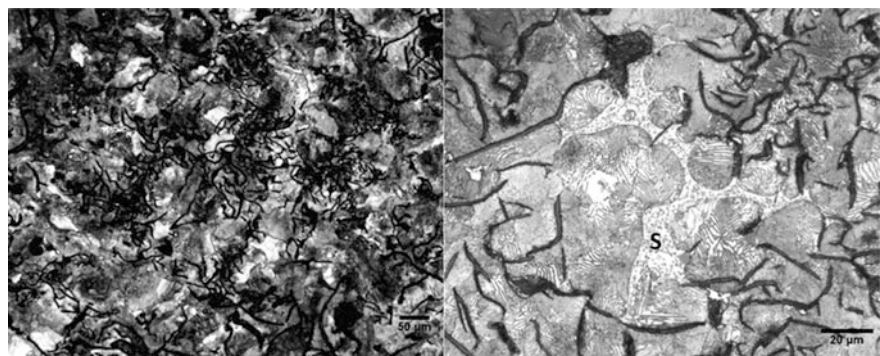


Fig. 10.69 Nucleus. Nital-2. Grey cast iron with pearlitic matrix (areas of steadite, S)

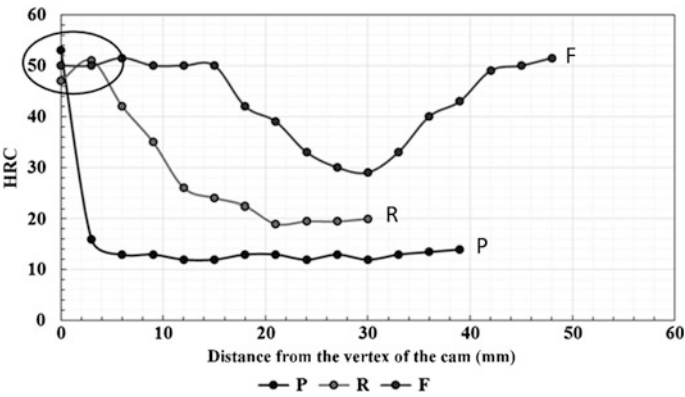


Fig. 10.70 Hardness profiles. 50 HRC $\simeq$ 480 HB (A 370)

automobiles): the crankshaft is obtained through machining and experience, after quenching and tempering, a surface treatment of nitriding with the purpose of increasing its resistance to fatigue. Steels usually contain 0.3–0.4% C, alloyed (low alloy) with Mn–Cr–Mo.

The maximum power of an engine (CV) is calculated by applying the equation: $P(\text{CV}) = C \text{ (kg m)} \cdot N \text{ (r.p.m.)} / 716$ (the reader could deduce it). The torque motor is calculated with the formula: $C = 2\pi\tau_{\text{max}}r_0^3/3$, τ_{max} : maximum shearing stress, r_0 : diameter of the part (the reader could deduce it). Thus, for a 100 CV engine, working between 3000 and 6000 rpm and $r_0 = 1.5$ cm, the maximum shearing stress varies according to the following equations:

$$C_1 = 100 \cdot 716/3000 \simeq 24 \text{ kg m} \rightarrow \tau_{\max} = 44 \text{ MPa} (\sigma_{\max}) \quad (10.336)$$

$$C_2 = 100 \cdot 716/6000 \simeq 12 \text{ kg m} \rightarrow \tau_{\max} = 22 \text{ MPa} (\sigma_{\min}) \quad (10.337)$$

Fluctuating stress, between 44 and 22 MPa must not originate fatigue and catastrophic failure.

Chemical analysis (Table 10.20):

Types of steel. Composition ranges:

The steel used in this crankshaft has the composition of the AISI-SAE 1035 (G10350 UNS) whose ranges of composition are mentioned in Table 10.21.

Types of cast iron. Composition ranges (Table 10.22):



Fig. 10.71 Macrography of a crankshaft (steel, upper; ductile iron, lower)

Table 10.20 Chemical analysis of the crankshaft

Crankshaft	C (%)	Si (%)	Mn (%)	P (%)	S (%)	Mg (%)	EC
Steel	0.36	0.31	0.74	0.012	0.018		
Cast iron	>4.23	1.85	0.71	0.019	0.026	0.10	>4.86

Table 10.21 Composition ranges for the steel

%C	%Si	%Mn	%P (max.)	%S (max.)
0.32–0.38		0.60–0.90	0.040	0.050

Table 10.22 Composition ranges for the cast iron

T. C.	%Si	%Mn	%P (max.)	%S (max.)	%Ce (option)	%Mg
3.60–3.80	1.80–2.80	0.15–1.0	0.030	0.020	0.005–0.20	0.03–0.06

Calculation of the residual magnesium:

$$Mg_{\text{added}} = 0.75 \cdot S_{\text{cast iron}} + Mg_{\text{residual}}/\eta \tag{10.338}$$

When $\eta = 1$:

$$0.1 - 0.026 \cdot 0.75 \rightarrow Mg_{\text{residual}} = 0.08 \tag{10.339}$$

Optical metallurgy of the steel crankshaft (Fig. 10.72):

Ferritic–pearlitic structure in the crankshaft manufactured in steel. Ferritic matrix. Pearlite as disperse constituent. The austenitic grain size was determined by using some micrographs, being the average intersected length, $\bar{L}_3 = 0.039 \text{ mm}$ ($39 \mu\text{m}$), standard deviation $\sigma = 0.0028 \text{ mm}$ ($\simeq 3 \mu\text{m}$), equivalent to a grain size of 6 ASTM. The steel was hot forged at temperatures of around $1000 \text{ }^\circ\text{C}$.

It can be demonstrated that a nitriding treatment performed at $500 \text{ }^\circ\text{C}$ for one hour provides a nitride layer of approximate $10 \mu\text{m}$, as is the case (Fig. 10.73) (see *Solidification and Solid-State Transformations of Metal and Alloys*, Pero-Sanz et al. Elsevier (2017)).

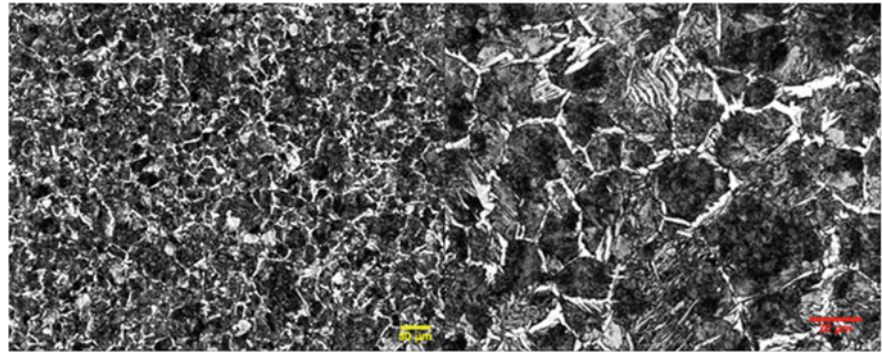


Fig. 10.72 Steel. Nital-2

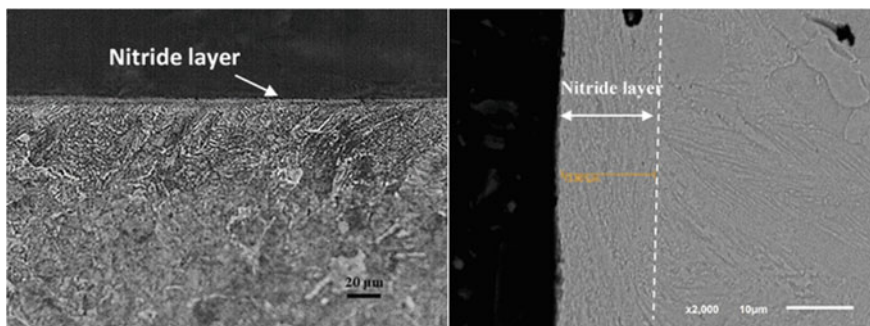


Fig. 10.73 Forged steel. Nitride layer. Nital-2. 46 HRC surface hardness

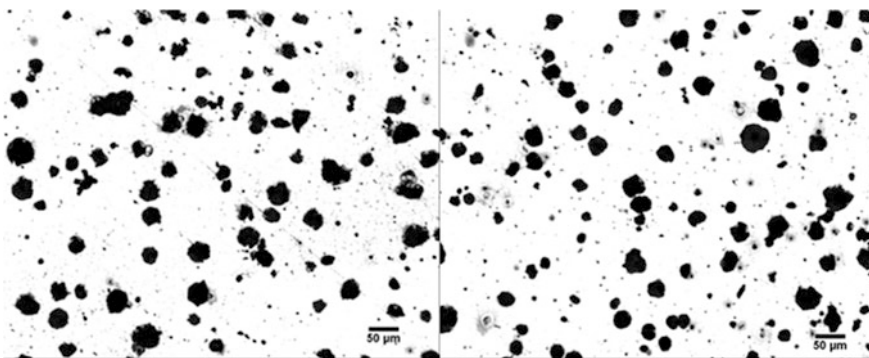


Fig. 10.74 Cast iron. Polished state

Metallography of the crankshaft manufactured in cast iron (polished state) (Fig. 10.74).

Spheroidal graphite over polished specimen. By comparison with micrographs at $100\times$ similar to standard cards of the Metallgesellschaft AG, the approximate values obtained by image analysis were: **nodules**/ $\text{mm}^2 \simeq 200$ nodules, **size** $\simeq 25\ \mu\text{m}$ and **fraction of area**, $f_A \simeq 9.5\%$, which is adapted to the enclosed standard card. (Fig. 10.75)

Class and degree of nodularity ASTM-A247 (Figs. 10.76 and 10.77).

It is adapted to a Class 6 with a degree of nodularity of the 90%, approximately.

Metallography of the crankshaft manufactured in cast iron (etched with Nital-2): (Fig. 10.78).

It is a ductile iron in as-moulded state, with direct ferritizing between the eutectic and eutectoid temperatures. The structure (matrix constituent) is ferritic–pearlitic (*bull's eye* ductile iron as American denomination).

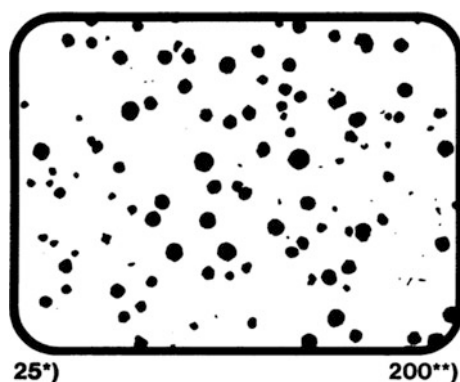
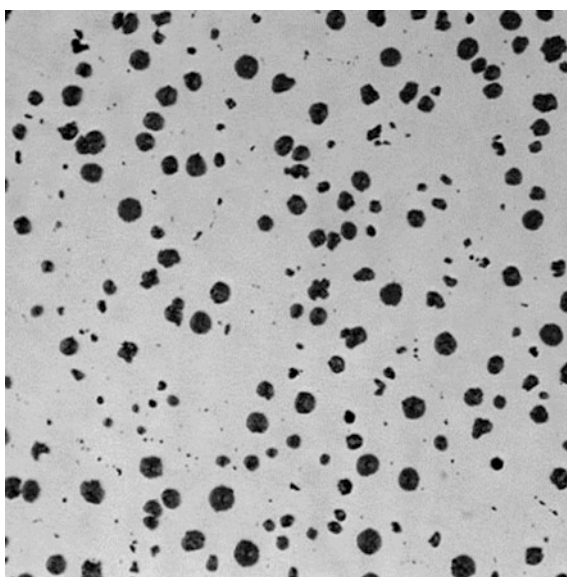


Fig. 10.75 Nodules/mm² $\simeq$ 200 nodules, size $\simeq$ 25 μ m

Fig. 10.76 Class 6 (ASTM A247)



Fraction of ferrite:

Spheroidal cast iron with ferritic–pearlitic matrix. The fraction of ferrite, by comparison with the standard cards of the Metallgesellschaft AG enclosed, is between 30 and 45% ferrite in the interval (Fig. 10.79).

