

Basics of Ferroalloys

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2.1 INTRODUCTION: BACKGROUND FOR FERROALLOYS DEVELOPMENT AND PRODUCTION

The history of ferroalloys is relatively short compared to bronze or iron development. Ancient iron artifacts investigated are mostly fairly pure iron, containing carbon as the only alloying element. Carbon control by carburizing/decarburizing treatments was traditionally understood by blacksmiths and was used throughout the “Iron Age” to adjust steel properties. Steel produced via the direct reduction route in bloomeries remained naturally unalloyed because iron oxide was reduced at such low temperatures that iron was formed in the solid state. Other components like manganese and silicon, which are typical in modern steels, were found only as natural impurities, yet mainly in slag inclusions in steel. When higher shaft furnaces were developed from bloomeries, stronger air blasting through tuyeres was needed. Temperature in the combustion zones was increased, and the iron formed dissolved more carbon and melted: thus, a blast furnace process was discovered. This development happened in the late Medieval Age in Central Europe. The product was carbon-saturated cast iron

that typically contained a small percentage of silicon and eventually also some manganese, depending on the ore composition. Pig iron from blast furnaces was used as foundry iron for castings or converted to steel by difficult and time-consuming refining process. These processes were gradually developed, but steel from bloomeries kept its dominance until the 19th century. In the early 19th century, two main methods were used to refine hot metal from blast furnaces to steel. They were puddling with an oxidizing flame in a reverberatory furnace and the crucible process in which iron oxide (ore, scale) was added into hot metal to react with carbon and to get low-carbon steel (Flemings and Ragone, 2009; Tylecote, 1984). Principally some alloying would have been possible, but several prerequisites had to be met before rational alloying could be carried out. First, the breakthrough inventions in chemistry during the end of the 18th and early 19th centuries with the discovery of elements (like nickel, oxygen, manganese, chromium, molybdenum, and silicon from 1751 to 1824) and the understanding of chemical reactions like combustion/oxidation and reduction made it possible to recognize essential events of contemporary iron and steel-making processes and to start developing new processes (Engels and Nowak, 1983). Second, there should be some evidence of beneficial influences of additions on steel properties, which requires an understanding of steel microstructure and the influencing mechanisms of alloying elements. Third, it should be possible to produce potential alloying materials at a reasonable price. During the last half of the 1800s, these prerequisites gradually began to be fulfilled.

In steelmaking the decisive breakthrough was the invention of the converter process by Henry Bessemer in 1855. He realized that oxygen from air blown inside the carbon-rich hot metal burned the carbon dissolved in iron melt. He also succeeded in developing a proper reactor and technology for the Bessemer process. Bessemer's steel converter was, however, lined with acid silica refractory. Even if it could operate at temperatures up to 1600°C, the lining life was short. Because of the acid environment, the low-basicity slag was unsuitable for phosphorus removal. This was a big problem at that time in Great Britain, where plenty of P-bearing iron ores were available. The problem was solved when S.G. Thomas and P.C. Gilchrist succeeded in developing basic doloma lining, introduced in 1878–1879 (Barracough, 1990). Doloma is a calcia-magnesia mixture obtained by burning natural dolomite ($(\text{Ca}, \text{Mg})\text{CO}_3$) mineral. Basic Thomas converters gradually replaced acid Bessemer converters. Also the open-hearth process (involving a reverberatory furnace heated by flame), developed by the Siemens and Martin brothers in 1860–1870, which started with acid lining, adopted basic lining and the new steelmaking practice as well. Thus, basic lining was available for electric furnaces when they started to be used for steelmaking in the beginning of the 1900s and for the production of ferroalloys too.

In parallel with Bessemer's process development, Scottish metallurgist Robert Mushet discovered a way to add manganese-containing *spiegeleisen* in liquid steel to “kill” it. The term *killing* stemmed from the prevention of steel

melt “boiling” (actually carbon-oxygen reaction and formation and removal of CO gas, which appears as boiling). Certain additions like spiegeleisen were observed to eliminate this “wild” state and to “kill” the steel. Manganese was thus first used for steel deoxidation. Its beneficial effect to avoid hot shortness by binding excess sulfur was soon recognized (Tylecote, 1984). Spiegeleisen was already produced in the 18th century in blast furnaces, containing 8% to 15% Mn and ~5% C. Mushet was also one of those who developed the first “tool steels” with 1% to 2% Mn and high tungsten content in the 1860s. Robert Hadfield invented the first high-manganese steel in the 1880s by introducing a work hardening steel with 11% to 14% Mn and 1% C (Tylecote, 1984). This steel grade has remained principally unchanged and still has a firm position in impact- and wear-resistance type working applications (e.g., in railway crossings). At this time, it also became evident that alloying or modifying steel with pure elements is not economical. Further, it might be technically challenging or impossible (e.g., dissolution of metallic tungsten in a steel melt would take an enormously long time).

At that time metallurgists started to consider the addition of alloying elements to steel in the form of a ferroalloy—an alloy of iron with at least one other element (except carbon, which is as cementite, Fe_3C , or graphite in cast irons). Small-scale production of ferroalloys began in the 1860s with the use of the crucible process. Chromium or manganese ore was reduced by coal in graphite crucibles, which were heated to high temperatures to get liquid high-carbon ferroalloy (~25% Cr). High-Mn ferromanganese production was also started in a blast furnace by the French Terre Noire Co in 1877 with 80% Mn and 6% to 7% C. It was also demonstrated that FeSi could be produced in a blast furnace, as could low-content FeTi and FeV ferroalloys. On the other hand, production of FeCr in the same way was found difficult because of the high melting point of the slag formed during smelting (Volkert and Frank, 1972). When electric furnace technology was introduced at the end of the 1800s, electric smelting of ferroalloys gradually progressed in the early 1900s, and today all ferroalloys that require furnace technology are produced exclusively in electric furnaces.

