Part 3

Steels and cast irons

«*It is now truer than ever that steels are the most important group of engineering materials, for they are continually evolving to meet new needs and challenges, and this is really the main justification for doing research in this field.*»
R.F.K. Honeycombe 29th Hatfield memorial lecture 6 December 1979 [Hon80]

«*Steel, the most versatile of the structural materials is present in practically all the sectors - buildings and public works, transport (automobiles, marine engineering), packaging, furniture, tools, mechanical engineering, industrial and consumer goods,...*

Moreover, due to its intrinsic low cost and ease of recovery, steel is particularly suited to the development of multiple-use cycles, and this is already reflected by the highest effective recycling rate of all materials.»
M Giget "Functional properties and choice of materials", Chapter 2 of "The book of steel" [Bér96a].

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Steel Design

The most modern quality of steel is undoubtedly its great versatility. In spite of the fact that world steel consumption is no longer increasing, the range of available grades has risen significantly in response to ever more stringent and precise market demands. For the potential user, the first step in the steel selection process is to compare the technical properties of the different grades with the characteristics required for the intended application [Ash92], [Ash99], [Ash02]. For the steel designer, property combinations can be improved and optimised only by a detailed scientific analysis of the metallurgical mechanisms involved. A clear understanding of the underlying phenomena provides the flexibility needed to tailor properties to meet particular needs in a reliable and reproducible manner. However, it is not only the final functional properties of a component that must be considered, but also the ease and cheapness of manufacture, including the cost of raw materials. Recyclability and environmental considerations are also becoming increasingly important. The best material is the one that meets all these requirements at the lowest total life cost.

14-1 Mechanical properties

Strengthening mechanisms

Mechanical strength is often the major property requirement, usually expressed in terms of the yield and ultimate tensile stress in a uniaxial tensile test. There are four basic strengthening mechanisms that can be used in different ways to improve the mechanical properties of steels (and alloys in general), corresponding to strain hardening, grain refinement, solid solution strengthening, and precipitation hardening. The first two can also be employed in pure metals, while the last two depend on the physical-chemical equilibria in alloy systems. In order to evaluate the effect of the various parameters involved in the different mechanisms, a number of empirical formulae have been established, usually based on the observed increase in 0.2 % yield stress (the flow stress at 0.2 % permanent or plastic strain, often also called the 0.2 % proof stress). The formulae contain proportionality coefficients which provide an indication of the comparative efficiency of different contributions to strengthening [Pic78].

Strengthening by grain refinement

Grain boundaries usually represent obstacles to dislocation motion, due to the difference in orientation of the two crystals that they separate. The propagation of a strain vector across the interface generally requires the activation of new slip systems, with an associated increase in flow stress. The smaller the grain size, the larger the number of obstacles and the greater the degree of strengthening. However, since grain boundaries are local regions of excess energy, there is a natural tendency for their total area to decrease by grain growth during high temperature processing and heat treatment cycles. To achieve a fine grain size it is necessary to promote recrystallisation with a high nucleation density, generally by controlled thermomechanical processing, and to prevent subsequent grain growth. The mobility of grain boundaries can be impeded by the presence of precipitate particles and certain elements in solid solution. A fine primary solidification grain size can often exert a beneficial influence, even after several subsequent solid state phase transformations.
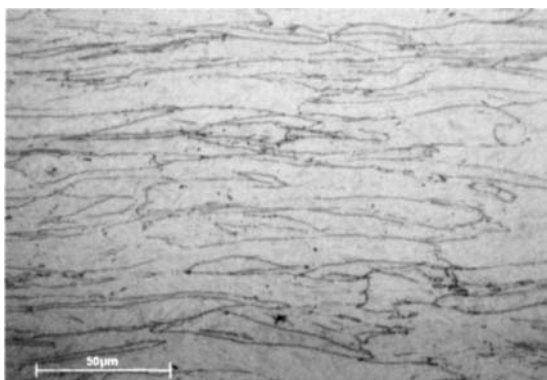
Strain hardening

The stiffening produced when metals are cold worked and the subsequent softening that can be achieved by appropriate heating are phenomena that have long been known and exploited by smiths, even though their origins have become understood only in more modern times. Strain hardening, or work hardening, occurs in all cold forming processes, including forging, rolling, wire-drawing, sheet drawing, etc. We now know that plastic deformation involves the generation and movement of crystal dislocations. The distorted dislocation core structures and their associated longer range elastic stress fields interact with one another and their motion is impeded. New dislocations must be created for deformation to continue and this requires a higher stress. The number of dislocations, and therefore the number of obstacles and the resulting flow stress, thus increase with strain. Dislocation density is measured as the total length of dislocations per unit volume and is usually expressed in units of cm^{-2}. For example, in an annealed single crystal, a typical value would be of the order of $10^7 cm^{-2}$, whereas levels of 10^{10} to $10^{12} cm^{-2}$ are observed after common cold working operations. The strengthening that accompanies strain hardening is associated with a loss of residual ductility. It is therefore usually necessary to limit the amount of cold work in order to achieve an acceptable balance between strength and ductility.

