STEEL

1. Introduction

Steel, the generic name for a group of ferrous metals composed principally of iron (qv), is the most useful metallic material known on account of its abundance, durability, versatility, and low cost. In the form of bars, plates, sheets, structural shapes, wire pipe and tubing, forgings, and castings, steel is used in the construction of buildings, bridges, railroads, aircraft, ships, automobiles, tools, cutlery, machinery, furniture, household appliances, and many other articles on which the convenience, comfort, and safety of society depends. Steel is also an essential material for spacecraft and supporting facilities as well as in practically every kind of material needed for national defense (see BUILDING MATERIALS, SURVEY; TOOL MATERIALS).

The durability and versatility of steel are shown by its wide range of mechanical and physical properties. By the proper choice of carbon content and alloying elements, and by suitable heat treatment, steel can be made so soft and ductile that it can be cold-drawn into complex shapes such as automobile bodies. Conversely, steel can be made extremely hard for wear resistance, or tough enough to withstand enormous loads and shock without deforming or breaking. In addition, some steels are made to resist heat and corrosion by the atmosphere and by a wide variety of chemicals.

About 1 billion metric tons of raw steel are produced annually throughout the world (2004) with China responsible for ~25%. Its usefulness is enhanced by the fact that it has historically been inexpensive. The price as of early 2004 ranged from 40–50 c/kg for the common grades to several dollars per kg for special steels such as certain tool steels. Prices, that have remained relatively constant since the early 1980s occasionally benefit from import restrictions, currency exchange rates, and (at the time of writing) from sudden increases in the price of items used in manufacturing, notably scrap that more than doubled in price because of high demand from China.

The uses of steel are too diverse to be listed completely or to serve as a basis of classification. Inasmuch as grades of steel are produced by more than one process, classification by method of manufacture is also not advantageous. The simplest classification is by chemical composition into the large groups of carbon steels, alloy steels, and stainless steels. Within these groups are many subdivisions based on specific chemical composition, physical or mechanical properties, and/or uses.

It has been known for many centuries that iron ore, embedded in burning charcoal, can be reduced to metallic iron (1,2). Iron was made by this method as early as 1200 BC. Consisting almost entirely of pure iron, the first iron metal closely resembled modern wrought iron, which is relatively soft, malleable, ductile, and readily hammer-welded when heated to a sufficiently high temperature. This metal was used for many purposes, including agricultural implements and various tools.

It is not known when the first metal resembling modern carbon steel was made intentionally. It has been speculated that steel was made in India ~100 BC. Remains of swords with steel blades have been found in Luristan, a western province of Iran (formerly Persia), at sites dated at ~800 BC.

Most modern steels contain $>98\%$ iron. However, steel also contains carbon, which, if present in sufficient amounts (usually $> 0.3\%$ up to $\sim 2\%$), gives a property unmatched by any of the metals available to the ancients. This property is the ability to become extremely hard if cooled very quickly (quenched) from a high enough temperature, as by immersing it in water or some other liquid. Its hardness and the ability to take and hold a sharp cutting edge make steel an extremely valuable metal for weapons, tools, cutlery, surgical instruments, razors, and other special forms.

It was not until the eighteenth century that carbon was recognized as a chemical element, and it is quite certain that no early metallurgist was aware of the basis of the unique properties of steel as compared to those of wrought iron. Carbon can be alloyed with iron in a number of ways to make steel, and all methods described herein have been used at various times in many localities for perhaps 3000 or more years.

For example, low carbon wrought-iron bars were packed in air-tight containers together with charcoal or other carbonaceous material. By heating the containers to a red heat and holding them at that temperature for several days, the wrought iron absorbed carbon from the charcoal; this method became known as the cementation process. If the iron is made in primitive furnaces, carbon can be absorbed from the charcoal fuel during and after its reduction. The Romans, eg, built and operated furnaces that produced a steel-like metal instead of wrought iron. In neither of the two foregoing cases did the iron or steel reach sufficiently high temperatures to become molten.

In ancient India, a steel called *wootz* was made by placing very pure iron ore and wood or other carbonaceous material in a tightly sealed pot or crucible heated to high temperature for a considerable time. Some of the carbon in the crucible reduced the iron ore to metallic iron, which absorbed any excess carbon. The resulting iron–carbon alloy could give an excellent grade of steel. In a similar way, pieces of low carbon wrought iron were placed in a pot along with a form of carbon and melted to make a fine steel. In the eighteenth century, a variation of this method, in which bars that had been carburized by the cementation process were melted in a sealed pot to make steel of the best quality, became known as the crucible process.

Before the invention of the Bessemer process for steelmaking in 1856, only the cementation and crucible processes were of any industrial importance and of course were available in limited quantities. Although both of the latter processes had been known in the ancient world, their practice seems to have been abandoned in Europe before the Middle Ages. The cementation process was revived in Belgium ~ 1600, whereas the crucible process was rediscovered in the British Isles in 1740. Both processes were practiced in secret for some time after their revival, and little is known of their early history. The cementation process flourished in the United Kingdom during the eighteenth and nineteenth centuries and continued to be used to a limited extent into the early part of the twentieth century. At red heat, a low carbon ferrous metal, in contact with carbonaceous material such as charcoal, absorbed carbon that, up to the saturation point of $\sim 1.70\%$, varied in amount according to the time the metal was in contact with the carbon and the temperature at which the process was conducted. A type of muffle furnace or pot furnace was used and the iron and charcoal were packed in alternate layers.

In the softer grades (average carbon content ∼0.50%), the composition of the bar was uniform throughout. In the harder grades (average carbon content as high as 1.50%), the outside of a bar might have a carbon content of 1.50–2.00%, whereas the center contained 0.85–1.10%. Steels made by this method were called cement steels.

The crucible process gave steels that were not only homogeneous throughout, but were free from occluded slag originating in the wrought iron used to make cement steel. Crucible steel was so superior to cement steel for many purposes that the crucible process quickly became the leader for the production of the finest steels. Its drawback was, however, that each crucible held only ∼50 kg steel.

The various steelmaking processes were all eventually supplanted (3,4). The first of the newer techniques was the historic pneumatic or Bessemer process, introduced in 1856. Shortly thereafter, the regenerative-type furnace, known in the 1900s as the open-hearth furnace, was developed in Europe. Adapted to steelmaking, the open-hearth process was the principal method for producing steel throughout the world until 1970. As of this writing (2004), it is essentially phased out.

Since 1970, the most widely used processes for making liquid steel have been the oxygen steelmaking processes, in which commercially pure oxygen (99.5% pure) is used to refine molten pig iron. In the top-blown basic oxygen process, oxygen is blown down onto the surface of the molten pig iron containing such coolants as scrap steel or iron ore for temperature control. In the bottom-blown basic oxygen process (Q-BOP), the oxygen is blown upward through the molten pig iron. The direction in which the oxygen is blown has important effects on the final steel composition and on the amount of iron lost to the slag. Many plants today use a combination of top and bottom blowing.

Liquid steel is also made by melting steel scrap in an electric-arc furnace. This process is now a significant contributor to large-scale production and today makes about 30% of the steel in Japan and at least 50% in the United States. As demand has gone up, the world price of premium scrap has increased substantially—maybe 50 to >100% in some cases recently. Since scrap is a major part of electric melting costs, this is now a major criterion and leads to price surcharges.

Pig iron (with more predictable costs), and iron and steel scrap are the sources of iron for steelmaking in basic-oxygen furnaces. Electric furnaces historically relied on iron and steel scrap, although newer iron sources such as direct-reduced iron (DRI), iron carbide, and even pig iron are becoming both desirable and available (see Iron). In basic-oxygen furnaces, the pig iron is used in the molten state as obtained from the blast furnace; in this form, it is referred to as hot metal.

Pig iron consists of iron combined with numerous other elements. Depending on the composition of the raw materials used in the blast furnace, principally iron ore (beneficiated or otherwise), coke, and limestone, and the manner in which the furnace is operated, pig iron may contain 3.0–4.5% carbon, 0.15–2.5% or more manganese, as much as 0.2% sulfur, and 0.025–2.5% phosphorus; silicon can be as low as 0.15% with modern techniques and is almost always $< 0.8\%$. Sulfur, phosphorus, and silicon can be and today usually are, reduced significantly by treating the hot metal between the blast furnace and the steelmaking vessel. During the steelmaking process, many but not all solutes are reduced, often drastically.

Steelmaking processes were historically either acid (silica rich refractory linings) or basic (calcium or magnesium rich). Acid processes have virtually disappeared. Basic slags, rich in lime, are able to absorb much of the unwanted sulfur and phosphorus, and also do not react so vigorously with the furnace linings, which are predominantly magnesite or dolomite. In electric melting, when the power loading is high, it may be necessary to water-cool these linings.

Oxidation is employed to convert a molten bath of pig iron and scrap, or scrap alone, into steel. Each steelmaking process has been devised primarily to provide some means by which controlled amounts of oxygen can be supplied to the molten metal undergoing refining. The increase in oxygen potential in the iron bath may be thought of most simply as burning out impurities either as a gas (eg, CO) or an oxide (eg, MnO, P_2O_5, or SiO_2) which dissolves in the slag. More exactly, it is an ionic liquid–metallic liquid equilibration where the distribution coefficient depends on compositions of slag and metal and also on temperature. The impurities, including the majority of the sulfur, exist largely as ions in the slag. As the purification of the pig iron proceeds, owing to the removal of carbon, the melting point of the bath is raised, and sufficient heat must be supplied to keep the bath molten.

In general, steels having similar chemical compositions and thermal treatment have similar mechanical and physical properties, no matter by which process they are made, unless the patterns of inclusions (oxides, silicates, and sulfides) are very different when toughness and large plastic deformations can be affected.

Methods exist to make impure iron directly from ore, ie, to make DRI without first reducing the ore in the blast furnace to make pig iron that has to be purified in a second step. These processes, generally referred to as direct-reduction processes, are employed where natural gas is readily available for the reduction (see also IRON). Carbonization of iron ore to make iron carbide as an alternative source of iron units is in its infancy and has been slow to develop.

2. Electric Furnace Processes

The principal electric furnace steelmaking processes are the electric-arc furnace, induction furnace, consumable-electrode melting, and electroslag remelting. The main raw material for all these processes is solid steel. As implied by the term “steelmaking”, in the first two processes steel is made that is different in composition and shape from the starting material, which is usually steel scrap and/or DRI. The starting material used for the last two processes closely resembles the desired steel ingot subsequently rolled or forged, and yields very high quality steel for applications with extremely strict requirements.

2.1. Electric-Arc Furnace.

The electric-arc furnace is by far the most popular electric steelmaking furnace. The carbon arc was discovered by Sir Humphry Davy in 1800, but it had no practical application in steelmaking until Sir William Siemens of open-hearth fame constructed, operated, and patented furnaces operating on both direct- and indirect-arc principles in 1878. At that early date, the availability of electric power was limited and very expensive. Furthermore, carbon electrodes of the quality to carry sufficient current for steel melting had not been developed (see FURNACES, ELECTRIC).

The first successful direct-arc electric furnace, patented by Heroult in France, was placed in operation in 1899. The patent covered single- or multiphase furnaces with the arcs placed in series through the metal bath. This type of furnace, utilizing three-phase ac power, was historically the most common for steel production.

The first direct-arc furnace in the United States was a single-phase two-electrode rectangular furnace of 4-t capacity at the Halcomb Steel Company (Syracuse, New York), which made its first heat in 1906. A similar but smaller furnace was installed 2 years later at the Firth-Sterling Steel Company in McKeesport, Pennsylvania. In 1909, a 15-t three-phase furnace was installed in the South Works of the Illinois Steel Company, in Chicago, Illinois, which was, at that time, the largest electric steelmaking furnace in the world. It was the first round (instead of rectangular) furnace and operated on 25-cycle power at 2200 V.

Electric-arc furnaces offer the advantages of low construction costs, flexibility in the use of raw materials, the ability to produce steels over a wide range of compositions (carbon, alloy, and stainless) and to operate below full capacity without major operating problems.

The biggest change in steelmaking in the last quarter of the twentieth century is the fraction of steel made by remelting scrap or, increasingly, other iron units, in an electric-arc furnace (EAF). This change was originally to serve a relatively nondemanding local market, but has increased in both quality and quantity of products to compete with mills using the blast furnace/oxygen steelmaking route (5,6). As of 2004, market share is at least 40–50%. Because the cost of entry into the market is attractive for electric melting relative to integrated plants, and because they can serve local markets, a plethora of new plants has been built or is being planned as of today. With many million metric tons of new capacity having advanced features now installed, competition is expected to remain fierce.

Early processes used three-phase ac, but increasingly the movement is to a single dc electrode with a conducting hearth. The high power densities and intense temperatures necessitate both water cooling and improved basic refractory linings. Scrap is charged into the furnace, which usually contains some of the last heat as a liquid heel to improve melting efficiency. Oxygen is blown to speed the reactions, which do not differ in any significant way from basic-oxygen furnace (BOF) steelmaking. Oxy-fuel burners are also used to accelerate scrap heating and reduce electricity consumption. Various techniques are applied to ensure adequate separation of melt and slag to permit effective ladle treatment. A fairly common practice is to use eccentric bottom tapping (Fig. 1), which minimizes vortexing.

Historically, much of the refining was done in the furnace, including a second slag made after the first meltdown and refining by oxygen blowing. Thus it had relatively low productivity. Today the furnace is usually strictly a melting unit of 50–200 t. Final treatment takes place in a ladle furnace, which allows refining, temperature control, and alloying additions to be made without delaying the next heat. The materials are continuously cast with various degrees of sophistication, including slabs down to 50 mm in thickness. Direct casting to sheet is in the advanced prototype stage.

The degree to which electric melting can replace more conventional methods is of great interest and depends in large part on the availability of sufficiently pure scrap or other iron units at an attractive price. Some improvements in quality are also needed to make the highest value products. Advances in electric furnace technology are being aggressively countered by developments and cost control in traditional steelmaking. The "quality gap" continues to decrease.

The energy needed to melt steel is much less than that required to reduce iron oxide to a molten product. The latter can be >2000 kWh/t for the chemical reaction alone. To melt steel from room temperature takes <400 kWh/t. By using some preheat from waste gases, actual electrical usages in best practice can be <395 kWh/t, an advance from 450 to 500 kWh/t needed in the 1980s.

The best labor practices in integrated mills can now be <3 man- h/t for sheet, whereas electric furnaces are easily <1 h/t. The best plants are ~0.5 h/t. At labor costs of $18–$28/h, this represents a real financial advantage. Thus electric melting has taken the segments of the market wherever the product is "good enough" and by continual improvements it is nibbling away at other segments. As of this writing (2004), deep drawing sheet, tinplate, electrogalvanized steel, and some high quality bars are still largely in the integrated sector.

2.2. Induction Furnace. The high frequency coreless induction furnace is used in the production of complex, high quality alloys such as tool steels. It is used also for remelting scrap from fine steels produced in arc furnaces, for melting chrome–nickel alloys and high manganese scrap, and more recently for vacuum steelmaking processes.

The induction furnace was first patented in Italy in 1877 as a low frequency furnace. It was first commercially applied, installed, and operated in Sweden. The first installation in the United States was made in 1914 by the American Iron and Steel Company in Lebanon, Pennsylvania; however, it was not successful. Other low frequency furnaces have been operated successfully, especially for stainless steel.

Most commonly, the melting procedure is essentially a dead-melt process, ie, the solid constituents of the charge melt smoothly and mix with each other. Little if any refining is attempted in ordinary induction melting, and no chemical reactions occur where gaseous products agitate the molten bath. The charge is selected to produce the composition desired in the finished steel with a minimum of further additions, except possibly small amounts of ferroalloys as final deoxidizers. For ordinary melting, the high frequency induction furnace is not used extensively.

2.3. Vacuum and Atmosphere Melting. A coreless high frequency induction furnace is enclosed in a container or tank that can be either evacuated or filled with a gaseous atmosphere of any desired composition or pressure. Provision is made for additions to the melt, and for tilting the furnace to pour its contents into an ingot mold also enclosed in the tank or container without disturbing the vacuum or atmosphere in the tank (Fig. 2).

Although vacuum melting has often been employed as a remelting operation for very pure materials or for making electrodes for the vacuum consumable-electrode furnace, it is generally more useful in applications that include refining. Oxygen and hydrogen are removed from the molten metal in vacuum melting, as well as carbon when alloys of very low carbon content are being produced (7,8). Nitrogen is more difficult to remove completely.

2.4. Consumable-Electrode Melting. This refining process produces special-quality alloy and stainless steels by casting or forging the steel into an electrode that is remelted and cast into an ingot in a vacuum (Fig. 3). These special steels include bearing steels, heat-resistant alloys, ultrahigh strength missile and aircraft steels, and rotor steels.

A consumable-electrode furnace consists of a tank that encloses the electrode and a water-cooled copper mold. After the furnace has been evacuated, power is turned on and an arc is struck between the electrode and a starting block that is placed in the mold before operation begins. Heat from the arc progressively melts the end of the electrode. Melted metal is deposited in a shallow pool of molten metal on the top surface of the ingot being built up in the mold. Rate of descent of the electrode is automatically controlled to maintain the arc. The remelting operation removes gases (hydrogen, oxygen, and to some degree nitrogen) from the steel, improves its cleanliness, produces an ingot that exhibits practically no center porosity or segregation, and improves hot workability and the mechanical properties of the steel at both room and high temperatures. A second remelting can further improve quality—of course at extra cost.

2.5. Electroslag Remelting. Remelting of electroslag has the same general purpose as consumable-electrode melting, and a conventional air-melted ingot serves as a consumable electrode. No vacuum is employed. Melting takes place under a layer of slag that removes unwanted impurities. Grain structure and orientation are governed by controlled cooling during solidification.

2.6. Powder Techniques. Highly alloyed materials made by the processes described are particularly susceptible to segregation of alloying elements during solidification both on a macro- and a microscale. Much plastic working may be necessary to minimize this susceptibility before service applications.

An ingenious method to avoid or reduce segregation of alloying elements involves preparing small spheres of material by the atomization of a liquid stream through a nozzle to produce a powder. This powder can be compacted, often hot and triaxially by gas pressure, to form a material where, on further heating, the residual pores close by diffusion to approach 100% density quite closely.

3. Oxygen Steelmaking Processes

In oxygen steelmaking, 99.5% pure oxygen gas is mixed with hot metal, causing the oxidation of the excess carbon and silicon in the hot metal and thereby producing steel. In the United States, this process is called the basic-oxygen process (BOP) (4,9,10). The first U.S. commercial installation began operation in 1955.

Blowing with newly cheap oxygen was investigated in Germany and Switzerland some years before the first commercial steelmaking plants to use this method began operation in Austria in the early 1950s. This operation was designed to employ pig iron produced from local ores that were high in manganese and low in phosphorus. The process spread rapidly throughout the world, largely displacing open hearths.

3.1. Top-Blown Basic Oxygen Process.

The top-blown basic oxygen process is conducted in a cylindrical furnace somewhat similar to a Bessemer converter. This furnace has a dished bottom without holes and a truncated cone-shaped top section in which the mouth of the vessel is located. The furnace shell is made of steel plates ~50-mm thick; it is lined with refractory 600–1200-mm thick (11).

A jet of gaseous oxygen is blown at high velocity onto the surface of a bath of molten pig iron and scrap at the bottom of the furnace by a vertical water-cooled retractable lance inserted through the mouth of the vessel (Fig. 4). The furnace is mounted in a trunnion ring and can be tilted backward or forward for charging and tapping.

When the furnace is tilted toward the charging floor, which is on a platform above ground level, solid scrap is dumped by an overhead crane into the mouth of the furnace. Scrap can form up to 30% of the charge unless it is preheated, when up to 45% may be used. The crane then moves away from the furnace and another crane carries a transfer ladle of molten pig iron to the furnace and pours the molten pig iron on top of the scrap.

The manganese residue of the blown metal before ladle additions is generally higher than in an open-hearth process and is closely related to the amount of manganese in the furnace charge. High slag fluidity and good slag–metal contact promote transfer of phosphorus from the metal into the slag, even before the carbon reduction is complete. Efficiency of sulfur elimination is as good as or better than that in the basic open-hearth process because the bath action is more vigorous, the operating temperatures are higher, and the fuel does not contain sulfur.

Because the basic-oxygen process uses a refining agent containing practically no nitrogen, the product has a low nitrogen content. Oxygen residues depend on the carbon content.

Residual alloying elements such as copper, nickel, or tin are usually considered undesirable. Their main source is purchased scrap. Because of the generally high consumption of hot metal in the basic-oxygen process, the residual alloy content is usually sufficiently low, depending on the quality of the purchased scrap.

No external heat source is required. In all types of steelmaking that employ pig iron, which melts at temperatures well below low carbon steel, the heat balance between exothermic oxidation of elements, such as C, Si, and Mn, and the cooling provided by scrap or sometimes other endothermic coolants, such as iron ore, are critical issues. The numerical factors are well understood and are routinely contained in computer programs used by operators. If the balance is such that the temperature after blowing is too high, refractory consumption is increased significantly.

After charging, Fig. 6 the furnace is immediately returned to the upright position, the lance is lowered into it to the desired height above the bath, and the flow of oxygen is started. Striking the surface of the liquid bath, the oxygen immediately forms iron oxide, part of which disperses rapidly through the bath. Carbon monoxide generated by the reaction of iron oxide and carbon is evolved, giving rise to a violent circulation that accelerates refining. Some of the sensible heat of combustion of this carbon monoxide can be captured enabling more scrap to be melted for a given bath composition.

Slag-forming fluxes, chiefly burnt lime, fluorspar, and mill scale (iron oxides), are added in controlled amounts from an overhead storage system shortly before or after the oxygen jet is started. These materials, which produce a slag of the proper basicity and fluidity, are added through a chute built into the side of a water-cooled hood positioned over the mouth of the furnace. This hood collects the gases and the dense reddish brown fume emitted by the furnace during blowing, and conducts them to a cleaning system where the solids are removed from the effluent gas before it is discharged to the atmosphere. Without access to sintering machines, which are largely closed by environmental constraints but used to be valuable facilities to recycle dusts of various types, easy disposal is a problem (12). Most proposed solutions attempt to recycle the iron units into the system.

The oxidizing reactions take place so rapidly that a 300-metric-ton heat, eg, can be processed in 30 min or less. The intimate mixing of oxygen with the molten pig iron permits this rapid refining. Mixing oxygen with the molten pig iron gives a foamy emulsion of oxygen, carbon monoxide, slag, and molten metal that occupies a volume about five times that of the slag and molten metal. The furnace must be big enough to accommodate this foamy mixture.

The mechanism of carbon elimination is similar to those of the earlier open-hearth processes, ie, oxidation of carbon to carbon monoxide and carbon dioxide. The chemical reactions and results are the same in both cases. The progress of the reaction is plotted in Figure 5.

The general reaction, whereby silicon is oxidized to silica and transferred to the slag, applies to the basic-oxygen process. Oxidation of silicon is important mainly because of its thermal effects. Only a trace of silicon remains in the steel at the end of the refining period. The amount of silicon in pig iron varies from $\sim$0.8% to as low as 0.15%. Lower silicon values lead to lower slag volumes but take more energy in the blast furnace, and produce less heat during steelmaking.

