Humankind has used iron products since at least 1200 B.C. Even though iron is one of the five most abundant elements in the Earth’s crust by weight, occurrences of metallic iron in nature are scarce and normally associated with meteorites. Thus, to make iron products, humanity has developed processes to extract it from iron oxides, the most common iron ores. As the most common fuels in nature are rich in carbon, which under the right conditions can reduce iron oxides to metallic iron, carbon has played a decisive role in the development of products made of iron and its alloys.

The presence of carbon in the steps to manufacture iron-based products probably led to the observation that this element has important effects on the properties of iron alloys. This observation gave rise to the main iron-based alloys: steels and cast irons. Iron and its alloys have been produced for many centuries by artisanal methods that have comprised many different processes for reducing iron (i.e. converting it from an oxidized state) from its naturally occurring ores together with some mechanical work and some control of heating and cooling conditions (see Chapter 2, “Processes in Steel Production,” in this book). A turning point came when it was noticed that substantial alloying with carbon significantly lowered the alloy melting point: this made possible, around the 18th century, the production of liquid iron alloys on an industrial scale and thus of large quantities of iron-based alloys. Thus, from around 40,000 t/yr in 1856, humankind entered the 21st century regularly producing 1,000 Mt/yr of steel. (Unless otherwise noted, the units of the International System, SI, are used in this book. Here, in particular, steel production is given in millions of metric tons.)

The evolution of steel usage as an engineering material is related to many technical and economic aspects. In particular, in the last decades of the 20th century, the accumulated knowledge of the relations between chemical composition, structures, properties, and performance, together with the effect of processing on these features, has reached a level that allows continuous scientific development of new alloys and improvement of available ones.
One of the important tools in this development has been (and still is) metallography. The understanding of the relationships between properties and structure in the scale of micrometers (μm, \(10^{-6}\) m) to millimeters (mm, \(10^{-3}\) m) depends largely on metallography, a science established on the basis of the initial research of Henry Clifton Sorby in Sheffield, England, around 1860. Together with a variety of other important tools for characterizing metals, metallography has become so essential to the understanding of the behavior of steels that almost all materials engineering courses dedicate a significant amount of time to teaching this topic. Furthermore, it is essentially impossible to find an industrial establishment producing or processing steel that does not rely on metallographic techniques at some stage of development, quality control, or failure analysis.

For at least the last two centuries, iron-based alloys (mixtures of metals, or of a metal and another element that exhibit metallic behavior or have a metallic bonding character) have occupied an important position among industrial materials. The two main families of iron alloys are steels and cast irons. Steels are the most widely used iron-based alloys. One of the most important differences between steels and cast irons is the ability of steels to deform plastically.

Many factors contribute to the importance of steel as an industrial material. Iron ores are abundant, and modern steel plants have achieved low production costs. Furthermore, steels can achieve remarkable combinations of physical and mechanical properties. Today steels are also valued for their ability to be recycled. When steels are discarded, they degrade quickly to oxides that are not harmful; moreover, they require relatively low amounts of energy to be produced and even less to be recycled. Because most steels are magnetic, they are easy to separate from other materials during recycling. Thus, steel is a highly sustainable material.

The ability to properly manipulate steel characteristics to obtain the right combination of chemical composition and structure (at various scales) for a given application allows one to achieve extraordinary performance with steel, combined with outstanding combinations of physical and mechanical properties.

Structure is a fundamental concept in materials science, materials engineering, and metallurgy. Although the atomic structure is important in defining some aspects of material behavior, the classical study of structures begins at the crystalline structure level. Most metals and industrial alloys, including the vast majority of steels, are used in conditions under which the atoms are regularly organized in a lattice, forming a crystal. The way the atoms are organized in a metal or in an alloy determines several properties of the metal. Ferrous alloys having the face-centered cubic (FCC) structure, for instance, are nonmagnetic, whereas alloys with the body-centered cubic (BCC) structure are ferromagnetic at room temperature.

Structure—from the crystalline structure level (nm, \(10^{-9}\) m)—plays a role in determining steel performance. However, steel items seldom are composed of a single crystal or even of a single phase. The way different crystals organize themselves in a polycrystalline material, their size and shape, as well as the amount of each phase that might be present in the material are the characteristics normally occurring in the range of dimensions conventionally referred to as microstructural (μm scale).
The mass production of steel at rates compatible with a world production on the order of 1000 Mt/yr (1649 Mt in 2013) results in heterogeneities in chemical composition and properties in larger dimensions, at a scale conventionally called macrostructural (mm scale). Figure 1.1 schematically depicts steel structural features in the ranges discussed. Properly controlling structure (at all scales) is one of the most important tools for producing steels with proper properties and performance.