Figure 14-1-1 shows the microstructure of a low alloy steel that has been heavily cold rolled, the individual grains being flattened to a so-called pancake shape. The high dislocation density represents a large amount of stored mechanical energy, so that such structures are unstable when the material is subsequently heated. The dislocation density decreases during heat treatment, and depending on the time and temperature, three thermally activated softening processes can occur, corresponding to recovery, recrystallisation and grain growth.

Recovery is the process with the lowest activation energy and corresponds to a reduction in the density of dislocations and their rearrangement into lower energy configurations. It

Figure 14-1-1:
Optical micrograph of a low alloy steel hot rolled in the austenite field at a temperature sufficiently low to prevent recrystallisation. The individual grains have been flattened to a "pancake" morphology. Etching in 4 % picric acid reagent has revealed the prior austenite grain boundaries.
Document Arcelor Recherche, Fr

involves diffusion-dependent processes such as climb and cross-slip and enables the mutual annihilation of dislocations of opposite sign. The extent of softening depends on the temperature and time, and eventually leads to a network of more-or-less two-dimensional dislocation sub-boundaries surrounding regions of perfect crystal. The latter process is sometimes called polygonisation. The sub-boundaries still represent obstacles to dislocation motion, while *the deformed grain morphology remains unchanged,* so that the associated softening is relatively limited. To achieve maximum softening, it is necessary to raise the temperature to a level where recrystallisation becomes possible. The minimum temperature necessary depends on the alloy and the degree of cold work, but is generally around 0.5 *Tm,* where *Tm* is the absolute melting temperature (solidus for an alloy). New grains with low dislocation density and a relatively equiaxed morphology *nucleate and grow* in the deformed matrix, leading to a fully recrystallised structure when the process is complete, that is, when the cold worked regions have been totally consumed. The density of recrystallisation nuclei is greater the larger the amount of prior strain, while extended holding times and higher annealing temperatures lead to a reduction in the number of grains, and therefore the total grain boundary area, by the grain growth phenomenon. Certain grains grow at the expense of others by boundary migration. The increase in grain size is accompanied by additional softening. Grain refinement is possible when these parameters are appropriately controlled.

Table 14-1-2: :
The different stages of softening during static annealing, Tm is the melting point in Kelvins

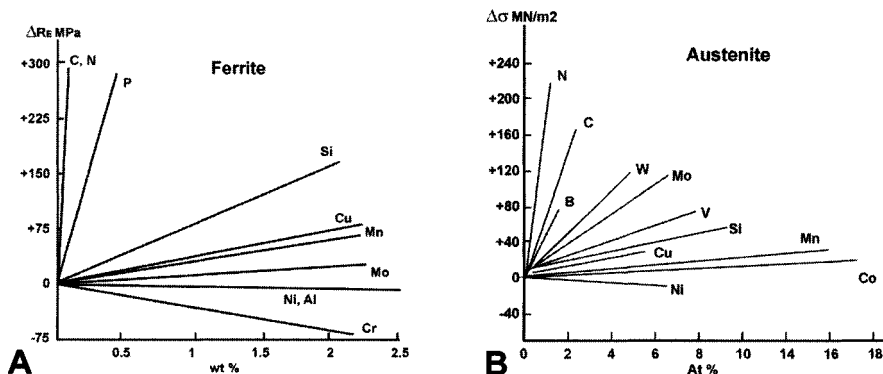| I: Cold working	II: Recovery, T<0.5 Tm	III: Recrystallisation T ≈ 0.5 Tm	IV: Grain growth, T>0.5 Tm
High dislocation density.	Decrease in dislocation density, polygonisation	**Nucleation and growth** of new grains with low dislocation density.	Reduction in the number of grains.
High hardness, low ductility.	Slight softening.	Marked softening, depending on the final grain size.	Marked softening, depending on the final grain size.

Figure 14-1-3:
A) Solid solution strengthening in HSLA type ferrite-pearlite steels.
B) Solid solution strengthening in austenite. [Pic78].

A similar result can be obtained when the initial dislocation-rich structure is produced by warm or hot working, and in practice, grain refinement is usually achieved by controlled thermomechanical processing cycles, often by the hot rolling of materials under conditions where concomitant precipitation prevents grain growth. In this case, the recrystallisation process can be either *dynamic* (during deformation) or *static* (after deformation or between passes).