Refractory lining life is an important maintenance cost, but developments using a nitrogen lance to splash slag over the walls have reduced this by increasing lining life by a factor of $\sim$10 (from 2000 to 20,000 heats).

After the oxygen blowing is completed, the lance is withdrawn and the furnace is tilted to a horizontal position. Historically, temperature and composition were measured at this point, and if the reaction was not perfect, a further, short reblow or scrap addition was carried out. Today sufficient sensors (qv) and models are available so that the number of reblows is virtually zero, thereby contributing to productivity. In general, rather than aiming to make a variety of compositions during blowing, a generic low carbon steel is made and modified in the ladle. The furnace is tilted toward its taphole side and the steel is tapped into a waiting ladle with the slag held back by various schemes. After the steel has been tapped, the furnace is inverted by tilting toward its opposite side and the remaining slag is dumped into a slag pot. The furnace is then turned to charging position and is ready for the next heat.

3.2. Bottom-Blown Basic-Oxygen Process. The bottom-blown basic-oxygen process, called oxygen bottom metallurgy (OBM) in Europe (Maxhültte) and Quelle basic-oxygen process (Q-BOP) (*quelle* is “fountain” or “gusher” in German) in the United States and Japan, is also conducted in a furnace similar to a Bessemer converter. The furnace comprises two parts, the bottom and the barrel. Both the bottom and barrel consist of an outer steel shell that is ~50-mm thick and lined with refractory that is 600–1200-mm thick. The bottom contains 6–24 tuyeres or double pipes (Fig. 7). Oxygen is blown into the furnace through the center pipes and natural gas or some other hydrocarbon is blown into the furnace through the annular space between the two pipes (13–15).

Considerable heat is generated when the oxygen gas oxidizes the carbon, silicon, and iron in the molten pig iron. If special precautions are not taken, the temperature of the refractory immediately adjacent to the oxygen inlet increases when the oxygen is blown upward through the furnace bottom, as in a Bessemer converter. No commercial refractory has been found that withstands such temperatures without cooling. Surrounding the oxygen jet with a cylindrical stream of a hydrocarbon such as methane imparts the required cooling by endothermic decomposition of the hydrocarbon. The bottom-blown oxygen process is critically dependent on this technique.

Both the OBM and the Q-BOP processes are operated in about the same way as the top-blown process. The furnace is charged with steel scrap and hot metal, and oxygen is blown into this mixture to produce steel of the desired composition. However, the method of adding lime to the furnace is different. In the bottom-blown processes, finely powdered lime is added to the oxygen before it is blown into the furnace. Thus, the oxygen serves as a carrier gas to transport the powdered lime pneumatically into the furnace. The powdered lime dissolves rapidly in the slag, permitting increased oxygen-blowing flow rate and thus a decrease in blowing time. Furthermore, slopping is avoided, ie, the sudden ejection of appreciable amounts of slag and metal from the furnace. In the top-blown process, pebble-sized lime is used with pieces 2.5–7.5 cm in diameter.

The chemistry of the bottom-blown processes is similar to that of the top-blown process. However, the slags in the bottom-blown processes contain significantly less iron oxide, causing a ~2% increase in yield, that is, in the amount of liquid steel produced from a given charge of hot metal and scrap. Because bottom blowing is generally closer to thermodynamic equilibrium, the final carbon can be as low as 0.01% without excessive oxidation of iron into the slag, a source of serious yield loss. In top-blown vessels, the carbon is usually 0.03%.

Decrease in the iron oxide content of the slag also causes an increase in the amount of manganese remaining in the liquid steel at the end of the oxygenation stage (oxygen blow). Manganese is desirable in the finished steel and almost always has to be added after the steel is tapped from the furnace into a ladle. Thus, a smaller amount of manganese can be added to bottom-blown steel during tapping, which results in decreased costs. However, the low iron oxide content of the slag increases the slag viscosity, and liquid steel is entrapped in the slag (also a yield loss), unless sufficient fluorspar or other slag fluidizer is added to the charge.

3.3. Top- and Bottom-Blown Basic-Oxygen Processes.

During the 1970s, several combinations of top and bottom blowing were developed. In the lance bubbling equilibrium (LBE) process, nitrogen or argon is injected through a number of porous refractory plugs installed in the furnace bottom, while oxygen is top-blown into the furnace through a lance. The bottom injection of nitrogen or argon causes more intimate mixing of slag and metal, and hence most of the advantages of the Q-BOP bottom-blowing process are obtained in furnaces designed for top blowing. The Linz-Donawitz-Kawasaki gas (LD–KG) process is similar to the LBE process but the nitrogen or argon is injected through tuyeres in the furnace bottom rather than through porous refractory plugs (15).

4. Determination of Chemical Composition

The chemical composition of a given steel may be specified by some customers within rather narrow limits for each element (other than residual elements), so the chemical composition of the steel during refining is followed closely. However, it is no longer necessary to obtain nearly instantaneous analysis during a blow. By blowing fully and then using the ladle to add alloys and control temperature, accurate composition control has become much simpler. Robots are now used to carry out analysis in some shops.

5. Scrap as Raw Material

Scrap consists of the by-products of steel fabrication and worn-out, broken, or discarded articles containing iron or steel (17,18). It is a principal source of the iron for steelmaking; the other source is iron from blast furnaces, either molten as it comes from the furnace (hot metal) or in solid pig form. Scrap is of great practical value. Every ton of scrap consumed in steelmaking is estimated not only to displace and conserve for future use 3.5–4 t of natural resources, including iron ore, coal, and limestone, but also to contribute positively to the goal of total recycling. The amount of home scrap, ie, the various trimmings that accumulate during production, has been greatly reduced. The introduction of almost-complete continuous casting has limited the discards from ingots that historically made up a large part of home scrap.

Purchased scrap comes in two basic categories. Industries that have a steady supply of discards from such operations as stamping, drawing, machining, and forging count on resale of what is often a premium product (if identity has been maintained) as part of their routine costs. Less economically desirable material comes from salvaging the values in products such as ships, automobiles, railroad equipment, and buildings. A whole industry has grown up to recycle the many millions of scrapped automobiles, a mixture of steels, polymers, copper, etc. Following removal of some discrete components such as batteries, the hulk passes through a shredder, the products are given further separation, and a usable scrap becomes available. The shredded polymers give rise to a product known as fluff, which, as of this writing, is not recyclable and must be landfilled.

Scrap can have many compositions and sizes, which translate to charge density, and its economic value is based in part on these. During the latter 1980s and early 1990s, the price spiked as high as $190/t for the best-quality scrap. (In spring 2004, prices reached $300/ton as noted above) At such prices, electric melting becomes marginal without surcharges), and the smaller amount used in BOF melting helps to cushion the price to some degree. Another issue arises in scrap quality. For the most demanding brands of sheet steel, certain impurities affect the product and thus are made in integrated shops. As a result, there is increasing demand for sources of iron units other than scrap that is free of impurities. Examples are iron carbide, which is still its early use, and iron ore treated by reducing gases to give direct-reduced iron. Several million metric tons per year of the latter are on the world market.

The choice of metallic charge is a complex issue, involving the markets to be served and the prices expected. Nevertheless, scrap of all types is expected to remain important because the energy of melting is so much lower than that for reduction from ore. Preheating of scrap using the sensible heat of the previous melt is being practiced increasingly and can be significant in the thermal balance. For instance, the amount of scrap in a BOF can approach 45% rather than 30% if cold scrap is used.

Scrap is a worldwide commodity. The United States alone exports some 10,000,000 t/year—with recent shortages, calls for export limits have been made. The total circulation of scrap in the United States is in the range of 70–90×10^6 t/year, including that for foundry operations, which is $\sim 10 \times 10^6$t/year; modest quantities are charged to blast furnaces when this is economical.

The ability to tap an array of iron units to provide flexibility in all parts of the business cycle is a topic of great interest in keeping costs of raw steel down in the international arena. This is being combined with efforts to reduce the time for a given process by even a few seconds.

5.1. Chemical Composition. A standard problem in purchased scrap is the accuracy of analysis of composition. For home scrap, this may not be much of an problem, but sampling (qv) difficulties and analytical costs can be troublesome in other cases. The difficulty of estimating the alloy content, whether this is to be used to reduce the amount of additional additives necessary in the ladle or to avoid possible troubles from copper or tin, is a continuing worry. Elements such as lead in free machining steels, which can harm furnace linings, are becoming of less concern as alternative elements replace lead. Volatile elements such as lead, zinc, and antimony vaporize and may require adequate capture mechanisms. Elements such as aluminum can add to the heat of oxidation in the furnace and allow higher amounts of scrap. Finally, there is a long-standing interest in purifying scrap to allow higher economic value but these efforts have only been effective sporadically.

6. Addition Agents

In steelmaking, various elements are added to the molten metal to effect deoxidation, control of grain size, improvement of the mechanical, physical, thermal, and corrosion properties, and other specific results. Originally, the chemical element to be incorporated into the steel was added to the bath in the form of an alloy that consisted mainly of iron but was rich in the desired element. Such alloys, because of their high iron content, became known as ferroalloys and were mostly produced in iron blast furnaces. Later, the production of alloys for steelmaking was carried out in electric-reduction and other types of furnaces, and a number of these alloys contain very little iron. For this reason, the term addition agent is preferred when describing the materials added to molten steel for altering its composition or properties; ferroalloys are a special class of addition agents.

Included in the ferroalloy class are alloys of iron with aluminum, boron, calcium, chromium, niobium, manganese, molybdenum, nitrogen, phosphorus, selenium, silicon, tantalum, titanium, tungsten, vanadium, and zirconium. Some of these chemical elements are available in addition agents that are not ferroalloys, as well as in almost pure form. These include relatively pure metals such as aluminum, calcium, cobalt, copper, manganese, and nickel; easily reducible oxides of molybdenum, nickel, and tungsten; carbon, nitrogen, and sulfur in various forms; and alloys consisting principally of combinations of two or more of the foregoing elements. Some rare-earth alloys are also used for special purposes, but only to a minor extent. Addition agents are predominantly introduced in the ladle.

The economical manufacture of alloy steels requires consideration of the relative affinity of the alloying elements for oxygen as compared with the affinity of iron for oxygen. For example, copper, molybdenum, or nickel may be added with the charge or during the working of the heat and are fully recovered. The advent of ladle metallurgy has led to the easily oxidized elements, such as Al, Cr, Mn, B, Ti, V, and Zr, being added after the oxygen content of the bath has been reduced. A marked increase in yield has resulted.

7. Ladle Metallurgy

The finished steel from any furnace, whether basic-oxygen or electric, is tapped into ladles. Most ladles hold all the steel produced in one furnace heat. Some slag is allowed to float on the surface of the steel in the ladle to form a protective blanket. Excess slag is prevented from entering the ladle by controlling its exit from the furnace taphole.

A ladle consists of a steel shell, lined with refractory brick, having an off-center opening in its bottom equipped with a nozzle (Fig. 8). A valve makes it possible to enlarge or close the opening to control the flow of steel through the nozzle. Simple stopper-rod valves have been replaced by more elaborate slide gate systems involving spring-loaded refractory disks, each containing a central hole and sliding relative to the other. Better flow control and positive shutoff are achieved—both are important in practice.

Ladle metallurgy, the treatment of liquid steel in the ladle, is a field in which several new processes, or new combinations of old processes, continue to be developed (19,20). The objectives often include one or more of the following on a given heat: more efficient methods for alloy additions and control of final chemistry; improved temperature and composition homogenization; inclusion flotation; desulfurization and dephosphorization; sulfide and oxide shape control; and vacuum degassing, especially for hydrogen reduction and generation of carbon monoxide to make interstitial-free (IF) steels. Electric arcs or induction coils are normally used to raise the temperature of the liquid metal (ladle arc furnace).

7.1. Argon Treatment. In early ladle furnaces, argon was used to provide better mixing of additives, such as ferroalloys, to even out temperature gradients and to float out inclusions such as oxides and sulfides. Argon could be added through a porous plug in the bottom of the ladle or through a lance inserted in the bath. Expensive ferroalloys can be added through the area where the slag is displaced by rising bubbles of argon without significant oxidation loss. These are the composition adjustment by capped argon stirring (CAS) and sealed argon bubbling (SAB) processes. At first, there was no cover on the ladle, but as of the 1990s almost all ladles have covers to prevent atmospheric oxidation.

In the argon–oxygen decarburization (AOD) process, argon or argon–oxygen mixtures are blown in through bottom tuyeres to lower the carbon content of the bath by making escape of carbon monoxide in the argon bubbles easier. Although this process works on carbon steel, better alternatives are available. The predominant use of AOD is in making stainless steels more weldable by lowering the carbon content to 0.03% max.

When the ladle is fitted with a tight cap, other processes become attractive, especially if the steelmaking slag, which contains considerable iron oxide and hinders sulfur removal, can be substantially separated from the melt before further treatment. Sulfur in solution can be removed as sulfide by injecting CaSi or Mg [the Thyssen Niederrhein (TN) process] or 90% CaO–10% CaF_2 (Kimitsu injection (KIP) process). Thermodynamically, calcium is more effective than magnesium in reducing S; CaF_2 increases sulfide capacity of slags, as does increasing the basicity, ie, increasing Al_2O_3 and reducing SiO_2. CaF_2 also increases fluidity. When the proper oxygen–sulfur balance is present in liquid steel, calcium additions can give hard, spherical inclusions which do not deform during rolling, as does, eg, MnS. Thus Ca additions can lead to better properties in the direction normal to the rolling direction by avoiding needle shaped inclusions. With a capped ladle, addition of ferroalloys into the plume of argon bubbling up through the steel through a synthetic slag (with little or no FeO) is also effective (capped argon bubbling (CAB) process).

7.2. Vacuum Processes. More complete control over ladle treatment is achieved by the ability to seal a vessel well enough so that a good vacuum can exist over the steel. Although the expense can be justified for steels with the most difficult property requirements, for many purposes less elaborate treatments are adequate. Many possible configurations exist (21).

Some early processes involved stream degassing, where on entering the vacuum chamber the molten steel fragmented into large numbers of droplets, thus offering a large surface for loss of gases such as hydrogen. This was not very effective in inclusion or carbon removal. Another process was the Dortmund-Hoerder (DH) process, where an evacuated vessel can be lowered into the ladle for 10–20 cycles and thus the steel is exposed to an adequately low vacuum [0.13 kPa (1 mm Hg)]. Ferroalloy additions can be made *in situ*.

A more complicated system is found in the Ruhrstahl-Heraeus (RH) process (Fig. 9), which has two hollow legs as compared to only one in the DH. By bubbling argon into one leg, a pressure difference is created circulating steel though the vacuum chamber and back into the vessel. Oxygen and carbon dissolved in the steel react to form CO, which escapes. Reduction of carbon from 0.08 to 0.03% and oxygen from 400 to 50 ppm occurs, at which point the steel can be economically killed with aluminum. The higher carbon contents at entry improve the yield of iron in the BOF vessel. In the Ruhrstahl-Heraeus oxygen blowing (RH-OB) process, even higher carbon contents (0.10%) can be treated, with oxygen blown into the degasser, thus further improving yield. For interstitial-free steels, the start carbon, which may be 0.03%, is reduced to no more than 20 ppm. Oxygen and nitrogen are also held at levels near 20 ppm. A very high quality sheet steel is produced with exceptional deep-drawing properties.

The simpler vacuum oxygen decarburization (VOD) process used originally for stainless steels can be used for carbon steel by placing the ladle in an evacuated tank, introducing argon into the bottom of the ladle, and blowing oxygen through a lance. The carbon can be reduced to 0.01%.

In other systems, extra energy to maintain temperature can be supplied by an arc, chemical heating by injecting Al and O_2, or by induction stirring with or without vacuum. Sulfur and oxygen are reduced even without a vacuum; hydrogen is reduced if a vacuum is present.

A principal purpose of ladle metallurgy is to produce a well-stirred and homogeneous bath. Thus considerable effort has been spent on the fluid dynamics necessary to ensure this. Water has been a valuable modeling agent.

All special processes involve extra capital and operating costs, time, and a realistic analysis of markets and procedures. Because of increasing quality demands, some form of ladle treatment has become routine in steelmaking.

8. Casting

8.1. Continuous Casting. At one time, all steel for hot working was cast into ingots. Today very little steel is cast as ingots, except for limited quantities where the typical 250-mm cast slab thickness is inadequate for the final product, eg, heavy plate. For certain special property requirements, bottom pouring of the ingot through a refractory riser is common.

The possibility of casting molten steel continuously into useful shapes equivalent to conventional semifinished shapes, such as slabs and billets, and thus eliminating the ingot and primary-mill stages of rolled-steel production, led to continuous attempts to solve the problem by many investigators using a variety of machine designs. Because of the high melting point, high specific heat, and low thermal conductivity of steel, success did not come easily in the case of ferrous metals. For nonferrous metals, on the other hand, continuous-casting quickly proved practical.

The obvious rewards available to successful casting provided a strong driving force. Early machines built in the 1930s and 1940s were not practical, but progress was made in the 1960s, which included such novel ideas as following the caster with a rolling mill to change the otherwise fixed cross-section, a constraint that limits yield. Some mills today have the ability to reduce the width up to 30 cm by a high-powered press.

Around 1970, a great surge in capacity was nearly complete in Japan, and casters had been an integral concept. The decision was made by Nippon Steel to eliminate any ingot casting at their then-new sheet works in Oita. Thus the casters had to work without fail and new levels of operating confidence were achieved. Consortia of steel companies and equipment builders arose to provide reliable casters, and to permit second generation improvements such as molds having widths that could be varied during operation and sensors that could measure necessary variables of interest to long strings of casts. Slowly it became possible to reach truly continuous operation with runs of a week or more, making width and composition chances along the way. Improvements in the steel supplied were critical (22–24).

For various reasons, including financial ones, the United States was slower than Japan and Europe to install continuous slab casters for the production of sheet. Electric melters cast billets continuously from about 1975 onward. Casting was done crudely at first but the sophistication increased rapidly, culminating in dramatic change by operation of a thin-slab caster at one of Nucor's plants, followed by many other electric melters. This opened up another avenue of attack for them on sheet markets, once the exclusive province of integrated mills.

Although the continuous casting of steel appears deceptively simple in principle, many difficulties are inherent to the process. When molten steel comes into contact with a water-cooled mold, a thin solid skin forms on the wall (Fig. 10). However, because of the physical characteristics of steel, and because thermal contraction causes the skin to separate from the mold wall shortly after solidification, the rate of heat abstraction from the casting is low enough that molten steel persists within the interior of the section for some distance below the bottom of the mold. The thickness of the skin increases because the action of the water sprays as the casting moves downward and, eventually, the whole section solidifies.

The mass of the solidifying section is supported as it descends by driven pinch rolls that control the speed of descent. Any tendency for the casting to adhere to the mold wall may cause the skin to rupture—the dreaded but increasingly rare "breakout". However, molds that move up and down for a predetermined distance at controlled rates during casting have practically eliminated the sticking problem. The continuous-cast section issuing from the withdrawal or supporting rolls may be disposed of in several ways, some of which are illustrated in Figure 11.

A number of other designs of continuous-casting machines are being used in the production of semifinished sections. For example, bars and light structural sections are made from billets, ie, rounds or round-cornered squares having sizes in the range of 100–250 mm, and often having several (typically up to six) strands in parallel. At one time, rounds were cast in a rotating mold but the hoped-for better quality can be obtained more easily using a stationary mold and more care with the liquid feed (Fig. 12).

Many other casting schemes have been tried. There has been some measure of success but limited general application. Examples are horizontal casting, pressure casting (Fig. 13**a**) (25), and wheel-belt casting. The most important development in the 1980s was the thin-slab ($\sim$50 mm) caster, which has the potential of reducing the number of hot rolling stands from eight or nine down to perhaps five or less (Figs. 13**b**,**c**). Today, essentially all electric shops making flat rolled products use thin-slab casters as they await the successful demonstration of direct-sheet carbon steel casting, already in early commercial stages at the Crawfordsville plant of Nucor Steel. This logical extension of thin slabs to cast carbon or stainless steel directly to sheet in the 1-mm range is a possibility long recognized but difficult to realize—the concept was in a patent by Sir Henry Bessemer $>$150 years ago. A schematic of a twin-roll sheet caster is in Fig. 14. (25a).

Continuous casting is almost universal. It gives a higher yield than ingot casting and avoids the cost of rolling ingots into slabs because the slabs are produced directly from liquid steel. Excessive segregation during solidification can create problems of low ductility in regions of high carbon and alloy content, and cause cracking during processing. In general, segregation increases with increasing thickness, ie, with slower cooling rates. Continuous-cast slabs are only $\sim$20–25-cm thick and exhibit much less segregation than slabs rolled from ingots that are 3–5 times as thick. Consequently, there is usually less variation in steel composition from one heat to the next in continuous-cast steel than there is from the top to the bottom in a single ingot.

Continuous-cast aluminum-killed steel is similar in composition and properties to ingot-cast aluminum-killed steel. It contains 0.025–0.060% aluminum and has excellent deep-drawing characteristics. Whereas earlier developments merely involved care in shielding the liquid stream from the atmosphere which could produce undesirable inclusions, great care is taken in later efforts not only to prevent chemical contamination but to understand and control the fluid flow in the mold and the tundish, the latter a buffer between the ladle and the mold, and holding up to 70 t of liquid steel. The aim is to avoid mixing of metal and slag and also to give time and opportunity for any inclusions that do form in the mold to float to the top and be absorbed in a special slag.

A vast array of sensors provides data to the operators so that accidents such as breakouts from thin spots in the solidifying shell very rarely occur and the internal and surface quality are extremely good. In fact, the surface is good enough so that cooling to room temperature for defect removal is often not necessary if certain criteria are met, and slabs can be and are charged while still hot for rolling, thereby saving much of their sensible heat.

9. Plastic Working of Steel

Plastic working of a metal such as steel is the permanent deformation accomplished by applying mechanical forces to a metal surface. The primary objective is usually the production of a specific shape or size (mechanical shaping), although increasingly it also involves the improvement of certain physical and mechanical properties of the metal (mechanical treatment). These two objectives can often be readily attained simultaneously.

Plastic deformation of steel can be accomplished by hot working or cold working. Prior to hot working, the steel is heated to 1090–1310°C, depending on the grade and the work to be accomplished. The force required to deform the metal is very sensitive to the rate of application and the temperature of working; however, after deformation, the basic strength of the steel is essentially unchanged. In cold working, on the other hand, steel is not heated before working, the force required to cause deformation is relatively insensitive to the application rate and temperature variations, but the yield strength of the steel is increased significantly.

The principal hot-working techniques are hammering, pressing, extrusion, and rolling the first two of which are called forging. Other less common methods include rotary swaging, hot spinning, hot deep-drawing, roll forging, and die forging. Although at high temperatures the material is not very strong when compared to its room temperature strength, the shape changes are made in several stages for reasons of mechanics. For example, the maximum reduction that can be obtained in a single roll pass is 10–40% because the ability of the rolls to drag the piece through depends on geometric factors and the coefficient of friction. Thus to reduce a 250-mm slab to a 2-mm hot band takes ~10 separate reductions. During this process the austenite crystals (grains) normally present may recrystallize several times (see below) and the recrystallization can have a significant effect on final properties (26–31).

