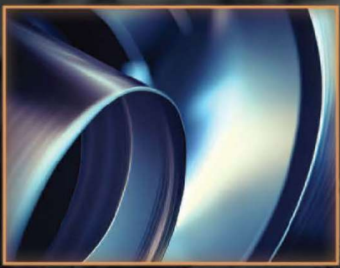

HIGH ELECTRICAL RESISTANT MATERIALS

Ferrochrome Slag Resource Ceramics

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Scrivener Publishing

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High Electrical Resistant Materials

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Contents

Preface

Since waste materials are currently endangering our environment, ways of utilizing them have become a global challenge. Currently, R&D work is being carried out to utilize these materials for producing value-added products. In the present investigation, an effort has been made to utilize fly ash (FA) and pond ash (PA) (waste materials from thermal power plants) and high-carbon ferrochrome (HCFC) slag (by-product of the ferrochrome industry) for producing a novel material called ceramics. Kaolin/K-feldspar is mixed with PA/HCFC slag to produce ceramics with formation of mullite.

The FA/PA/HCFC slag-based ceramics can replace porcelain-based ceramics, and some permanent ceramic structures can be constructed with such wastes. Thus, it is no wonder that scientists are trying to develop ceramics utilizing waste materials.

The present text will highlight the mechanism involved in the formation of ceramics from FA/PA/HCFC slag. This will perhaps be the first attempt to use FA/PA/HCFC slag for developing ceramics. Properties and structures made with ceramics are found to be comparable with those made with porcelain-based ceramics. Systematic investigations are currently being carried out to develop new ceramic products using these FA/PA/HCFC slag materials. Performances of these materials above ambient temperature are being evaluated, and results indicate the possible replacement of porcelain with these newly invented ceramics.

The Authors
December 2023

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Fundamentals of Ferrochrome (FeCr) Alloy and Its Slag

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Abstract

The manufacture of alloy steel consumes chromium in large quantities. Therefore, there is an ever-increasing demand for chromium. Manufacturers use chromium in the alloy steel used for tool steel, high-speed steel, stainless steel, and ball-bearing steel. In addition, nichrome (Ni-Cr) alloy is used as a heating element for electric furnaces.

Chromium is a ferrite stabilizer and a strong carbide former. Addition of chromium improves strength, oxidation resistance, and corrosion resistance properties. Therefore, the global production of chromium has gained importance over the years.

Chromium is not obtained in its free state; therefore, chromium ore is reduced by normal smelting process. Carbothermal reduction of chromium ore enables production of ferrochrome. Usually, an electrical furnace is used for production of chromium, which consumes high electric energy. As a result, the cost of ferrochrome production is enhanced. During the production, chromium is lost through formation of slag. Hence, ferrochrome slag is thought to be a useful raw material for production of high temperature insulation bricks, construction work using geopolymer made from chromium slag, etc. Therefore, R&D scientists are trying to find suitable uses for other applications.

In this chapter, the fundamentals of ferrochrome slag chemistry are discussed. Results obtained by different workers are cited and thermodynamics models used by different groups of researchers are briefly discussed. Physicochemical properties

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are also described which may be helpful for future R&D work. Important consideration is also given to environmental issues. Chromium is present in two ionic forms, i.e., trivalent and hexavalent chromium, with the hexavalent form being detrimental to human health. Therefore, this chapter also discusses how unutilized chromium slag pollutes the environment, making it a human health hazard.

Keywords: Chromite ore, ferrochrome production process, ferroalloys, slags, environmental aspects of slag, compositions of slag, thermodynamics of slags, oxidation state of slag, slag properties (i.e., viscosity, electrical resistivity)

1.1 Introduction

Industrialization is a process of socioeconomic development. However, industrial activities are associated with generation of wastes. Production and dumping of wastes pollute our environment as well as water due to the leaching effect when these wastes are submerged in water [1, 2]. Hence, appropriate actions are needed to safeguard atmospheric pollution and subsurface contamination. In recent times, increased construction activities that have arisen due to industrial and population growth have resulted in the scarcity of available conventional construction materials. Hence, nonhazardous wastes are often utilized for construction work [3, 4]. This will reduce waste disposal problems and the costs associated with construction work.