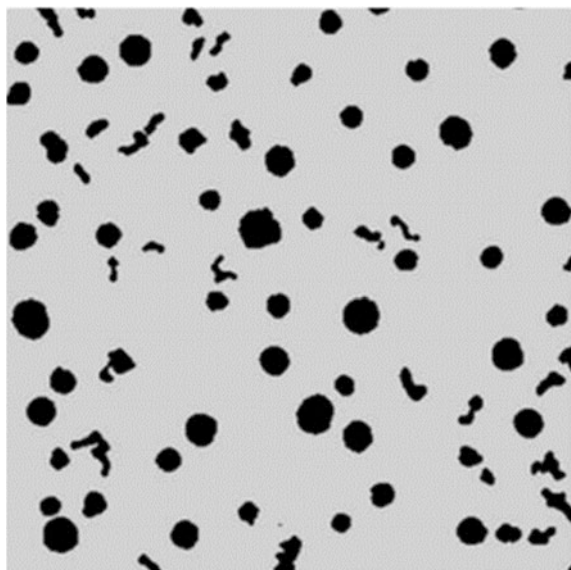


Fig. 10.77 Nodularity 90% (ASTM A247)

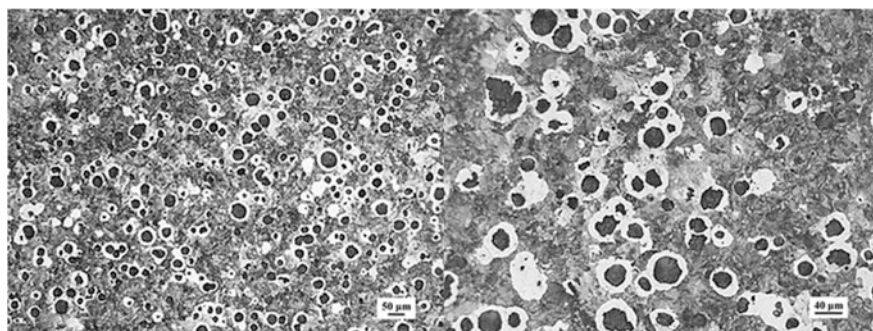


Fig. 10.78 Cast iron. Nital-2

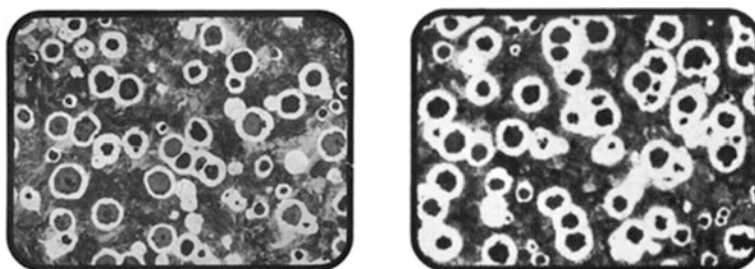


Fig. 10.79 Standard cards for 30% (left) and 45% (right) of ferrite

Mechanical properties:

1. Hardness test. ASTM A 370-77 standard (Table 10.23):

$$P = 187.5 \text{ kg}, d = 2.5 \text{ mm}$$

The steel crankshaft has been subjected to a superficial treatment with chemical modification (nitriding), which provide a hardness higher than 45 HRC (see metallography of the crankshaft manufactured in forged steel) (Table 10.24).

2. Tensile test ASTM A48-76 standard (Figs. 10.80, 10.81 and 10.82; Table 10.25):

A ductile iron of degree 100-40-15 can be deduced.

In tests performed in specimens of ductile iron, the reduction in area is lower than the 1%. In the case of specimens of forged steel, the value of the reduction of area is of the 55%.

Table 10.23 Hardness of the crankshaft

Specimen	HB
Forged steel	234
Ductile iron	224

Table 10.24 Hardness values

HR 15 N	HR 30 N
85	65
83	63
86	64
85 (49 HRC-ASTM E140)	64 (45 HRC-ASTM E140)

Fig. 10.80 Tensile test forged steel specimens (FS)





Fig. 10.81 Tensile test ductile iron specimens (DI)

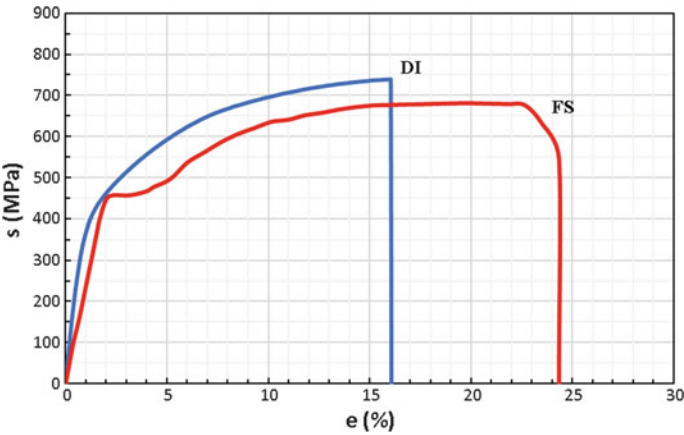


Fig. 10.82 Engineering stress–strain curves for the forged steel (FS) and ductile iron (DI)

Table 10.25 Results from the analysis of the strain–stress curve

Specimen	Yield strength MPa (ksi)	Ultimate tensile strength MPa (ksi)	Elongation ($L_0 = 5d$)
Forged steel	486 (71)	700 (102)	24.8
Ductile iron	300 (44)	747 (109)	15.0

3. Fractography of the ductile iron (tensile test):

The fracture is originated, invariably, by cleavage, from a peripheric zone densely nodulized (more density and size of the graphite) (Figs. 10.83, 10.84, 10.85 and 10.86).

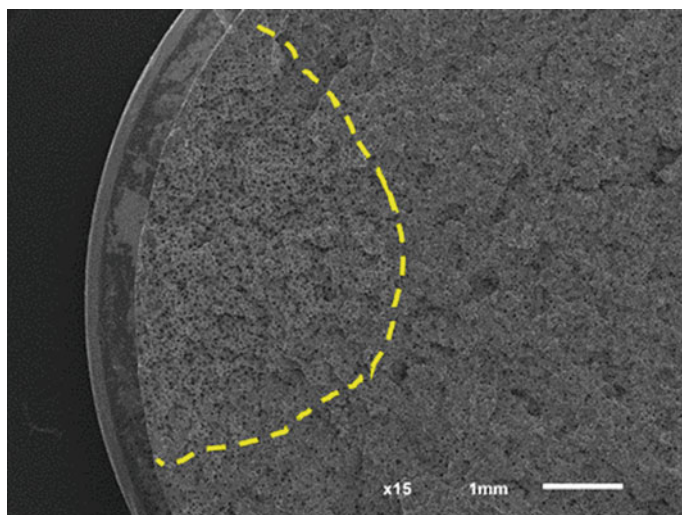


Fig. 10.83 Fracture surface (peripheric concentration of graphite)

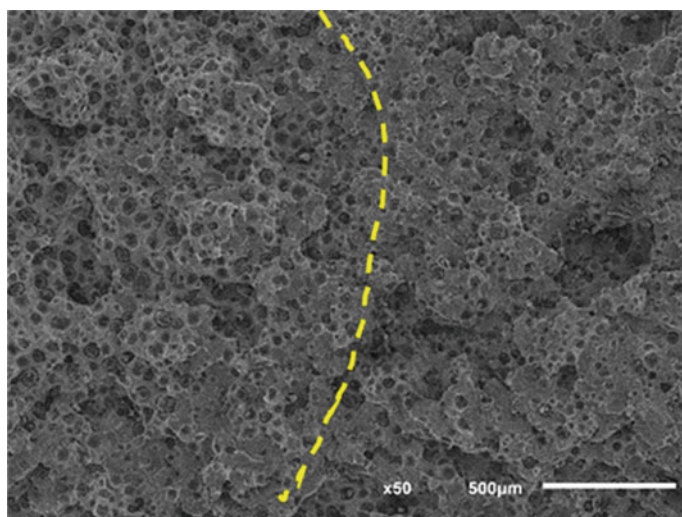


Fig. 10.84 Transition between the zone of peripheric concentration of graphite and the interior zones of fracture

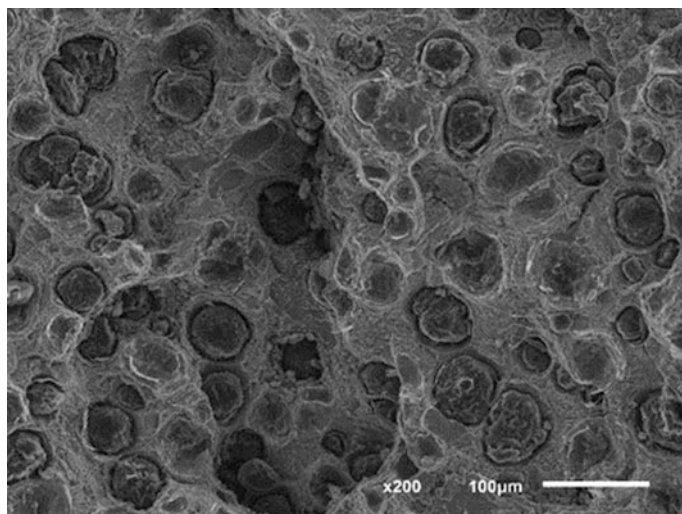


Fig. 10.85 Peripheral concentration of graphite

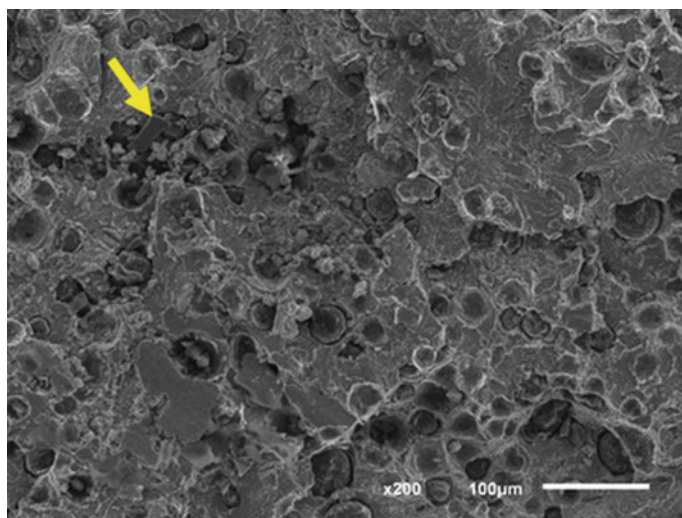


Fig. 10.86 Final zone of fracture. Detail: zone with presence of inclusions (arrow)

EDAX (X-ray dispersive energy) analysis shows inclusions, indicated with arrows, oxides and SiC, as it is demonstrated in the following figures (zones 1 and 3). The zone 2 corresponds with a non-spheroidal graphite particle: the nodulization is not perfect (Fig. 10.87; Table 10.26).