Cold working is generally applied to bars, wire, strip, sheet, and tubes. It reduces the cross-sectional area of the piece being worked on by cold rolling, cold drawing, or cold extrusion. Similar limitations on reduction per pass apply, although recrystallization does not occur. Trying to get reductions which are too large per pass can lead to loads high enough to break rolls. Cold working imparts improved mechanical properties, better machinability, good dimensional control, bright surface, and production of thinner material than can be accomplished economically by hot working (see METAL TREATMENT). These desirable properties must be balanced in each case against a loss of ductility. The thickness of available hot-rolled material is has been decreasing steadily towards 1 mm. and hot-rolled material is becoming a less-expensive competitor for some material traditionally cold-rolled and annealed.

10. Metallography and Heat Treatment

The great advantage of steel as an engineering material is its versatility. Properties can be closely controlled and changed by heat treatment. Thus, if steel is to be formed into some intricate shape, it can be made very soft and ductile by heat treatment; on the other hand, alternative heat treatments can also impart high strength with good ductility and toughness.

The physical and mechanical properties of steel depend on its microstructure, ie, the nature, distribution, and amounts of its metallographic constituents as distinct from its chemical composition. The amount and distribution of iron and iron carbide determine most of the properties, although most plain carbon steels also contain manganese, silicon, phosphorus, sulfur, oxygen, and traces of nitrogen, hydrogen, and other chemical elements such as aluminum and copper. These elements may modify, to a certain extent, the main effects of iron and iron carbide, but by and large the influence of iron carbide always predominates. This is true even of medium alloy steels, which may contain considerable amounts of nickel, chromium, and molybdenum. These elements also serve other purposes.

There are two allotropic forms of iron: ferrite and austenite. Ferrite in both its low or α (up to 910°C) and high or δ; (1390°C to mp 1536°C) is body-centered cubic (bcc). The spaces between atoms (interstices) are larger in the face-centered cubic γ (fcc) austenite than in ferrite and can accommodate more small interstitial atoms such as carbon and nitrogen. Thus the solubility in austenite is 2 wt% for carbon and 2.8 wt% for nitrogen, as opposed to a few hundredths of a percent for ferrite. This effect is critical in the heat treatment of steels where ferrite and austenite may also contain different amounts of alloying elements (manganese, silicon, nickel, etc). The atomic arrangement in the two allotropic forms of iron is shown in Figure 15.

Cementite, the term for iron carbide in steel, is the form in which most of the carbon appears in steels. It has the formula Fe_3C, and thus consists of 6.67 wt% carbon and the balance iron. Cementite is very hard and brittle. As the hardest constituent of plain carbon steel, it scratches glass and feldspar, but not quartz. It exhibits about two-thirds the induction of pure iron in a strong magnetic field, but has a much lower Curie temperature.

Most commercial steels contain at most a few tenths of a percent of carbon. In fact, the great bulk of sheet steel that accounts for ~60% of commercial production has <0.1%. Thus when these materials are heated to temperatures where austenite is stable, the carbon readily dissolves. Iron–nitrogen alloys are essentially not commercial. The limiting temperatures and compositions for austenite are given by the phase diagram (Fig. 16). By controlling the cooling rate from the austenite range, the carbon comes out of solution in a range of microstructures that have very specific properties (32–35).

A nonalloyed carbon steel having 0.76% carbon, the eutectoid composition, consists of austenite above its lowest stable temperature, 727°C (the eutectoid temperature). On reasonably slow cooling from above 727°C, transformation of the austenite occurs above ~550°C to the series of parallel plates of α plus cementite known as pearlite. The spacing of these plates depends on the temperature of transformation, from 1000 to 2000 nm at ~700°C and <100 nm at 550°C. The corresponding Brinell hardnesses (BHN), which correspond approximately to tensile strengths, are about BHN 170 and BHN 400, respectively.

Eutectoid steels are not common, although small volumes are used as rails, high strength wire, and in some inexpensive tool steels. Above (hyper-) or below (hypo-) eutectoid, a primary precipitation of cementite or ferrite occurs until the austenite reaches the eutectoid composition when it transforms as before. Normally, these proeutectoid components form at grain boundaries. At lower temperatures of precipitation, however, they may also form on certain well-defined planes in the austenite crystals. The amount of proeutectoid constituents offers a rough guide to the composition of the steel. This guide is more accurate at slow-cooling rates.

If small specimens are prepared in which the austenite can be cooled to 250–500°C sufficiently rapidly to avoid the above microconstituents, and transformed at temperatures in this range, the formation of a completely different phase, a bcc α-phase supersaturated with carbon and containing small cementite particles (bainite), which is both strong and tough, occurs. Bainite was rarely found in plain carbon steels, but it can be obtained in commercial practice by judicious alloying and is increasing in importance.

Finally, if all of the above sets of phases can be suppressed by sufficiently rapid cooling, the austenite transforms to a phase known as martensite. This phase contains all of the carbon in the austenite. The result is a body-centered structure supersaturated in carbon. The crystal structure is body-centered tetragonal, ie, a cube extended in one direction, where the degree of tetragonality, and thus lattice strain, increases linearly with carbon. Martensite begins to form at a well-defined temperature known as M_s and continues to form as the temperature continues to drop. For most steels, the transformation is complete (defined as M_f) before reaching room temperature, but in high carbon and certain alloy steels, some austenite may remain at room temperature and requires special consideration. Martensite forms by a lattice shear reaction without diffusion of the carbon atoms, and usually has a plate or needle-like morphology. Because of its lattice strain, it is normally too brittle for service until some of the carbon is precipitated by a second heating between 200 and 700°C, ie, tempering. Material given this treatment can have unsurpassed combinations of strength and toughness, and is the underpinning of much of the industrial world.

11. Iron–Iron Carbide Phase Diagram

The iron–iron carbide phase diagram (see Fig. 16) shows the ranges of compositions and temperatures in which the various stable or metastable phases, such as austenite, ferrite, and cementite, are present in slow-cooled steels. This diagram covers the temperature range from 600°C to the melting point of iron, and carbon contents from 0 to 5%. In steels and cast irons, carbon can be present either as iron carbide (cementite) or as graphite. Under equilibrium conditions, only graphite is present because iron carbide is metastable with respect to iron and graphite. However, in commercial steels, although not in cast irons, iron carbide is essentially always present instead of graphite. When a steel containing carbon solidifies, the carbon in the steel typically solidifies as iron carbide. Although the iron carbide in a steel can change to graphite and iron when the steel is held at elevated temperatures for several days or weeks, iron carbide in steel under normal conditions is quite stable for many years, even, eg, in power stations.

The portion of the iron–iron carbide diagram of interest herein is that part extending from 0 to 2% carbon. The range from 3 to 4.5% carbon covers most of the cast irons, a fascinating set of materials used as-cast, sometimes heat-treated, but not deformed either hot or cold (and not discussed further here). Application of the phase diagram to heat treatment can be illustrated by considering the changes occurring on heating and cooling steels of selected carbon contents.

Iron occurs in two allotropic forms, α or δ and γ (see Fig. 15). The temperatures at which phase changes occur are known as the critical temperatures. For pure iron, these temperatures are 910°C for the $\alpha{-}\gamma$ phase change and 1390°C for the $\gamma{-}\delta$ phase change. The boundaries in Figure 16 show how these temperatures are affected by composition.

The only changes occurring on heating or cooling pure iron are the reversible changes at ~910°C from bcc α-iron to fcc γ-iron and from the fcc γ-iron to bcc δ-iron at ~1390°C.

Eutectoid steels are those that contain 0.76% carbon. The diagram shows that at $< 727°\text{C}$ the constituents are α-ferrite and cementite. At 600°C, the α-ferrite may dissolve up to 0.007% carbon. Up to 727°C, the solubility of carbon in the ferrite increases until, at this temperature, the ferrite contains ~0.02% carbon. The phase change on heating a eutectoid carbon steel occurs at 727°C, which is designated as A_1, the eutectoid or lower critical temperature. On heating such a steel just above this temperature, all ferrite and cementite transform to austenite of eutectoid composition, albeit slowly, and on slow cooling the reverse change occurs.

When a eutectoid steel is slowly cooled from the austenite range, the ferrite and cementite form in alternate layers of microscopic thickness. Under the microscope at low magnification, the diffraction effects from this mixture of ferrite and cementite give an appearance similar to that of a pearl, hence the material is called pearlite. (The spacing is of the same order as the wavelengths of visible light).

Hypoeutectoid steels are those that contain less carbon than the eutectoid steels. If the steel contains $> 0.02\%$ carbon, the constituents present at and $<$ 727°C are usually ferrite and pearlite. The relative amounts depend on the carbon content. As the carbon content increases, the amount of ferrite decreases and the amount of pearlite increases.

The first phase change on heating, if the steel contains $> 0.02\%$ carbon, occurs at 727°C. On heating just above this temperature, the pearlite slowly changes to eutectoid austenite at a rate controlled by carbon diffusion. The excess ferrite, called proeutectoid ferrite, remains unchanged. As the temperature rises further above A_1, the austenite dissolves more and more of the surrounding proeutectoid ferrite, becoming lower and lower in carbon content until all the proeutectoid ferrite is dissolved in the austenite at the upper critical temperature, A_3, which now has the same average carbon content as the steel.

On slow cooling, the reverse changes occur. Ferrite precipitates, generally at the grain boundaries of the austenite, which becomes progressively richer in carbon. Just above A_1, the austenite is substantially of eutectoid composition, 0.76% carbon.

The behavior on heating and cooling hypereutectoid steels (steels containing $>0.76\%$ carbon) is similar to that of hypoeutectoid steels, except that the excess constituent is cementite rather than ferrite. Thus, on heating above A_1, the austenite gradually dissolves the excess cementite until at the A_{cm} temperature, ie, the highest temperature at which austenite and cementite can coexist (see Fig. 16), the proeutectoid cementite has been completely dissolved and austenite of the same carbon content as the steel is formed. Similarly, on cooling below A_{cm}, cementite precipitates and the carbon content of the austenite approaches the eutectoid composition. On slow cooling below A_1, this eutectoid austenite changes to pearlite and the room temperature composition is therefore pearlite and proeutectoid cementite.

Some confusion occurred in early iron–carbon equilibrium diagrams, which indicated a critical temperature at ~768°C. Although there are changes in specific heat in this vicinity, leading to changes in slope of cooling curves, this is the Curie temperature, (ϑ), where ferromagnetic α becomes paramagnetic. This is a second-order phase transformation as contrasted to the first-order transformation, which is the one of interest and importance in heat treatment. In older literature the Curie temperature was called A_2, a terminology no longer used.

The iron–carbon diagram may be significantly altered by alloying elements, and its pseudoquantitative application should be limited to plain carbon and low alloy steels. The most important phase-diagram effects of the alloying elements are that the number of phases that may be in equilibrium is no longer limited to two as in the iron–carbon diagram; that the temperature and composition range, with respect to carbon, over which austenite is stable may be increased or reduced; and that the eutectoid temperature and composition may change. We shall see that the effect of alloys on rates of austenite decomposition is usually more important than the equilibrium effects.

Alloying elements either enlarge the austenite field or reduce it. The former include manganese, nickel, cobalt, copper, carbon, and nitrogen and are referred to as austenite stabilizers.

The elements that decrease the extent of the austenite field include chromium, silicon, molybdenum, tungsten, vanadium, tin, niobium, phosphorus, aluminum, and titanium. These are known as ferrite stabilizers.

Manganese and nickel lower the eutectoid temperature, whereas chromium, tungsten, silicon, molybdenum, and titanium generally raise it. All these elements seem to lower modestly the eutectoid carbon content.

11.1. Grain Size. The crystal structures shown in Figure 15 exist as a regular array over a distance of several thousand unit cells in a given direction to give a crystal commonly called a grain. Eventually, however, these run into a region where the orientation of the cells differs by rotation in all three directions. The region where the grains abut is a surface where no atoms are at their equilibrium spacing and is known as a grain boundary. Grain boundaries can usually be observed readily in an optical microscope, especially if they are etched in a mild reagent for accentuation. Typical grain sizes, ie, the average distance between boundaries, are in the range of 5000–50000 nm.

Austenite. A significant aspect of the behavior of steels on heating is the grain growth that occurs when the austenite, formed on heating above A_3 or A_{cm} (see Fig. 16) is heated even higher. The austenite, like any metal, consists of polyhedral grains with curved boundaries where the grain boundary energy is balanced in three dimensions. As formed at a temperature just above A_3 or A_{cm}, the size of the individual grains is small, but as the temperature is increased above the critical temperature, the grain size increases. The final austenite grain size depends primarily on the maximum temperature to which the steel is heated although the time of heating can have a secondary effect.

In practice, either deliberately or otherwise, phases other than iron carbide may be present. These are typically carbides (qv) or nitrides (qv) of aluminum, vanadium, niobium, and/or titanium, which do not dissolve easily in austenite. Those found at grain boundaries serve to prevent the boundaries from moving as easily as such boundaries would in the absence of these phases. As long as these particles exist, growth in size of austenite grains is severely constrained. When the temperature is increased so that the particles go into solution, the grains coarsen rapidly. The grain size of the austenite has a marked influence on transformation behavior during subsequent cooling and on the size and distribution of the constituents of the final microstructure.

During much conventional processing, especially to sheet and strip, an austenitic slab is being reduced in cross-section typically by deformation through a series of rolls each of which imposes 10–40% decrease in thickness. At high temperatures, the deformed structure recrystallizes, ie, new small grains form and may coarsen even before reaching the next roll. As the temperature drops upon passage through the mill, recrystallization and grain growth occur with increasing difficulty. By controlling the rolling schedule, it is possible to obtain very fine grain sizes in austenite prior to its subsequent transformation. If rolling occurs to temperatures too low to allow recrystallization the grains may be deformed from near-spherical to pancake shaped. The general effects of austenite grain size on the properties of heat-treated steel are summarized in Table 1.

Microscopic Grain Size Determination. The microscopic grain size of steel is customarily determined from a polished plane section prepared in such a way as to delineate the austenite grain boundaries. Grain size can be estimated by several methods. Results can be expressed as diameter of average grain in millimeters (reciprocal of the square root of the number of grains per mm^2), number of grains per unit area, number of grains per unit volume, or a grain size number obtained by comparing the microstructure of the sample at a fixed magnification to a series of standard charts.

11.2. Phase Transformations. *Austenite.* Close to equilibrium, that is with very slow cooling, austenite transforms to pearlite when cooled below the A_1 (see Fig. 16) temperature. When austenite is cooled more rapidly, this transformation occurs at a lower temperature. The faster the cooling rate, the lower the temperature at which transformation occurs. Furthermore, the structure of the ferrite–carbide aggregate formed when the austenite transforms varies markedly with the transformation temperature, and the properties are found to vary correspondingly. Thus heat treatment involves a controlled supercooling of austenite. In order to take full advantage of the wide range of structures and properties that this treatment permits, a more detailed knowledge of the transformation behavior of austenite and the properties of the resulting aggregates is essential. For most specimens, heat flow from the interior of the piece to the surface controls the cooling rate of internal points. Thus understanding the effects of this issue becomes relevant.

Isothermal Transformation Diagram. To separate the effects of transformation temperature from those of heat flow, it is essential to understand the nature of the transformation of austenite at a given, preselected temperature below the A_1. Information needed includes the starting time, the amount transformed as a function of time, and the time for complete transformation. A convenient way to accomplish this is to form austenite in specimens so thin (usually ~1-mm thick) that heat flow is not an issue, rapidly transfer the specimens to a liquid bath at the desired temperature, and follow the transformation with time. The experiment is repeated at several other transformation temperatures. On the same specimens, the microstructure and properties of the transformation products can be assessed. These data can be summarized on a single graph of transformation temperature versus time known as an isothermal transformation (IT) diagram or, more usually, a time–temperature–transformation (TTT) diagram. A log scale is used for convenience. This concept, put forward in 1930, revolutionized the understanding of heat treatment.

Figure 17 shows a typical curve for a eutectoid steel, along with representative microstructures and hardness as a surrogate for mechanical properties. For noneutectoid steels, ferrite or cementite begins to form at austenite grain boundaries at temperatures below the A_3 or A_{cm}, respectively, but these reactions do not go to completion. Rather, the precipitation is interrupted by formation of the more rapidly growing pearlite giving a two-phase structure. Schematically, that would give, eg, a ferrite start time to the left of the pearlite start time, merging at around 550°C, ie, the knee of the TTT curve.

There are several important points relating to these curves. (*1*) The start of transformation occurs at increasingly short times down to ~550°C, during which interval pearlite forms. The pearlite has a finer spacing as formation temperature decreases, becoming thus harder and stronger. During the period from beginning to end of transformation, colonies of pearlite form and grow relatively slowly until all the austenite is consumed. (*2*) Below 550°C to just > 200°C, the start of transformation takes longer and longer as the transformation temperature falls and the product of transformation is bainite. The hardness increases as the transformation temperature decreases. (*3*) At the M_s temperature, martensite begins to form more or less instantaneously. The fraction that forms depends nonlinearly on the undercooling below M_s, as shown schematically by the indications of 50 and 90% transformation of austenite. For this steel, M_f is below room temperature so some untransformed austenite is present. Martensite, usually acicular, is harder and stronger than any of the other constituents but is much too brittle in this steel to put in service without further treatment (tempering). (*4*) This curve is valid only for eutectoid steel having a specific austenite grain size. Other compositions and grain sizes have different TTT curves. Curves are collected in various reference books (32–34). (*5*) The effect of austenite grain size is real but relatively small. The effects of alloying elements can be very large (Fig. 18) and provide a practical tool to enable desired structures to be produced in large sections where heat flow is a factor and the overall structure may be nonuniform.

Because almost no steel undergoes isothermal transformation, the effect of heat transfer is critical. Heat is lost from the surface, either to air or to a liquid such as water or oil. Although this leads to a complex set of equations, these are well known and characterized. Basically, all transformations are shifted to lower temperatures as a result of heat transfer. A primary concern in some cases is that for certain steels and cooling rates, it may be impossible to avoid the formation of ferrite and pearlite in parts of the specimen. This may be undesirable from a property standpoint. Increasing the surface cooling rate, superficially attractive as a way of avoiding ferrite and pearlite formation, has drawbacks because of possible distortion or even cracking during the quench. The solution is to change the position of the TTT curve to longer times along the x axis to allow the same structures to form at slower cooling rates. This is usually achieved by alloying because increasing austenite grain size has more negatives than positives.

11.3. Constituent Properties.

Pearlite. Pearlites, softer than bainites and martensites, are less ductile than the lower temperature bainites and, for a given hardness, far less ductile than tempered martensite. As the transformation temperature decreases within the pearlite range, the interlamellar spacing decreases, and these fine pearlites, formed near the nose of the isothermal diagram, are both harder and more ductile than the coarse pearlites formed at higher temperatures. Thus, although as a class pearlite tends to be soft and not very ductile, its hardness and toughness both increase markedly with decreasing transformation temperatures.

Bainite. In a given steel, bainite microstructures are generally found to be both harder and tougher than pearlite, although less hard than martensite. Bainite properties generally improve as the transformation temperature decreases. Lower bainite compares favorably with tempered martensite at the same hardness and can exceed it in toughness. Upper bainite, on the other hand, may be somewhat deficient in toughness as compared to fine pearlite of the same hardness (33).

Martensite. Martensite is the hardest and most brittle microstructure obtainable in a given steel. The hardness of martensite increases nonlinearly with increasing carbon content up to the eutectoid composition. The hardness of martensite at a given carbon content varies only very slightly with the cooling rate or with usual alloying elements.

Although for some applications, particularly those involving wear resistance, the hardness of martensite is desirable in spite of the accompanying brittleness, this microstructure is mainly important as the starting material for tempered martensite structures, which have definitely superior and easily controllable properties for most demanding applications.

Tempered Martensite. Martensite is tempered by heating to a temperature ranging from 170 to 700°C for 30 min to several hours. This treatment causes the martensite to transform to ferrite interspersed with small particles of iron carbides. Higher temperatures and longer tempering periods cause the cementite particles to increase in size and the steel to become more ductile and lose strength. Tempered martensitic structures are, as a class, characterized by very desirable toughness at almost any strength. Figure 19 describes, within ±10%, the mechanical properties of tempered martensite, regardless of composition. For example, a steel consisting of tempered martensite having an ultimate strength of 1035 MPa (150,000 psi) might be expected to exhibit elongation of 16–20%, reduction of area of between 54 and 64%, yield point of 860–980 MPa (125,000–142,000 psi), and Brinell hardness of ~295–320. Because of its high ductility at a given hardness, this is the structure that is generally preferred.

11.4. Transformation Rates.

The main factors affecting transformation rates of austenite are composition, grain size, and homogeneity. In general, increasing carbon and alloy content as well as increasing grain size tend to lower transformation rates. These effects are reflected in the isothermal transformation curve for a given steel. In practice, it is generally desirable to use as low a carbon content as possible for achieving the desired mechanical properties because toughness, internal stress, distortion, and weldability are thus improved.

Continuous Cooling. The basic information depicted by an isothermal transformation diagram illustrates precisely the structure formed if the cooling is interrupted and the reaction completed at a given temperature. The information is also useful for interpreting behavior in the more usual case when the cooling proceeds directly without interruption, as in the case of annealing, normalizing, and quenching. In these processes, the residence time at a single temperature is generally insufficient for the reaction to go to completion. Instead, the final structure consists of an association of microstructures that were formed individually at successively lower temperatures as the piece cooled. However, the tendency to form the various structures is still capable of being represented usefully if schematically on a modified TTT diagram.

The final microstructure after continuous cooling depends on the time spent at the various transformation temperature ranges through which a piece is cooled. The transformation behavior on continuous cooling thus represents an integration of these times by constructing a continuous-cooling transformation diagram at constant rates similar to the isothermal transformation diagram (see Fig. 18). This diagram lies below and to the right of the corresponding isothermal transformation diagram if plotted on the same coordinates. That is, transformation on continuous cooling starts at a lower temperature and after a longer time than the intersection of the cooling curve and the isothermal diagram would predict. This displacement is a function of and increases in direct proportion with the cooling rate.

Figure 18 contains several superimposed cooling-rate curves. The changes occurring during these cooling cycles illustrate the manner in which diagrams of this type can be correlated with heat-treating processes and used to predict the resulting microstructure in a commonly used Cr–Ni–Mo alloy steel (Type 4340).

Considering first a relatively low cooling rate (<22°C/h), the steel is cooled through the regions in which transformations to ferrite and pearlite occur for the constitution of the final microstructure. This cooling rate corresponds to a slow cooling in the furnace, such as might be used in annealing.