Almost every metal exhibits, at ambient pressure (1 atm or $1.013 \times 10^5$ Pa), a single stable crystal structure from room temperature to its melting point. The most common metal structures are the FCC and hexagonal close-packed (HCP), both compact structures, and the BCC structure, which is not compact. In this respect, iron is exceptional in exhibiting polymorphism. Depending on temperature, iron can have two different crystal structures at ambient

1.3 Crystal Structure of Iron-Based Alloys
pressure. At low temperatures (up to 910 °C, or 1670 °F) iron is BCC. Above this temperature, FCC becomes more stable. At temperatures above 1394 °C BCC becomes stable again, up to the melting point of iron at 1535 °C (2795 °F). Thus, different phases (regions of a material that are chemically uniform and physically distinct) of iron are stable at different ranges of temperature and pressure (Fig. 1.2).

Causing and controlling the transformations between these two structures is one of the most important and most widely used tools in the control of steel product microstructure. How atoms are arranged in a given crystal structure depends on how these atoms interact. When other elements are mixed with the iron atoms, forming an alloy, the relative stability of the different phases is changed. Carbon addition to iron, for instance, causes important changes in the relative stability of iron phases and introduces the possibility of new phases forming. One of the ways of representing these changes is through a phase equilibrium diagram, as shown in Fig. 1.3. This diagram shows that carbon additions of up to around 4.2% (mass percent, as are all compositions in this book unless otherwise noted) lower the melting point and that additions up to around 0.8% C increase the stability of the FCC phase with respect to the BCC phase. Thus, adding alloying elements to iron allows one to tailor the relative stability of the phases and affect the structure that will be formed in a steel. These elements have other important effects, which are discussed in more detail later.

1.4 Steel Characterization

The combination of chemical composition and structure defines steel properties. Many analytical chemistry methods and techniques can be used to characterize chemical composition. Structure can also be characterized by a

![Fig. 1.2](a) Body-centered cubic (BCC) structure. The lattice parameter for pure iron at room temperature is 2.86 Å. (b) Face-centered cubic (FCC) structure. The lattice parameter for pure Fe at room temperature is approximately 3.66 Å.
wide range of techniques, depending, among other factors, on the scale of the structure. Table 1.1 presents some structural characterization techniques related to the dimensional scale at which they are applicable. Metallographic techniques (both micro- and macrographic) are applied to the structure characterization at the microscopic and macroscopic scales, respectively. The structural characteristics that are most relevant to the development and control of steel features are in the range of 10 nm to 1 mm. For this reason, metallography has a paramount role in steel characterization. The various metallographic characterization techniques are discussed in more detail in Chapter 4, “Metallographic Technique: Macrography,” Chapter 5, “Metallographic Technique: Micrography,” and Chapter 6, “Metallographic Technique: Electron Microscopy and Other Advanced Techniques,” all in this book.

Besides carbon, which is not always a desirable alloying element, many chemical elements may be present in a steel. Elements not intentionally added are called residuals. Elements added to steel to affect its behavior are usually called alloying elements. However, many elements that are not classified as residuals or alloying elements are critical to the behavior of steels and are frequently omitted from discussions on steel chemical compositions. Figure 1.4 lists the main functions of alloying elements as normally accepted. Besides these, elements coming from scrap (such as copper, arsenic, antimony, zinc, and lead) and those coming from the atmosphere (such as nitro-

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**Fig. 1.3** The Fe-C phase equilibrium diagram at 1 atm. The phase transformations of Fe are indicated on the vertical axis (0% C), corresponding to pure Fe. The range of temperatures in which FCC (called $\gamma$, or austenite) is stable increases with the addition of C up to around 0.8%, and then decreases. The BCC phase (called ferrite) is able to dissolve only 0.018% C in its low-temperature range ($\alpha$). Above this limit, other phases are more stable and are formed. The metastable Fe-C phase diagram is frequently used and is discussed in Chapter 7, “Equilibrium Phases and Constituents in the Fe-C System,” in this book.

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1.5 Chemical Composition of Steels
gen, hydrogen, and oxygen, the last of which is the main refining agent in steelmaking and dissolves significantly in liquid steel; see Chapter 2, “Processes in Steel Production”) also must be considered when discussing residuals in steels. Several elements can be residuals in some steels and deliberate additions in others. For instance, copper is added to weathering steels to promote the formation of a patina. Also, lead can be used to promote machinability, although this use is declining because of its environmental impact.

The main effects of elements added to steel, summarized in Fig. 1.4, are discussed in detail in the following chapters.

<table>
<thead>
<tr>
<th>Scale (approximate dimensions)</th>
<th>Characterization techniques</th>
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</thead>
<tbody>
<tr>
<td>Crystalline structure (Å)</td>
<td>X-ray diffraction</td>
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<tr>
<td></td>
<td>Transmission electron microscopy (electron diffraction)</td>
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<tr>
<td>Structural features in the range of 10–100 nm (dislocations, stacking faults, ultrafine grains, etc.)</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>100 nm–1000 µm</td>
<td>Scanning electron microscopy</td>
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<td>Atom force microscopy</td>
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<td>1–1000 µm</td>
<td>Optical microscopy</td>
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<td>Confocal laser microscopy</td>
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<tr>
<td>1–1000 mm</td>
<td>Macrography</td>
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Fig. 1.4  Schematic presentation of the main effects and functions of chemical elements added to steel. In parentheses, some specific examples of each function are presented. Evidently, some elements have more than one function in the alloy design of a given steel.