The occurrence of silicon in iron has its historical origin in blast furnace iron making. Advisedly or by accident, relatively high Si contents (several percents) were obtained in pig iron depending on the blasting practice, blast furnace burden material, charcoal, and other factors. Generally, high silicon in cast iron promotes graphite formation and thus improves ductility. In the early 1900s, however, the exact explanation was not known, and the knowledge of how to produce good-quality castings was more art than science. In the early 1800s, Swedish chemist Jacob Berzelius produced a kind of ferrosilicon by crucible reduction. He also succeeded in separating elemental silicon, which he called “silicium,” in 1824 (Engels and Nowak, 1983). Berzelius observed that silicon burned in air and formed silica (silicon oxide). The production of elemental silicon turned out to be very difficult, so ferrosilicon was produced

instead. It was possible to produce Si-containing hot metal in blast furnaces up to 20% Si in the late 19th century. The product was used for steel deoxidation and alloying. When the electric furnace was developed at the turn of the century, the production technology for FeSi was also developed.

Smelting in an electric furnace and reduction with carbon (coke, charcoal, coal) thus constitute the method on which production of most ferroalloys was founded and special furnace constructions and technologies were developed. In ferroalloys production furnaces are designed to operate in submerged arc mode (submerged arc furnace [SAF]), in which the high resistivity of the charge is utilized for smelting.

The processes described so far are based on carbothermic reduction operating at high temperatures. Sinter or pellets prepared from concentrates and eventually lumpy ore are reduced by coke to form the ferroalloy. The heat for the reactions is generated by electric arcs (with plasma temperatures \sim 18 000° to 20 000°C) formed between the tips of the electrodes in the furnace. The temperatures of materials near the arc zone may reach \sim 2800° to 3000°C, whereas the temperatures in the main reaction zone are typically around 1600° to 1800°C. Because of the strongly endothermic reduction reactions in the smelting process of a ferroalloy, huge amounts of electricity are consumed. In modern FeCr and FeMn processes, typical electricity consumptions are 3000 to 3500 kWh/t ferroalloy, and in the FeSi process typical electricity consumption can reach up to 7000 or 8000 kWh/t FeSi for a high-silicon (75% Si) ferroalloy.

2.2 FERROALLOYS IN THE DEVELOPMENT OF STEELS

As mentioned, old historical iron artifacts were made of almost pure iron containing only carbon as the alloying element. Properties like hardness, strength, and toughness were controlled by changing carbon content with the use of carburizing or decarburizing treatments, skills that had been mastered by blacksmiths. Historical “super steels” like “Damascus” steel and “Bulat” steel, which used Indian “Wootz” iron as a raw material, had amazing properties that are difficult to attain with modern technologies. Rather, in these steels the properties were based on complicated and sophisticated processing with a combination of high and low carbon source materials, which form a composite layered structure via forging-folding-welding tens and maybe hundreds of times (Reibold et al., 2006; Smith, 1988). Famous Japanese *katana* swords were made of Tatara iron, which contained some titanium within iron sand (ilmenite $\text{FeO}\cdot\text{TiO}_2$) and was typically used as an iron source. Also, traditional Japanese sword masters used a folding/forging technique.

Generalized steel alloying was not possible until the 19th century. When understanding of basic chemistry, including analytical chemistry, progressed, it became possible to measure steel composition. At the same time, great advancements were attained in materials investigations and characterization. An important tool in materials research was optical microscopy, which could

reveal the microstructure of steel and find relations between steel composition, microstructure, and properties. A contemporary of Bessemer, H.C. Sorby in Sheffield, was one pioneer who examined steel microstructure (Tylecote, 1984). The value of metallography was appreciated in Europe by 1885. At that time a French research group at Creusot-Loire investigated relations between the microstructure and heat treatment of steels. The polymorphic forms of iron and different microstructures were identified (austenite, ferrite, cementite, pearlite, martensite, and, somewhat later, bainite in the 1920s). The invention of electron microscopy in the 1930s and its development as a common tool for materials scientists further improved knowledge about steel structure and phenomena influencing its structure and properties.

In most steels, carbon is the base element influencing the structure, but by adding different alloying elements, the formation of microstructures and their properties could be controlled. Further, new precipitated phases could be obtained, like carbides (with Cr, Mo, Nb, Ti, V, W, etc.), nitrides, or carbonitrides (Al, Nb, Ti, V). Edgar C. Bain, who in the early 1920s discovered the structure named bainite, and H.W. Paxton, gave a comprehensive summary of the behavior of different alloying elements in steels and their influences on microstructure and properties in the book *Alloying Elements in Steel* (Bain and Paxton, 1966). In the following 50 years, enormous progress was made in the development of new steels with improved performance properties. Improved knowledge of thermodynamics, kinetics, and mechanisms of precipitates formation and phase transformations in different steels has been the basis for creating new steel grades and manufacturing methods. The processes and science of heat treatments have strongly evolved. One example is the thermo-mechanical controlled rolling process, which can produce better mechanical properties in steels with less alloying but a cheaper and faster process route (DeArdo et al., 1990). Figure 2.1 summarizes the most important properties of steels and the process stages where these properties are mainly determined.

Because of great innovations in steelmaking processes, steels can be produced with high “purity” (a low content of impurities like S, P), a low content of interstitial atoms (N, H, and C in ultra-low-carbon grades), and ultimate cleanliness (low oxygen content, strict inclusion control, and the absence of harmful precipitates). Technological developments in processes also have given means to new evolutions in microalloyed and high-alloyed steels. The requirements for the alloying materials depend not only on the need of alloying to attain the desired analysis limits, but depending on the process stage and circumstances, sometimes quite strict requirements can be set regarding the chemistry and physical state of the alloys. Consequently, a wide variety of alloy materials have become available with various compositions specified to certain purposes and in different forms (e.g., lumps, grains, powder, wire, cored wire). Except for different carbon grades, the ferroalloys can be categorized—for example, according to Al-, Ti-, Ca-, Mg-, P-, or S-contents as well as metallic impurities (Cr, Ni, Cu, Sn, As, Sb, etc.).