At a higher cooling rate (22–83°C/h), such as might be obtained on normalizing a large forging, the ferrite, pearlite, bainite, and martensite fields are traversed and the final microstructure contains all these constituents. At cooling rates of 1,167–30,000°C/h, the microstructure is free of proeutectoid ferrite and consists largely of bainite and a small amount of martensite. A cooling rate of at least 30,000°C/h is necessary to obtain the fully martensitic structure desired as a starting point for tempered martensite. This rate, 30,000°C/h, corresponds to the cooling rate at the center of a 60-mm bar quenched in agitated oil. Thus, the final microstructure, and therefore the properties of the steel, depends on the transformation behavior of the austenite and the cooling conditions, and can be predicted with considerable confidence if these factors are known.

12. Hardenability

Hardenability refers to the depth of hardening or to the size of a piece that can be hardened adequately under given cooling conditions, and not to the maximum hardness that can be obtained in a given steel (36). The maximum hardness depends almost entirely on the carbon content, whereas the hardenability (depth of hardening) is far more dependent on the alloy content and, to a lesser degree, on the grain size of the austenite. Steels in which IT diagrams indicate a long time interval before the start of transformation to pearlite are useful when large sections are to be hardened, because if steel is to transform to bainite or martensite, it must escape any transformation to pearlite. Therefore, the steel must be cooled through the high temperature transformation ranges at a rate rapid enough for transformation not to occur even at the nose of the IT diagram. This rate, which just permits transformation to martensite without earlier transformation at a higher temperature, is known as the critical cooling rate for martensite. It furnishes one method for expressing hardenability. For example, in the steel of Figure 19 the critical cooling rate for martensite is 30,000°C/h or 8.3°C/s.

Although the critical cooling rate can be used to express hardenability, cooling rates ordinarily are not constant but vary during the cooling cycle. Especially when quenching in liquids, the cooling rate of the steel always decreases as the steel temperature approaches that of the cooling medium. In fact, quoted cooling rates are properly those that occur at a specified temperature, normally 700°C. It is therefore customary to express hardenability in terms of depth of hardening in a standardized quench. The quenching condition used in this method of expression is a hypothetical (and mathematically exact) one in which the surface of the piece is assumed to come instantly to the temperature of the quenching medium. This condition implies no barrier to heat transfer at the steel–bath interface, ie, an infinite heat-transfer coefficient at this surface. This is known as an ideal quench. The diameter of a round steel bar, which is quenched to the desired microstructure, usually 50% martensite and 50% softer products, or a corresponding hardness value, at the center in an ideal quench, is known as the ideal diameter, D_I. The relationships between the cooling rates of the ideal quench and those of other cooling conditions are known. Thus, the hardenability values in terms of ideal diameter can be used to predict the size of round or other shape which have the same cooling rate when cooled in actual quenches where cooling severities are known. The cooling severities (usually referred to as severity of quench), which form the basis for these relationships are called H values. The H value for the ideal quench is infinity. Those for some commonly used cooling conditions are given in Table 2.

Hardenability is most conveniently measured by a test in which a steel sample is subjected to a continuous range of cooling rates. In the end-quench or Jominy test, a round bar, 25-mm diameter and 100-mm long, is heated to the desired austenitizing temperature to control the austenite grain size and quenched in a fixture by a stream of water impinging on only one end. Hardness measurements are made on flats that are ground along the length of the bar after quenching. The results are expressed as a plot of hardness versus distance from the quenched end of the bar. The relationships between the distance from the quenched end and cooling rates in terms of D_I are known, and the hardenability can be evaluated in terms of D_I by noting the distance from the quenched end at which the hardness corresponding to the desired microstructure occurs and using this relationship to establish the corresponding cooling rate or D_I value. Published heat flow tables or charts relate the ideal diameter value to cooling rates in quenches or cooling conditions where H values are known. Thus, the ideal diameter value can be used to establish the size of a piece in which the desired microstructure can be obtained under the quenching conditions of the heat treatment to be used. The hardenability of steel is such an important property that it has become common practice to purchase steels to specified hardenability limits. Composition often thus becomes a secondary specification. Such steels are called H steels.

13. Heat-Treating Processes

In almost all heat-treating processes, steel is heated above the A_3 point and then cooled at a rate that results in the microstructure that gives the desired properties (34,37). Process annealing and stress-relieving are exceptions.

13.1. Austenitization. The steel is first heated above the temperature at which austenite becomes stable. The actual austenitizing temperature should normally be high enough to dissolve the carbides completely in a practical time—often 30–60 min, and take advantage of the hardening effects of any alloying elements present. In some cases, such as tool steels or high carbon steels, undissolved carbides may be deliberately retained for extra wear resistance. The temperature should not be high enough to produce pronounced grain growth. It is important to heat long enough for complete solution. For low alloy steels in a normally loaded furnace, 1.8 min/mm of diameter or thickness usually suffices.

Excessive heating rates may create high stresses, resulting in distortion or cracking. Certain types of continuous furnaces, salt baths, and radiant-heating furnaces provide very rapid heating, but preheating of the steel may be necessary to avoid distortion or cracking, and sufficient time must be allowed for uniform heating throughout. Unless special precautions are taken, heating causes scaling or oxidation, and may result in loss of carbon near the surface (decarburization). Controlled-atmosphere furnaces or salt baths can minimize these effects.

13.2. Quenching. The primary purpose of many quenching operations is to cool rapidly enough to suppress at least some, and perhaps all, transformation at temperatures above the M_s temperature. For material to be used in bending or torsion, where the maximum stress is at the surface, it is often extravagant in alloy use to produce martensite throughout the piece. There can be other advantages. By careful selection and processing, which control the timing of volume changes during austenite transformation, compressive stresses can be retained in the surface and thereby contribute to improved fatigue life. For material where the stresses are applied in tension or compression, transformation to martensite throughout the piece is generally advisable.

The cooling rate required depends on the size of the piece and the hardenability of the steel. The preferred quenching media historically are water, oils, and brine. The temperature gradients set up by quenching create high thermal and transformational stresses that may lead to cracking and distortion. A quenching rate no faster than necessary should be employed to minimize these stresses. Water and brine are often too stringent for satisfactory use, whereas oil can be a fire hazard. Oils also deteriorate upon use and today can be a difficult disposal problem. Thus polymer–water mixtures have found application. These mixtures can have a range of heat abstraction rates and some of the problems with oil can be avoided. Agitation of the cooling medium accelerates cooling and improves uniformity. Cooling should be long enough to permit complete transformation to martensite. Then, in order to minimize time-dependent cracking from quenching stresses, the article should be transferred immediately to the tempering furnace (Fig. 20).

13.3. Tempering. Quenching forms hard, often brittle martensite having high residual stresses. Tempering relieves these stresses and precipitates excess carbon as carbides; it improves ductility, although at some expense of strength and hardness. The operation consists of heating at temperatures below the lower critical temperature, A_1.

Measurements of stress relaxation on tempering indicate that, in a plain carbon steel, residual stresses are significantly lowered by heating to temperatures as low as 150°C, but that temperatures of 480°C and above are required to reduce these stresses to adequately low values. The times and temperatures required for stress relief depend on the high temperature yield strength of the steel, because stress relief results from the localized plastic flow that occurs when the steel is heated to a temperature where its yield strength is less than the internal stress. This phenomenon may be affected markedly by composition, and particularly by alloy additions.

The toughness of quenched steel, as measured by the notch impact test, first increases on tempering up to 200°C, then decreases on tempering between 200 and 310°C, and finally increases rapidly on tempering at 425°C and above. This behavior is characteristic and, in general, temperatures of 230–310°C should be avoided. Where this range is unavoidable because of strength requirements, eg, for aircraft landing gear, additions of 1–2% silicon change the rate of carbide formation and can move the brittle range to higher tempering temperatures to allow acceptable toughness.

In some more highly alloyed steels, there is the possibility of precipitation of alloy carbides from the ferrite at ~500°C and an actual increase in hardness. For steels needing high temperature strength, eg, tools and pressure vessels in refineries, these are often an attractive (albeit more expensive) choice. In order to minimize cracking, tempering should follow quenching immediately. Any appreciable delay may promote cracking.

The tempering of martensite results in a contraction, and if the heating is not uniform, dangerously high stresses result. Similarly, heating too rapidly may be dangerous because of the sharp temperature gradient set up between the surface and the interior. Recirculating-air furnaces can be used to obtain uniform heating. Oil baths are commonly used for low temperature tempering, salt baths can be used over a bigger range at higher temperatures. Some steels lose toughness on slow cooling from ~540°C and above, a phenomenon known as temper brittleness. Rapid cooling after tempering is desirable in these cases.

Martempering. A modified quenching procedure known as martempering minimizes the high stresses created by the transformation to martensite during the rapid cooling characteristic of ordinary quenching (Fig. 21). In practice, it is ordinarily carried out by quenching in a molten salt bath just above the M_s temperature. Transformation to martensite does not begin until after the piece reaches the temperature of the salt bath and is then allowed to cool relatively slowly in air. Because the large temperature gradient characteristic of conventional quenching is absent, the stresses produced by the transformation are much lower and a greater freedom from distortion and cracking is obtained. After martempering, the piece may be tempered to the desired strength.

Austempering. Lower bainite is generally as strong as and somewhat more ductile than tempered martensite. Austempering, which is an isothermal heat treatment that results in lower bainite, offers an alternative heat treatment for obtaining optimum strength and ductility if the specimens are sufficiently small.

In austempering the article is quenched to the desired temperature in the lower bainite region, usually in molten salt, and kept at this temperature until transformation is complete (Fig. 22). Usually, the piece is held twice as long as the period indicated by the isothermal transformation diagram. The article may then be quenched or air-cooled to room temperature after transformation is complete, and may even be tempered to lower hardness if desired.

13.4. Normalizing.

In this operation, steel is heated above its upper critical temperature (A_3) and cooled in air. The purpose of this treatment is to refine the hot-rolled structure (often quite inhomogeneous), depending on the finishing temperature after hot-rolling, and to obtain a carbide size and distribution that is more favorable for carbide solution on subsequent heat treatment than the earlier as-rolled structure.

In alloy steels, particularly if these have been slowly cooled after rolling, the carbides in the as-rolled condition tend to be massive and are difficult to dissolve on subsequent austenitization. The carbide size is subject to wide variations, depending on the rolling and slow cooling. Here, again, normalizing tends to establish a more uniform and finer carbide particle size that facilitates subsequent heat treatment. Although an expense, this process provides more uniform quality in the finished product.

The usual practice is to normalize at 50–80°C above the upper critical temperature. For some alloy steels, however, considerably higher temperatures may be used. Heating may be carried out in any type of furnace that permits uniform heating and good temperature control.

13.5. Annealing.

Annealing has two different purposes: to relieve stresses induced by hot- or cold-working, and to soften the steel to improve its machinability or formability. It may involve only a subcritical heating to relieve stresses, recrystallize cold-worked material, or spheroidize carbides; alternatively, it may involve heating above the upper critical temperature (A_3) with subsequent transformation to pearlite or, less commonly, directly to a spheroidized structure on cooling.

The most favorable microstructure for machinability in low or medium carbon steels is coarse pearlite. The customary heat treatment to develop this microstructure is a full annealing, illustrated in Figure 23. It consists of austenitizing at a relatively high temperature to obtain full carbide solution, followed by slow cooling to give transformation exclusively in the high temperature end of the pearlite range. This simple heat treatment is reliable for most steels. It is, however, rather time-consuming because it involves slow cooling over the entire temperature range from the austenitizing temperature to a temperature well below that at which transformation is complete.

Isothermal Annealing. Annealing to coarse pearlite can be carried out isothermally by cooling to the proper temperature for transformation to coarse pearlite and holding until transformation is complete. This method, called isothermal annealing and illustrated in Figure 24, may save considerable time over the full-annealing process described previously. Neither the time from the austenitizing temperature to the transformation temperature, nor the one from the transformation temperature to room temperature, is critical. Both may be shortened within limits. If extreme softness of the coarsest pearlite is not necessary, the transformation may be carried out near the nose of the IT curve, where the transformation is completed rapidly and the operation further expedited. The pearlite in this case is much finer and harder.

Isothermal annealing can be conveniently adapted to continuous annealing, usually in specially designed furnaces. This is commonly referred to as cycle annealing.

Spheroidization Annealing. Coarse pearlite microstructures are too hard for optimum machinability in the higher carbon steels. Such steels are customarily annealed to develop spheroidized microstructures by holding the as-rolled, slowly cooled, or normalized materials just below the lower critical temperature range. Such an operation is known as subcritical annealing. Full spheroidization may require long holding times at the subcritical temperature. The method may be slow, but it is simple and may be more convenient than annealing above the critical temperature.

Using some modifications, the annealing procedures described to produce pearlite can give spheroidized microstructures. If free carbide remains after austenitizing, transformation in the temperature range where coarse pearlite ordinarily would form proceeds to spheroidized rather than pearlitic microstructures. Thus, heat treatment to form spheroidized microstructures can be carried out like heat treatment for pearlite, except for the lower austenitizing temperatures. Spheroidization annealing may thus involve a slow cooling similar to the full-annealing treatment used for pearlite, or it may be a treatment similar to isothermal annealing. An austenitizing temperature not more than 55°C above the lower critical temperature is customarily used for this type of annealing.

Process Annealing. Process annealing is the term used for subcritical annealing of cold-worked materials. It customarily involves heating at a temperature high enough to cause recrystallization of the cold-worked material and to soften the steel. The most important example of process annealing is the box annealing of cold-rolled low carbon sheet steel. The sheets are enclosed in a large box that can be sealed to permit the use of a controlled atmosphere to prevent oxidation. Annealing is usually carried out between 590 and 715°C. The operation usually takes ~24 h, after which the charge is cooled slowly within the box. The entire process takes several days.

An alternative way to anneal the low carbon sheet and certain higher strength steels used in large tonnages for automobiles, appliances, and containers is to pass the sheet, after cold rolling, continuously through a long furnace having a carefully designed temperature profile. Usually it is desirable to have a certain crystallographic texture in the sheet after annealing, and to exercise control over the amounts of carbon and nitrogen remaining in solution in the ferrite. The control requirements are thus severe, but the savings in time over box annealing, as well as the very small scatter in properties, makes this an attractive option when capital is available. Developments using a hydrogen atmosphere during box annealing for better heat transfer have largely restored the competitiveness against continuous annealing processes; the latter of course also continue to improve.

13.6. Carburizing. In carburizing, low carbon steel acquires a high carbon surface layer by heating in contact with carbonaceous materials. On quenching after carburizing, the high carbon skin forms martensite, whereas the low carbon core remains comparatively soft. The result is a highly wear-resistant exterior over a very tough interior. This material is particularly suitable for gears, camshafts, etc. Carburizing has historically been carried out by packing the steel in boxes with carbonaceous solids, sealing to exclude the atmosphere, and heating to ~925°C for a period of time depending on the depth desired. This method is called pack carburizing. Alternatively, today, the steel may be heated in contact with carburizing gases, in which case the process is called gas carburizing; or, alternatively, the steel may be heated in liquid baths of carburizing salts, in which case it is known as liquid carburizing. The M_f of the high carbon case may be below room temperature, which means that some soft retained austenite may be present. Further heat treatments may be necessary to eliminate this or minimize its effects.

13.7. Nitriding. The nitrogen case-hardening process, termed nitriding, consists of subjecting machined and, preferably, heat-treated Cr–Mo steel parts containing aluminum at ~500°C to the action of a nitrogenous medium, commonly ammonia gas, under conditions whereby surface hardness is imparted without requiring any further treatment. Wear resistance, retention of hardness at high temperatures, and resistance to certain types of corrosion are also imparted by nitriding. The hardness of nitrided steels arises primarily from the presence of 0.9–1.4% aluminum, which leads to large numbers of small precipitates of aluminum nitride [24304-00-5].

An intermediate treatment that adds both carbon and nitrogen to steel surfaces can be obtained by exposing the parts to a bath of molten cyanide at just above the critical temperature of the core for about one hour followed by direct quenching. The hardened area is about 0.25-mm deep.

14. Carbon Steels

Plain carbon steels, by far the largest volume of steel produced, have the most diverse applications of any metallic engineering materials. These include castings, forgings, tubular products, plates, sheet and strip, wire and wire products, structural shapes, bars, and railway materials such as rails, wheels, and axles. Carbon steels are made by all modern steelmaking processes and, depending on their carbon content and intended purpose, may be rimmed, semikilled, or fully killed (33). Rimmed steels having good surfaces are almost extinct; While desirable when ingots were common, they are difficult to produce by modern continuous casting process. Semikilled have the oxygen content controlled largely by Si and Mn; today these are largely higher carbon grades where the oxygen in solution from the melt is lower. Killed steels use Al to reduce oxygen in the steel, usually after ladle treatment, and are used for almost all low carbon sheet products.

The American Iron and Steel Institute (AISI) has published standard composition ranges for plain carbon steel. Each composition range is assigned an identifying number according to an accepted method of classification (Table 3). In this system, carbon steels are assigned to one of three series: 10xx (nonresulfurized), 11xx (resulfurized), and 12xx (rephosphorized and resulfurized). Modern low carbon steels are often of such low carbon that the lowest Society of Automotive Engineers (SAE) designation, 1005, is not helpful. Material is ordered to property and performance specifications. Normal practice makes an upper limit of 0.015% for sulfur and phosphorus easily attainable, and by ladle metallurgy this can readily be reduced to 0.003%. Sulfur in amounts as high as 0.33% max may be deliberately added to the 11xx and as high as 0.35% max to the 12xx steels to improve machinability. In addition, phosphorus up to 0.12% max may be added to the 12xx steels to increase stiffness.

In identifying a particular steel, the letters x are replaced by two digits representing average carbon content. For example, an AISI 1040 steel would have an average carbon content of 0.40%, with a tolerance of ±0.03%, giving a range of 0.37–0.44% carbon.

14.1. Properties.

The properties of plain carbon steels are governed principally by carbon content and microstructure. These properties can be controlled by heat treatment as discussed. About half the plain carbon steels are used in the hot-rolled form, although increasingly the property combinations are enhanced by controlled cooling following the last stand of the hot mill for structural shapes, sheet, and strip. The other half are cold-rolled to thin sheet or strip and used directly or with an annealing treatment such as described above.

Certain properties of plain carbon steels may be modified by residual elements other than the carbon, manganese, silicon, phosphorus, and sulfur that are always present, as well as gases, especially oxygen, nitrogen, and hydrogen, and their reaction products. These incidental elements are usually acquired from scrap, deoxidizers, or the furnace atmosphere. The gas content depends mostly on melting, deoxidizing, ladle treatments, and casting procedures. Consequently, the properties of plain carbon steels can depend heavily on the manufacturing techniques.

The average mechanical properties of as-rolled 2.5-cm bars of carbon steels as a function of carbon content are shown in Figure 25. This diagram is an illustration of the effect of carbon content when microstructure and grain size are held approximately constant. Although the diagram is representative, the great bulk of tonnage used is at low carbon levels. These levels are often $<$ 0.2% C; much is $<$ 0.1% C.

14.2. Microstructure and Grain Size. The carbon steels having relatively low hardenability do not contain martensite or bainite in the cast, rolled, or forged state. The constituents of the hypoeutectoid steels are therefore ferrite and pearlite, and of the hypereutectoid steels, cementite and pearlite.

As of today, most of the low carbon steels do not rely primarily on pearlite for strength. Although the pearlite does contribute somewhat to tensile strength, the resulting reduction in ductility and toughness make it much more attractive to improve strength, ductility, weldability, and toughness simultaneously by concentrating on reducing the ferrite grain size in a lower carbon material (38). The yield strength, σ_y, has been shown (39) to increase with the inverse square root of the ferrite grain size, d.

$$\sigma_{\mathrm{y}} = A + B \cdot d^{-1/2}$$

Thus where 25–50 μm was once considered quite appropriate for a ferrite grain size, 5 μm has become not at all unusual. These smaller grain sizes can be produced directly from hot rolling by controlled recrystallization of the austenite to a fine grain size, which in turn leads to many more independently nucleated ferrite grains. The addition of small amounts of carbide and nitride formers, such as Nb, V, and Ti, helps to keep the grain sizes small, and by precipitation in the ferrite at lower temperatures, assisted by water cooling of the material out of the last rolling stand, gives extra strengthening. These materials, a relatively recent but increasingly important development, are commonly known as microalloyed or high strength low alloy (HSLA) steels (38,39).

14.3. Microstructure of Cast Steels. Cast steel is generally coarse-grained because austenite forms at high temperature and the pearlite is usually coarse, in as much as cooling through the critical range is slow, particularly if the casting is cooled in the mold. In hypoeutectoid steels, ferrite ordinarily precipitates at the original austenite grain boundaries during cooling, although ferrite often precipitates as plates within individual austenite grains, especially if these are large. In hypereutectoid steels, cementite is similarly precipitated. Such large-grained mixtures of ferrite or cementite and coarse pearlite have poor strength, toughness, and ductility properties, and heat treatment is usually necessary to reduce the grain size and thereby obtain suitable microstructures and properties in cast steels.

14.4. Hot Working. Many carbon steels are used in the form of as-rolled finished sections. The microstructure and properties of these sections are determined largely by composition, rolling procedures, and cooling conditions. The rolling or hot working of these sections is ordinarily carried out in the temperature range in which the steel is austenitic, with four principal effects: considerable homogenization occurs during the heating for rolling, tending to eliminate some, but never all, of the dendritic segregation present in the ingot; the dendritic structure is broken up during rolling; recrystallization takes place during rolling, and the final austenitic grain size is determined by the temperature at which the last passes are made (the finishing temperature); and dendrites and inclusions are reoriented, with markedly improved ductility, in the rolling direction.

The inhomogeneities in composition inherent in the solidification process are in practice never totally removed. Rolling serves to reduce the length scales over which these inhomogeneities occur to a few tens of micrometers normal to the rolling direction. Although this can lead to some anisotropy of properties, such as toughness and ductility, in the directions parallel and normal to the rolling direction, it rarely is seriously deleterious to engineering applications.

The austenite grain size at the end of hot rolling, during which the steel recrystallizes several times, is sensitive to undissolved particles. These may be products of the steelmaking process during deoxidation, or occur as deliberate additions of carbide and/or nitride formers as in HSLA. The ultimate microstructure, and thus properties and performance, depends on how and at what temperature this austenite transforms during the subsequent cooling. Section size has important ramifications. A large I-beam cools slowly, but hot-rolled sheet is normally coiled from the mill directly at a predetermined temperature into a large torus weighing several tons, which thus also cools slowly.

14.5. Cold Working. The manufacture of wire, sheet, strip, bar, and tubular products often includes cold working, with effects that may be eliminated by annealing. However, some products, particularly wire, are used in the cold-worked condition to give inexpensive strength. The most pronounced effects of cold working are increased strength and hardness and decreased ductility. The effect of cold working on the tensile strength of plain carbon steel is shown in Figure 26. The yield strength also increases, generally more rapidly than tensile strength, so cold working is a cost-effective method of strengthening if ductility is not critical.

Upon reheating cold-worked steel to the recrystallization temperature (∼450°C) or above, depending on composition, extent of cold working, and other variables, the original microstructure and properties may be substantially restored.