Solid solution strengthening

The presence of alloying elements in interstitial or substitutional solid solution can cause strengthening. Substitutional alloying elements whose atomic size is different to that of the solvent metal locally distort the crystal lattice. The resultant elastic stress fields interact with those around dislocations, requiring a higher applied stress for glide to continue. In the case of interstitial solutes, the local lattice distortion depends on the size and shape of the interstices and the type of atom concerned. A carbon atom in an octahedral interstice in fcc iron induces a symmetrical stress field, whereas the same atom in a tetrahedral site in bcc iron generates a non-symmetrical stress field. The non-symmetrical distortion due to interstitial atoms in the body-centred tetragonal lattice of martensite produces a strengthening effect much larger than that for normal solid solution strengthening.

It can be energetically more favourable for certain alloying elements to position themselves at dislocations. For example, this is the case for interstitial elements such as carbon and nitrogen, whose mobility allows them to diffuse to dislocations, where they form a so-called Cottrell atmosphere, which tends to pin the dislocation, impeding its movement, since if it breaks away, the overall energy of the system is increased. This is the cause of the strain-aging phenomenon observed in extra mild steels. Nitrogen can diffuse to dislocations at ambient temperature, while carbon diffusion becomes significant above about 100 °C. A higher stress is required to move the dislocations, but once they have torn free

from their atmosphere they can glide under a lower stress, leading to a yield drop. This effect is used in the bake-hardening steels, whose name derives from the fact that the atmospheres form during the baking treatment used to cure paint coatings. At medium temperatures, from 200 to 400 °C, the interstitial atoms are sufficiently mobile to catch up with the dislocations again when they are held up by obstacles. Under these conditions, a repeated series of yield drops can be observed during a tensile test. The phenomenon is described as dynamic strain aging and is also known as the Portevin-Le Chatelier effect [Cah83].

The solid solution strengthening effects of common alloying elements in ferrite are well established (Fig. 14-1-3 A). Unfortunately, the elements with the greatest strengthening effects (C, N and P) have very low solubilities, so that their practical interest is small, except when trapped in supersaturated solid solution, as in the case of martensite. The situation for austenite is illustrated in Figure 14-1-3 B. The most efficient strengtheners are again the interstitial elements, whose solubilities remain relatively low and which can form unwanted precipitate phases. The most potent substitutional elements (W, Mo, V) are ferrite stabilisers, so that their concentrations must often be limited for this reason.

Precipitation hardening
Particles of a second phase generally act as obstacles to dislocation motion. The nature of the interaction depends on the mechanical properties of the precipitate phase, together with the crystal structure and orientation. Matrix dislocations may shear precipitates that are coherent if their size and shear stress are sufficiently small. A large lattice mismatch may induce coherency stresses that interact with dislocations, providing a contribution to strength. In the case of incoherent particles, since the slip planes are not continuous, dislocations must loop round the precipitates, by the classical Orowan mechanism, or climb over them at high temperatures. The stress necessary for looping is inversely proportional to the particle spacing. For coherent precipitates that are stronger than the matrix, the stress necessary for shear increases with particle size, so that above a critical dimension looping becomes easier, since for a constant volume fraction the distance between particles is greater the larger the precipitate diameter.

The yield stress of the material therefore depends on the size, strength, volume fraction and coherency of the precipitate phase. For example, in martensitic steels, heat treatment in the range 500–600 °C can cause the continuous precipitation of coherent carbides, provided that the temperature-time combination is not excessive. The process is often referred to as *secondary hardening*, since it occurs after the primary hardening due to the martensite transformation and offsets the softening associated with the reduction in interstitial solution hardening. The maximum hardness is obtained when the carbide particle size is about 10 nm. Further particle coarsening (overaging) leads to a rapid loss in strength. The high strength resulting from precipitation hardening is often difficult to maintain at high temperatures, since the precipitates coarsen rapidly and lose coherency, and may even begin to redissolve. An exception concerning phases whose size remains stable due to high coherency is described in § 20-3.

Even at low temperatures, coarse second phase particles have only a limited strengthening effect, particularly when they are intrinsically weak. This is true for pearlite, for ferrite islands in duplex stainless steels, and for secondary carbides in austenitic materials.