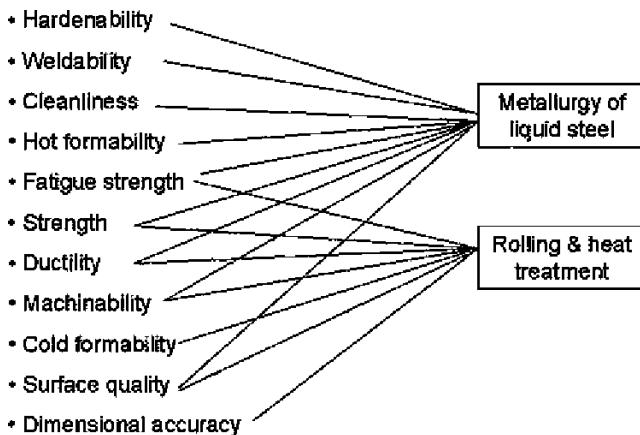


FIGURE 2.1 Relations of steel properties to metallurgical treatments of steel in liquid and solid states.

2.3 A CASE: FERROALLOYS FOR STAINLESS STEELS

Among high-alloyed steels, stainless steels are a special case because of their large production amount and central position as users of ferrochromium. Furthermore, other ferroalloys are also used extensively for stainless steel production. The history of stainless steel is quite short, as the effect of chromium on the improved corrosion resistance of iron was only recognized in the early 1800s. However, at that time it was not yet possible to produce chromium or chromium ferroalloy had to be produced industrially. Reducing chromium from chromite ore ($\text{FeO}\cdot\text{Cr}_2\text{O}_3$) is difficult and needs high temperatures $\sim 1700^\circ\text{C}$ for efficient reduction and liquid slag formation during the process. High temperature also sets strict requirements for a furnace and its lining material.

The first trials to produce “stainless steels” were performed soon after 1900. The “stainless era” is usually said to have begun in 1912 when austenitic Cr-Ni stainless steel was patented by the company Krupp, followed by ferritic and martensitic stainless steels created by other inventors (Tylecote, 1984). Acid-resistant Mo-containing stainless steels were introduced later in the 1920s. In the following decade, fundamentals of main types of stainless steels and their properties were duly examined, but production grew slowly because of the obstacle of a too-high carbon content. Today it is evident that in most stainless steels, carbon content should be very low (typically below 0.05%) to avoid the formation of carbides, which impair corrosion resistance and cause the “sensitization” phenomenon (a type of grain boundary corrosion). In the steelmaking process, the carbon problem is linked to chromium: when carbon is oxidized for removal, Cr also starts to oxidize. This meant that high-carbon FeCr could not be used for stainless steel without drastic chromium losses

during steelmaking. A lot of chromium should be added after decarburization by using low-carbon FeCr, which is more expensive than a high-carbon grade. Low-carbon FeCr should also have a higher Cr:Fe ratio to minimize the amount of alloying required, but so-called charge FeCr typically had rather low Cr:Fe (containing only 50% to 55% Cr). Therefore, to produce low-carbon FeCr, ores with a high chromium content are preferred. Special processes were developed to decarburize FeCr—for example, single or double treatment with slag to make “affine” (<4% C) and “sur-affine” (<0.5% C) FeCr grades. The stainless steel production exceeded 1 Mt/year in 1950. Stainless steel production received a boost with the invention of the argon-oxygen decarburization (AOD) process, taken into operation in the 1960s. It made possible the use of high-carbon FeCr and to decarburize the melt by diluting oxygen by Ar gas and thus lowering the partial pressure of CO, which is formed (Krivsky, 1973). In 1976, the world production of stainless steels exceeded 5 Mt, reaching 10 Mt in 1988, 20 Mt in 2002, and 30 Mt in 2010 (based on data from www.worldstainless.org, 2012), as shown in Figure 2.2.

Stainless steels can be divided in several groups depending on their alloying and structure. Austenitic stainless steels (ASTM classification 300 series) form the biggest group, accounting for 55% to 60% of all stainless (Fig. 2.3). A classic example is 18/8 steel with 18% Cr and 8% Ni. If better corrosion resistance, especially against pit corrosion, is required, the nickel content is raised to 11% to 14% and molybdenum is added (2% to 4%). The carbon

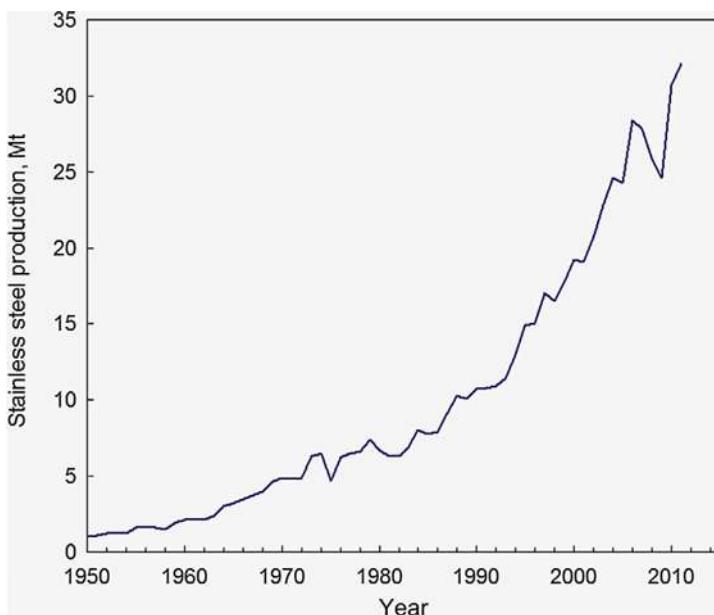


FIGURE 2.2 Growth dynamics of the worldwide production of stainless steel.