14.6. Heat Treatment. Although many wrought (rolled or forged) carbon steels are used without a final heat treatment, this may be employed to improve the microstructure and properties for critical applications if the cost can be justified.

The option of annealing a hot- or cold-rolled structure depends on the type of further processing to be applied. For example, the forces required to cold draw a section prior to final machining may be too high if the specimen is not given a full anneal above the A_3, followed by slow cooling to produce a fairly coarse ferrite–pearlite structure. The moderate cold work produced by the drawing to a final size is helpful to obtaining good chip formation during machining.

At the other extreme, the exceptional ductility requirements of a material to be shaped by drawing, flanging, or other large plastic deformation modes necessitate careful combinations of advanced steelmaking, hot rolling, cold rolling, and annealing. The demands of consumers for aesthetic and functional requirements are passed through such product manufacturers as autos, appliances, and the steelmaker. The increase in quality and reproducibility in these materials in the last two decades has been impressive.

The tendency toward lower carbon steels has minimized the utilization of pearlite as a structural constituent. The growing use of HSLA steels has greatly reduced the quenching and tempering of carbon steels to provide noticeably stronger materials without the use of expensive alloys. Normalizing is still used to reduce variability in hot-rolled material if the economics can be justified.

14.7. Residual Elements. In addition to carbon, manganese, phosphorus, sulfur, and silicon that are always present, carbon steels may contain small amounts of hydrogen, oxygen, or nitrogen, introduced during the steelmaking process; nickel, copper, molybdenum, chromium, and tin, which may have been present in the scrap; and aluminum, titanium, vanadium, or zirconium, which may have been introduced during deoxidation.

Nitrogen can be a relatively harmful element in BOP steels unless special precautions are taken. A smaller atom than carbon, nitrogen is more soluble and has a higher diffusivity. Thus nitrogen can be particularly deleterious to the properties of sheet steel, where, unless care is taken, deformation can be quite inhomogeneous. This can lead to ugly surface markings totally unsuitable in automobile or appliance applications. The effect can be masked for a time by a light skin pass prior to leaving the rolling mill, but as nitrogen diffuses over a period of several days at room temperature during shipment or storage, the effect reappears. To avoid this, steel normally killed with aluminum ties up nitrogen as AlN in addition to its other functions. Nitrogen is not easily removed by vacuum treatment.

During the 1990s, the ability to produce interstitial-free steels (42) low in carbon and nitrogen has been achieved, whereby the carbon and oxygen left in solution after steelmaking react to form carbon monoxide under a vacuum in the ladle degasser. The bubbles leaving also serve to carry off some of the nitrogen. Steels made in the electric furnace tend to have higher nitrogen and are thus not able to make the most difficult types of deep-drawing sheet as of this writing. However, the high nitrogen can be combined with nitride formers (V, Nb, and/or Ti) to take it out of solution in the ferrite and enable high strength low alloy (HSLA) steels with yield strengths in the 500+ Mpa range, or even higher.

An embrittling effect in heavier sections, the mechanism of which is still debated, is possible with a hydrogen content of more than $\sim$3 ppm. The content of hydrogen and other gases can, however, be reduced by vacuum dagassing.

Alloying elements such as nickel, chromium, molybdenum, and copper, which may be introduced with scrap, can increase the hardenability, although only slightly, because the concentrations are ordinarily low. However, the heat-treating characteristics may change, and for applications in which ductility is important, as in low carbon steels for deep drawing, the increased hardness and lower ductility imparted by these elements needs to be carefully watched.

Tin, even in low amounts, is harmful in steels for deep drawing. For most applications, however, the effect of tin in the quantities ordinarily present is negligible.

Aluminum is generally desirable as a grain refiner and tends to reduce the susceptibility of carbon steel to aging associated following deformation. In structural steels, aluminum tends to promote graphitization and is therefore undesirable in steels used at high temperatures. The other elements that may be introduced as deoxidizers, such as titanium, vanadium, or zirconium, are ordinarily present in such small amounts as to be ineffective, and need slightly larger amounts to lead to HSLA steels. Copper and tin can create a rough surface condition during hot rolling through a process called hot shortness. Here the copper and tin form a liquid alloy that can penetrate grain boundaries and cause surface cracks.

15. Alloy Steels

For slightly $< 10\%$ of products, alloying elements are introduced to produce properties not available for carbon steels where the functional elements are usually only considered to be carbon, silicon (to 0.6%), and manganese (to 1.65%). Copper, which may be present up to 0.6 wt %, is relatively rare compared to the ubiquitous silicon and manganese.

The principal classes of alloy steels in decreasing order of volume are HSLA (usually as hot-rolled), AISI alloy steels (usually quenched and tempered), stainless steels (cast or wrought), electrical steels (largely iron–silicon), alloy tool steels, and nonstainless heat-resistant steels. One or more alloying elements may be critical to the resulting properties. Some very specialized steels have been developed to meet exceptionally harsh service requirements. Even though the tonnage of these specialized steels may be small, the importance to modern technology may be huge if the task is only feasible with the specific alloy (see HIGH TEMPERATURE ALLOYS; TOOL MATERIALS).

15.1. Functions of Alloying Elements.

Alloy steels may contain up to $\sim$50% of alloying elements which directly enhance properties, although 30% is a more common upper limit. Examples are the increased corrosion resistance of high chromium steels, the enhanced electric properties of silicon steels, and at much lower levels the improved strength of the HSLA steels, and the improved hardenability and tempering characteristics of AISI alloy steels.

15.2. High Strength Low Alloy Steels.

Until the 1970s, increasing the strength of steel involved producing dispersions of carbides by quenching and tempering (accompanied by cost and joining problems), increasing the fraction of pearlite (resulting in ductility and toughness problems), or cold working (ductility problems). As the understanding of the origin of properties developed, other mechanisms began to be attractive to produce inexpensive steels having good combinations of the properties essential for service needs. The most important advance was to refine the ferrite grain size, and be able to disperse small amounts of very fine alloy carbides or carbonitrides. In this way, toughness and ductility were improved simultaneously. Processing improvements on reliable composition control and tight control of the rolling schedules lead to very attractive and economical combinations of properties in the hot-rolled condition (38,40–43). Because the carbon content is lower, the weldability is also improved, and in a few cases the corrosion resistance in ambient air has also been better.

Several types of processing that contribute to these desirable properties are as follows: (*1*) Controlled rolling of steels having small amounts of carbon and nitrogen containing V, Ti, Nb, and/or Zr in the austenite produces fully recrystallized fine austenite grains; rolling to low temperatures in the austenite range or into the austenite–ferrite range produces deformed pancake grains. Subsequent cooling leads to very fine ferrite grains. The pancake grain structure can lead to anisotropy of properties or in extreme cases to delamination. (*2*) Accelerated cooling from the hot mill after controlled rolling in the austenite range produces equiaxed ferrite while avoiding acicular ferrite, not so slowly, however, that growth of carbonitride precipitates occurs during coiling, thus leading to a strength loss, but slowly enough that carbonitrides can precipitate in the ferrite during coiling. (*3*) Sufficiently rapid cooling of low ($<$0.08%) carbon in steels having enough hardenability produces low carbon bainite. Adequate toughness in these steels requires controlled rolling (38). (*4*) Simple normalizing for some steels, eg, those containing vanadium, can give sufficient ferrite grain refinement for these steels to be attractive. (*5*) Intercritical annealing, ie, in the $\alpha + \gamma$ range, of carbon steels containing 1.5% manganese gives martensite islands in a ferrite matrix after rapid cooling. This is a product with a low initial yield strength but rapid work hardening and increased ductility. These dual-phase steels are useful in parts needing good yield strength which are to be deformed before service, eg, auto wheels, and are a growing fraction of the market with the plan to make lighter vehicles. (*6*) A more recent entry in this field are the TRIP (the acronym for TRansformation Induced Plasticity) that aided steels which are low alloy but contain ferrite, bainite and austenite at room temperature; during forming some of the austenite transforms to martensite increasing both strength and uniform extension.

There are several hundred types of steels that use these principles separately or in combination. Some of these are generic, many are proprietary. Among them are various microalloyed ferrite–pearlite steels having limited pearlite amounts and the low carbon bainites, as well as the dual-phase steels.

Some other steels that fall into related categories are the various long-standing proprietary weathering steels, eg, USS's Cor-Ten A (dating from 1930 but still useful!), which uses small amounts of copper and phosphorus to improve atmospheric corrosion resistance. These elements also produce significant solid solution hardening. Phosphorus is also used for its strengthening effects alone, although the toughness is degraded.

- Other alloy effects in these steels are in the control of the shape of sulfide inclusions. Manganese(II) sulfide, MnS, is a common form in which sulfur is present; this is soft and ductile at rolling temperatures and is thus in the form of stringers. This leads to poor through thickness ductility; ie, the ductility perpendicular to the rolling direction. Other sulfides, eg, calcium sulfide, CaS, and titanium(II) sulfide, TiS, are sufficiently stronger so that during hot rolling these remain essentially spherical and give more nearly isotropic mechanical properties. There is a developing market for these inclusion-shape-controlled steels.

Finally, hydrogen in relatively small amounts can lead to cracking, especially as the strength increases. If the presence of hydrogen cannot be adequately lowered by the ladle treatment, combinations of low carbon and silicon, inclusion shape control, and $< 0.25\%$ copper can be helpful in minimizing loss of toughness.

15.3. Interstitial-Free Steels. In some ways, interstitial-free (IF) steels are primarily carbon steels having deliberately low yield strength. Many of the same principles apply as for other alloy steels (42). It has long been known that the maximum ductility in steel sheet, which is so important in formability, depends on the carbon and nitrogen in solution in the ferrite. If these can be reduced < 50 ppm, not only does the ductility approach 50% and the yield strength decrease, but the harmful effects of strain aging and quench aging essentially disappear. By vacuum treatment in the ladle, carbon and nitrogen in solution are reduced; by adding small quantities of carbide and nitride stabilizers, any residual interstitials are tied up as precipitates. These IF steels are becoming increasingly important both on their own and as a base for the hot dip galvanizing commonly used for increased corrosion resistance.

15.4. AISI Alloy Steels. The American Iron and Steel Institute defines alloy steels as follows: “steel is considered to be alloy steel when the maximum of the range given for the content of alloying elements exceeds one or more of the following limits: manganese, 1.65%; silicon, 0.60%; copper, 0.60%; or in which a definite range or a definite minimum quantity of any of the following elements is specified or required within the limits of the recognized field of constructional alloy steels: aluminum, boron, chromium up to 3.99%, cobalt, columbium (niobium), molybdenum, nickel, titanium, tungsten, vanadium, zirconium, or any other alloying element added to obtain a desired alloying effect” (44). Steels that contain 4% or more of chromium are included by convention among the special types of alloy steels known as stainless steels (45,46).

Steels that fall within the AISI definition have been standardized and classified jointly by AISI and SAE (see Table 3). These represent by far the largest alloy steels production and are generally known as AISI alloy steels. They are also referred to as constructional alloy steels.

The effect of the alloying elements on AISI steels is indirect because alloying elements control microstructure through their effect on hardenability. These elements permit the attainment of desirable microstructures and properties over a much wider range of sizes and sections than is possible with carbon steels.

15.5. Quenched and Tempered Low Carbon Constructional Alloy Steels. A class of quenched and tempered low carbon constructional alloy steels has been very extensively used in a wide variety of applications such as pressure vessels, mining and earth-moving equipment, and in large steel structures (see TANKS AND PRESSURE VESSELS).

As a general class, these steels are referred to as low carbon martensites to differentiate them from constructional alloy steels of higher carbon content, such as the AISI alloy steels, that develop high carbon martensite upon quenching. The low carbon martensites are characterized by a relatively high strength, minimum yield strengths of 690 MPa (100,000 psi), good toughness down to -45°C, and weldability with joints showing full joint efficiency when welded with low hydrogen electrodes. They are most commonly used in the form of plates, but also as sheet products, bars, structural shapes, forgings, and semifinished products. Several steel-producing companies manufacture such steels under various trade names. Compositions are proprietary.

15.6. Alloy Tool Steels. Alloy tool steels are classified roughly into three groups. The first consists of alloy tool steels, to which alloying elements have been added to impart hardenability higher than that of plain carbon tool steels. Accordingly, these steels may be hardened in heavier sections or using less drastic quenches to minimize distortion. The second group is that of intermediate alloy tool steels, which usually contain elements such as tungsten, molybdenum, or vanadium. These form hard, wear-resistant carbides, often by secondary hardening during tempering ∼500°C. The last are high speed tool steels that contain large amounts of carbide-forming elements, which serve not only to furnish wear-resisting carbides, but also to increase secondary hardening thereby allowing operation at red heat.

15.7. Stainless Steels. Stainless steels are more resistant to rusting and staining than plain carbon and low alloy steels (47–50). This superior corrosion resistance results from the presence of chromium. Although other elements, such as copper, aluminum, silicon, nickel, and molybdenum, also increase corrosion resistance; in specific ways, these are usually minor relative to chromium in their usefulness.

Germany, the United Kingdom, and the United States shared in the early development of stainless steels. In the United Kingdom in 1912, during the search for steel that would resist fouling in gun barrels, a corrosion-resistant composition containing 12.8% chromium and 0.24% carbon was reported. It was suggested that this composition be used for cutlery. In fact, the composition of AISI Type 420 steel (12−14% chromium, 0.15% carbon) is similar to that of the first corrosion-resistant steel.

The higher chromium−iron alloys were developed in the United States from the early twentieth century on, when the effect of chromium on oxidation resistance at 1090°C was first noticed. Oxidation resistance increased markedly as the chromium content was raised $> 20\%$. For steels containing appreciable quantities of nickel, 20% chromium seems to be the minimum amount necessary for oxidation resistance at 1090°C.

The austenitic iron−chromium−nickel alloys were developed in Germany ∼1910 in a search for materials for use in pyrometer tubes. Further work led to the widely used versatile 18% chromium−8% nickel steels, the so-called 18−8.

The many compositions would appear to make the role of individual elements difficult to understand. There is, however, an understandable pattern. The corrosion resistance is primarily dependent on the chromium content, which is in four general ranges, reflecting the nature of the protective oxide film formed. These ranges fall ∼5%, 10−13%, 18%, and 25%, and the grades listed contain these amounts of chromium. Increasing the chromium content is valuable for resisting general (uniform) corrosion. However, under some circumstances very localized and potentially damaging corrosion can occur. Examples are (*1*) pitting corrosion, which can be deep enough to penetrate sheet and that can be mitigated by the addition of 2−3% molybdenum, hence Grades 316 and 317; (*2*) grain boundary attack where carbides have formed at grain boundaries, which can be prevented by low carbon contents, hence the L grades ($<0.03\%$C), by avoiding heat treatments, especially welding, which permit carbide precipitation or by adding carbide formers such as Ti or Nb, hence Grades 321 and 347; and (*3*) stress corrosion cracking (SCC), whereby cracks, usually transgranular, form under the simultaneous action of stress, from an applied load or more insidiously from residual stresses, and specific environments, especially chlorides in contact with austenitic steels. Composition changes do not give effective control cheaply and great care remains necessary to avoid SCC in process units operating at a few hundred degrees.

The next step to comprehending the many grades of stainless steel lies in understanding the crystal structure of the iron-rich matrix. The austenite field in iron exists over an increasingly small temperature range as chromium is added and disappears at ~12% chromium. Thus, to make the martensitic grades, it is important to be able to form 100% austenite first. Fortunately, carbon extends this range so it is possible to have all austenite prior to quenching in a 12% chromium carbon steel, or, if the carbon is high enough, even in a 17% chromium steel.

For the ferrite grades, it is necessary to have at least 12% chromium and only very small amounts of elements that stabilize austenite. For these materials, the structure is bcc from room temperature to the melting point. Some elements, such as Mo, Nb, Ti, and Al, which encourage the bcc structure, may also be in these steels. Because there are no phase transformations to refine the structure, brittleness from large grains is a drawback in these steels. They find considerable use in structures at high temperatures where the loads are small and toughness is not critical.

Austenitic steels are extremely valuable structural components in a wide variety of applications. Adding several percent of nickel to an iron–chromium alloy can allow austenite to exist metastably or stably down to ambient temperature. Depending on composition, the M_s can be near or even above room temperature. A bcc phase, or sometimes a hexagonal close-packed ϵ phase, can then form martensitically, especially if the material is plastically deformed, eg, Type 301, and can give very high strengths. Using more nickel, the austenite is stable and formable and increasingly finds both industrial and domestic uses. The several types in the 300 series have other specific alloys largely to control the various forms of localized corrosion or to improve the creep strength.

The standard AISI types with the Unified Numbering System (UNS) designation are identified in Table 4. A number of proprietary types have not been listed. These are for specific uses, which justify their substantial cost.

Martensitic Stainless Steels. Martensitic stainless steels include Types 403, 410, 414, 416, 420, 431, 440A, 440B, 440C, 501, and 502 (see Table 4). The most widely used is Type 410, which contains 11.50–13.50% chromium and <0.15% carbon. In the annealed condition, this grade may be drawn or formed. It is an air-hardening steel, offering a wide range of properties by heat treatment. In sheet or strip form, Type 410 is used extensively in the petroleum industry for ballast trays and liners. It is also used for parts of furnaces operating < 605°C, and for blades and buckets in steam turbines.

Type 420, with ~0.35% carbon and a resultant increased hardness, is used for cutlery. In bar form, it is used for valves, valve stems, valve seats, and shafting where corrosion and wear resistance are needed. Type 440 may be employed for surgical instruments, especially those requiring a durable cutting edge. The necessary hardness for different applications can be obtained by selecting grade A, B, or C, with increasing carbon content in that order.

Other martensitic grades are Types 501 and 502. The former has >0.10% and the latter <0.10% carbon. Both contain 4–6% chromium. These grades are also air-hardened, but do not have the corrosion resistance of the 12% chromium grades. Types 501 and 502 have wide application in the petroleum industry for hot lines, bubble towers, valves, and plates.

Ferritic Stainless Steels. Ferritic steels are iron–chromium alloys not hardenable by heat treatment. In alloys having 17% chromium or more, an insidious embrittlement occurs in extended service ~475°C. This can be mitigated to some degree but not eliminated. Grades commonly include Types 405, 409, 430, 430F, and 446 (see Table 4); newer grades are 434, 436, 439, and 442.

The most common ferritic grade is Type 430, containing 0.12% carbon or less and 14–18% chromium. Because of its high chromium content, the corrosion resistance of Type 430 is superior to that of the martensitic grades. Furthermore, Type 430 may be drawn, formed, and, using proper techniques, welded. At one time widely used for automotive and architectural trim, it is also employed in equipment for the manufacture and handling of nitric acid (qv), to which it is resistant. Type 430 does not have high creep strength but is suitable for some types of service up to 815°C, and thus has application in combustion chamber for domestic heating furnaces.

Type 409, developed as a less expensive replacement for Type 430 in automotive applications such as trim and catalytic converters, has become the principal alloy in this area.

The high (23–27%) chromium content of Type 446 imparts excellent heat resistance, although its high temperature strength is only slightly better than that of carbon steel. Type 446 is used in sheet or strip form up to 1150°C. Some variants of Type 446 are available for severe applications. This grade does not have the good drawing characteristics of Type 430, but may be formed with care. Accordingly, Type 446 is widely used for furnace parts such as muffles, burner sleeves, and annealing baskets. Its resistance to nitric and other oxidizing acids makes it suitable for chemical-processing equipment.

Austenitic Stainless Steels. Austenitic steels, based on iron–chromium–nickel alloys, are not hardenable by heat treatment and are predominantly austenitic. They include Types 301, 302, 302B, 303, 304, 304L, 305, 308, 309, 310, 314, 316, 316L, 317, 321, and 347. The L refers to 0.03% carbon max, which is readily available today. In some austenitic stainless steels, all or part of the nickel is replaced by manganese and nitrogen in proper amounts, as in one proprietary steel and Types 201 and 202 (see Table 4).

The most widely used austenitic stainless steel is Type 304, commonly known as 18–8. It has excellent corrosion resistance and, because of its austenitic structure, excellent ductility. It may be deep-drawn or stretch formed. It can be readily welded, but carbide precipitation must be avoided in and near the weld by cooling rapidly enough after welding. Where carbide precipitation presents problems, Types 321, 347, or 304L may be used. The applications of Types 304 are wide and varied, including kitchen equipment and utensils, dairy installations, transportation equipment, and oil-, chemical-, paper- (qv), and food-processing (qv) machinery.

The low nickel content of Type 301 causes it to harden faster than Type 304 on account of reduced austenite stability. Accordingly, although Type 301 can be drawn successfully, its drawing properties are not as good as those of Type 302 or 304, but it can be cold-rolled to very high strength. Type 301, because of its lower carbon content, is not as prone as Type 304 to give carbide precipitation problems in welding, and can be used to withstand severe corrosive conditions in the paper, chemical, and other industries. The austenitic stainless steels are widely used for high temperature services.

Types 321 and 347 have additions of titanium and niobium, respectively, and are used in welding applications and high temperature service under corrosive conditions. Type 304L may be used as an alternative for Types 321 and 347 in welding (qv) and stress-relieving applications $< 426^\circ C$.

The addition of 2–4% molybdenum to the basic 18–8 composition produces Types 316 and 317, which have improved corrosion resistance. These grades are employed in the textile, paper, and chemical industries where strong sulfates, chlorides, and phosphates, and reducing acids such as sulfuric, sulfurous, acetic, and hydrochloric acids, are used in such concentrations that the use of corrosion-resistant alloys is mandatory. These are also used in some surgical implants (see BIOMATERIALS, PROSTHETICS, AND BIOMEDICAL DEVICES). Types 316 and 317 have the highest creep-rupture strengths of any commercial stainless steels, although Types 347 and 310 may show lower creep rates in certain ranges.

The austenitic stainless steels most resistant to oxidation are Types 309, 310, and 314 where the higher Si contributes significantly. Because of their high chromium and nickel contents, these steels resist scaling at temperatures up to 1090 and 1150°C and consequently are used for furnace parts and heat exchangers. They are somewhat harder and not as ductile as the 18–8 types, but may still be drawn and formed. Types 309 and 310 can be welded readily and have increasing use in the manufacture of industrial furnace equipment (see HIGH TIMEPRATURE ALLOYS). For applications requiring better machinability, Type 303 containing sulfur or selenium may be used.

15.8. High Temperature Service, Heat-Resisting Steels. The term high temperature service covers many types of operations in many industries. Conventional high temperature equipment includes steam (qv) boilers and turbines, gas turbines, cracking stills, tar stills, hydrogenation vessels, heat-treating furnaces, and fittings for diesel and other internal-combustion engines. Numerous steels are available. Where unusual conditions occur, modification of the chemical composition may adapt an existing steel grade to service conditions. In some cases, however, entirely new alloy combinations must be developed to meet service requirements. For example, the aircraft and missile industries have encountered design problems of increased complexity, requiring metals of great high temperature strength for both power units and structures. Steels are constantly under development to meet these requirements (52).