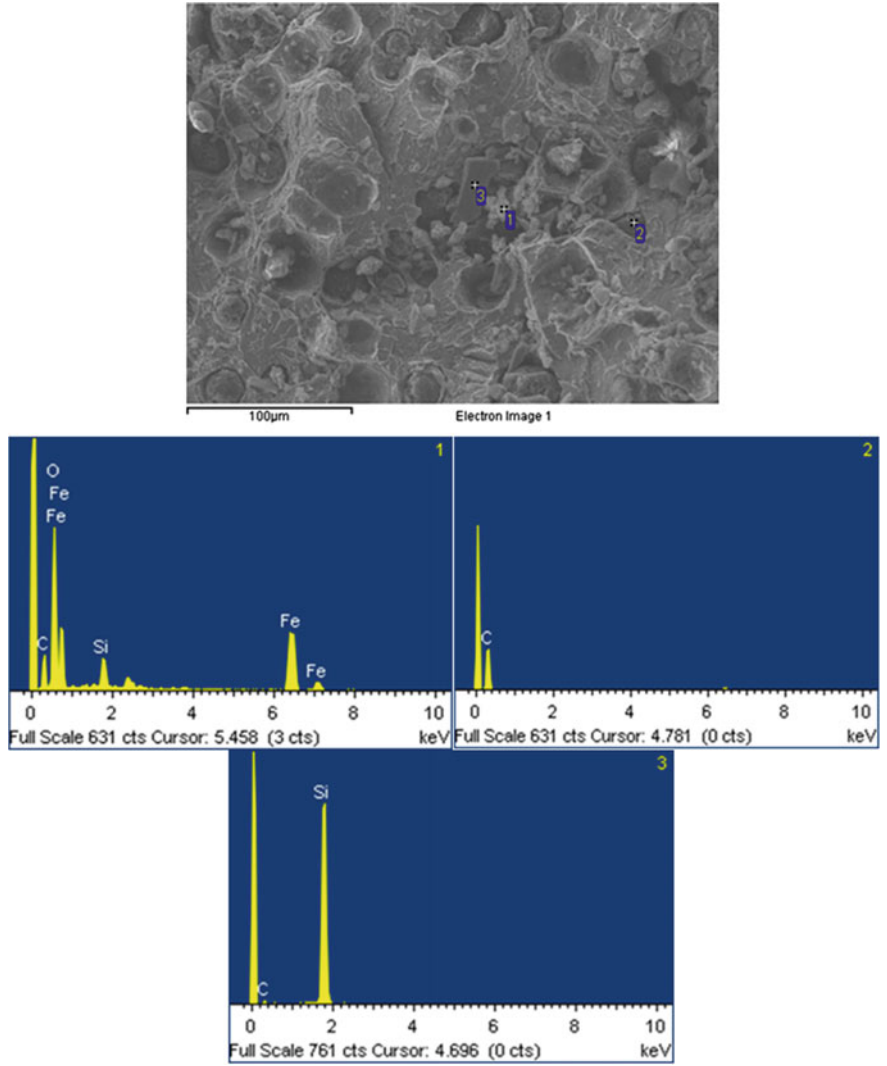


Fig. 10.87 EDAX analysis images. Result of the EDAX analysis: profile 1 (iron oxide), profile 2 (graphite) and profile 3 (SiC)

Table 10.26 Point analysis from EDAX

Elements profile	%C	%O	%Si	%Fe	Total
1	20.45	47.39	3.04	29.13	100.00
2	100.00				100.00
3	37.77		62.23		100.00

4. Resilience test:

Resilience tests were carried out with a Hounsfield hammer. This hammer, as opposite to the typical ones (Charpy and Izod), is light and compact: the mobile weight is divided into two weights that move in opposite directions, being located the specimen in the centre of percussion of the two hammers. All the device can be fixed with screws to any table, being not necessarily a big and permanent table as for the hammers previously mentioned.

The weight in the percussion centre of each hammer is of 12 lb (5.443 kg), falling the hammers from a height of 2 ft (0.609 m), which generates a potential energy of 48 ft lb. (6.629 kg m), being the relative falling speed of 22.7 ft/s (6.91 m/s)*. The results obtained with the Hounsfield hammer (Fig. 10.88; Table 10.27), multiplied by 2.4 are approximately equivalent to the Izod resilience.

*Specimens are cylinders 55 mm in length and 5 mm in diameter, machined from the crankshaft centres.



Fig. 10.88 Broken resilience specimens

Table 10.27 Resilience results

Specimen	Hounsfield (lb ft)	Izod (lb ft)	CVN (KCV) (lb ft)
Forged steel	36.5	87.6	110.0
Ductile iron	3.0	7.2	17.5

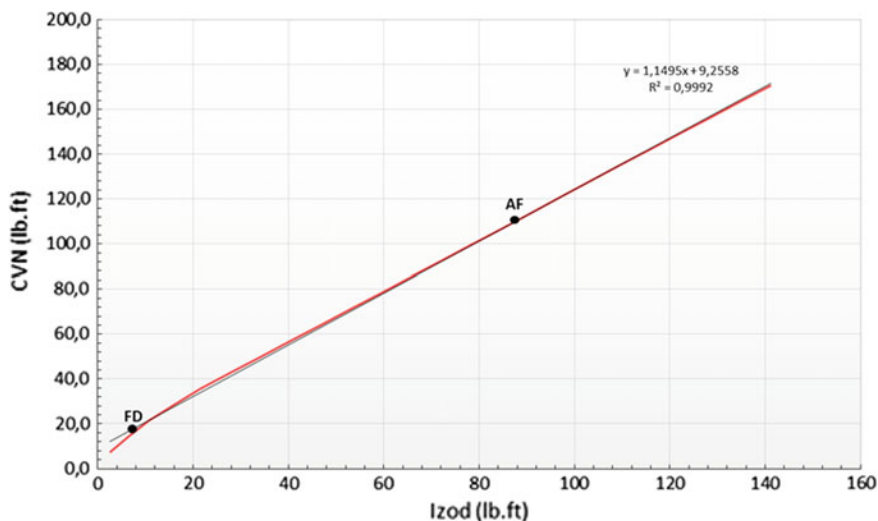


Fig. 10.89 Equivalence Izod-Charpy V notch. Values of resilience for the ductile iron (FD or DI) and forged steel (AF or FS)

The equivalence between Izod and CVN (Charpy V Notch) tests performed from data of the EURONORM 10-55 is represented in Fig. 10.89 expressed in lb ft, as well as the values of resilience obtained for the ductile iron (FD or DI = 7.2 lb ft Izod, equivalent to a 17.5 lb ft CVN) and the forged steel (AF or FS = 87.6 lb ft Izod, equivalent to a 110 lb ft CVN). The resilience of the steel is clearly higher to that one of the ductile iron, according to the obtained results.

5. Fractography of the crankshafts (resilience tests):

SEM observations are carried out from the surface surfaces both for the forged steel and for the ductile iron crankshafts. The facies presented for the steel is of ductile fracture (dimples, D) in the beginning of the crack (final notch), with circumferential propagation along the periphery of the specimen. The final fracture is predominantly brittle (cleavage, C), although ductile zones in the boundaries of ferritic grains (matrix constituent of this hypoeutectoid steel) are observed (Figs. 10.90, 10.91, 10.92, 10.93 and 10.94).

As opposed to the crankshaft manufactured in steel, the fracture through resilience in specimens of ductile iron is totally brittle (cleavage) but being observed cross plastic deformation in fracture (Figs. 10.95, 10.96, 10.97 and 10.98).