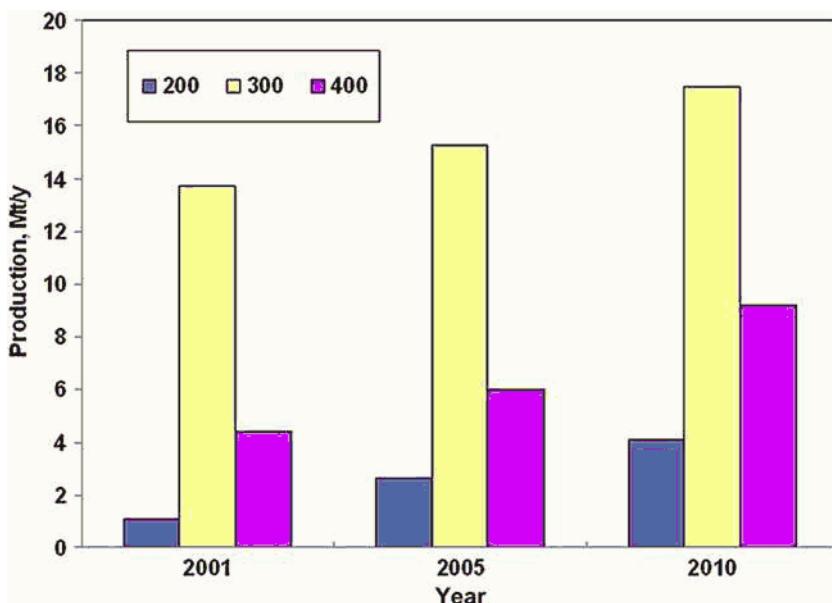


FIGURE 2.3 Share of stainless steel grades by category (200, 300, and 400 series).

maximum is normally 0.03% C (“L” grades), but in high temperature grades may be typically up to 0.08% C (“H” grades).

The second major group is represented by ferritic stainless steels, some 30% of all the stainless (400 series) (see Fig. 2.3). Here, chromium content is from 10.5% to 30%, and it can contain some Mo and even Ni. Carbon content is limited, like in austenitic steels. A relatively new group of stainless steels is “duplex stainless steels,” which have approximately same fraction of austenite and ferrite in their structure. An example analysis is 21% to 23% Cr, 4.5% to 6.5% Ni, 2.5% to 3.5% Mo, 2% Mn, and C_{max} 0.03%. Duplex steels have better mechanical properties because of their structure.

Martensitic stainless steels belong to ferritic steels but have a higher carbon content (0.1 to 1% C), which makes them hardenable when quenching after heat treatment. Corrosion resistance is not as good as it is in corresponding low-carbon grades but good mechanical properties make these steels applicable in different tools, dental and surgical instruments, cutlery, and so on. A typical martensitic stainless steel has 12% to 14% Cr, <2% Ni, 0.2% to 1% Mo, 1% Mn, 1% Si, and 0.3% C.

Because of the high contents of alloying elements in stainless steels, their price is sensitive to changes in alloying costs. When nickel prices climbed up, increased attention was paid to finding substitutes for nickel in austenitic 300 series stainless steels. A common austenite stabilizer is manganese. In the 200 series stainless steels, Cr content is kept to 16% to 19%, but Ni content is

decreased to around 5% (in some grades only 1% to 2% Ni) and Mn content is raised to 5% or 10% Mn. Also copper (Cu) and nitrogen (N) can partly substitute for nickel. Significant production of these Cr-Mn-Ni stainless steels, known since the 1930s, began in the United States in the 1950s ([ASM Handbook, 1990](#)). After the year 2000, production of the 200 series steels increased, especially in China and India, and exceeded 10% of the total stainless steel production in 2005; it is currently on the level of 12% to 14% (see [Fig. 2.3](#)).

2.4 RECENT FERROALLOYS PRODUCTION AND MARKETS DEVELOPMENT

As the ferroalloys are primarily used in steelmaking, different grades of alloys have been developed to fulfill the varying requirements of the steel industry. As discussed earlier, most of the chromium is added in the form of high-carbon charge FeCr (50% to 55% Cr, 2% to 5% Si, 6% to 8% C, and the balance is Fe). Also, for different alloying purposes, different Cr-alloys are produced with higher Cr and lower carbon contents than in Charge HC (high-carbon) FeCr. Typical composition is 60% to 70% Cr, 2% to 3% Si, and in different carbon categories: high-carbon (HC) grades with 5% to 8% C, medium-carbon (MC) grades with 1% to 4% C, and low-carbon (LC) grades with 0.1% to 0.5% C. Even lower carbon contents are available. The world leader in ferrochrome production is South Africa with 3.6 Mt in 2008; China is second with 2.2 Mt, followed by India and Kazakhstan with about 1 Mt/year. Kazakhstan, South Africa, and India have the largest chromite resources known. Russia and Finland are the next big producers with productions of about 0.25 Mt/year. [Figure 2.4](#) shows the progression of the world's ferrochromium production. Over 80% of all FeCr goes into stainless steel and high-alloyed steels. The rest is used in low-alloyed steels (typically 0.3% to 2.0% Cr) to improve hardenability and strength. Concerning the need of FeCr for stainless steels, it is noteworthy that a significant share of the all Cr units (on average 30% to 40%) comes from recycled stainless scrap and the rest (60% to 70%) comes from "virgin" ferrochrome alloy.

Ferroalloys production is firmly coupled with steel production, and the time-dependent production rates follow each other. The total world steel production is presented in [Figure 2.5a](#) and the total ferroalloys production in [Figure 2.5b](#), except for ferrochrome even ferromanganese, silicomanganese, and ferrosilicon. In 2008–2010 about 5.7 Mt of ferromanganese, 8.5 to 9.5 Mt of silicomanganese, and 7.5 to 8 Mt of ferrosilicon were produced annually.