Toughness

At ordinary temperatures, there are two basic ways in which a crystalline material can react under heavy loading ; by shear, generally involving the movement of dislocations, or by decohesive failure, often termed cleavage, particularly when it occurs along clearly defined crystal planes. Pure shear is associated with high ductility, with necking down to a fine point in a tensile test. In contrast, pure cleavage gives zero reduction in area, that is, brittle behaviour. Fortunately, the stress necessary for cleavage is usually higher than that for shear in most defect-free metallic materials, but in non-compact crystal structures (other than fcc and cph), this may no longer be true at low temperatures. However, cleavage can be promoted in conditions where dislocation movement is inhibited, such as under very high strain rates or strongly triaxial loading. The latter situation exists at the tip of a notch or microcrack (for example, caused by the fracture or disbonding of a hard brittle particle, by fatigue, by gas evolution, etc.). The increase in stress associated with strain hardening can eventually lead to local decohesive failure at such defects, so that many metals show at least a small amount of brittle fracture. Ductile fracture absorbs a large amount of energy, whereas pure brittle failure, once initiated, can be self propagating.

The tendency of a material to fail in a more-or-less ductile or brittle manner is called its toughness. An indication is given by the reduction in area at failure in a tensile test, but it is usually measured under conditions where cleavage fracture is promoted by the presence of a machined notch or fatigue crack. The most common test is the Charpy V-notch impact test, in which the standard specimen is struck opposite the notch by a heavy falling pendulum. The toughness is expressed in terms of the kinetic energy absorbed by the fracture. A more rigorous technique is fracture toughness testing, in which a sharp crack is produced in fatigue and then extended under monotonic loading until the appearance of an instability in the load-displacement curve. The fracture toughness is expressed in terms of the stress σ and crack length a at the onset of unstable propagation. The stress intensity factor K $(= \sigma \sqrt{a})$ is given in units of MPa.$\sqrt{m}$. The fracture toughness is generally inversely proportional to the yield strength (*cf.* Figure 17-2-4) and the higher its value, the larger the specimen required for a valid measurement, different criteria being used depending on the type of behaviour observed.
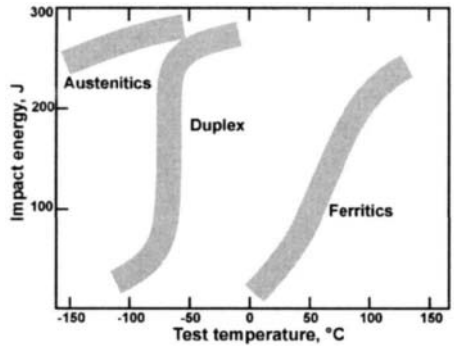
In a brittle material, there is no plastic deformation at the crack tip, which remains sharp. The increasing elastic stress concentration induces cleavage, generally along preferred crystal planes, or possibly along grain boundaries. The resulting fracture surface is strongly facetted (Figures 7-1-6, 14-1-5 B and 21-4-7 A). The absence of plastic work leads to a low overall energy dissipation.

In a ductile material, the stress concentration at the crack tip causes the emission of dislocations, leading to blunting and reduction of the local stress concentration. The load must

Figure 14-1-4:
Schematic Charpy impact-temperature curves for
different types of stainless steel.
Adapted from a Ugine document, Arcelor Group.

be increased to produce further propagation. Some cleavage fracture usually occurs at locally brittle points such as inclusions or hard precipitate particles. However, the ductile metal in between stretches plastically and thins down to form narrow necks. The resulting fracture surface consists of ductile dimples, with the brittle particles situated in their centres. A large amount of energy is dissipated during fracture due to the extensive plastic work.

The mobility of dislocations depends on the crystal structure and is highly temperature sensitive in bcc structures, where cross-slip plays an important role. Large differences in fracture energy can be observed depending on the temperature, with a transition from ductile to brittle behaviour as the temperature decreases. The transition is often close to ambient temperature for carbon steels (*cf.* Figure 17-2-2 for the effect of carbon), the fracture mode being mixed over a certain range of temperature. This is illustrated in Figure 14-1-4, where the energies at 20°C range from 20 to 70 J. The relative proportions of ductile and brittle fracture areas vary in the transition zone. Figure 14-1-5 shows schematic impact strength-temperature curves for austenitic, duplex and ferritic stainless steels. Face-centred-cubic austenitic structures do not show a ductile/brittle transition, remaining ductile at all temperatures.

In order to improve toughness, brittle precipitate particles should be avoided, particularly at grain boundaries, while the facility of cross-slip depends on the composition and is enhanced by the presence of nickel.