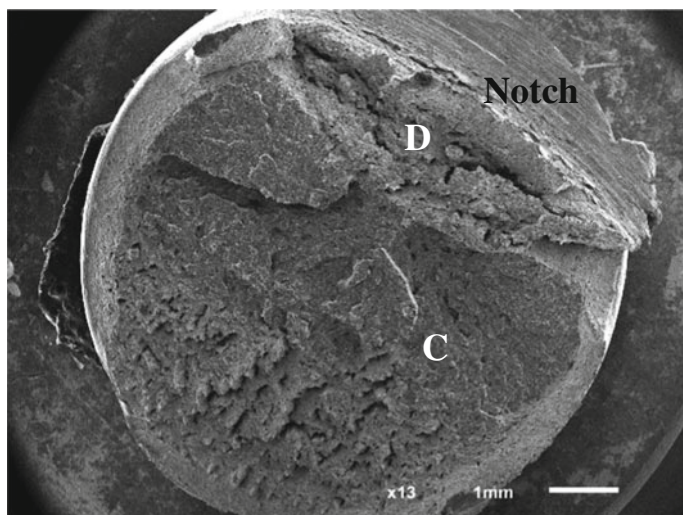


Fig. 10.90 Resilience specimen for a crankshaft manufactured in forged steel

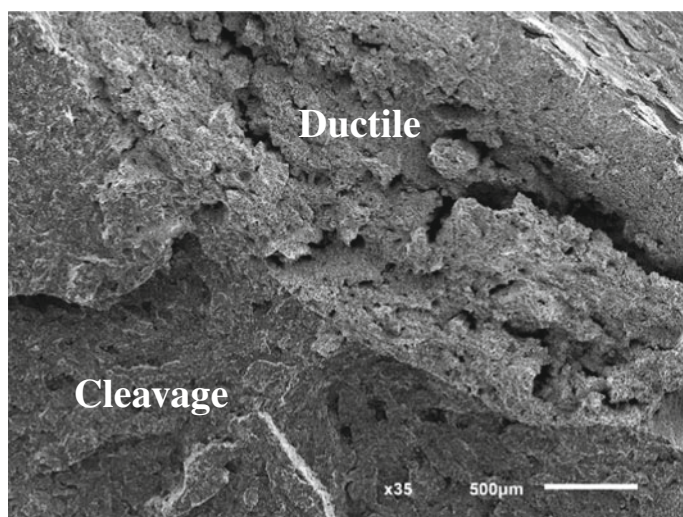


Fig. 10.91 Ductile–brittle transition zones near to the notch

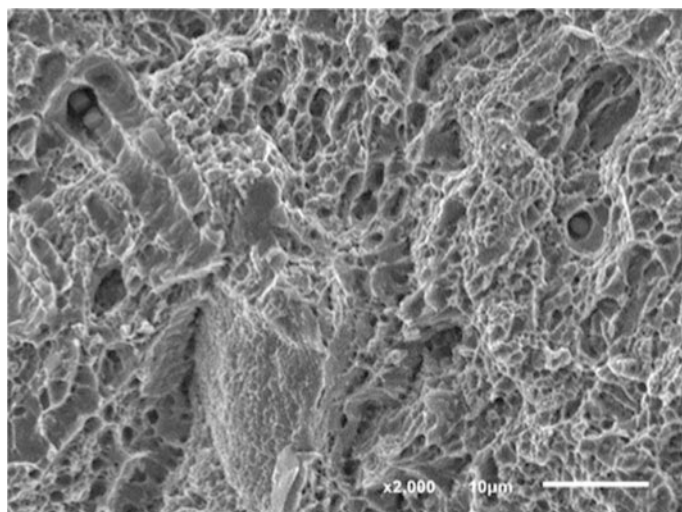


Fig. 10.92 Ductile fracture (dimples) in the zone near to the notch

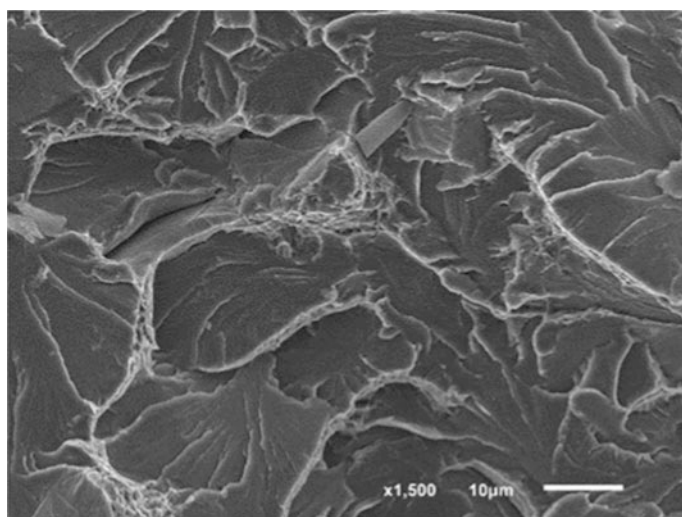


Fig. 10.93 Brittle fracture (cleavage) in the final zone of fracture

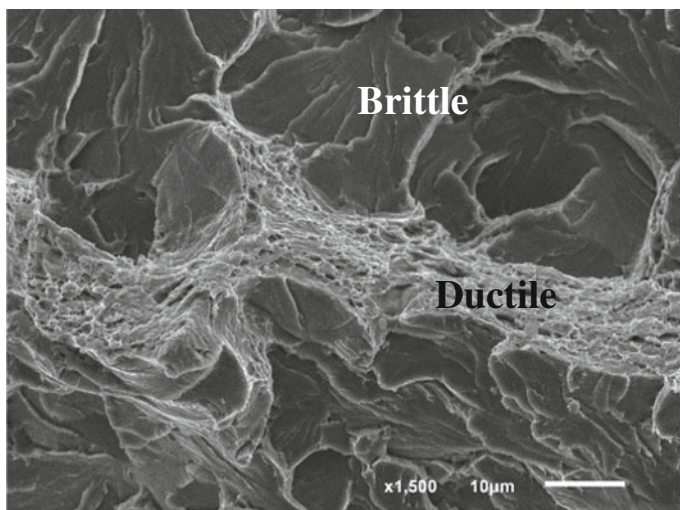


Fig. 10.94 Final zone of fracture. Surface of ductile fracture in the ferrite (matrix constituent). Brittle fracture in the pearlite (disperse constituent)

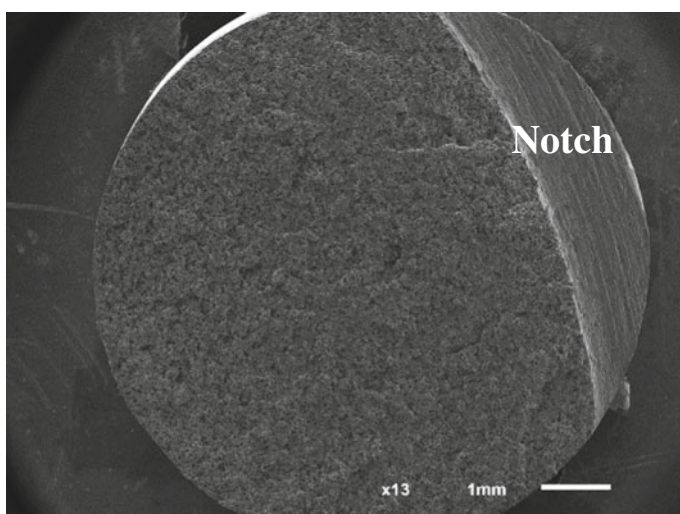


Fig. 10.95 Resilience specimen of the crankshaft manufactured in cast iron. Plastic deformation in the fracture is not observed

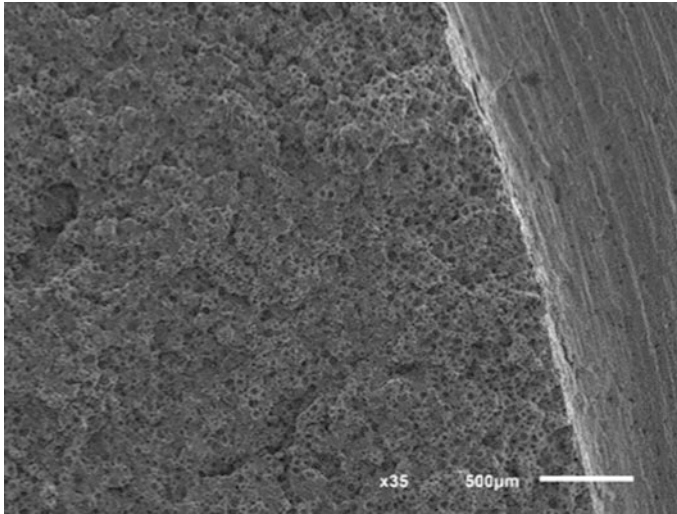


Fig. 10.96 Zone of notch background. Ductile fracture is not observed (dimples)

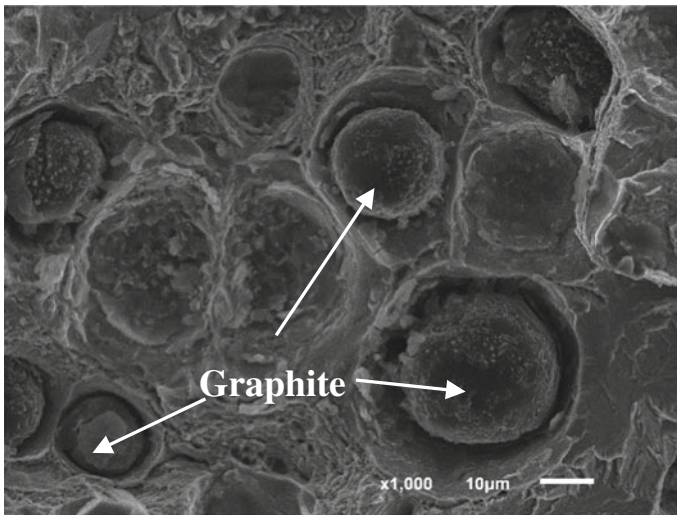


Fig. 10.97 Brittle fracture (cleavage) in the resilience specimen. Decohesion between graphite nodules and matrix

From the equation proposed by Rolf and Novak:

$$\left(\frac{K_{IC}}{\sigma_y}\right)^2 = 5\left(\frac{CVN}{\sigma_y} - 0.05\right) \quad (10.338)$$

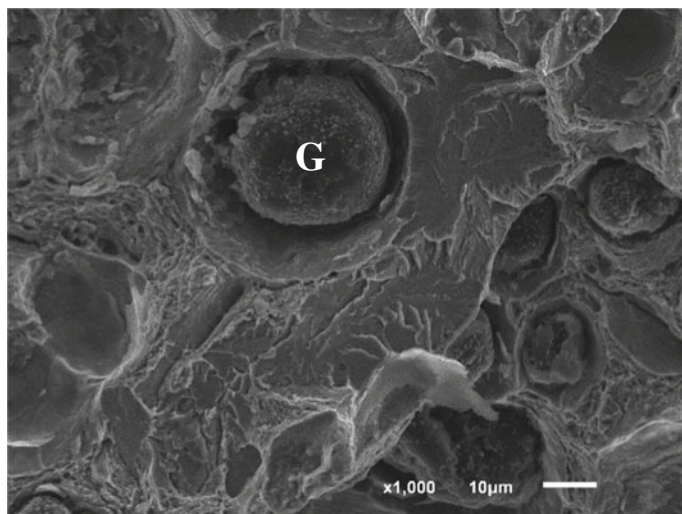


Fig. 10.98 Detail of the decohesion graphite matrix observed in a resilience specimen

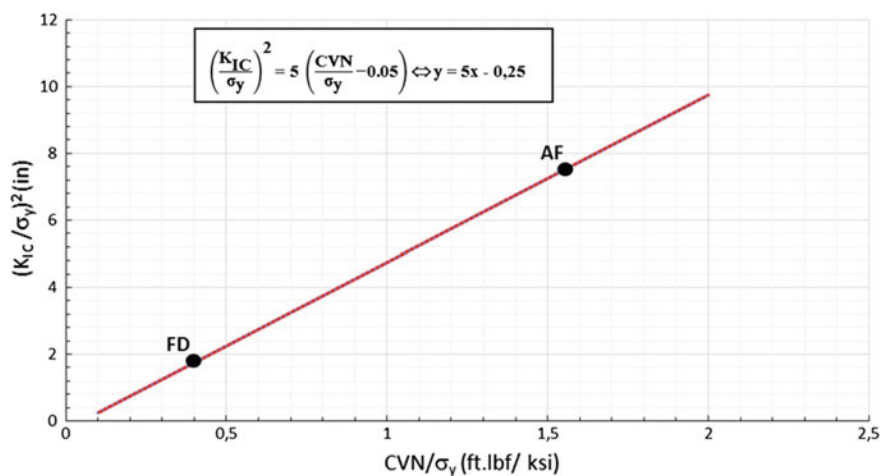


Fig. 10.99 Fracture toughness facing to Charpy V notch

The fracture toughness for the steel (AF) and the ductile iron (FD) were calculated (Fig. 10.99).

A value of fracture toughness K_{IC} of $194 \text{ ksi}\sqrt{\text{in.}}$ ($212 \text{ MPa}\sqrt{\text{m}}$) for the forged steel and $58 \text{ ksi}\sqrt{\text{in.}}$ ($63.5 \text{ MPa}\sqrt{\text{m}}$) for the ductile iron were obtained, which corroborates the obtained results in the resilience tests. The toughness of the steel is three times higher than that of the cast iron.

6. Conclusions:

The steel crankshafts can be manufactured in carbon steels, as is the case, forged and nitrided or from alloyed steels, as quenched and tempered and nitrided. The success of the ductile iron in the manufacture of crankshafts is, fundamentally, economic and is limited to vehicles of small or medium power. Forged steel crankshafts are used in high power vehicles or in extreme working conditions. For instance, the steel 722M24HT (BS 970) 0.24% C–3% Cr–0.5% Mo, quenched and tempered and nitrided, can be used in competition vehicles.

Fundamentals of the Cupola Furnace: Applications—Mass and Energy Balances

11

Abstract

This chapter describes the process of cast irons production in cupola furnace, main type of furnace used in the production of this engineering material. Different solved problems about mass and energy balances will help the reader in the understanding of the cast irons production. The importance of raw materials is also considered in this chapter, as optimization problems in the utilization of the raw materials are presented. Solved problems regarding the desulphurization and dephosphorization are also included.