Ferrochrome slag is such a waste material which is obtained from ferrochromium (FeCr) industries [5]. The FeCr alloy is used in the stainless-steel manufacturing process [6]. Chromium in stainless steel improves properties such as corrosion/oxidation resistance, hardness, tensile strength at elevated temperatures, wear and abrasion resistance, etc. [7].

The FeCr alloy is manufactured from its ore by reducing it with coke. The process is carried out at 1,500 °C in an electric arc furnace. Molten slag and metal are slowly tapped in a mold and subsequently cooled in air to enable formation of stable, dense, crystalline phase [8].

The main constituents of FeCr slag are SiO_2, Al_2O_3, FeO, Cr_2O_3, CaO and MgO [9]. Slag products are crushed and ground into sizes ranging between 6.3 mm and 300 mm. Hence, with increased production of ferrochrome, FeCr slag production (HC FeCr, 52% Cr) has increased.

Mineral chromite with chemical composition $FeCr_2O_4$ (ferrous chromic oxide), is a submetallic mineral belonging to the spinel group (with a generic formula of $R^{+2}O.R^{+3}O_4$). It is the only economic mineral mined for chromium production. Because of the high heat stability of chromite, it is also used as a refractory material for high temperature vessels such as furnaces [10]. Two main products are achieved from refining of chromite: ferrochromium and metallic chromium [10]. The smelting operation must be carried out with chromite ore in order to produce the two products mentioned above. One of the major problems encountered during chromite smelting is the issue of energy consumption (i.e., electricity). A large amount of energy is required to smelt chromite to produce ferrochromium or metallic chromium. According to Keesara [11], approx. 4,000 kWh of energy per ton material weight is required for smelting of chromite. This is due to the high melting temperature of chromium. Regarding economic benefits, revenue generated from a ferrochromium plant is dependent on Cr/Fe ratio [12]. The higher the ratio, the higher the revenue earned by the plant. Thus, the economy of the total process depends largely on quality of ore, cost of energy, transportation cost, and others. Hence, one has to consider these factors before venturing into or manufacturing chromium from available ore. During chromite smelting, energy requirement and its cost depend to a large extent on the technology used in smelting the ore. New technologies have been developed to reduce the energy required for smelting chromite and producing ferrochrome. These technologies, together with the conventional chromite smelting technique, are subsequently discussed in this chapter.

1.2 Chromite Smelting Technologies

Production of ferrochrome involves four primary processes: Conventional smelting process, Outokumpu process, DC-arc process, and Premus process. The aim of these processes is to smelt chromite ore in a submerged electric arc furnace. These technologies are discussed below.

1.2.1 Conventional Smelting Process

Traditional chromite smelting technology involves charging chromite ore into a submerged electric arc furnace (Figure 1.1). Coke and coal are used as reductants. Quartzite is used as a fluxing material which removes undesirable oxides in the form of slags. Metal/ferrochrome and slag produced are tapped from the furnace for further processing. According to Naiker [13], the primary advantages of the conventional smelting process are the low capital investment incurred and the flexibility offered in choosing raw materials in the production process. However, in terms of energy requirement, the process is not efficient as it is an energy-intensive process, requiring up to 4,000 kWh per ton of material produced. The conventional

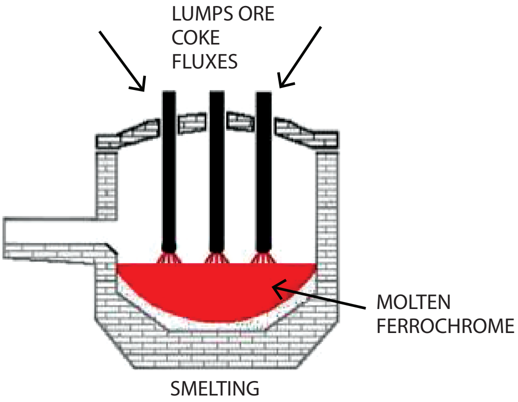

Figure 1.1 Schematic diagram of smelting using submerged electric arc furnace (EAF) [14].

smelting process requires about 1.0 indexed energy cost per ton of ferrochrome alloy produced.