> *Spectacular examples of brittle fracture occurred in certain of the Liberty ships built with all-welded hulls during the second world war. Fractures initiated at low temperatures in the North Atlantic were able to propagate right through the structure, the vessel breaking in two.*
>
> *The tragic case of the Titanic, which sank on its maiden voyage in 1912, is another illustration. The steel employed, which represented a standard quality for the time, tore in a brittle manner in 2 °C water when the ship hit an iceberg. The sister ship Olympic remained in service for 20 years [Fe198]. The development of steels with*
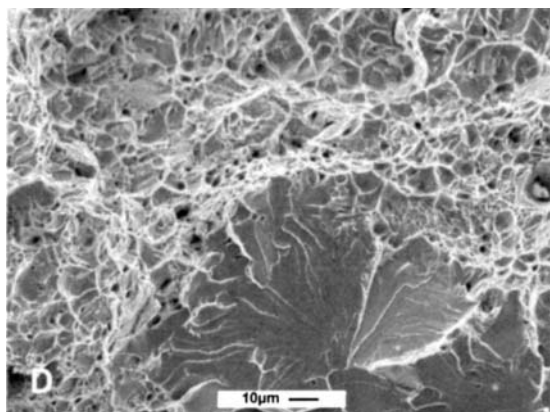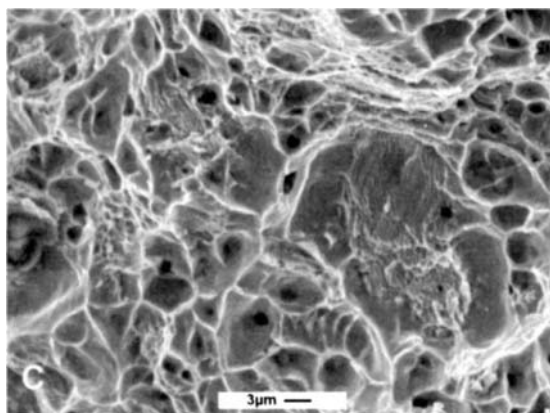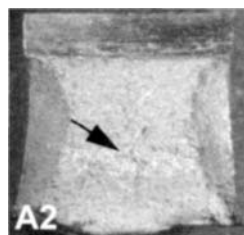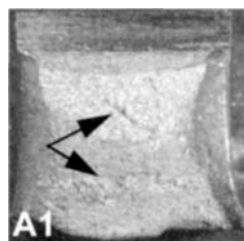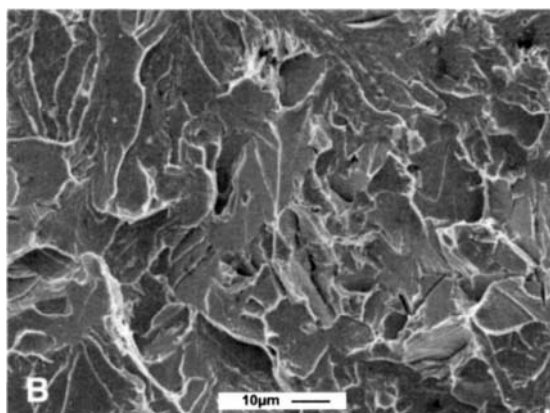
Figure 14-1-5:
Charpy fracture surfaces for a 1035 (C35E4) ferrite-pearlite steel.

A1, A2) Standard 1 cm^2 cross-section specimens broken at 20 °C, showing bright brittle zones (arrows) and dark ductile zones.

B) Scanning electron micrograph of the brittle zone, showing flat areas of cleavage radiating from a central point and forming a so-called river pattern. The deep grooves correspond to grain boundary fracture.

C) Scanning electron micrograph of the ductile zone, showing dimples in many of which a precipitate particle is clearly visible. One large dimple contains a region of pearlite.

D) Scanning electron micrograph of the transition between the ductile and brittle zones, revealing the difference in size of the two fracture morphologies.

Courtesy INPG, Grenoble, Fr.

improved toughness in the second half of the 20th century enabled their safe use in severe low temperature applications such as ice-breakers and arctic pipelines.

Formability

Formability is the ability of a material to be shaped by processes such as deep drawing, bending or rolling. It is greater the lower the yield strength and the greater the capacity to undergo plastic strain without fracture. Strain hardening is generally an advantage provided that it is not excessive, since it prevents local thinning (necking). Indeed, this is the principle of the so-called TRIP steels (TRansformation Induced Plasticity), in which strain-induced martensite formation maintains a high work hardening coefficient. While the intrinsic ductility of the material is of prime importance, forming behaviour can be impaired by the presence of inclusions that are either brittle or have weak interfaces. Ductile inclusions that can deform with the matrix are generally harmless, whereas hard and brittle phases, such as carbides, should be avoided. The inclusion population (cleanness) is determined essentially by the melting and refining practice, which must be carefully controlled (*cf.* § 15-4) [Phi02].