11.1 Cast Iron Production in Cupola Furnace

A cupola furnace is a small blast furnace, approximately one order of magnitude smaller. It is used in the manufacture of cast irons and exceptionally used in the reduction of ores. The charge usually comprises pig iron, steel scraps and small amounts of fluxes (limestone) and coke. In the cupola, the charge does not experience reduction, on the contrary, the charge is oxidized and part of the silicon (in the form of SiO_2), manganese (in the form of MnO) and iron (in the form of FeO) pass to the slag. The coke with the injected air forms CO and CO_2 . Part of the coke can pass to the charge (recarburation). The cupola consumes less coke than the blast furnace and the proportion of CO_2 in the gases is usually higher than that of CO . As opposed to the blast furnace, the cupola furnace works intermittently depending on the requirements, when the moulds for the casting of the cast iron are ready. The following introductory exercise is solved (Fig. 11.1).

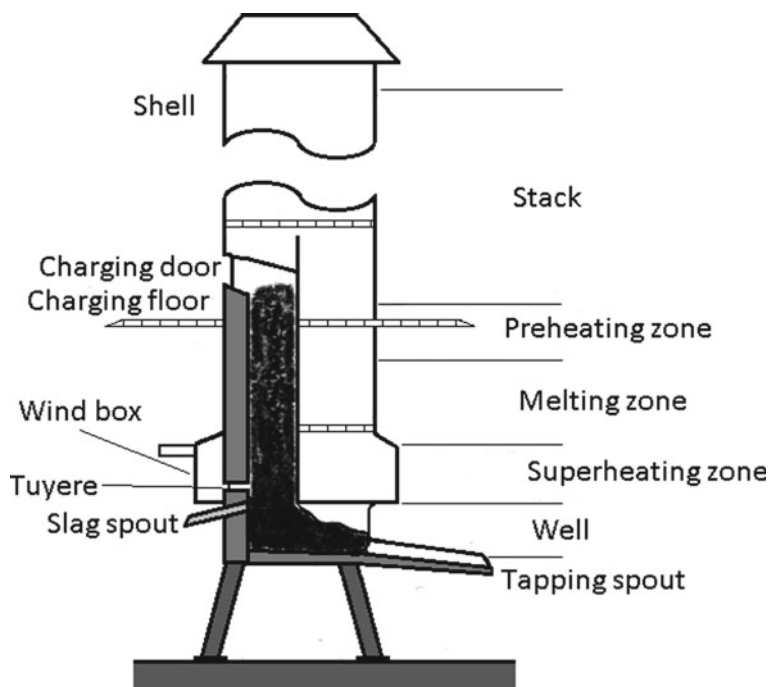


Fig. 11.1 Cupola furnace

Exercise 11.1. An iron ore is reduced in a shaft furnace (cupola furnace) in accordance with the following reaction:



The necessary carbon monoxide is obtained through the combustion of coke at the bottom of the furnace. The coke contains 90% C, of which 4% is absorbed by the reduced iron and 86% is burned to CO, no CO being formed in the combustion.

Required:

1. The volume of CO necessary to reduce 1 metric tonne of iron as required by the equation.
2. The theoretical weight of coke required in reducing 1 metric tonne of iron.
3. The volume of air used in burning this amount of coke.
4. The volume and percentage composition of the gases formed in the combustion.

5. The volume and percentage composition of the gases resulting from the combustion plus the reduction reaction.
6. The volume of air used per tonne of coke, measured at 600 °C and 1800 mm Hg total pressure.

Question

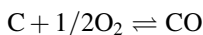
1. The volume of CO necessary to reduce 1 metric tonne of iron is calculated as follows:

$$\frac{9 \cdot 22.41 \text{ CO}}{112 \text{ g Fe}} \cdot \frac{10^6 \text{ g Fe}}{t \text{ Fe}} \cdot \frac{1 \text{ m}^3 \text{ CO}}{1000 \text{ l CO}} \simeq 1800 \text{ m}^3 \text{ CO} \quad (11.1)$$

2. The theoretical weight of coke required in reducing 1 metric tonne of iron is:

$$\frac{9 \cdot 12 \text{ g C}}{112 \text{ g Fe}} \cdot \frac{10^3 \text{ g Fe}}{1 \text{ kg Fe}} \cdot \frac{1 \text{ kg coke}}{0.86 \text{ kg C}} = 1121 \text{ kg coke} \quad (11.2)$$

3. The amount of air used in burning the coke is:



$$\frac{11.21 \text{ O}_2}{\text{mol C}} \cdot \frac{1121 \cdot 0.86 \cdot 10^3 \text{ g C}}{12 \text{ g C/mol}} \cdot \frac{1 \text{ m}^3}{1000 \text{ l}} \cdot \frac{100 \text{ m}^3 \text{ air}}{21 \text{ m}^3 \text{ O}_2} \simeq 4284 \text{ m}^3 \text{ air} \quad (11.3)$$

4. The percentage composition of the gases formed in the combustion is:

$$4284 \text{ m}^3 \text{ air} \cdot \frac{79 \text{ m}^3 \text{ N}_2}{100 \text{ m}^3 \text{ air}} = 3384 \text{ m}^3 \text{ N}_2 \quad (11.4)$$

$$\begin{aligned} &1800 \text{ m}^3 \text{ CO} \\ &65.3\% \text{ N}_2 - 34.7\% \text{ CO} \end{aligned}$$

5. Volume and percentage composition of the gases resulting from the combustion and reduction reactions:

$\text{N}_2 = 3384 \text{ m}^3$; $1800 \text{ m}^3 \text{ CO}$ generate (see general equation)

$$\begin{aligned} 3 \cdot 1800 \text{ m}^3 / 9 &= 600 \text{ m}^3 \text{ CO}_2; 6 \cdot 1800 \text{ m}^3 / 9 = 1200 \text{ m}^3 \text{ CO} \\ &\rightarrow 23\% \text{ CO} - 11.5\% \text{ CO}_2 - 65.5\% \text{ N}_2 \text{ (flue gases)} \end{aligned}$$

6. The volume of air used per tonne of coke if it is injected at 600 °C and 1800 mm Hg total pressure:

$$\text{no. of air mol} : 4284 \text{ m}^3 \cdot \frac{10001}{\text{m}^3} \cdot \frac{1 \text{ mol}}{22.41} = 191250 \text{ mol} \quad (11.5)$$

By applying the perfect gases law,

$$\begin{aligned} V &= 191250 \text{ mol} \cdot 0.082 \frac{\text{atm l}}{\text{mol K}} \cdot (600 + 273) \text{ K} \cdot \frac{1 \text{ m}^3}{10001} \cdot \frac{760 \text{ mm Hg/atm}}{1800 \text{ mm Hg}} \cdot \frac{90\% \text{ C}}{100 \text{ coke}} \\ &= 5200 \text{ m}^3 \text{ air/t cok} \end{aligned} \quad (11.6)$$

Exercise 11.2. Mass balance of a cupola furnace. Using the raw materials listed below, calculate a 100 kg cupola charge, which is used to produce metal of the following composition: 3.6% C, 0.8% Mn, 2.50% Si, max. 0.20% P, max. 0.13% S.

Raw materials compositions:

Pig iron: 4% C, 0.5% Mn, 1% Si, 0.04% P, 0.06% S

Scrap (steel punchings): 0.05% C, 0.1% Mn, 0.02% Si, 0.020% P, 0.020% S

FeMn: 80% Mn, 20% Fe

FeSi: 50% Si, 50% Fe

Assume that the majority of the carbon will come from the pig iron.

Question

$$x : \text{kg of pig iron} : 100 \cdot 3.6 = 4 \cdot x \rightarrow x = 90 \text{ kg of pig iron}$$

$$y : \text{kg of FeMn} : 80 \cdot y + 0.8 \cdot 90 = 100 \cdot 0.8 \rightarrow y = 0.1 \text{ kg of FeMn}$$

$$z : \text{kg of Si} : 50 \cdot z + 1 \cdot 90 = 100 \cdot 2.4 \rightarrow z = 3.2 \text{ kg of FeSi}$$

$$w : \text{kg of scrap} : 100 - 90 - 3.2 - 0.1 = 6.7 \text{ kg of scrap}$$

Adjustment (second approximation) in C, Mn and Si:

$$100 \cdot \% \text{ C} = 90 \cdot 4 + 6.7 \cdot 0.05 \rightarrow \% \text{ C} \simeq 3.6\%$$

$$100 \cdot \% \text{ Mn} = 90 \cdot 0.8 + 80 \cdot 0.1 + 6.7 \cdot 0.1 \rightarrow \% \text{ Mn} \simeq 0.81\%$$

$$100 \cdot \% \text{ Si} = 90 \cdot 1 + 50 \cdot 3.2 + 6.7 \cdot 0.02 \rightarrow \% \text{ Si} \simeq 2.50\%$$

S and P contents:

$$\begin{aligned}\%S \cdot 100 &= 90 \cdot 0.06 + 6.7 \cdot 0.02 \rightarrow \%S = 0.085\% < 0.13\% \\ \%P \cdot 100 &= 90 \cdot 0.04 + 6.7 \cdot 0.02 \rightarrow \%P = 0.037\% < 0.20\%\end{aligned}$$

Considering the price of the raw materials (pig iron, scrap, FeMn and FeSi), solve through linear programming (EXCEL), the optimal economic adjustment from the composition. Compare it with the previous one:

Data prices: pig iron (7 \$)/(100 kg); scrap (6 \$)/(100 kg); FeSi (33 \$)/(100 kg); FeMn (30 \$)/(100 kg).

Calling *a* (pig iron), *c* (scrap), *m* (manganese) and *s* (silicon), constraint equations are:

$$a + c + m + s = 100$$

(11.7)

$$4 \cdot a + 0.05 \cdot c = 360$$

(11.8)

$$1 \cdot a + 0.02 \cdot c + 50 \cdot s = 250$$

(11.9)

$$0.8 \cdot a + 80 \cdot m + 0.1 \cdot c = 80$$

(11.10)

$$0.04 \cdot a + 0.020 \cdot c < 20$$

(11.11)

$$0.06 \cdot a + 0.020 \cdot c < 13$$

(11.12)

The objective function to be minimized is:

$$P = 7 \cdot a + 6 \cdot c + 33 \cdot s + 30 \cdot m$$

(11.13)

NOTE: Consider that ferroalloys are expensive and can noticeably (it is not the case) influence in the price of the charge. Assume, for instance, that some residual carbon exists in the ferroalloys.

We use SOLVER from Excel to solve the problem. The following results were obtained (Table 11.1):

Table 11.1 Results of the optimization problem

Decision variables		Objective function	
A	89.9	P (\$/100 kg)	779
C	6.8		
S	3.2		
M	0.1		
Total	100		

Solutions are like those described at the beginning of the exercise.

Exercise 11.3. Application of the linear programming (method based on the simplex algorithm) to the calculation of the optimal charge (minimum cost) in a cupola furnace. The raw materials and their prices are the same as in the previous exercise. The metal produced has the following chemical composition: 3.00–3.30% C, 1.80–2.10% Si, 0.70–1.00% Mn, $P < 0.07\%$ and $S < 0.15\%$. 100 kg cupola charge.