The temperatures needed for high performance turbines are so high that iron base alloys are not contenders. The melting point of iron (1536°C) is high but not high enough. For several years, nickel-based alloys strengthened by compounds such as Ni_3Al have been used in single crystal form. The next generation seems likely to be based on intermetallic compounds, such as titanium aluminide, TiAl, if ductility problems can be controlled.

A number of steels suitable for high temperature service are given in Table 5.

The design of load-bearing structures for service at room temperature is generally based on the yield strength or for some applications on the tensile strength. The metal is expected to behave essentially in an elastic manner, is the structure undergoes an elastic deformation immediately upon load application and no further deformation occurs with time. When the load is removed, the structure returns to its original dimensions.

At high temperature, the behavior is different. A structure designed according to the principles employed for room temperature service continues to deform with time after load application, even though the design data may have been based on tension tests at the temperature of interest. This deformation with time is called creep: the design stresses at which it can be important are relatively low.

In spite of the fact that plain carbon steel has lower resistance to creep than high temperature alloy steels, its price allows it to be widely used in such applications up to 540°C, where rapid oxidation commences and a chromium-bearing steel must be employed. Low alloy steels containing small amounts of chromium and molybdenum have higher creep strengths than carbon steel and are employed where materials of somewhat higher strength are needed. Above ~540°C, the amount of chromium required to impart oxidation resistance increases rapidly. The 2% chromium steels containing molybdenum are useful up to ~620°C, whereas 10–14% chromium steels may be employed up to ~700–760°C. Above this temperature, the austenitic 18–8 steels are commonly used. Their oxidation resistance is considered adequate up to ~815°C. For service between 815 and 1090°C, steels containing 25% chromium and 20% nickel, or 27% chromium, are used. The behavior of steels at high temperature is quite complex, and only the simplest design considerations have been mentioned herein (see HIGH TEMPERATURE ALLOYS).

15.9. Miscellaneous High Strength Steels. Strengths above 1400–1700 MPa (203,000–246,500 psi) are not often used or required in steels because of difficulties in joining, ductility, and/or toughness. For specialized uses however, it is possible to achieve such strength (see HIGH PRESSURE TECHNOLOGY) (53).

One of the earliest materials for ultrahigh strength was piano wire, heavily cold-drawn fine pearlite where the strength can be > 3500 MPa (507,500 psi). For many steels, any form of carbon as a contributor to strength needs great care. It is possible to quench and temper a 0.40% carbon alloy steel to give a usable yield in the range of 1800–2000 MPa (261,000–290,000 psi) by melting and adding enough silicon so that the tempering temperature can be raised to give adequate ductility. This process has been used, for instance, for aircraft landing gear, where weight is critical and high costs are acceptable.

A different way of reaching high strengths is to use alternative precipitates to cementite and alloy carbides. Early efforts in this area came from making stainless steels of very low carbon, by using an unstable austenite (M_s above room temperature) so a body-centered phase can exist in large amounts after cooling. After dissolving the precipitable elements, eg, Mo, Al, Nb, and Cu, in austenite at ~1000°C, the material can be cooled without quenching to ambient temperature and subsequently aged ~500°C to form the hardening compound in the bcc phase. Yield strengths up to 1590 MPa (230,550 psi) can be obtained, although this can be reduced when necessary to optimize other properties in these precipitation hardening (PH) steels.

An important item in this array of materials is the class known as maraging steels. This group of high nickel martensitic steels contain so little carbon that they are often referred to as carbon-free iron–nickel martensites (54). Carbon-free iron–nickel martensite with certain alloying elements is relatively soft and ductile and becomes hard, strong, and tough when subjected to an aging treatment at ~480°C.

The first iron–nickel martensitic alloys contained ~0.01% carbon, 20 or 25% nickel, and 1.5–2.5% aluminum and titanium. Later an 18% nickel steel containing cobalt, molybdenum, and titanium was developed, and still more recently a series of 12% nickel steels containing chromium and molybdenum came on the market.

By adjusting the content of cobalt, molybdenum, and titanium, the 18% nickel steel can attain yield strengths of 1380–2070 MPa (200,000–300,000 psi) after the aging treatment. Similarly, yield strengths of 12% nickel steel in the range of 1035–1380 MPa (150,000–200,000 psi) can be developed by adjusting its composition.

15.10. Silicon Steel Electrical Sheets. Selected silicon steels are characterized by relatively high permeability, high electrical resistance, and low hysteresis loss when used in magnetic circuits. First patented in the United Kingdom 1900, these silicon steels permitted the development of more powerful electrical equipment and have furthered the rapid growth of the electrical power industry. Steels containing 0.5–5% silicon are produced in sheet form for the laminated magnetic cores of electrical equipment and are referred to as electrical sheets (54).

The grain-oriented steels, containing ~3.25% silicon, are used in the highest efficiency distribution and power transformers and in large turbine generators. They are processed in a proprietary way and have directional properties related to a preferred orientation of the large crystals.

The nonoriented steels are subdivided into low, intermediate, and high silicon steels. The first contain ~0.5–1.5% silicon, used mainly in rotors and stators of motors and generators. Steels containing ~1% silicon are used for reactors, relays, and small intermittent-duty transformers.

Intermediate silicon steels (2.5–3.5% Si) are used in motors and generators of average to high efficiency and in small- to medium-size intermittent-duty transformers, reactors, and motors.

High silicon steels (historically 3.75–5.00% but more recently 6% Si) are used in power transformers and high efficiency motors, generators, and transformers, and in communications equipment.

16. Economic Aspects

The production of steel is of great importance in most countries because modern civilization depends heavily on steel, the raw material for many industries. As a result, most countries have an active steel industry, which at one time was heavily subsidized but as of this writing is becoming somewhat more privatized. The world trade in steel was frequently a source of hard currency where the United States was the main contributor. Trade is much more at market prices that reflect the real cost of production. Under these conditions, the United States in its own market is very often the low cost producer following massive cost reduction in the 1980s. The United States can export a few million tons per year at a profit.

16.1. Production. World production of raw steel, largely continuously cast, is shown in Table 6. United States production is now ~100,000,000 t/year, over 90% of which is continuously cast. The amount melted in electric furnaces in 2003 is at least 50% and is still increasing.

The leading producers in 1979 were the USSR, United States, Japan, Germany, and, barely, China. By 2000, China and South Korea had grown enormously in capacity. China continues to expand hugely with a reported target of 300+ MM tons/year. The United States, and Japan have at best slightly increased capacity, mergers in Europe make individual countries inappropriate, and the USSR (now CIS) has dropped significantly. Countries such as India and those in the Pacific rim and Latin America have become increasingly important steel producers as they build infrastructure. World growth in the latter part of the twentieth century was small although the last few years have seen a 15+% increase (almost entirely from China). The redistribution of individual producers has been very significant as difficult economic times led to closures, bankruptcies and mergers worldwide.

16.2. Prices. Through the 1970s the world price of steel continued to increase with inflation. Around 1980, however, overcapacity was ~25% and prices became flat at best. On a basis depreciated for inflation they mostly dropped and a huge restructuring of the industry took place. Plants closed worldwide and capacity slowly came into better alignment with demand by ~1990. Quality and customer service improved dramatically and, by 1995, modest price increases began to stick. The challenge from competitive materials intensified, but on the whole the steel industry has not lost a principal market since beverage cans were lost to aluminum in the 1970s. Much tonnage of carbon steel was available in the mid-1990s at \$0.15–\$0.30/#, not very different from the 1979 price and of much better quality. Since almost all countries had the capacity to produce more steel than they consumed, and cash flow is an important consideration in a capital intensive operation, there was a great deal of concern with "unfair" trade (selling price less than production price), tariffs, etc, which along with currency variations led to a great deal of political infighting. As noted earlier a tightness of basic materials, notably scrap, has sent prices much higher, even doubling in some cases. How long this will continue is speculative.

16.3. Products. The production amounts of various products in the United States are shown in Table 7. Sheet, both hot- and cold-rolled, dominates at ~60% of production. Coated material, mostly galvanized, is playing an increasingly important role as demands for longer life become an issue (Fig. 27) (56). Dominant customers remain the automotive and construction industries.

At one point in the mid-1980s, imports reached 26% of consumption. As of the last few years, imports were averaging 20% and included some semifinished slabs finished in the United States because of insufficient domestic capacity for cast slabs to make sheet. The situation remains fluid.

17. Health and Safety Factors

The hazards and environmental problems associated with steelmaking are many and varied, but have been sharply reduced by industrywide efforts. Since the early 1980s, increasingly stringent environmental regulations have been imposed by local, state, and federal government in the United States (57). There have been many arguments as to the cost-effective nature of some of these. Some other nations have largely equivalent regulations, but many do not, which can give them a competitive advantage.

17.1. Accidents. In an industry that has massive equipment, high temperature operations, and many moving objects, the potential for accidents is always present. Safety is taken seriously and is the direct responsibility of the plant superintendent. Accidents do occur, although in the United States the rate in the steel industry compares favorably with heavy industry as a whole.

17.2. Health Hazards. There are many sources of industrial hygiene (qv) and occupational health hazards. Some are direct, eg, radiant heat, noise, and exposure to local concentrations of noxious gases such as carbon monoxide near blast furnaces. Others are long-term, eg, the acid fumes from pickling baths or (less and less as ovens are shut down) the possible leakage of organic vapors and certain tiny solid particles from coke ovens. The use of protective clothing, masks, eye shields, ear protection, etc, is routine and rigorously enforced. Even though constant vigilance and training are essential, the hazards are contained effectively when sensors monitoring potential dangers are employed along with good work practices and engineering controls such as radiation shields, ventilation, air conditioning of control stations, mufflers, and soundproof enclosures. Networking between companies in the safety area, which makes a further contribution to overall safety, is excellent in the United States.

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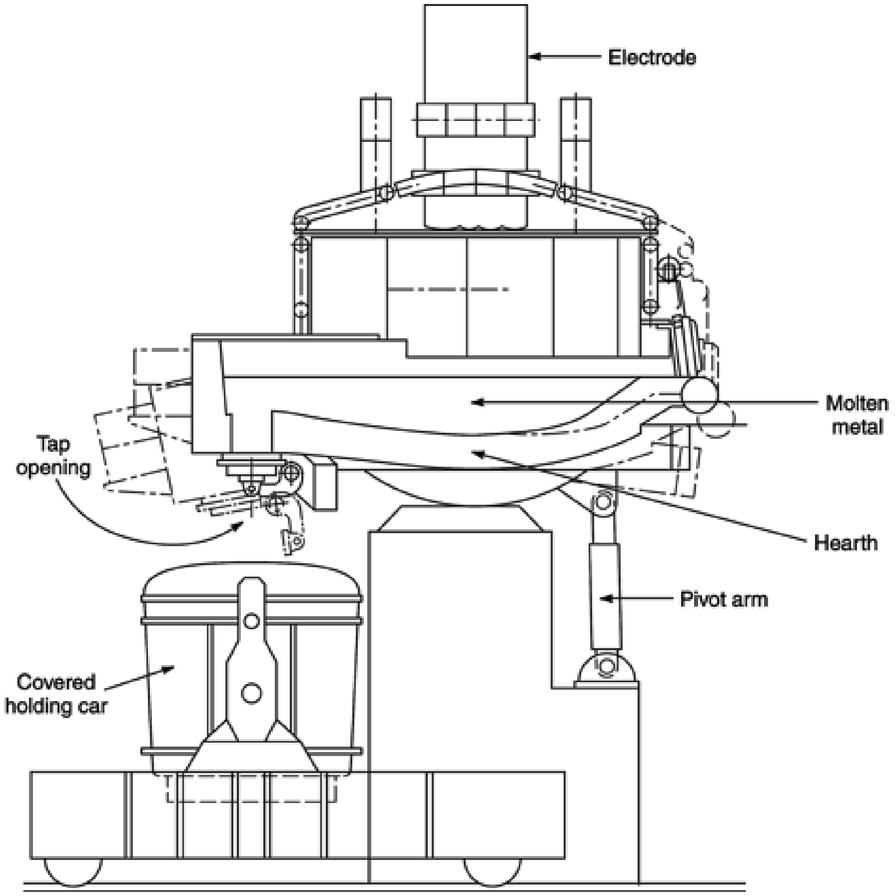

Fig. 1. Eccentric bottom tapping (EBT) electric furnace. Courtesy of Mannesmann.

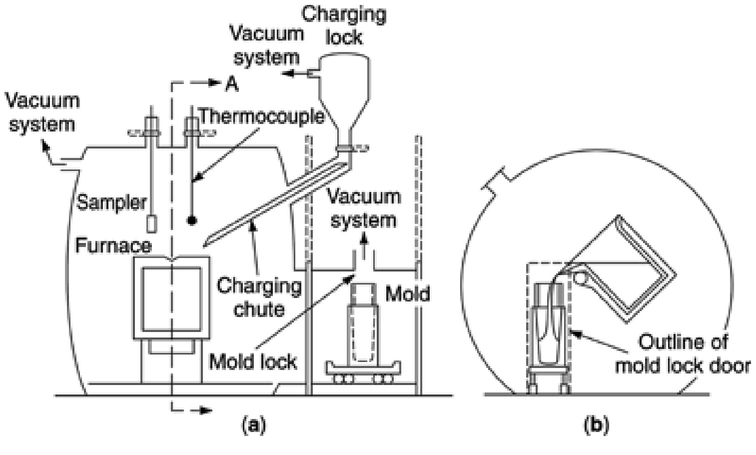

Fig. 2. Schematic arrangement of a furnace in a vacuum chamber equipped with charging and mold locks for vacuum induction melting (1): (**a**) front cross section; and (**b**) section A during pouring.

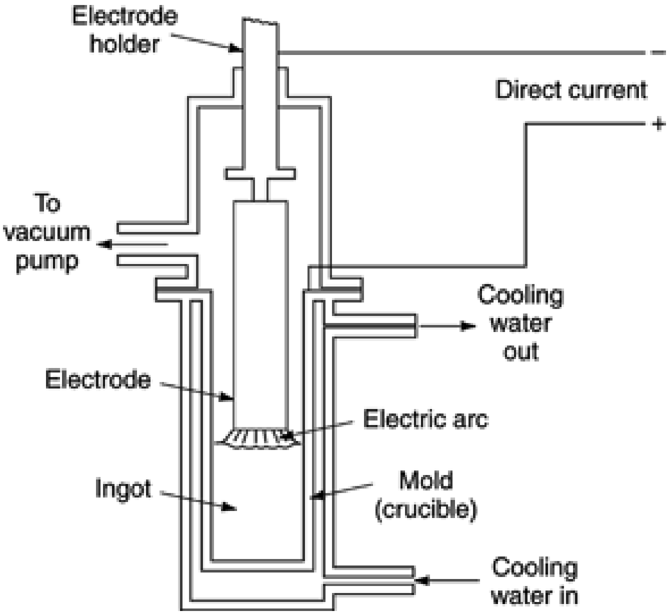

Fig. 3. Schematic representation of the principle of design and operation of a consumble-electrode furnace for melting steels in a vacuum (1).

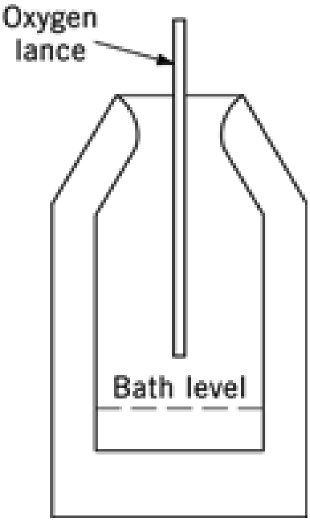

Fig. 4. Sketch of a basic-oxygen steelmaking furnace, where an oxygen lance is inserted through the mouth of the furnace (1).

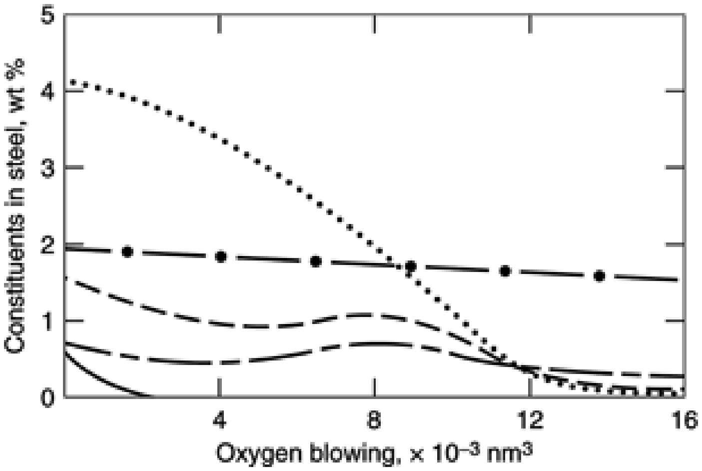

Fig. 5. Progress of refining in the basic-oxygen steelmaking process, where (—) corresponds to Si; (———) to Mn; (·····) to C; (– – –) to P; and (—•—) to S. The values for phosphorus are one-tenth those indicated on the ordinate; the values for sulfur are one-hundredth those indicated. The time elapsed is ~20 min in most cases.

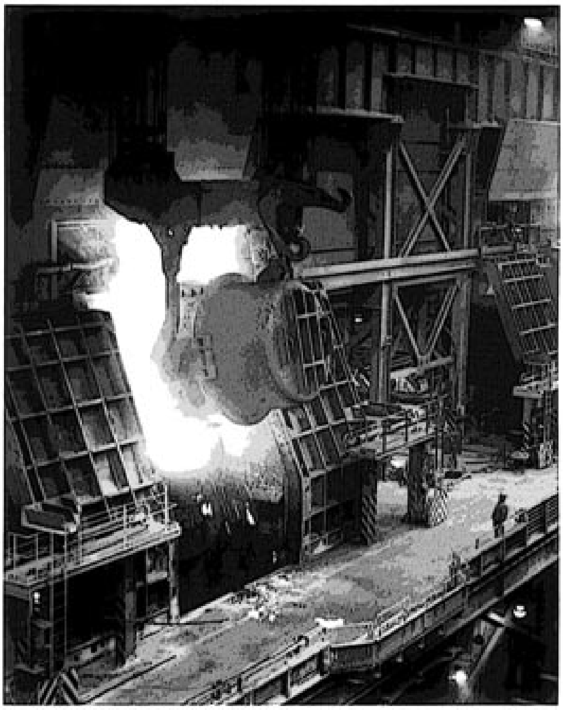

Fig. 6. Liquid blast-furnace iron (hot metal) being charged into a 200-metric ton Q-BOP furnace in preparation for making a heat of steel.

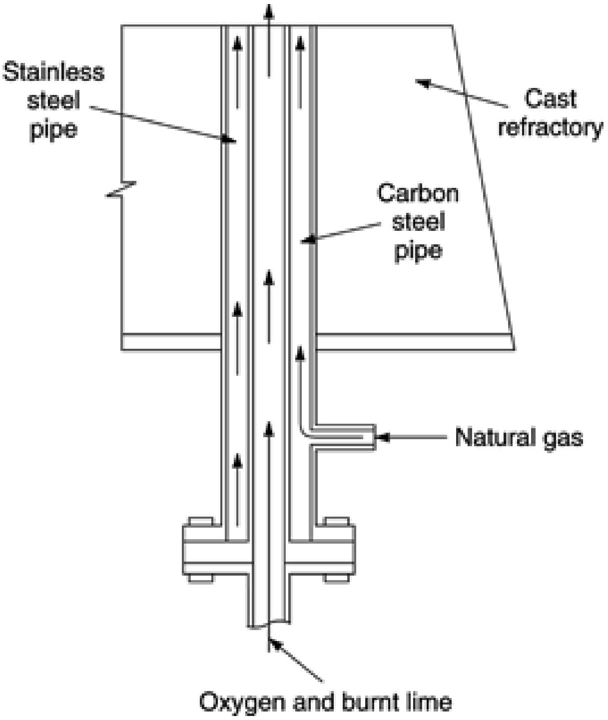

Fig. 7. Tuyere for bottom-blown basic-oxygen process (13,14).

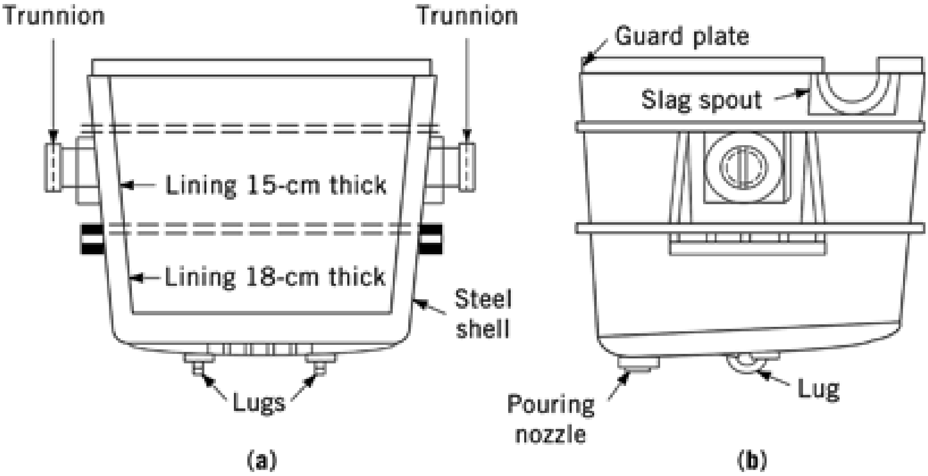

Fig. 8. Steel ladle: (**a**) vertical section through the trunnions, and (**b**) side view.

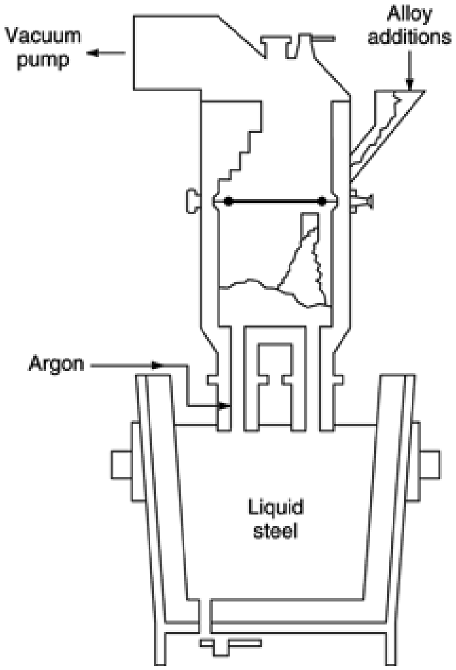

Fig. 9. Schematic diagram of the RH degasser.