A comparison of the production of the mentioned "bulk" ferroalloys since the 1980s reveals some interesting features. Concerning manganese alloys, there has been a clear transition from FeMn to SiMn ([Fig. 2.6](#)): in the beginning of the 1980s FeMn was produced much more than SiMn, in the beginning of 2000 the produced amounts were equal, but in 2010 the FeMn/SiMn ratio was ~0.6 ([Brown, 1984](#); [Corathers et al., 2012](#); [Fenton, 1996](#)).

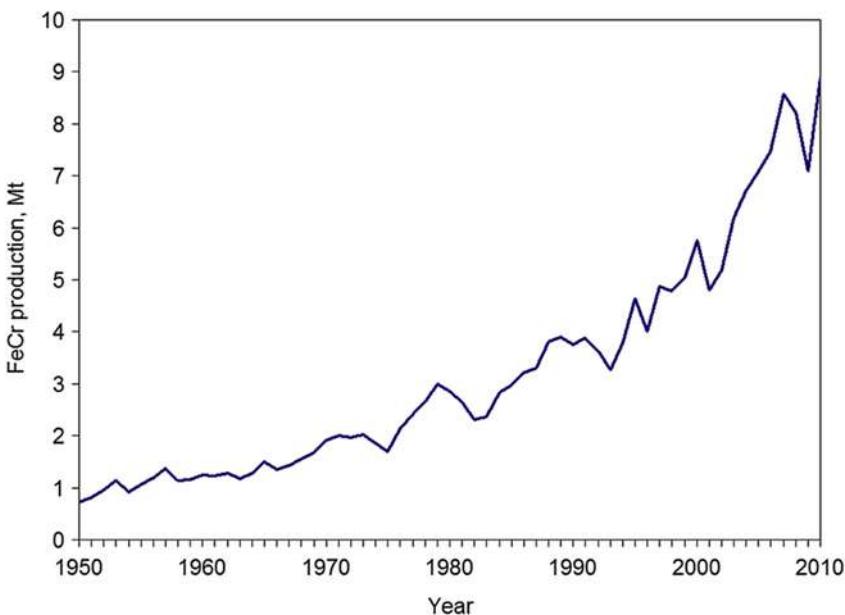


FIGURE 2.4 World production of ferrochromium.

There have been some changes in production technology: ferromanganese production in blast furnaces has reduced from 30% to about 10%, and most FeMn production now occurs via submerged arc furnaces (SAF). All silicomanganese is produced in SAFs. Silicomanganese is a suitable addition to be used for the deoxidation of most steels, whereas ferromanganese and ferrosilicon are used mainly for alloying purposes. Nevertheless, the growing trends shown in Figure 2.6 are comparable with the trend of steel production.

By calculating the apparent ferroalloy consumption per all kinds of steels produced, eventual trends in “alloying degree” can be observed (Fig. 2.7). The average consumption of ferroalloys has been 2.2% to 2.4% of the mass of steel, but it has grown to 3% in recent years. However, this does not refer to real growth of “degree of alloying” but describes the fast growth of high-alloyed stainless steels. As most chromium is added as charge FeCr with low Cr content (50% to 55%), the quantity of the ferroalloy addition is still emphasized.

Despite the volatility of metals markets, ferroalloys production is rather steady as it represents one of the major backbones of steelmaking. Besides steels, ferroalloys are used also for special materials production (foundry castings, superalloys, low-iron and nonferrous alloys, welding materials, etc.). Figure 2.8 presents a map of the producing countries. Countries with reported ferroalloys production are marked (data collected from various sources as of 2010). Nevertheless, there is also local ferroalloys production