Question

Slack variables: p , q and r

Artificial variables: u , v , w , x , y , z , α , β and γ

Carbon balance:

$$\frac{4.6}{100} \cdot a + \frac{0.02}{100} \cdot b + \frac{7}{100} \cdot d + u - p \geq 3.00 \quad (11.14)$$

$$\frac{4.6}{100} \cdot a + \frac{0.02}{100} \cdot b + \frac{7}{100} \cdot d + v \leq 3.30 \quad (11.15)$$

Silicon balance:

$$\frac{0.4}{100} \cdot a + \frac{0.01}{100} \cdot b + \frac{50}{100} \cdot c + w - q \geq 1.80 \quad (11.16)$$

$$\frac{0.4}{100} \cdot a + \frac{0.01}{100} \cdot b + \frac{50}{100} \cdot c + x \leq 2.00 \quad (11.17)$$

Manganese balance:

$$\frac{0.2}{100} \cdot a + \frac{0.01}{100} \cdot b + \frac{75}{100} \cdot d + y - r \geq 0.7 \quad (11.18)$$

$$\frac{0.2}{100} \cdot a + \frac{0.01}{100} \cdot b + \frac{75}{100} \cdot d + z \leq 1 \quad (11.19)$$

Phosphorus balance:

$$\frac{0.04}{100} \cdot a + \frac{0.01}{100} \cdot b + \alpha < 0.07 \quad (11.20)$$

Sulphur balance:

$$\frac{0.01}{100} \cdot a + \frac{0.02}{100} \cdot b + \beta < 0.15 \tag{11.21}$$

$$a + b + c + d + \gamma = 100 \tag{11.22}$$

Economic function to be optimized:

$$P = 7 \cdot a + 10 \cdot b + 33 \cdot c + 33 \cdot d + M \cdot (u + w + y + \gamma) \tag{11.23}$$

The high value of M (for instance, 1000) forces the artificial variables u, w, y, γ to take values close to 0. The cost coefficients of the slack variables (p, q, r) are 0, so they do not have influence in the economic function.

We use SOLVER from Excel to solve the problem. The following results were obtained (Table 11.2):

Exercise 11.4. A cupola used to make iron castings is charged with pig iron, flux and coke. The flux is pure CaCO_3 , and 25 kg are used per tonne of pig iron charged. The coke is 86% C, 5 SiO_2 , 7 Al_2O_3 , 2 FeO and 120 kg, which is used per tonne of pig iron.

The gas from the cupola contains equal parts of CO and CO_2 in volume. No carbon is oxidized from the pig iron.

The slag from the cupola carries (%): 11 FeO , 46 SiO_2 , 3 MnO , 25 CaO , 15 Al_2O_3

The cast iron produced carries 3.8% C, besides some manganese and silicon.

Required: Per tonne of pig iron charged:

1. The weight of the slag.
2. The volume of air consumed in oxidizing silicon, manganese and iron.
3. The volume of air consumed in oxidizing the carbon of the coke.
4. The volume and percentage composition of the gas.

Table 11.2 Results of the optimization problem

Decision variables		Objective function	
A	70.50	P (\$/100 kg)	875
B	25.73		
C	3.03		
D	0.74		
Total	100.00		

Question

1. Weight of slag/t pig iron:

$$25 \text{ kg CaCO}_3 \rightarrow 25 \text{ kg CaCO}_3 \cdot \frac{56 \text{ kg CaO}}{100 \text{ kg CaCO}_3} = 14 \text{ kg CaO} \quad (11.24)$$

Then, the amount of slag per tonne of pig iron is:

$$14 \text{ kg CaO}/0.25 = 56 \text{ kg slag} \quad (11.25)$$

2. Volume of air consumed (m^3) consumed in oxidizing silicon, manganese and iron (all of them end in the slag):

$$\text{Mn} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{MnO}, \quad \text{MnO} = 56 \cdot 0.03 = 1.68 \text{ kg MnO} \quad (11.26)$$

$$\frac{16 \text{ g O}_2}{71 \text{ g MnO}} \cdot 1.68 \text{ kg MnO} = 379 \text{ g O}_2 \rightarrow \text{O}_2 = \frac{379}{32} \cdot 22.41 \cdot \frac{100 \text{ g air}}{21 \text{ g O}_2} = 1.262 \text{ m}^3 \quad (11.27)$$

$$\text{Fe} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{FeO}, \quad \text{FeO} = 56 \cdot 0.11 - 120 \cdot 0.02 (\text{cok}) = 3.76 \text{ kg FeO} \quad (11.28)$$

$$\frac{16 \text{ g O}_2}{72 \text{ g FeO}} \cdot 3.76 \text{ kg FeO} = 836 \text{ g O}_2 \rightarrow \text{O}_2 = \frac{836}{16} \cdot 11.21 \cdot \frac{100 \text{ g air}}{21 \text{ g O}_2} = 2.783 \text{ m}^3 \quad (11.29)$$

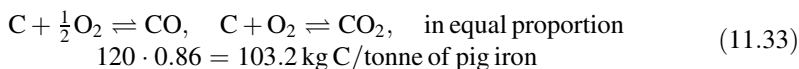
$$\text{Si} + \text{O}_2 \rightleftharpoons \text{SiO}_2, \quad \text{SiO}_2 = 56 \cdot 0.46 - 120 \cdot 0.05 (\text{coke}) = 19.76 \text{ kg SiO}_2 \quad (11.30)$$

$$\begin{aligned} \frac{32 \text{ g O}_2}{60 \text{ g SiO}_2} \cdot 19.76 \text{ kg SiO}_2 &= 10539 \text{ g O}_2 \rightarrow \text{O}_2 = \frac{10539}{32} \cdot 22.41 \cdot \frac{100 \text{ g air}}{21 \text{ g O}_2} \\ &= 35.129 \text{ m}^3 \end{aligned} \quad (11.31)$$

Volume of air consumed in oxidizing silicon, manganese and iron:

$$2.783 + 35.129 + 1.262 \simeq 39.2 \text{ m}^3 \quad (11.32)$$

3. Volume of air consumed in oxidizing the carbon of the coke:



$$\text{Volume CO} = \text{Volume CO}_2 = \frac{1}{2} \cdot (103.2/12) \cdot 22.41 \cdot 1000 \text{ g}/10001 = 96.32 \text{ m}^3 \quad (11.34)$$

$$\text{Air}(\text{CO}_2) = \frac{103.2}{2} \cdot \frac{1000}{12} \cdot \frac{22.41}{\text{mol}} \cdot \frac{100 \text{ air}}{21 \text{ O}_2} = 458.7 \text{ m}^3 \text{ air} \quad (11.35)$$

$$\text{Air}(\text{CO}) = \frac{103.2}{2} \cdot \frac{1000}{12} \cdot \frac{11.21}{\text{mol}} \cdot \frac{100 \text{ air}}{21 \text{ O}_2} = 229.3 \text{ m}^3 \text{ air} \quad (11.36)$$

4. Volume and percentage composition of the gas:

Total flue gases:

$$96.32 \text{ m}^3 \text{ CO}_2 + 96.32 \text{ m}^3 \text{ CO} + (458.7 + 229.3) \cdot \frac{79 \text{ N}_2}{100 \text{ air}} = 736.16 \text{ m}^3 \quad (11.37)$$

Composition:

$$74\% \text{ N}_2 - 13\% \text{ CO} - 13\% \text{ CO}_2 \text{ (stack gas)}$$

Exercise 11.5. The pig iron melted in a cupola had the following composition (%): 91.0 Fe, 3.6 C, 2.0 Si, 0.7 Mn, 0.7 P, 2 dirt. The dirt of the pig iron consisted of sand and clay and analysed 75% SiO₂ and 25% Al₂O₃. The temperature of the melted iron was 1300 °C and its melting point was 1180 °C.

25 kg of limestone were used per tonne of pig, analysing CaCO₃, 98%; SiO₂, 1%; Al₂O₃, 1%. The weight of coke used was 125 kg per tonne of pig, and it analysed C, 90%; SiO₂, 5%; Al₂O₃, 3%; FeO, 2%.

The gas produced percent carries 14 CO₂, 10 CO, 76 N₂. The slag made per cent carries 11 FeO, 46 SiO₂, 3 MnO, 25 CaO, 15 Al₂O₃.

The temperature of the gas leaving the cupola was 440 °C.

Required:

1. The cubic metres of gas produced and of blast used, per tonne of pig melted.

2. The percentage of Fe, Mn and Si of the pig that was oxidized during melting.
3. The weight of cast iron produced.
4. The percentage of the calorific power of the coke represented by the heat in the melted cast iron.
5. The percentage of the calorific power of the coke lost in the gases (a) by the sensible heat, (b) by incomplete combustion.

Question

1. The cubic metres of gas produced, and air injected per tonne of pig iron melted.

Carbon in the coke: $125 \cdot 0.9 = 112.5$ kg; x will be used in producing CO; and, y will be used in producing CO₂. As the relation CO₂/CO in the gas is $0.14/0.10 = 1.4$. Then,

$$\frac{y}{x} = 1.4; x + y = 112.5 \rightarrow x = 46.9 \text{ kg CO}; y = 65.6 \text{ kg CO}_2 \quad (11.38)$$

Combustion gases:

$$\begin{aligned} \text{CO} + \text{CO}_2 + \text{N}_2 &= \frac{46.9}{12} \cdot 22.4 \text{ m}^3 \text{ CO} + \frac{65.6}{12} \cdot 22.4 \text{ m}^3 \text{ CO}_2 + \frac{46.9}{12} \cdot 11.2 \\ &\quad \cdot \frac{79 \text{ m}^3 \text{ N}_2}{21 \text{ O}_2} + \frac{65.6}{12} \cdot 22.4 \cdot \frac{79 \text{ m}^3 \text{ N}_2}{21 \text{ O}_2} \\ &= 87.55 \text{ m}^3 \text{ CO} + 122.45 \text{ m}^3 \text{ CO}_2 + 625.13 \text{ m}^3 \text{ N}_2 \\ &= 835.13 \text{ m}^3 \text{ air} \end{aligned} \quad (11.39)$$

Injected for the coke combustion, it is necessary to add the air used in oxidizing the pig iron charge (Fe, Mn, Si).

The limestone is decomposed into CaO and CO₂. The CaO finishes completely in the slag:

$$25 \cdot 0.98 = 24.5 \text{ kg CaCO}_3 \quad (11.40)$$

$$24.5 \text{ kg CaCO}_3 \cdot \frac{56 \text{ kg CaO}}{100 \text{ kg CaCO}_3} = 13.72 \text{ kg CaO} \quad (11.41)$$

As 25% of the slag is CaO, the weight of the slag is:

54.88 kg of slag per tonne of pig iron

The amount CO₂ produced in the decomposition of the limestone is

$24.5/12 \cdot 22.4 = 5.49 \text{ m}^3$ of CO₂, which will be added to the stack gases that leave the furnace.