Hardness

The macroscopic hardness of a material provides a measure of its flow stress for a fixed amount of strain determined by the indenter geometry. The indenter is generally either a pyramidal diamond or a hard steel sphere, which is pressed into the specimen under a predetermined load. For a valid measurement of overall hardness, the volume beneath the indenter must contain a representative distribution of the different microstructural constituents present. The hardness of individual constituents can be evaluated in the same way with the aid of a microhardness indenter. Many phases commonly found in steels are very hard (Appendix 22-8). Indeed, their hardness is often used to advantage by embedding them in a relatively softer matrix (*e.g.* cast irons) or in a binder (*e.g.* tool steels) (*cf.* § 21-2). The behaviour of the material as a whole is determined by the properties of the particles and matrix and by the cohesion between them. High hardness generally confers good resistance to abrasive wear.

14-2   The effects of alloying elements

"Residual" elements

Commercial steels generally contain small amounts of many different elements, often considered as impurities or "tramp" elements. Some are introduced by contact with the atmosphere during melting and hot processing. They include oxygen, nitrogen and hydrogen, and can be present in solution or as compounds. Others, such as manganese, silicon, aluminium, magnesium and calcium, are deliberately used during refining of the liquid metal to remove oxygen and/or sulphur. The oxides and sulphides formed are mainly transferred to the slag, but small excess amounts of these additions can remain in

the metal. Manganese is often present in the raw materials and acts as a mild deoxidant, producing discontinuous MnO inclusions (and also sulphides). It prevents the formation of more harmful FeO at grain boundaries, but not the generation of CO. The evolution of CO bubbles during solidification causes frothing of the liquid and steels produced in this way are known as *rimming* grades. This can be prevented by the use of a more powerful deoxidant, such as silicon or aluminium. The steels are then said to be *killed*. Residual oxides containing these elements can be retained in the steels and represent a potential source of micro-cracks. Killed steels are more homogeneous, but the presence of higher carbon and silicon contents makes them harder and more difficult to process, and they are also more expensive.

Many residual elements are contained in the raw materials (*e.g.* Si, Al, P, As, S) and scrap (*e.g.* Ni, Cr, Cu, Sn) used to produce the steel. Lead, tin, antimony and arsenic are known to have deleterious effects, embrittling grain boundaries after welding or tempering [Gut77].

Deliberate micro-additions

A number of elements are added deliberately to steels in small amounts, from a few tens of ppm to the order of 1 %. Except for the interstitials, they have little influence on the distribution of the major phases. They can have numerous different effects, which are often interactive. Most of the mechanisms involved have already been discussed and are recalled briefly below to facilitate the interpretation of the summary table given in Appendix 22-7.

• Precipitation in the liquid phase (*e.g.* during solidification). Elements such as titanium and niobium have very low solubilities in the presence of carbon and nitrogen and are often used to tie up these species in a relatively harmless form. Manganese is often employed in a similar manner to scavenge sulphur. The formation of stable phases in the liquid can modify the solidification process by acting as nucleants.
• Precipitation due to interdendritic segregation, with the formation of minor phases at the end of solidification. Sulphur and phosphorus tend to segregate markedly in the inter-dendritic regions, leading to low incipient melting points and the risk of hot-shortness during processing. The presence of sufficient manganese will prevent sulphur segregation by forming MnS.
• Segregation to grain boundaries in the solid state of insoluble elements such as phosphorus, boron and sulphur, sometimes leading to precipitation by interaction with rapidly diffusing species, such as nitrogen (*e.g.* BN formation). Boron is believed to enhance grain boundary cohesion and sulphur to reduce it, while particles can provide strengthening by acting as pinning points, but when present in excessive quantities, may cause embrittlement.
• Precipitation during the tempering of martensite. Secondary hardening is produced by the precipitation of a fine dispersion of alloy carbides. The major carbide forming elements, in the order of increasing affinity for carbon (*i.e.* carbide stability), are Mn, Cr, W, Mo, V, Ti, Zr, Ta and Nb.

• Age hardening reactions. Apart from carbides, the addition of small amounts of insoluble elements can lead to precipitation strengthening, for example by copper particles (additions up to 3 % Cu) or intermetallic compounds (*e.g.* Ni_3Ti in maraging steels).

• Effects on quench hardenability. The aptitude of a steel to transform to martensite depends essentially on the Ms temperature and the rapidity of the pearlite and bainite transformations. Except for cobalt and aluminium, limited additions of all alloying elements increase hardenability. Strong carbide forming elements act indirectly, raising Ms due to removal of carbon from the austenite.