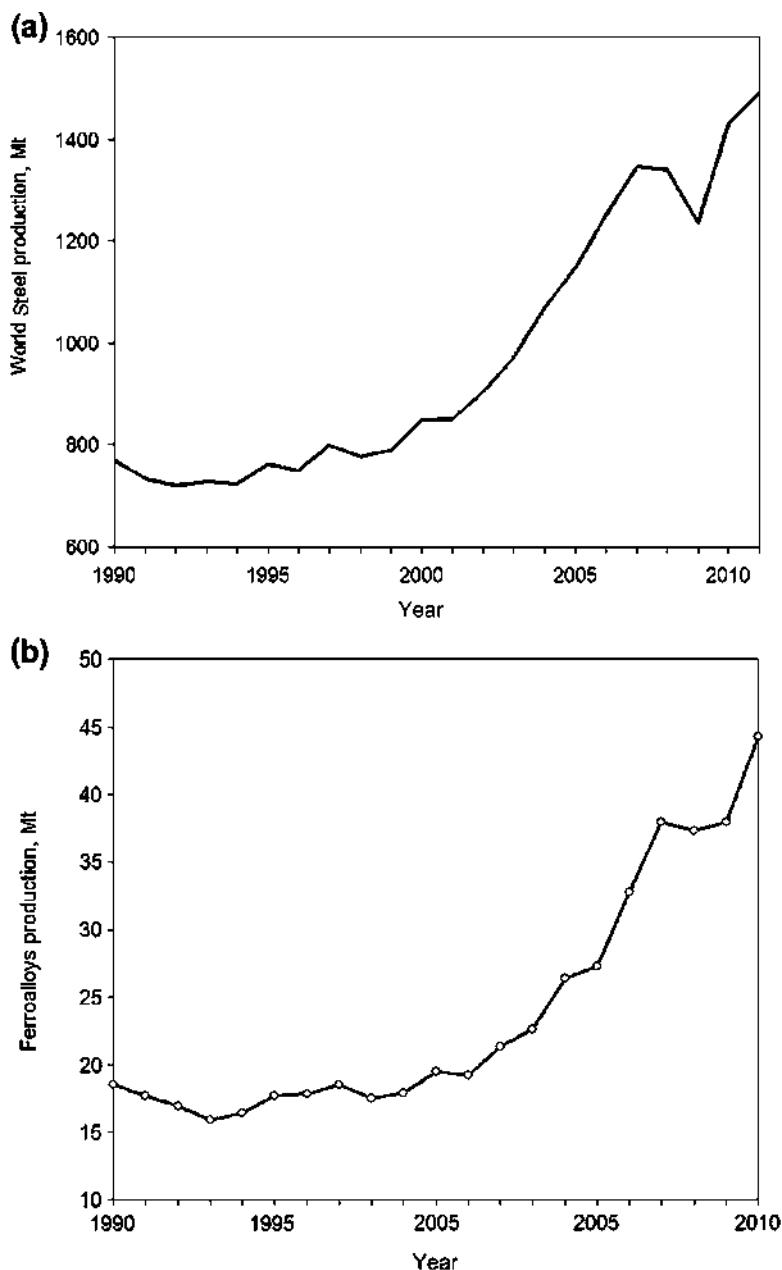


FIGURE 2.5 World production of steel (a) and ferroalloys (b).

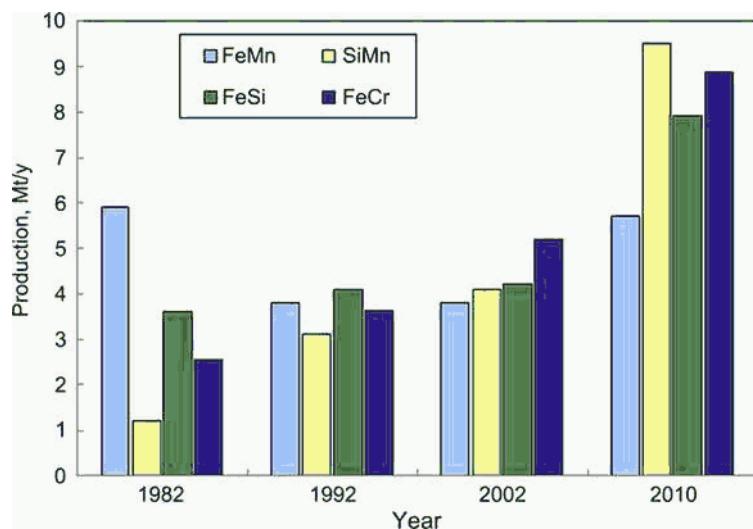


FIGURE 2.6 World production of FeMn, SiMn, FeSi, and FeCr alloys.

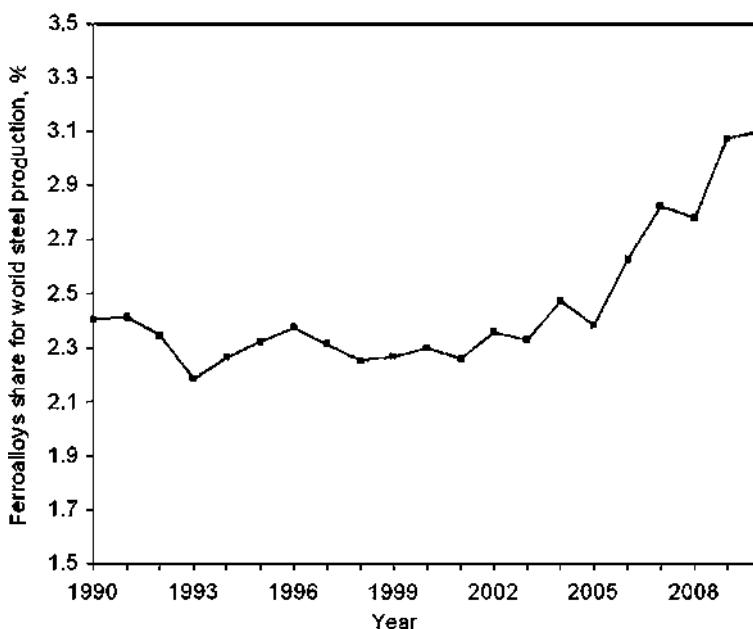


FIGURE 2.7 Average consumption of ferroalloys, percentage to steel.

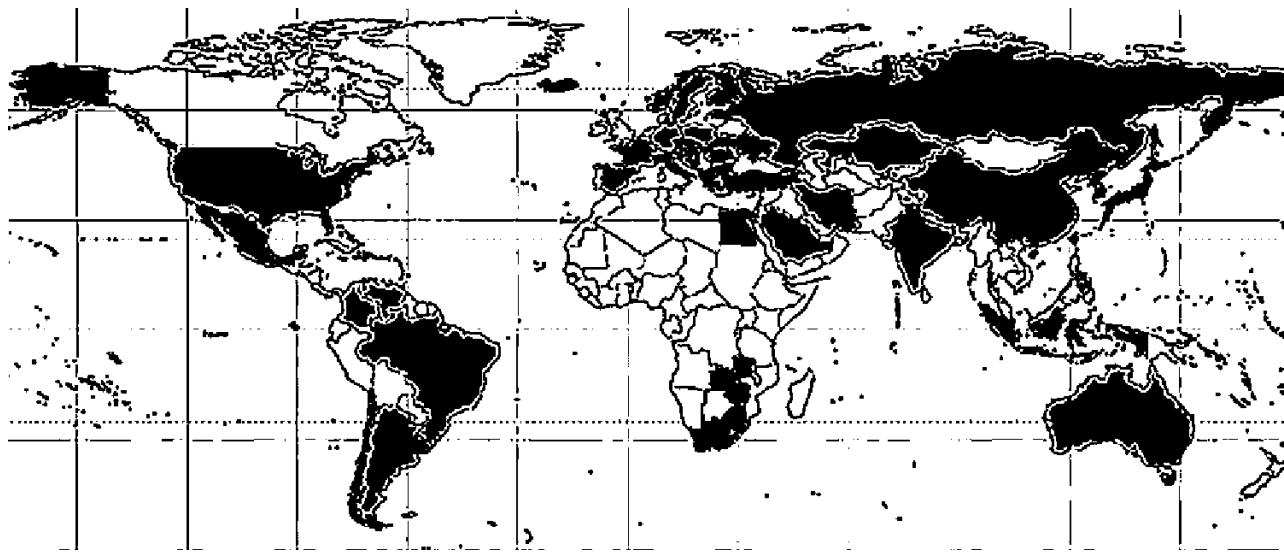


FIGURE 2.8 World map with major ferroalloys producers marked (2010).