2. The oxygen consumed by the charge.

FeO:

$$54.88 \text{ kg} \cdot 0.11 \cdot \frac{1}{72 \text{ g FeO}} \cdot 11.2 = 0.94 \text{ m}^3 \text{ O}_2; \text{N}_2 : 0.94 \cdot \frac{79}{21} = 3.54 \text{ m}^3 \text{ N}_2 \quad (11.42)$$

MnO:

$$54.88 \text{ kg} \cdot 0.03 \cdot \frac{1}{71 \text{ g MnO}} \cdot 11.2 = 0.26 \text{ m}^3 \text{ O}_2; \text{N}_2 : 0.26 \cdot \frac{79}{21} = 0.98 \text{ m}^3 \text{ N}_2 \quad (11.43)$$

SiO₂:

$$54.88 \cdot 0.46 - 125 \cdot 0.05(\text{coke}) - 15(\text{charge}) = 4 \quad (11.44)$$

$$\frac{4}{60} \cdot 22.4 = 1.49 \text{ m}^3 \text{ O}_2 \rightarrow \text{N}_2 : 1.49 \cdot \frac{79}{21} = 5.60 \text{ m}^3 \text{ N}_2 \quad (11.45)$$

In the gases, we have

$$\begin{aligned} &87.55 \text{ m}^3 \text{ CO (combustion)} + 122.45 \text{ m}^3 \text{ CO}_2(\text{combustion}) \\ &\quad + 5.49 \text{ m}^3 \text{ CO}_2 \text{ (decomposition limestone)} \\ &= 215.49 \text{ m}^3 \text{ CO}_2 \end{aligned} \quad (11.46)$$

$$\begin{aligned} &625.13 \text{ m}^3 \text{ N}_2 (\text{combustion}) + (3.54 + 0.98 + 5.60) \text{ m}^3 \text{ N}_2 (\text{oxidation of the charge}) \\ &= 635.25 \text{ m}^3 \text{ N}_2 \end{aligned} \quad (11.47)$$

In total,

$$850.74 \text{ m}^3 \text{ flue gases : } \\ \mathbf{87.55 \text{ m}^3 \text{ CO}(10\% \text{ CO}) / 127.94 \text{ m}^3 \text{ CO}_2(15\% \text{ CO}_2) / 635.25 \text{ m}^3 \text{ N}_2(75\% \text{ N}_2)}$$

3. Weight of cast iron produced:

$$\text{Fe} : 910 - 6.04 \cdot \frac{56}{72} \simeq 905.3 \rightarrow 93.13\% \quad (11.48)$$

$$\begin{aligned} \text{Si} : 20 - 4 \cdot \frac{28}{60} &\simeq 18.1 \\ &\rightarrow 1.86\% \text{ (maybe the charge should be calibrated with FeSi)} \end{aligned} \quad (11.49)$$

$$\begin{aligned} \text{Mn} : 7 - 1.64 \cdot \frac{55}{71} &\simeq 5.7 \\ &\rightarrow 0.59\% \text{ (maybe the charge should be calibrated with FeMn)} \end{aligned} \quad (11.50)$$

$$\text{P} : 7 \rightarrow 0.72\% \quad (11.51)$$

$$\text{C} : 36 \rightarrow 3.70\% \text{ (slight re-carburation)} \quad (11.52)$$

$$\text{TOTAL} : 972.1 \text{ kg} \quad (11.53)$$

4. Percentage of the calorific power of the coke represented by the heat in the melted cast iron. Data: heat of fusion of the pig iron: 230 cal/g; specific heat of the pig iron: 0.15 cal/g °C; heat of combustion of the coke: 8100 kcal/kg; specific heat of the coke: 0.363 cal/g.

Heat in the pig iron (cast iron):

$$\begin{aligned} 230 \frac{\text{cal}}{\text{g}} + 0.15 \frac{\text{cal}}{\text{g} \cdot ^\circ\text{C}} (1300 - 1180)^\circ\text{C} &= 248 \frac{\text{cal}}{\text{g}} = 248 \frac{\text{kcal}}{\text{kg}} \cdot 1000 \text{ kg} \\ &= 248000 \text{ kcal} \end{aligned} \quad (11.54)$$

Heat in the coke:

$$0.9 \cdot 125 \text{ kg} \cdot 8100 \frac{\text{kcal}}{\text{kg}} = 911250 \text{ kcal (complete combustion)} \quad (11.55)$$

Percentage of heat in the pig iron (cast iron):

$$248000 / 911250 = 0.27(27\%) \quad (11.56)$$

However, the combustion of the coke is incomplete (heat of combustion to CO_2 : 8100 kcal/kg; heat of combustion to CO : 2430 kcal/kg; from Ellingham diagrams).

Heat involved in the incomplete combustion:

$$\text{CO} : 2430 \text{ kcal/kg} \cdot 46.9 \text{ kg} = 113967 \text{ kcal} \quad (11.57)$$

$$\text{CO}_2 : 8100 \text{ kcal/kg} \cdot 65.6 \text{ kg} = 531360 \text{ kcal} \quad (11.58)$$

$$\text{TOTAL} : 645327 \text{ kcal} \quad (11.59)$$

Combustion efficiency:

$$\frac{645327}{911250} \simeq 0.71 \text{ (71\%)} \quad (11.60)$$

29% of the heat is lost

Latent heat in the gases. Data: for the CO , $c_e = 0.313 \text{ kcal/m}^3 \text{ }^\circ\text{C}$; for the CO_2 , $c_e = 0.415 \text{ kcal/m}^3 \text{ }^\circ\text{C}$; for the N_2 , $c_e = 0.313 \text{ kcal/m}^3 \text{ }^\circ\text{C}$

Total sensible heat:

$$\begin{aligned} & 87.55 \text{ m}^3 \text{ CO} \cdot 0.313 \frac{\text{kcal}}{\text{m}^3 \text{ }^\circ\text{C}} \cdot 440 \text{ }^\circ\text{C} + 127.94 \text{ m}^3 \text{ CO}_2 \cdot 0.415 \frac{\text{kcal}}{\text{m}^3 \text{ }^\circ\text{C}} \cdot 440 \text{ }^\circ\text{C} \\ & + 635.25 \text{ m}^3 \text{ N}_2 \cdot 0.313 \frac{\text{kcal}}{\text{m}^3 \text{ }^\circ\text{C}} \cdot 440 \text{ }^\circ\text{C} = 124931 \text{ kcal} \end{aligned} \quad (11.61)$$

This result supposes that in case of complete combustion, heat lost is

$$\frac{124931}{911250} \simeq 0.14 \text{ (14\%)} \text{ in flue gases} \quad (11.62)$$

Summarizing:

From the 645327 kcal produced by the coke, 248000 kcal (38%) are used in melting the charge, 124931 kcal (19%) leave the furnace with the gases and the remaining 47% are used in melting the slag and in losses through the furnace walls.

It should be remembered the importance of the cast iron temperature (pouring temperature) in the castability (fluidity) of the liquid. The corresponding exercises should be reviewed again (Chap. 10). Demonstrate that the value of the

heat for the carbon combustion into CO and CO₂ is like that showed previously (use Ellingham's diagram for the oxides).

Exercise 11.6. A cupola melts per hour 15 short tonnes of foundry iron containing 3.5% C, 2.2 Si, 0.8 Mn, 0.7 P and 5 tonnes of scrap containing 3.0% C, 1.8 Si, 1.1 Mn, 0.2 P.

The blast is computed on the basis of 30000 ft³ measured at room temperature, required to melt 1 tonne and scrap charge per minute. Assume the blast to be dry.

In melting, there is oxidize 20% of the Si in the iron and scrap charged, 15% of the Mn, 1% of the Fe, and no P, 5% of the carbon is also oxidized, but 1% of the carbon in the coke is absorbed by the iron in melting. Enough CaCO₃ is charged to give a slag of 30% CaO. The coke is 92% C and 8% SiO₂, and the ratio of weight of coke to weight of pig and scrap charged is 1:9.

Required:

1. The percentage composition of the resulting cast iron, slag and gases.
2. Composition and amount of slag (per minute).
3. The weight and percentage composition of the gases.

Question

1. Composition of the obtained cast iron:

$$1 \text{ short tonne} = 907.185 \text{ kg}$$

Charge per hour:

$$15 \text{ short tonne} \cdot \frac{907.185 \text{ kg}}{1 \text{ short tonne}} + 5 \text{ tonnes} \cdot \frac{1000 \text{ kg}}{1 \text{ tonne}} = 18617.5 \text{ kg} \quad (11.63)$$

Charge per minute:

$$18617.5/60 = 310.3 \text{ kg} \quad (11.64)$$

Coke per minute:

$$310.3/9 = 34.5 \text{ kg} \quad (11.65)$$

Average composition of the charge (per hour):

$$\text{Carbon : } 13617.75 \cdot 0.035 + 0.03 \cdot 5000 = 626.6 \text{ kg C} \quad (11.66)$$

$$\text{Silicon : } 13617.75 \cdot 0.022 + 0.018 \cdot 5000 = 389.6 \text{ kg Si} \quad (11.67)$$

$$\text{Manganese : } 13617.75 \cdot 0.008 + 5000 \cdot 0.0011 = 163.9 \text{ kg Mn} \quad (11.68)$$

$$\text{Phosphorus : } 13617.75 \cdot 0.007 + 5000 \cdot 0.002 = 105.3 \text{ kg P} \quad (11.69)$$

$$\text{Fe (balance) : } 17332.4 \text{ kg Fe} \quad (11.70)$$

$$\text{TOTAL : } 18617.8 \text{ kg charge} \quad (11.71)$$

Average composition of the charge:

$$93.1\% \text{ Fe, } 3.4\% \text{ C, } 2.1\% \text{ Si, } 0.9\% \text{ Mn, } 0.6\% \text{ P}$$

Losses through oxidation of the charge (minute):

$$\text{Si : } 310.3 \cdot 0.021 \cdot 0.2 = -1.30 \text{ kg} \quad (11.72)$$

$$\text{Mn : } 310.3 \cdot 0.009 \cdot 0.15 = -0.42 \text{ kg} \quad (11.73)$$

$$\text{Fe : } 310.3 \cdot 0.93 \cdot 0.01 = -2.89 \text{ kg} \quad (11.74)$$

$$\text{C : } 310.3 \cdot 0.034 \cdot 0.05 = -0.53 \text{ kg (by oxidation)} \quad (11.75)$$

$$\text{C : } 34.5 \cdot 0.92 \cdot 0.01 = +0.32 \text{ kg (recarburization by coke)} \quad (11.76)$$

$$\text{P : } 310.3 \cdot 0.006 = 1.86 \text{ kg} \quad (11.77)$$

The real charge has 5.22 Si/2.37 Mn/285.7 Fe/10.34 C/1.86 P, total 305.5 kg. Under that conditions, the average composition would be 93.52% Fe, 3.38% C, 1.71% Si, 0.78% Mn, 0.64% P, the average carbon content is kept constant, but the Si and Mn contents diminish, specially the first one. Maybe, it would be convenient adding to the pouring ladle FeSi and FeMn, as it was mentioned.