14-3   The common alloying additions

Stabilisation of ferrite or austenite

Elements that are liable to significantly modify the phase equilibria in the Fe-C system are considered as major alloying additions. Elements which extend the range of existence of the austenite field are said to be austenite or gamma stabilisers. The typical example, which is used as a reference, is nickel. Elements which decrease the austenite field and extend the range of the δ and α fields are called ferrite or alpha stabilisers. Chromium is considered as the reference in this case. The Fe-Ni and Fe-Cr phase diagrams are given in Figures 3-3-3 and 4-4-2 respectively. Figure 14-3-1 shows the effects of manganese, a gamma stabiliser, and silicon, a ferrite stabiliser, on the Fe-C diagram. The binary phase diagrams between iron and austenite stabilisers show two configurations. The elements Ni, Mn, Co, Pt, Pd, Ru, Rh, Os and Ir form a continuous range of solid solutions with austenite at high temperature, while the gamma field is limited in the systems with C, N, Cu, Au and Zn.

Two general types of binary diagram are also found for alpha stabilizing elements. The gamma loop is completely surrounded by ferrite in the systems with Cr, W, Mo, V, Ti, Si, Al, P, Be, As, Sn and Sb. In the case of S, B, Zr, Ta, Nb and Ce, the extent of the γ field is reduced without extending that of ferrite, being replaced by a two-phase equilibrium between austenite and an iron compound. The effect of the different alloying elements when associated with iron can be understood in terms of their crystal structures. Thus, most elements with fcc structures similar to that of austenite are gamma stabilisers. All the alpha stabilisers either themselves have bcc structures or form bcc compounds.

Nickel and chromium equivalents

In multi-component steels, it is useful to be able to evaluate the tendency to form ferrite or austenite by reference to the influence of chromium and nickel. Empirical formulae have been derived in which the ferrite or austenite stabilising effects of the different elements are expressed by a weighting coefficient referred to chromium or nickel. The sum of the ferrite-stabilising terms is called the chromium equivalent and that of the austenite stabilising terms the nickel equivalent. It is then possible to plot a two-dimensional diagram Ni_{eq} versus Cr_{eq} showing the ranges of existence of the different phases at ambient temperature
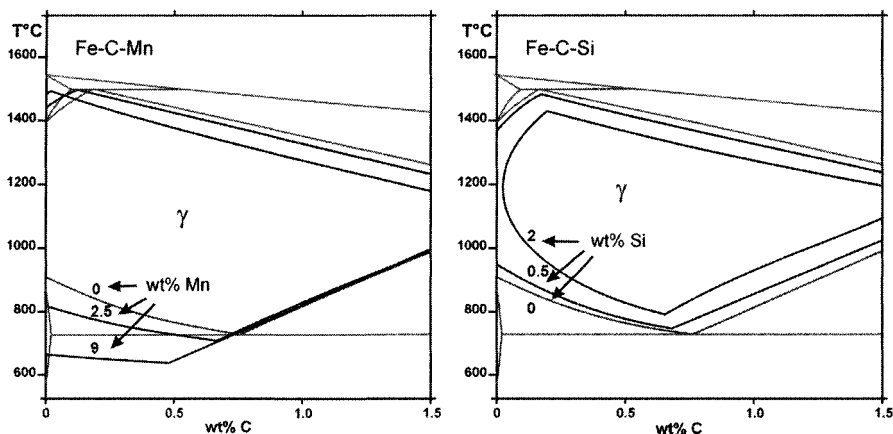
Figure 14-3-1:

Calculated isopleths showing the effect of manganese and silicon additions on the austenite phase field in the Fe-cementite-Mn and Fe-graphite-Si systems. The reference system (0% addition, grey) is Fe-cementite. Silicon is a ferrite stabiliser and reduces the extent of the austenite field. Manganese is a gamma stabiliser and extends the austenite field. The effects are quite significant even at low concentrations.
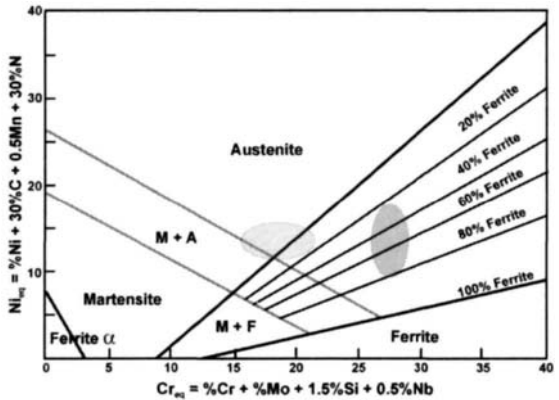
(Figure 14-3-2). The corresponding phase fields are shown by the black lines, which are valid for a particular austenitising temperature. Another important factor in practice is the tendency to form martensite on quenching, which depends on the Ms and Mf temperatures. This is represented in the diagram by the grey lines.