FIGURE 2.9 Periodic table showing ferroalloy major leading elements (dark gray) and co-occurring (minor) elements (light gray).

in-house in some metallurgical plants for that company's own use as well as occasional smelting campaigns to satisfy peak demands or to utilize locally available resources.

Finally, the modified periodic table (Fig. 2.9) shows the ferroalloys spectrum. Elements marked in dark gray are so-called leading elements (i.e., ferroalloys with these elements are produced explicitly), and the content of these elements is specified by standards and is monitored. Elements marked in light gray co-occur in ferroalloys but usually are not specifically separated. For example, cobalt often occurs in ferronickel during smelting, but the alloy is still ferronickel as nickel is the leading element in this case.

2.5 ENERGY AND EMISSIONS ISSUES OF THE FERROALLOYS INDUSTRY

2.5.1 Energy Demand for Ferroalloys Making

Today's ferroalloys are almost always produced by smelting in electric submerged arc furnaces (SAFs); only a comparatively small amount of ferromanganese is still produced in blast furnaces. A conventional SAF is an open furnace from which off-gas is mixed and combusted with a large amount of air. A "closed furnace," however, is designed to maintain CO-rich off-gas by collecting, cleaning, and storing it for further utilization. An intermediate type, referred to as a "semiclosed" furnace, is still common for FeSi and special alloys production. It is still possible to recover off-gas from this type of furnace, but it is less calorific. There is a strong trend toward closed furnaces with gas recovery and utilization; for instance, in ferrochrome production closed furnaces have rapidly increased ([Holappa, 2010](#)). As an example, some basic data of FeCr and FeMn ferroalloys making are reviewed in [Table 2.1](#).

TABLE 2.1 Consumption of Raw Materials and Energy When Producing HC FeCr and FeMn: Conversion of Coke to Electricity: 1 kg coke = 7.7 kWh

Ferroalloy Type	HC FeCr		HC FeMn
	Open	Closed	Closed
SAF type			
Feed type	Lumpy/fine, no preheating	Pellets, preheating	No preheating
Ore, kg/t	2400–3000	2300–2400	1900–2400
Reducing agent, kg/t	550–700	500–550	410–500
Fluxes, kg/t	100–400	200–300	—
Electrodes (paste), kg/t	8–25	7–10	8–25
Electricity, kWh/t	3800–4500	3100–3500	2200–3200
Potential coke energy, kWh/t	4200–5400	3900–4200	3100–3500
Total energy input, kWh/t	8000–9900	7000–7700	5300–6700

2.5.2 CO₂ Emissions from Ferroalloys Production

Ferroalloys production is an energy-intensive industry with a high consumption of electricity but only a moderate consumption of coke and minor consumption of other fuels and reductants. This affects direct CO₂ emissions. Table 2.2 has been calculated based on the literature data (Corathers et al., 2012; Lindstad et al., 2007; Sjardin, 2003) of emission factors for different processes and production numbers. For these ferroalloys, different grades (high, medium, low carbon; different silicon content) with different emission factors were integrated. Carbon dissolved in ferroalloys was not included as an emission in ferroalloys production.

As shown, the total emissions from four main ferroalloys with 32 Mt annual production were about 63 Mt, from which an approximate figure about 87 Mt CO₂ for total ferroalloys production (44 Mt) can be given as a rough estimate. However, the emissions data given in Table 2.2 are only for direct emissions from the combustion of carbon when coke and eventually coal are used for reduction as well as from electrodes consumption. One has to add indirect emissions generated in electricity production (see Table 2.1), so, depending on the method of electricity generation, the indirect CO₂ emissions

TABLE 2.2 Emission Factors, Production, and Estimated Global Emissions for Common Ferroalloys

Ferroalloy	Emission Factor, t CO ₂ /t Alloy	Production, Mt	Estimated CO ₂ Emissions, Mt
HC FeCr HC	1.3–1.63	8.9	14
HC FeMn	1.3–1.79	5.7	10
FeSi (45% to 90% Si)	2.5–4.8	7.9	23
SiMn	1.4–1.66	9.5	16
Total		32	63

can be large. **Table 2.3** shows CO₂ emission factors in the biggest ferroalloys-producing countries (see Graus and Worrell, 2011). Countries that have plenty of renewable energy (including nuclear power) naturally have low emission factors when compared with countries that are using coal power. In such conditions the total emission factor can be doubled compared to the value of the direct emission factor. The emission factor should be one decisive criterion when erecting and operating ferroalloys plants.

Although more data of energy and materials consumption in different processes/furnaces can be found in the literature, any direct comparison is impossible because of the use of different raw materials, process conditions, products, definitions of terms, and so on. A new approach for process

TABLE 2.3 CO₂ Emissions in Total Power Generation by Selected Countries in 2007 (g/kWh): The Values Are Heat-Corrected (Graus and Worrell, 2011).

Country	CO ₂ , g/kWh	Country	CO ₂ , g/kWh
Australia	921	Kazakhstan	488
Brasilia	71	Norway	3
China	823	Russia	363
Finland	164	South Africa	862
India	948	Ukraine	413
Japan	451		

evaluation is the best available technology (BAT) procedure. BAT was defined by EC Directive 96/61 Article 2(11) as follows:

The most effective and advanced stage in the development of activities and their methods of operation which indicates the practicable suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent, and where that is not practicable, generally to reduce the emissions and the impact on the environment as a whole.