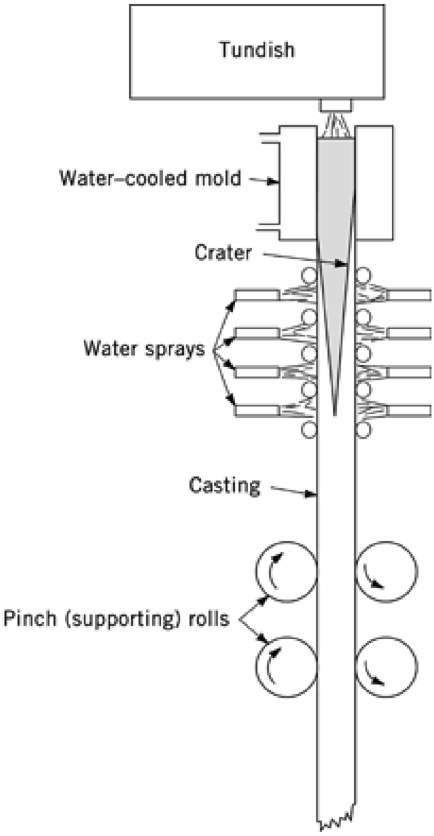

Fig. 10. Schematic representation of the process of cooling of steel (⌋) during continuous casting. The tundish is an increasingly important buffer between the ladle and the mold.

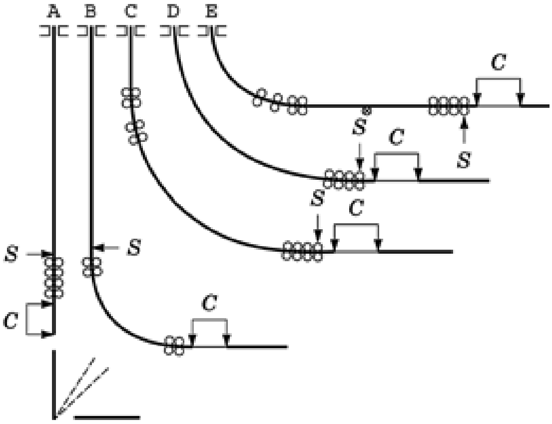

Fig. 11. Development of casting machines where *S* is the end of the supported length and *C* the cutoff zone; circles represent rolls. A is a vertical mold; B a vertical mold with bending; C a vertical mold with progressive bending; D a curved mold with straightening; and E a curved mold with progressive straightening (1).

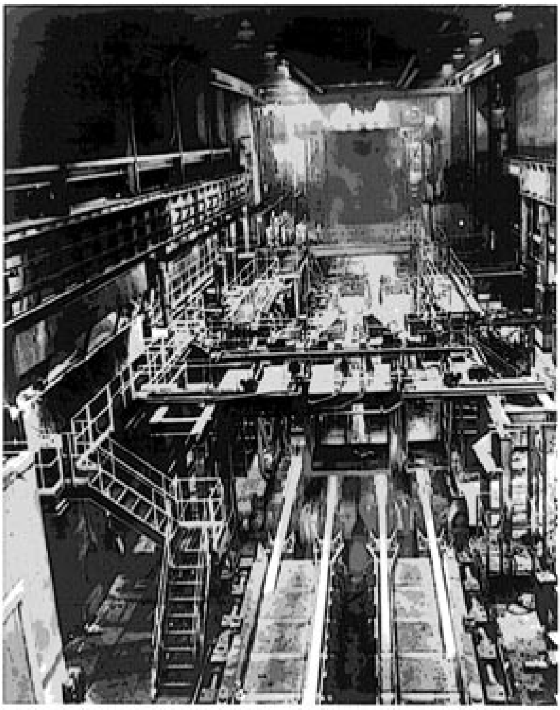

Fig. 12. Continuous casting of square steel blooms. The liquid steel is poured into molds (not shown) at top of photograph. The solidifying steel blooms move downward and then toward the camera. In the foreground, the blooms are cut to the proper length.

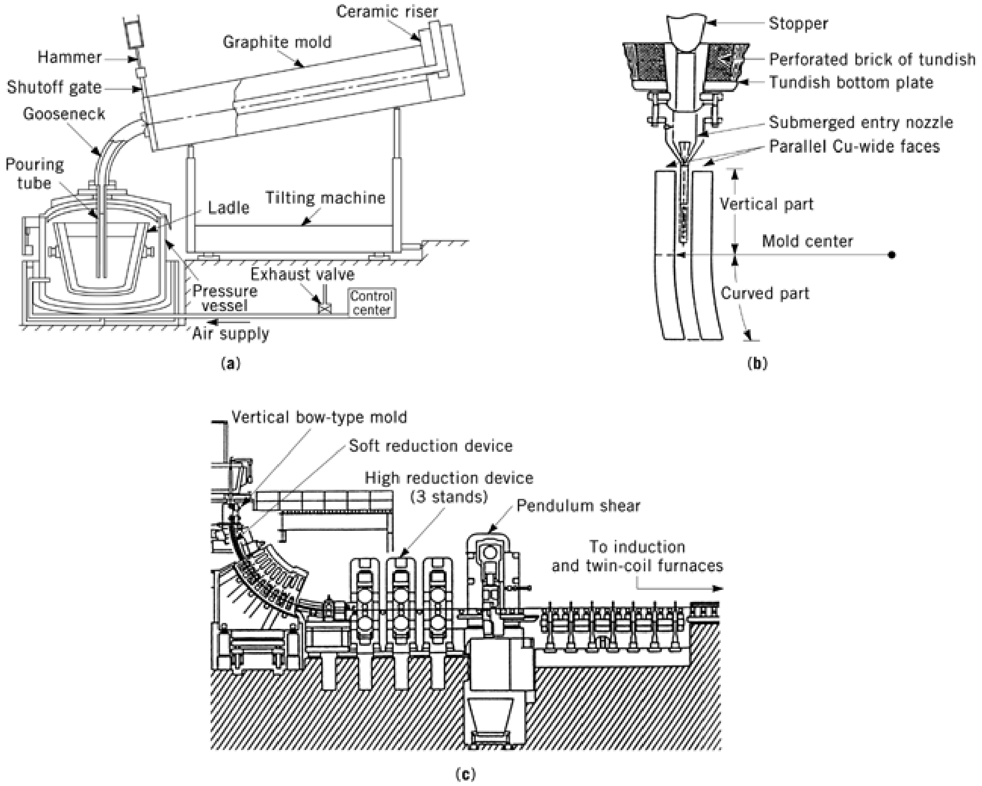

Fig. 13. (**a**) The bottom-pressure casting method as applied to slabs; (**b**) curve mold and submerged entry nozzle; and (**c**) portion of Arvedi caster for in-line strip production (ISP). Courtesy of the Iron & Steel Society.

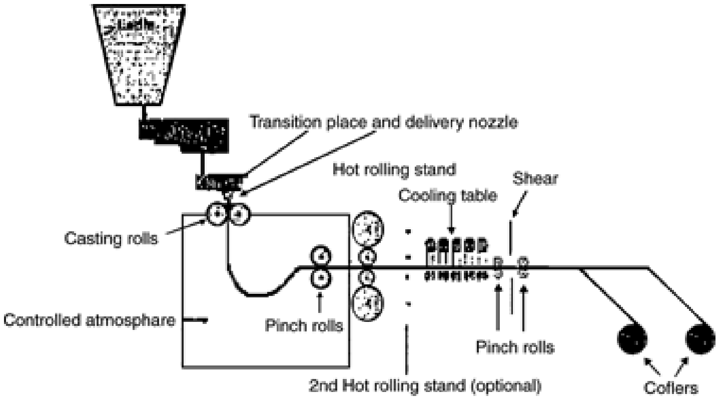

Fig. 14. Schematic of the Castrip twin-roll sheet caster at the Crawfordsville, IN plant of Nucor Steel (25a).

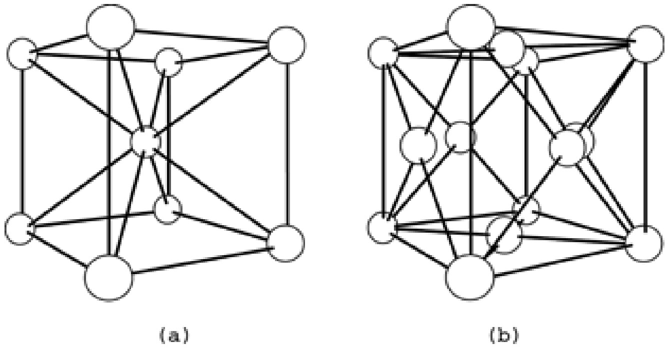

Fig. 15. Crystalline structure of allotropic forms of iron. Each white sphere represents an atom of (**a**) α- or δ-iron in bcc form; and (**b**) γ-iron in fcc form (1).

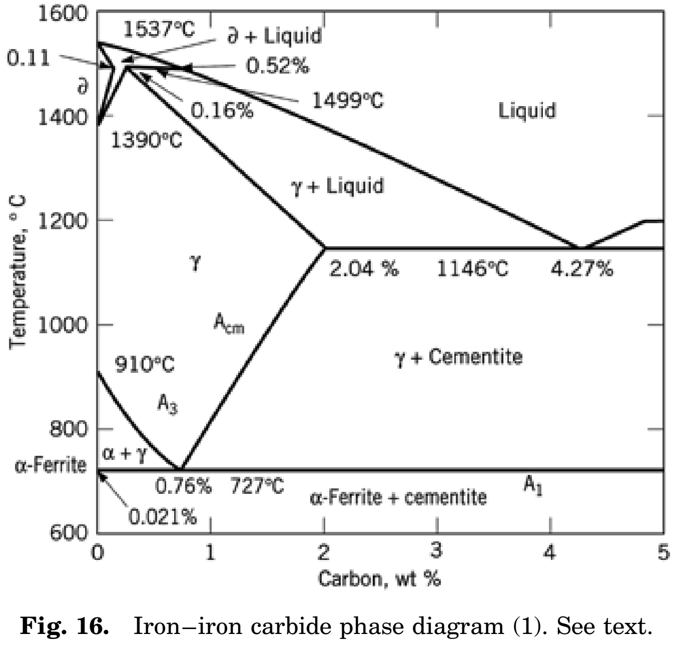

Fig. 16. Iron–iron carbide phase diagram (1). See text.

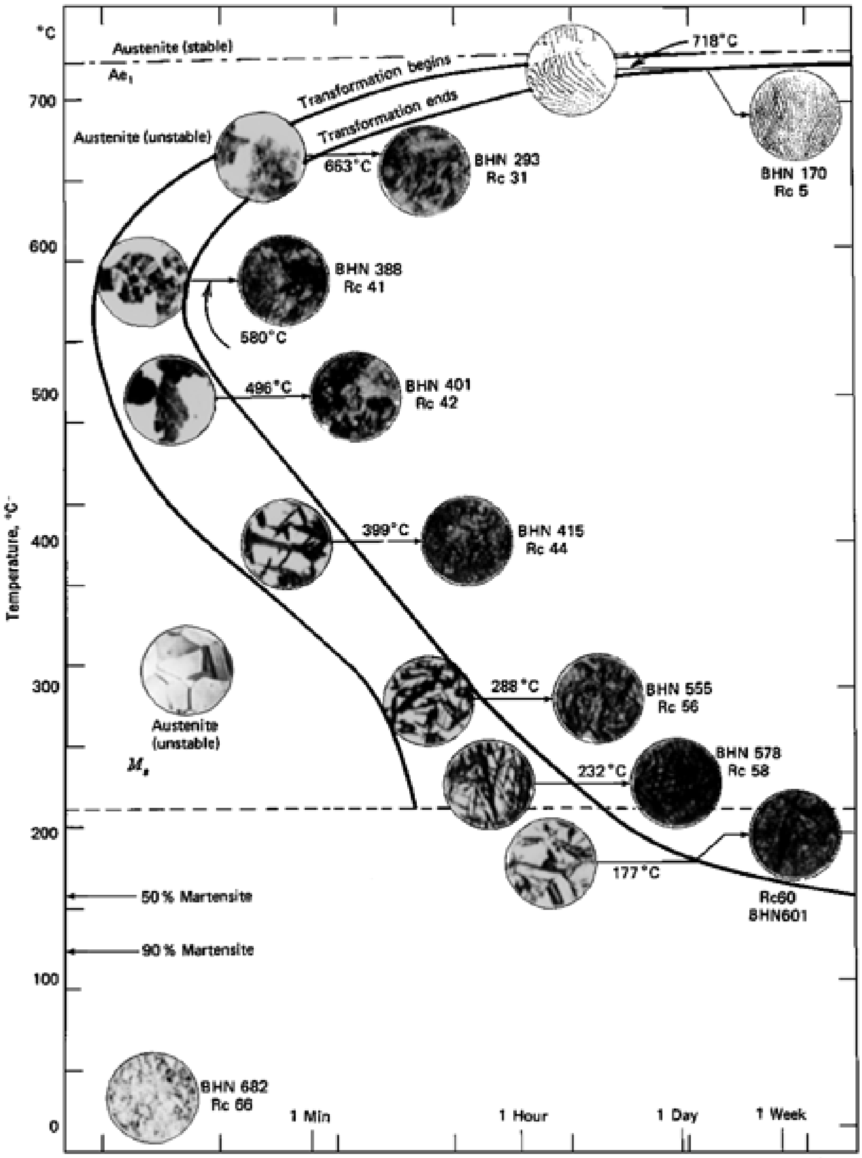

Fig. 17. Isothermal transformation (IT) diagram for a plain carbon eutectoid steel (1). Ae_1 is A_1 temperature at equilibrium; BHN, Brinell hardness number; Rc, Rockwell hardness scale C. C is 0.89%; Mn, 0.29%; austenitized at 885°C; grain size is ASTM 4–6. Photomicrographs originally ×2500.

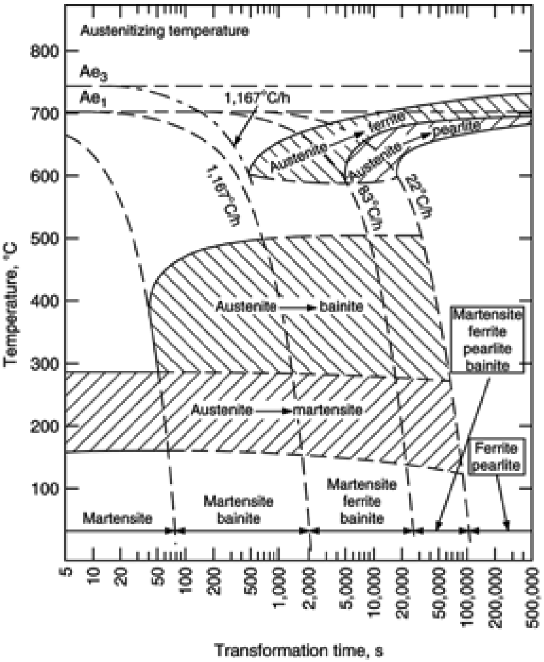

Fig. 18. Continuous-cooling transformation diagram for a Type 4340 alloy steel, with superimposed cooling curves illustrating the manner in which transformation behavior during continuous cooling governs final microstructure (1). Ae$_3$ is critical temperature at equilibrium. Ae$_1$ is lower critical temperature at equilibrium.

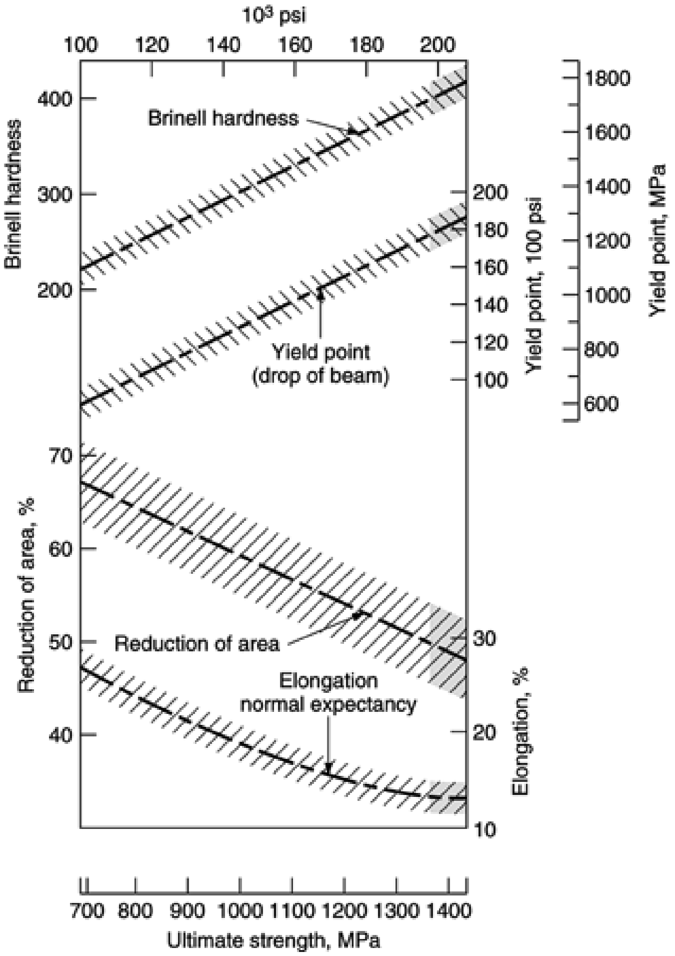

Fig. 19. Properties of tempered martensite (1). Fully heat-treated miscellaneous analyses, low alloy steels; 0.30–0.50% carbon. To convert MPa to psi, multiply by 145.

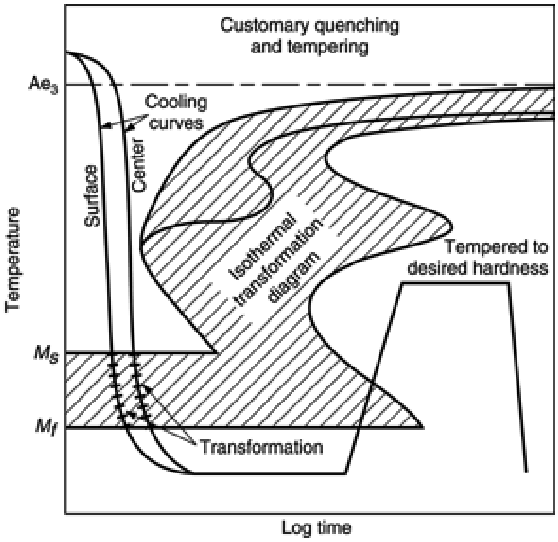

Fig. 20. Transformation diagram for quenching and tempering martensite. The product is tempered martensite.

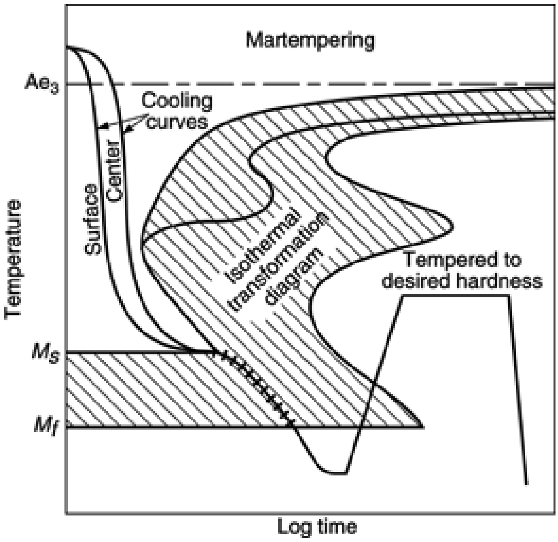

Fig. 21. Transformation diagram for martempering. The product is tempered martensite.

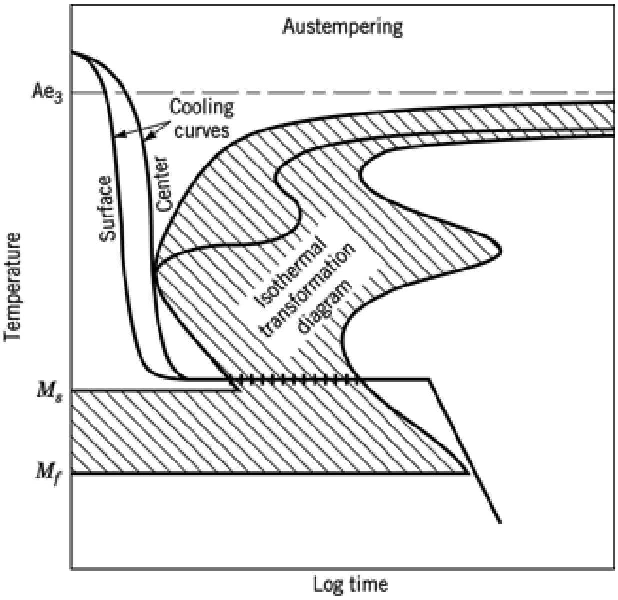

Fig. 22. Transformation diagram for austempering. The product is bainite.

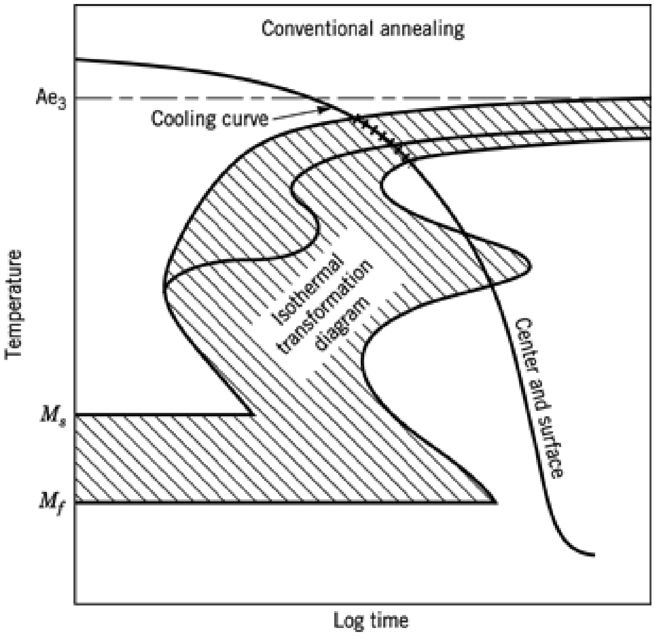

Fig. 23. Transformation diagram for full annealing. The product is ferrite and pearlite.

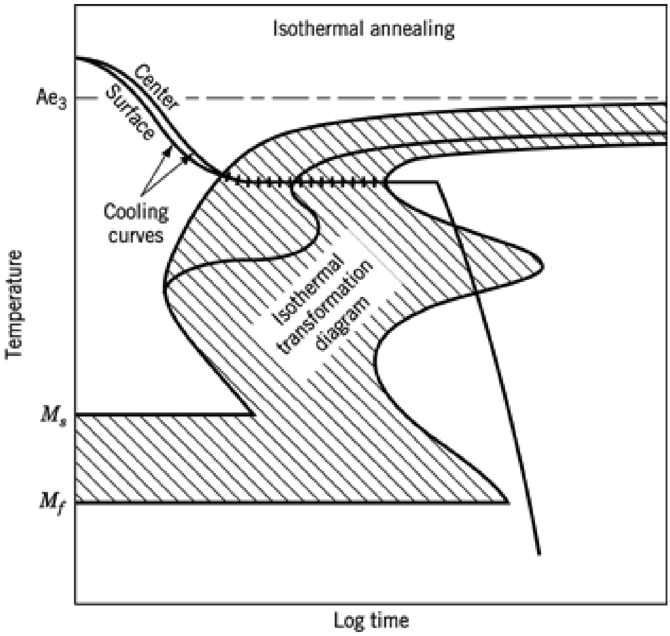

Fig. 24. Transformation diagram for isothermal annealing. The product is ferrite and pearlite.