2. Composition and amount of slag (per minute):

$$\text{SiO}_2 : 1.30 \text{ kg Si} \cdot \frac{60}{28} (\text{oxidation}) + 34.5 \cdot 0.08 = 5.55 \text{ kg SiO}_2 \quad (11.78)$$

$$\text{MnO} : 0.42 \text{ kg Mn} \cdot \frac{71}{55} = 0.54 \text{ kg MnO} \quad (11.79)$$

$$\text{FeO} : 2.89 \text{ kg Fe} \cdot \frac{72}{56} = 3.72 \text{ kg FeO} \quad (11.80)$$

$$\text{CaO} (x) \text{ as : } x/(x + 9.81) = 0.3 (\text{data}) \rightarrow x = 4.20 \text{ kg CaO} \quad (11.81)$$

That is to say, we have $9.81 + 4.20 = 14.01$ kg slag/minute whose composition is

$$39.6\% \text{ SiO}_2, 3.85\% \text{ MnO}, 26.55\% \text{ FeO}, 30\% \text{ CaO}$$

3. Weight and composition of the gases:

O₂ absorbed in the oxidation of the charge:

$$\begin{array}{c} \text{Si} + \text{O}_2 \rightleftharpoons \text{SiO}_2 \\ 1.30 \text{ kg Si} \cdot \frac{1 \text{ kmol Si}}{28 \text{ kg Si}} \cdot \frac{1 \text{ kmol O}_2}{1 \text{ kmol Si}} \cdot 22.41 \text{ l O}_2 = 1.04 \text{ m}^3 \text{ O}_2 \end{array} \quad (11.82)$$

$$\begin{array}{c} \text{Fe} + 1/2 \text{O}_2 \rightleftharpoons \text{FeO} \\ 2.89 \text{ kg Fe} \cdot \frac{1 \text{ kmol Fe}}{56 \text{ kg Fe}} \cdot \frac{1/2 \text{ kmol O}_2}{1 \text{ kmol Fe}} \cdot 22.41 \text{ l O}_2 = 0.59 \text{ m}^3 \text{ O}_2 \end{array} \quad (11.83)$$

$$\begin{array}{c} \text{Mn} + 1/2 \text{O}_2 \rightleftharpoons \text{MnO} \\ 0.42 \text{ kg Si} \cdot \frac{1 \text{ kmol Mn}}{55 \text{ kg Mn}} \cdot \frac{1/2 \text{ kmol O}_2}{1 \text{ kmol Mn}} \cdot 22.41 \text{ l O}_2 = 0.086 \text{ m}^3 \text{ O}_2 \end{array} \quad (11.84)$$

$$\text{TOTAL} : 1.716 \text{ m}^3 \text{ O}_2 \quad (11.85)$$

Per minute are blown:

$$\frac{30000 \text{ ft}^3}{60 \text{ min}} \cdot \left(\frac{0.3 \text{ m}}{\text{ft}} \right)^3 = 706.5 \frac{\text{m}^3}{\text{tonne} \cdot \text{minute}} \quad (11.86)$$

$310.5 \text{ kg charge} + 9.81 \cdot (\text{FeO} + \text{MnO} + \text{SiO}_2) \simeq 320 \text{ kg/min} \rightarrow$
 $706.5 \text{ m}^3/\text{tonne} \cdot \text{min} \cdot 0.320 \simeq 226 \text{ m}^3 (178.6 \text{ m}^3 \text{N}_2, 47.4 \text{ m}^3 \text{N}_2)$ for oxidizing the coke
 $(34.5 \cdot 0.92 \cdot 0.99 = 31.42 \text{ kg})$

(11.87)

Calling $x(\text{C} \rightarrow \text{CO})$ and $y(\text{C} \rightarrow \text{CO}_2)$:

$$\begin{aligned} \text{C} + \frac{1}{2}\text{O}_2 &\rightarrow \text{CO} \\ \frac{x}{12} \cdot 11.2 &= 0.93 \cdot x \end{aligned} \quad (11.88)$$

$$\begin{aligned} \text{C} + \text{O}_2 &\rightarrow \text{CO}_2 \\ \frac{x}{12} \cdot 22.4 &= 1.87 \cdot y \end{aligned} \quad (11.89)$$

$$x + y = 31.42 \quad (11.90)$$

$$0.93 \cdot x + 1.87 \cdot y = 47.4 \quad (11.91)$$

Solving:

$$y = 19.4 \text{ kg C (CO}_2\text{)} \quad (11.92)$$

$$x = 31.42 - 19.4 = 12 \text{ kg C (CO)} \quad (11.93)$$

Flue gases per minute:

$$\text{N}_2 = 178.6 \text{ m}^3 \quad (11.94)$$

$$\text{CO} = 11.22 \text{ m}^3 \quad (11.95)$$

$$\text{CO}_2 = 36.28 + \frac{4.20 \text{ kg CaO}}{56 \text{ g/mol}} \cdot 22.4 = 36.28 + 1.68 = 37.9 \quad (11.96)$$

Total gases: $227.7 \text{ m}^3/\text{min}$, with volume fractions of

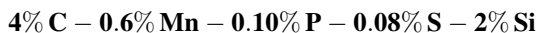
$$78\% \text{N}_2, 4.9\% \text{CO}, 17\% \text{CO}_2$$

11.2 Sulphur and Phosphorus in the Cupola Furnace

The cupola furnace is a traditional furnace for melting and manufacturing cast irons. The employed raw materials are usually pig iron, scraps of cast iron, scraps of steel, coke, limestone (as slag-forming element) and air blowing for the incomplete combustion (forced by the Boudouard equilibrium). The reached temperatures will be high enough for separating in liquid state, cast iron and slag. It should be remembered that the fluidity of the cast iron depends on its superheating above the melting point (1150–1200 °C). It is also possible to operate discontinuously (it is possible to stop melting processes during days).

- The blown air oxidizes the metallic charge, and FeO, MnO and SiO₂ are formed. The carbon content is usually kept constant by recarburization of charge from the coke. If Si and Mn are out of specification, it is necessary to use ferroalloys (expensive) added in the ladle. Phosphorus, apparently, does not oxidize, and for that reason its amount will be that introduced with the charge. In the manufacture of ductile irons, the phosphorus content should be kept below 0.05% (to avoid the formation of steadyite).
- Nothing has been told in previous exercises about the sulphur content (charge, coke). The slag seems to be oxidizing and acid (SiO₂/CaO < 1), all the contrary to that required for the removing (pick up) of sulphur (reducing and basic slag). Under that conditions, the sulphur contents in the cast iron should be controlled (<0.02%). On another note, the spheroidization of the carbon graphite by using magnesium would be not possible because the magnesium would prefer catching sulphur than nodulizing the carbon. Apart from that, excessive sulphur amount favours the chilling of the cast iron (see Chap. 10).
- Sulphur introduced with the coke could make difficult the manufacture of ductile irons, and for that reason, sulphur must be controlled also in the coke. See two last examples of desulphurization and dephosphorization in cupola irons.

Exercise 11.7. (Desulphurization of ductile irons) In the production of ductile iron, the sulphur content in the metal from the cupola should be 0.02% max. If the desulphurization ratio, %S (slag)/%S (metal), is 40, and that the coke weight is equal to 15% of the metal charge, what is the final slag weight per 100 kg of metal required for the condition given below?
S content in coke, 0.5%; ash, 8% (SiO₂), charge analysis:

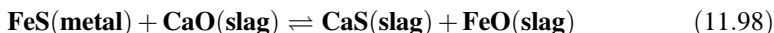


It has been demonstrated that sulphur is removed from liquid metal through two mechanisms:

1. The slag dissolves iron sulphide from the metal until equilibrium is reached, i.e. until the tendency of FeS to escape from the metal equals the tendency of FeS in the slag to escape to the metal. In other words,



2. Iron sulphide reacts with lime (CaO) at the slag-metal interface to produce calcium sulphide and iron oxide:



If the iron oxide level in the slag is already high, very little CaS can be found in the slag, and reaction (11.97) predominates.

Since the desired end result is the accumulation of sulphur in the slag and since it does not matter whether the sulphur appears there as FeS or CaS, we may, after analysing a given metal-slag combination for sulphur, express the desulphurizing power as $\%S(\text{slag})/\%S(\text{metal})$. This ratio may vary from as high as 400:1 to as low as 1:1, depending on the given situation.

Question

In the cast iron, we want to reduce the sulphur content from 0.08 to 0.02 (100 kg of cast iron), which means that the slag should pick up 0.06 kg of S. Moreover, there is $15 \cdot 0.005 = 0.075$ kg S in the coke. Total, 0.135 kg S. The percentage of sulphur in the slag, with a partition coefficient of 40, would be $40 \cdot 0.02 = 0.8\%$.

Expressing the basicity index (IB) in its easiest way: $\text{IB} = (\text{CaO}/\text{SiO}_2)_{\text{molar}}$, and considering that the charge does not oxidize, the amount of silica in the slag is $0.08 \cdot 15 = 1200$ g. Calling x to the amount of CaO:

$$(x/56)/(1200/60) = \text{IB} = \frac{x}{1120} \rightarrow x = 1120 \cdot \text{IB} \quad (11.99)$$

Imposing the condition:

$$[\%S](\text{slag}) = 0.8\% \quad (11.100)$$

$$0.8 = \frac{135}{1200 + 1120 \cdot \text{IB} + 135 \cdot (72/32)} \cdot 100 \rightarrow \text{IB} = 13.7 \quad (11.101)$$

$x = 15.4$ kg CaO, or $15.4 \cdot (100/56) = 27.5$ kg of limestone that should be added as flux. The slag would be composed of

304 g CaS (1.8%)

1200 g SiO₂ (7.1%)

15400 g CaO (91.1%) from 27.5 kg of limestone

TOTAL: 16904 g slag

What would be the amount of limestone required for melting the charge if the coke would be free of sulphur? Calculate the basicity index for the same partition coefficient of 40.

Question

$$[\%S](\text{slag}) = 0.8 = \frac{60}{1200 + 135 + 1120 \cdot IB} \cdot 100 \rightarrow IB = 5.5 \quad (11.102)$$

$$x = 6.156 \text{ kg CaO} \simeq 11.0 \text{ kg of limestone} \quad (11.103)$$

The consumption of fluxes would be significantly reduced, and the mass and energy balance of the process would be improved.

Exercise 11.8. (Dephosphorization of cupola iron). A base cupola iron containing 0.1% phosphorus is to be refined to 0.04% using a basic oxidizing slag. What slag weight will be required per 100 kg of metal, assuming that the slag–metal equilibrium will result in 6% $(\text{CaO})_4\text{P}_2\text{O}_5$ in the slag?

Question

If there is no phosphorus in the slag-making constituents to begin with, that is, if we assume that the lime, etc., are free of phosphorus, and since no phosphorus escape as gas we may write the following mass balance:

$$\begin{aligned} \text{P in metal as start} &= \text{P in metal after treatment with slag} \\ &+ \text{P in slag after exposure to metal} \end{aligned} \quad (11.104)$$

To visualize the problem, it is convenient to begin with an arbitrary weight of metal, say 100 kg. Then,

$$\text{Weight of P in 100 kg of ingoing metal} = 0.10 \text{ kg} \quad (11.105)$$

$$\text{Weight of P in 100 kg of outgoing metal} = 0.04 \text{ kg} \quad (11.106)$$

$$\text{Weight of P in slag} = 0.06 \text{ kg} \quad (11.107)$$

Now the phosphorus in the slag is present as $(\text{CaO})_4\text{P}_2\text{O}_5$, which contains

$$\frac{62 \text{ g P}}{366 \text{ g } (\text{CaO})_4\text{P}_2\text{O}_5} \cdot 100 = 17\% \text{ P} \quad (11.108)$$

Therefore, 0.06 kg of phosphorus would be present in

$$0.06 \text{ kg P} \cdot 100 \text{ kg (CaO)}_4\text{P}_2\text{O}_5 / 17 \text{ kg P} = 0.353 \text{ kg (CaO)}_4\text{P}_2\text{O}_5 \quad (11.109)$$

Since it is stated in the problem that, under the particular conditions of the experiment, the phosphorus partition results in 6% $(\text{CaO})_4\text{P}_2\text{O}_5$ in the slag, it follows that the total slag weight will be $0.353/0.06 \simeq 6$ kg per 100 kg of metal. In other words, a batch process of cupola furnace would be operating with a slag weight equal to 6% of the metal weight.

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