This definition implies that BAT not only covers the technology used but also the way in which the installation is operated, thereby ensuring a high level of environmental protection as a whole. BAT takes into account the balance between the costs and environmental benefits. The following list summarizes the most effective and advanced technologies for use on the ferroalloy production line (Holappa, 2011; Worrell et al., 2008):

- Concentrate sintering by utilizing CO gas from a smelting furnace.
- Preheat charge material for the smelting furnace by utilizing off-gas from the SAF.
- Prereduce the charge before smelting in the SAF. This is a potential but unestablished subprocess for certain ferroalloys.
- Smelt in closed SAFs with efficient off-gas recovery, filtering, and energy utilization in-plant or in neighbor users.
- Use of a semiclosed furnace (for FeSi) is acceptable if energy can be recovered from CO gas.
- Utilize latent heats of liquid ferroalloy and slag from the smelting furnaces.
- Improve the recovery of metals. Cr yield into FeCr is typically 90% to 95%, and for Mn in FeMn production the yield ranges from less than 80% to more than 90% depending on the slag practice and recycling.
- Integrate ferroalloy production with steel production, with other industries and for use within society. This might give excellent possibilities for energy recovery, electricity production, CO gas utilization, heat recovery, and utilization.
- Apply efficient gas cleaning for dust, heavy metals, and toxic emissions.
- Use a closed water system to remove particulates and harmful components.
- Recycle, reuse, and utilize solid wastes like slags as by-products.

From the viewpoint of energy, the first five aspects are most significant. Today only in one plant is the heat content of liquid FeCr directly utilized in stainless steel making (Holappa, 2010). Improvement of metals yields is a metallurgical problem but is also connected with recycling and process integration. The last three aspects listed are environmental issues and thus extremely important. When operating at high temperatures, a lot of dust is generated via vaporization and other mechanisms. In addition to valuable and harmless components, the dust often contains harmful, even poisonous, components. Therefore, the dust must be carefully collected and prevented from ending up in air, water, or soil.

It is reasonable to expect an energy-saving potential of 20% to 30% on a global level by adopting the best available techniques as widely as possible. With efficient integration, the benefit can be even higher. Another option is to introduce renewable biomaterial (i.e., charcoal) as a substitute reductant for coke and to mitigate greenhouse gas emissions by CO₂ recovery and sequestration. In large production units, this might be economically reasonable and realizable.

2.6 FUTURE OUTLOOK FOR THE FERROALLOYS INDUSTRY

Progress in the ferroalloys industry has closely followed developments in the steel industry, and this course will continue. The rapid growth in stainless steel use has driven a corresponding growth at least for chromium (FeCr) and nickel (Ni, FeNi, NiO): the average annual growth rate in this sector has been more than 5%. The demand for stainless steel has increased, particularly in China and India, the two largest countries by population. Such growth is assumed to continue, at least in India, and to extend to other developing regions in Southeast Asia, Africa, and South America. As the history of high-tonnage production is quite short, the amount of recycled stainless steel is limited, which means there will be a growing demand for primary alloying materials, especially Cr, Ni, and Mo. Concerning the other bulk ferroalloys FeMn, FeSi, and SiMn, the demand is bound more to low-alloyed carbon steels. Growth has been more moderate, 2% per year on average. Future growth is expected to take place almost solely in developing countries. At a 2% growth rate, the annual production of steel worldwide will exceed 2500 Mt by the 2040s, which means there will also be remarkable growth in different sectors of the ferroalloys industry.

What will be the requirements for the grades and quality of ferroalloys in the future? The base compositions of bulk ferroalloys come from the reconciliation of raw materials, production technology, and customers' wishes and requirements. A common meeting point for the seller and buyer is money (i.e., cost, price, and utility value). Especially in high-alloyed steels, the contents of major components (Cr, Mn, Si, etc.) and minor components (generally carbon, in FeCr silicon) have a strong influence on the processing time, slag, temperature control, and other details. These components are difficult to evaluate today but will become more critical in the future. A component regarded as an impurity, such as phosphorus, can be critical in stainless steel making, as its removal is practically impossible, whereas the amount of sulfur is relatively easy to decrease in the later stage of the converter process or even in the ladle stage. Concerning alloying and trimming additions in later process stages, typically in ladles, high contents of the alloy metal are important (e.g., in FeCr, FeMn, FeSi) to minimize the total addition. Depending on the steel grade to be produced, metallic impurities can be critical (e.g., aluminum and titanium) because they influence inclusions in steel and can cause problems in casting. Of course, gaseous components (nitrogen, oxygen, hydrogen) are important; most

often, high contents are harmful, causing problems in different stages of the steelmaking process until the final product is generated.

In 2009, Holappa (2010) surveyed worldwide experts in the field of ferroalloys production to ask about the importance of different factors concerning the sustainable production of ferroalloys. The 17 responses represented almost the same number of enterprises or institutions on six continents that dealt with central ferroalloys (FeCr, FeMn, FeSi). The survey consisted of questions concerning raw materials and pretreatment, energy issues, environmental issues, by-products, and economic aspects. Almost all the issues presented were regarded as important, and respondents believed their value would grow until 2020. Electric energy was ranked first among all factors. Economic issues (investment and operation costs, energy cost) had the next highest ranking, probably partly reflecting the recession that prevailed when the questionnaire was distributed. The next most important issue was energy efficiency, which included CO utilization, raw materials pretreatment (sintering/pelletizing), and emissions in air and water, almost all of which were given the same high weight. Overall, the ferroalloys industry has numerous challenges ahead, and it must undergo technological modernization and in-depth transformation in consideration of environmental issues. On the other hand, it is a rapidly and steadily growing branch, which makes regeneration easier and gives it the most potential.

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