Diagrams of this type were originally designed to predict the structures of welds. The first one was that of Schaeffler in 1949 [Sch49], subsequently modified by Delong in 1960 [Del60] and then in 1973 [Lon73]. Figure 14-3-2 is a frequently used version of the Schaeffler diagram [Lac93]. The various diagrams differ chiefly by the number of elements included in the formulae for the equivalents and the values of their corresponding coefficients (*cf.* Appendix 22-3). Special equivalent formulae have been adapted for cast microstructures and for different types of alloys, for example, 12 % Cr steels and duplex stainless grades [Kra80], [Cam00]. A recent comparison between the predictions of these formulae and thermodynamic calculations showed excellent agreement for ferrite stabilizing elements, but relatively poor concordance for austenite stabilisers, particularly manganese [Ind02].

Another effect of chromium is to promote the formation of embrittling σ phase in the temperature range from 500–820°C (*cf.* Fe-Cr phase diagram, Figure 4-4-2). Other elements, such as silicon and molybdenum, stabilise sigma phase, extending its range of existence. Several elements stabilise both ferrite and sigma and there is a certain tendency to confuse the two effects. In fact, σ phase is an electron compound, whose existence is extremely sensitive to the average number and configuration of shared electrons. At lower temperatures, below about 500°C, high chromium contents lead to the decomposition of

Figure 14-3-2:
Schaeffler diagram. The black lines represent the phase field boundaries, while the grey lines indicate the region where either the Mf point (lower line) or both the Mf and Ms points (upper line) lie above ambient temperature. Between them, transformation to martensite is only partial.

ferrite into two bcc phases, α and α' (or α-Cr), by either a classical or spinodal mechanism, depending on the composition. This latter tendency is not a general characteristic of the ferrite stabilising elements.

The classification of steels

There are many different types of steels and their classification is not simple. In keeping with the general theme of the present work, the criterion chosen here is that of a common room temperature microstructure within each category. In this respect, the empirical Schaeffler and Delong diagrams provide excellent guides.

- *Mild steels and micro-alloyed* (HSLA) steels have ferritic structures close to that of pure iron. They are very ductile and have good corrosion resistance. They are situated in the a ferrite region in the Schaeffler and Delong diagrams. They are widely employed for sheet forming operations and are often used in the coated condition. The HSLA grades combine high strength and toughness and are also manufactured in the form of long products for structural applications.

- *Hardenable steels* include low alloy grades that can be transformed to martensite, bainite or pearlite by controlled cooling from the austenite field. They are situated in the region labelled Martensite in the Schaeffler and Delong diagrams. The matrix of high carbon and alloy grades such as the high speed and tool steels also depends on heat treatment, but contains additional primary and secondary carbides. These materials are manufactured in the form of long products, for abrasion-resistant applications, such as cutting tools and bearings.

- *The martensitic stainless steels* have a chromium content sufficient to ensure good corrosion resistance (typically 12–17 %) while remaining within the gamma loop at high temperatures. They are situated in the M+F or martensite regions of Figure 14-3-2 depending on the carbon (and sometimes nickel) contents. They are used for applications requiring a combination of high strength, hardness and corrosion resistance, such

as engineering components, high temperature bolting, tooling, cutlery, etc. The precipitation hardened (PH) martensitic stainless steels are strengthened by fine particles of copper or intermetallic compounds. They are in fact stainless maraging grades.

- *The austenitic stainless steels* contain sufficient chromium to ensure good corrosion resistance, together with gamma stabilising elements, especially nickel, to promote an austenitic structure. Their compositions lie mainly within the light grey oval shown in Figure 14-3-2. They find many applications for equipment in the food and pharmaceutical industries, for domestic appliances, cooking utensils, sinks, etc.

- *The ferritic stainless steels* contain essentially alpha stabilising elements, particularly chromium, with compositions such that they lie outside the gamma loop in the phase diagram. They are situated in the ferrite field in the Schaeffler and Delong diagrams.

- *The duplex stainless steels* are high chromium, nickel-containing grades whose structure typically contains roughly equal proportions of ferrite and austenite. They are represented by the dark grey oval in Figure 14-3-2. They are employed for parts demanding a combination of high strength and excellent corrosion resistance for severe petroleum, chemical and nuclear engineering applications.

- *The heat-resisting alloys* and iron-containing superalloys are austenitic materials that maintain good strength and corrosion resistance at high temperatures. They find a wide range of applications in the fields of high temperature processing, heat treatment, power generation, aircraft and automobile engines, etc. This category is often at the limit of what can be reasonably termed steels and covers a variety of alloys and structures, each optimised for a particular high performance utilisation.

The roles of the different alloying elements are summarised in Appendix 22-7).