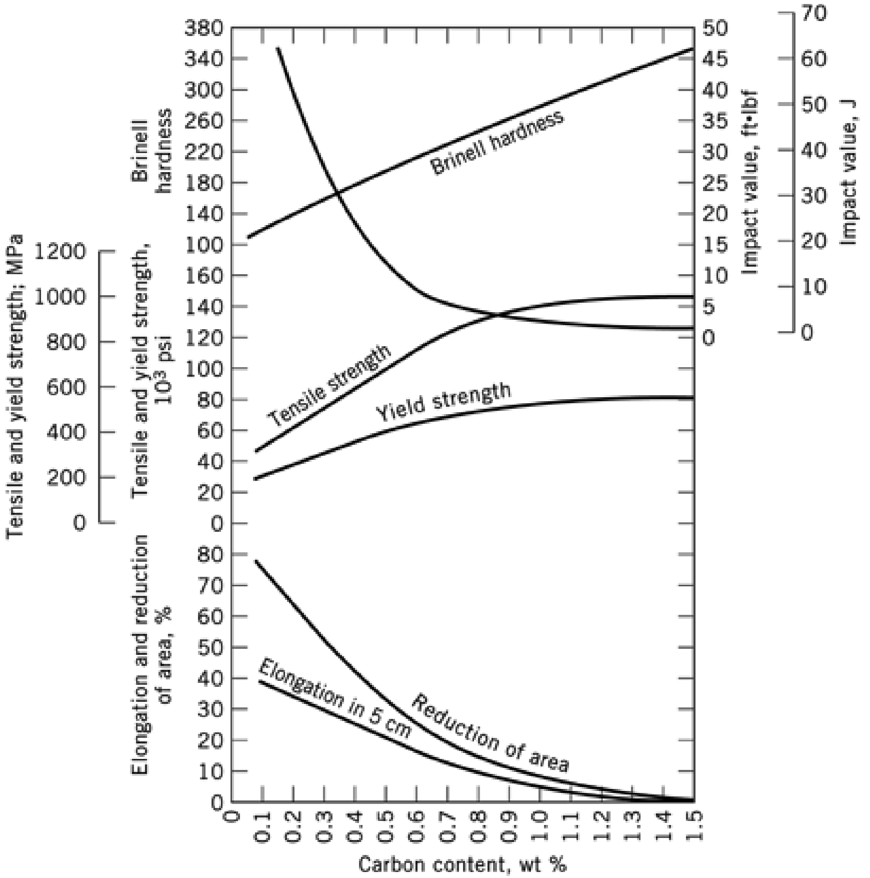

Fig. 25. Variations in average mechanical properties of as-rolled 2.5-cm bars of plain carbon steels, as a function of carbon content (1).

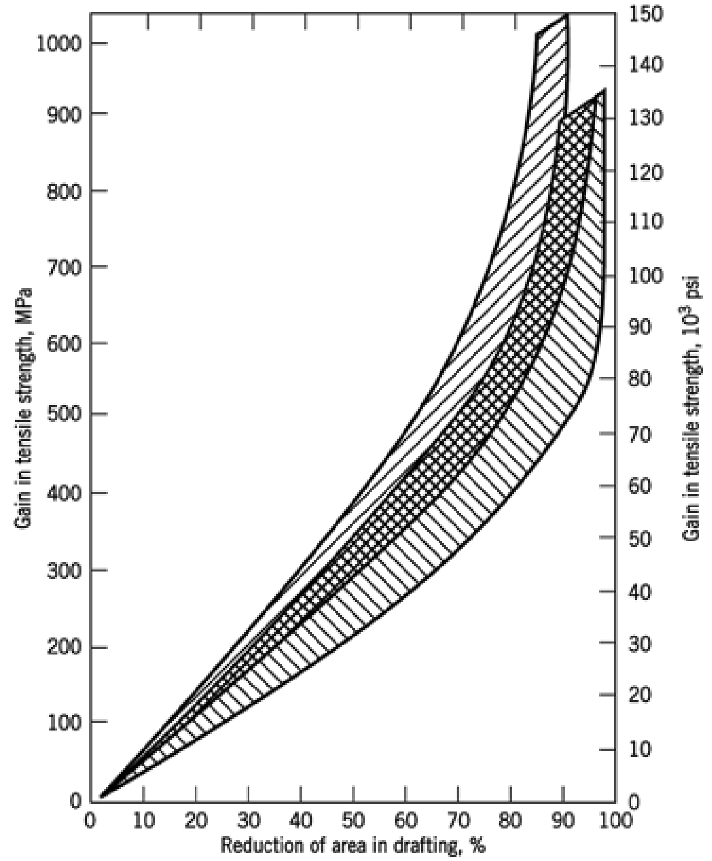

Fig. 26. Increase of tensile strength of plain carbon steel with increased cold working, where (⧅) represents 0.05–0.30 wt % carbon; (⊠) 0.30–0.60 wt %; and (⧄) 0.60–1.00 wt %.

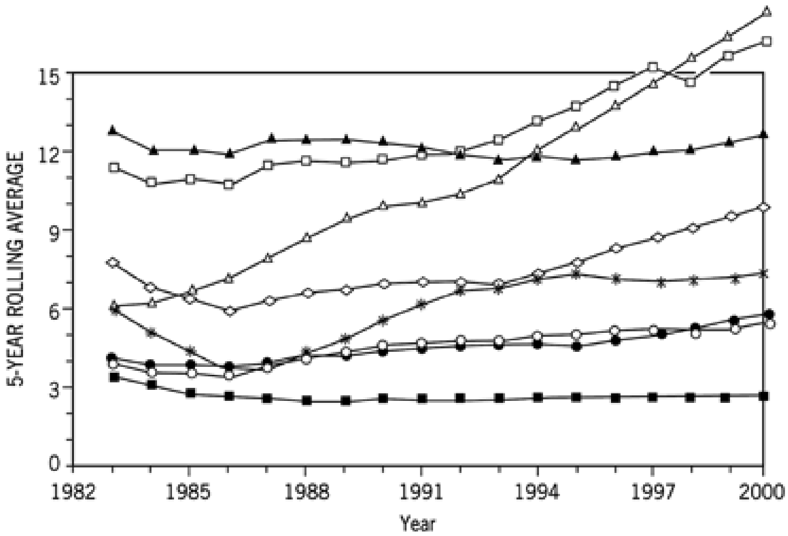

Fig. 27. United States shipments of steel mill products, where (—•—) represents bars-reinforcing, (—⋄—) hot-rolled and cold-finished bars, (—Ξ—) tinplate, (—N—) sheet-cold-rolled, (—◦—) structural shapes, (—∗—) plate, (—□—) sheet-hot-rolled, and (—△—) sheet-coated products.

Table 1. **Trends in Heat-Treated Products**

Property	Coarse-grained austenite	Fine-grained austenite
	Quenched and tempered products	
hardenability	increasing	decreasing
toughness	decreasing	increasing
distortion	more	less
quench cracking	more	less
internal stress	higher	lower
	Annealed or normalized products	
machinability		
rough finish	better	inferior
fine finish	inferior	better

Table 2. H **Values Designating Severity of Quench for Commonly Used Cooling Conditions**[a]

	Quenching medium		
Degree of medium agitation	Oil	Water	Brine
none	0.25–0.30	0.9–1.0	2
mild	0.30–0.35	1.0–1.1	2.0–2.2
moderate	0.35–0.40	1.2–1.3	
good	0.40–0.50	1.4–1.5	
strong	0.50–0.80	1.6–2.0	
violent	0.80–1.1	4.0	5.0

[a] H Values are proportional to the heat-extracting capacity of the medium.

Table 3. **Standard Numerical AISI–SAE**[a]

Series designation[b]	Types	Series designation[b]	Types
10xx	nonresulfurized carbon steel grades	47xx	1.05% Ni–0.45% Cr–0.20% Mo
11xx	resulfurized carbon steel grades	48xx	3.50% Ni–0.25% Mo
12xx	rephosphorized and resulfurized carbon steel grades	50xx	0.50% Cr
13xx	1.75% Mn	51xx	1.05% Cr
23xx	3.50% Ni	5xxxx	1.00% C–1.45% Cr
25xx	5.00% Ni	61xx	0.95% Cr–0.15% V
31xx	1.25% Ni–0.65% Cr	86xx	0.55% Ni–0.65% Cr–0.20% Mo
33xx	3.50% Ni–1.55% Cr	87xx	0.55% Ni–0.50% Cr–0.25% Mo
40xx	0.25% Mo	92xx	0.85% Mn–2.00% Si
41xx	0.95% Cr–0.20% Mo	93xx	3.25% Ni–1.20% Cr–0.12% Mo
43xx	1.80% Ni–0.80% Cr–0.25% Mo	98xx	1.00% Ni–0.80% Cr–0.25% Mo
46xx	1.80% Ni–0.25% Mo		

[a] The AISI (American Iron and Steel Institute) and the SAE (Society of Automotive Engineers) specifications are essentially the same. The list is simplified to show typical compositions. For ranges, see original tables.

[b] The first figure indicates the class to which the steel belongs; 1xxx indicates a carbon steel, 2xxx a nickel steel, and 3xxx a nickel–chromium steel. In the case of alloy steels, the second figure generally indicates the approximate percentage of the principal alloying element. Usually, the last two or three figures (represented in the table by x) indicate the average carbon content in points or hundredths of 1 wt %. Thus, a nickel steel containing ∼3.5% nickel and 0.30% carbon would be designated as 2330.

Table 4. **Compositions of Standard Stainless Steels**[a]

Type	UNS designation	Composition, wt %[b]							
		C	Mn	Si	Cr	Ni	P	S	Other
					Austenitic				
201	S20100	0.15	5.5–7.5	1.00	16.0–18.0	3.5–5.5	0.06	0.03	0.25 N
202	S20200	0.15	7.5–10.0	1.00	17.0–19.0	4.0–6.0	0.06	0.03	0.25 N
205	S20500	0.12–0.25	14.0–15.5	1.00	16.5–18.0	1.0–1.75	0.06	0.03	0.32–0.40 N
301	S30100	0.15	2.00	1.00	16.0–18.0	6.0–8.0	0.045	0.03	
302	S30200	0.15	2.00	1.00	17.0–19.0	8.0–10.00	0.045	0.03	
302B	S30215	0.15	2.00	2.0–3.0	17.0–19.0	8.0–10.0	0.045	0.03	
303	S30300	0.15	2.00	1.00	17.0–19.0	8.0–10.00	0.20	0.15[c]	0.6 Mo[d]
303Se	S30323	0.15	2.00	1.00	17.0–19.0	8.0–10.0	0.20	0.06	0.15[c] Se
304	S30400	0.08	2.00	1.00	18.0–20.0	8.0–10.5	0.045	0.03	
304H	S30409	0.04–0.10	2.00	1.00	18.0–20.0	8.0–10.5	0.045	0.03	
304L	S30403	0.03	2.00	1.00	18.0–20.0	8.0–12.0	0.045	0.03	
304LN	S30453	0.03	2.00	1.00	18.0–20.0	8.0–12.0	0.045	0.03	0.10–0.16 N
302Cu	S30430	0.08	2.00	1.00	17.0–19.0	8.0–10.0	0.045	0.03	3.0–4.0 Cu
304N	S30451	0.08	2.00	1.00	18.0–20.0	8.0–10.5	0.045	0.03	0.10–0.16 N
305	S30500	0.12	2.00	1.00	17.0–19.0	10.5–13.0	0.045	0.03	
308	S30800	0.08	2.00	1.00	19.0–21.0	10.0–12.0	0.045	0.03	
309	S30900	0.20	2.00	1.00	22.0–24.0	12.0–15.0	0.045	0.03	
309S	S30908	0.08	2.00	1.00	22.0–24.0	12.0–15.0	0.045	0.03	
310	S31000	0.25	2.00	1.50	24.0–26.0	19.0–22.0	0.045	0.03	
310S	S31008	0.08	2.00	1.50	24.0–26.0	19.0–22.0	0.045	0.03	
314	S31400	0.25	2.00	1.5–3.0	23.0–26.0	19.0–22.0	0.045	0.03	
316	S31600	0.08	2.00	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo
316F	S31620	0.08	2.00	1.00	16.0–18.0	10.0–14.0	0.20	0.10[c]	1.75–2.5 Mo
316H	S31609	0.04–0.10	2.00	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo
316L	S31603	0.03	2.00	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo
316LN	S31653	0.03	2.00	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo; 0.10–0.16 N
316N	S31651	0.08	2.00	1.00	16.0–18.0	10.0–14.0	0.045	0.03	2.0–3.0 Mo; 0.10–0.16 N
317	S31700	0.08	2.00	1.00	18.0–20.0	11.0–15.0	0.045	0.03	3.0–4.0 Mo
317L	S31703	0.03	2.00	1.00	18.0–20.0	11.0–15.0	0.045	0.03	3.0–4.0 Mo
321	S32100	0.08	2.00	1.00	17.0–19.0	9.0–12.0	0.045	0.03	

321H	S32109	0.04–0.10	2.00	1.00	17.0–19.0	9.0–12.0	0.045	0.03	5 × %C Ti[c]
330	N08330	0.08	2.00	0.75–1.5	17.0–20.0	34.0–37.0	0.04	0.03	
347	S34700	0.08	2.00	1.00	17.0–19.0	9.0–13.0	0.045	0.03	10 × %C Nb[c]
347H	S34709	0.04–0.10	2.00	1.00	17.0–19.0	9.0–13.0	0.045	0.03	−1.0 Nb
348	S34800	0.08	2.00	1.00	17.0–19.0	9.0–13.0	0.045	0.03	0.2 Co; Nb; 0.10 Ta
348H	S34809	0.04–0.10	2.00	1.00	17.0–19.0	9.0–13.0	0.045	0.03	0.2 Co; −1.0 Nb; 0.10 Ta
384	S38400	0.08	2.00	1.00	15.0–17.0	17.0–19.0	0.045	0.03	
					Ferritic				
405	S40500	0.08	1.00	1.00	11.5–14.5		0.04	0.03	0.10–0.30 Al
409	S40900	0.08	1.00	1.00	10.5–11.75	0.50	0.045	0.045	−0.75 Ti
429	S42900	0.12	1.00	1.00	14.0–16.0		0.04	0.03	
430	S43000	0.12	1.00	1.00	16.0–18.0		0.04	0.03	
430F	S43020	0.12	1.25	1.00	16.0–18.0		0.06	0.15	0.6 Mo
430FSe	S43023	0.12	1.25	1.00	16.0–18.0		0.06	0.06	0.15 Se
434	S43400	0.12	1.00	1.00	16.0–18.0		0.04	0.03	0.75–1.25 Mo
436	S43600	0.12	1.00	1.00	16.0–18.0		0.04	0.03	0.75–1.25 Mo; −0.70 Nb
439	S43035	0.07	1.00	1.00	17.0–19.0	0.50	0.04	0.03	0.15 Al; −1.10 Ti
442	S44200	0.20	1.00	1.00	18.0–23.0		0.04	0.03	
444	S44400	0.025	1.00	1.00	17.5–19.5	1.00	0.04	0.03	1.75–2.50 Mo; 0.025 N; −0.8 ()
446	S44600	0.20	1.50	1.00	23.0–27.0		0.04	0.03	0.25 N
					Duplex (ferritic–austenitic)				
329	S32900	0.20	1.00	0.75	23.0–28.0	2.50–5.00	0.04	0.03	1.00–2.00 Mo
					Martensitic				
403	S40300	0.15	1.00	0.50	11.5–13.0		0.04	0.03	
410	S41000	0.15	1.00	1.00	11.5–13.5		0.04	0.03	
414	S41400	0.15	1.00	1.00	11.5–13.5	1.25–2.50	0.04	0.03	
416	S41600	0.15	1.25	1.00	12.0–14.0		0.06	0.15	0.6 Mo
416Se	S41623	0.15	1.25	1.00	12.0–14.0		0.06	0.06	0.15 Se
420	S42000	0.15 min	1.00	1.00	12.0–14.0		0.04	0.03	
420F	S42020	0.15 min	1.25	1.00	12.0–14.0		0.06	0.15	0.6 Mo
422	S42200	0.20–0.25	1.00	0.75	11.5–13.5	0.5–1.0	0.04	0.03	0.75–1.25 Mo; 0.75–1.25 W; 0.15–0.3 V
431	S43100	0.20	1.00	1.00	15.0–17.0	1.25–2.50	0.04	0.03	
440A	S44002	0.60–0.75	1.00	1.00	16.0–18.0		0.04	0.03	0.75 Mo

Table 4. (*Continued*)

		Composition, wt %							
Type	UNS designation	C	Mn	Si	Cr	Ni	P	S	Other
440B	S44003	0.75–0.95	1.00	1.00	16.0–18.0		0.04	0.03	0.75 Mo
440C	S44004	0.95–1.20	1.00	1.00	16.0–18.0		0.04	0.03	0.75 Mo
				Precipitation-hardening					
PH 13-8 Mo	S13800	0.05	0.20	0.10	12.25–13.25	7.5–8.5	0.01	0.008	2.0–2.5 Mo; 0.90–1.35 Al; 0.01 N
15-5 PH	S15500	0.07	1.00	1.00	14.0–15.5	3.5–5.5	0.04	0.03	2.5–4.5 Cu; 0.15–0.45 Nb
17-4 PH	S17400	0.07	1.00	1.00	15.5–17.5	3.0–5.0	0.04	0.03	3.0–5.0 Cu; 0.15–0.45 Nb
17-7 PH	S17700	0.09	1.00	1.00	16.0–18.0	6.5–7.75	0.04	0.04	0.75–1.4 Al

[a] Ref. 51. Courtesy of ASM International.

[b] Single values are maximum values unless otherwise indicated.

[c] Value is minimum.

[d] Optional.

Table 5. **Alloy Composition of High Temperature Steels**

Ferritic steels	Stainless steels	AISI type
0.5% Mo	18% Cr–8% Ni[a]	304
0.5% Cr–0.5% Mo	18% Cr–8% Ni with Mo[a]	316
1% Cr–0.5% Mo	18% Cr–8% Ni with Ti[a]	321
2% Cr–0.5% Mo	18% Cr–8% Ni with Nb[a]	347
2.25% Cr–1% Mo	25% Cr–12% Ni[a]	309
3% Cr–1% Mo	25% Cr–20% Ni[a]	310
3% Cr–0.5% Mo–1.5% Si	12% Cr[b]	410
5% Cr–0.5% Mo–1.5% Si	17% Cr[b]	430
5% Cr–0.5% Mo, with Nb added	27% Cr[b]	446
5% Cr–0.5% Mo, with Ti added		
9% Cr–1% Mo		

[a] Austenitic.

[b] Ferritic.

Table 6. **World Raw-Steel Production, 1000 Metric Tons**

Country	1969	1979	1995	2003
Argentina	1,690	3,200	3,700	5,033
Australia	7,032	8,200	8,500	7,544
Austria	3,926	4,900	5,000	6,261
Belgium	12,832	13,100	11,600	11,128
Brazil	4,925	13,900	25,100	31,105
Bulgaria	1,515	2,500		
Canada	9,351	16,000	14,400	15,399
China	16,000	32,000	93,000	220,115
CIS and the former USSR	110,315	153,000	73,300[a]	105,887
Czechoslovakia	10,802	15,500	10,900[b]	11,378
France	22,510	23,600	18,100	19,803
Germany	50,456[c]	53,800[c]	41,800	44,841
Hungary	3,032	3,800	1,870	1,989
India	6,557	10,100	20,300	31,779
Italy	16,428	24,000	27,700	26,740
Japan	82,166	112,000	101,600	110,510
North Korea	2,000	5,100		
South Korea	373	7,600	36,700	46,306
Luxembourg	5,521	5,000	2,600	2,670
Mexico	3,467	7,000	12,100	15,237
Netherlands	4,712	5,800	6,400	6,587
Poland	11,251	19,500	11,900	9,047
Romania	5,540	12,000	6,500	5,776
South Africa	4,625	8,900	8,500	9,487
Spain	5,982	12,100	13,900	16,129
Sweden	5,322	4,700	4,900	5,707
United Kingdom	26,896	22,000	17,700	12,949
United States	128,151	124,000	83,100	91,360
Yugoslavia	2,220	3,500		1,286
others	9,038	21,500	59,100	73,087
Total	*574,635*	*748,300*	*730,355*	*945,140*

[a] Russia and Ukraine.

[b] Includes Czech Republic and Slovak Republic.

[c] Both FRG and GDR.

Table 7. **Net Shipments of U.S. Steel Products, 1000 Metric Tons**[a]

Steel products	1960	1970	1980	1994	2000
ingots and steel castings	307	833	404	192	140
blooms, slabs, billets, sheet bars	1,286	4,328	1,982	2,104	1,203
skelp	118	1	22		
wire rods	833	1,525	2,438	4,319	4,910
structural shapes (heavy)	4,387	5,049	4,410	4,996	7,402
steel piling	384	449	314	396	230
plates	5,562	7,316	7,330	7,764	8,898
rails					
standard (>30 kg/m)	606	779	984	449	654
all other	42	38	48	4	
joint bars	24	23	15	120[b]	128
tie plates	113	160	186		
track spikes	41	69	77		
wheels (rolled and forged)	221	226	144		
axles	101	147	175		
bars					
hot-rolled (includes light shapes)	6,274	7,355	6,270	7,966	9,562
reinforcing	2,009	4,437	4,249	4,473	6,893
cold finishing	1,257	1,352	1,438	1,621	1,756
tool steel	79	80	72	61	45
pipe and tubing					1,334
standard	1,949	2,317	1,608	1,036	1,334
oil country goods	1,086	1,186	3,277	1,211	1,791
line	2,440	1,900	1,082	1,031	976
mechanical	692	955	1,051	939	1,040
pressure	246	215	135	34	37
structural		455	516	176	150
stainless		29	37	23	17
wire					
drawn	2,213	2,143	1,263	715	579
nails and staples	291	272	157		
barbed and twisted	43	89	64		
woven wire fence	94	109	111		
bale ties and bailing wire	57	108	83		
black plate	523	553	457	288	314
tin plate	4,958	5,176	3,779	2,518	2,523
tin-free steel		777	887	857	815
all other tin mill products		65	55	91	90
sheets					
hot-rolled	7,249	11,175	10,991	14,205	19,236
cold-rolled	13,124	12,927	12,077	11,811	14,802
sheets and strip					
galvanized	2,773	4,359	4,757	13,275	18,413
all other metallic coated	237	500	655	1,554	2,138

Table 7. (*Continued*)

Steel products	1960	1970	1980	1994	2000
electrical	515	663	545	398	528
strip					
hot-rolled	1,209	1,173	607	646	864
cold-rolled	1,203	1,045	844	887	2,343
Total steel products	64,544	82,358	75,786	86,283	109,623

[a] All grades, including carbon, alloy, and stainless steels.

[b] Including joint bars, tie plates, track spikes, wheels (rolled and forged), and axles.