1.2.2 Outokumpu Process

The Outokumpu process involves grinding and pelletizing of ore fines, followed by sintering of green pellets and preheating before smelting [15, 16]. According to Goel [16], the ore and coke fines are normally wet-ground to about 35 percent under 37 microns (400 meshes) and are then pelletized to approximately +15 mm size. Figure 1.2 shows the flow sheet of the Outokumpu process. As seen in Figure 1.2, the preheating operation is done mainly in a rotary kiln and the energy required for sintering and preheating the pellets comes from CO gas generated in a submerged arc furnace. In the Outokumpu process, chromite ore is partly reduced in the rotary kiln during preheating, thereby reducing the amount of electric energy required for final smelting of the ore to ferrochrome.

1.2.3 DC-Arc Process

DC arc furnaces use a single solid carbon electrode as the cathode and produce a DC arc to an anode in the bottom of the furnace (Figure 1.3). The arc is normally an open or semi-submerged one [18]. Raw materials can be charged either directly into the furnace or by using a hollow electrode. The DC arc route is designed mainly to overcome the problem of ore fines encountered in the conventional chromite smelting process. Therefore, in

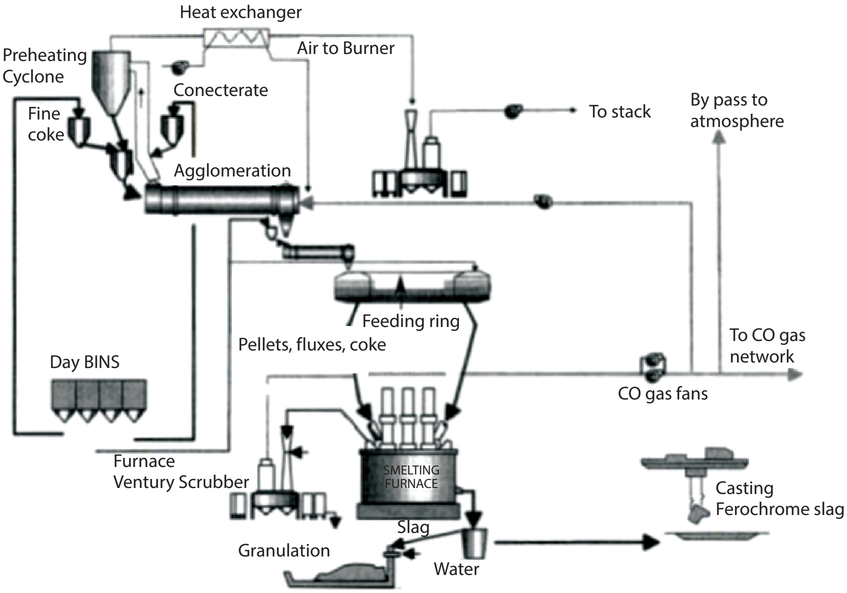

Figure 1.2 Outokumpu process [17].

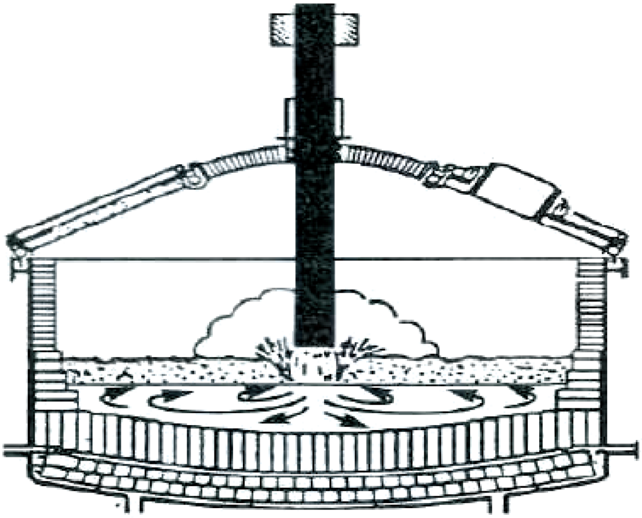

Figure 1.3 DC-arc process [19].

order to use this technology for producing ferrochrome, a compromise between coke consumption and energy requirement is necessary.

1.2.4 Premus Process

The Premus process is being used at the Lion ferrochrome plant in South Africa. It uses Xstrata's proprietary technology. This process is sophisticated, competitive and technologically advanced for the production of ferrochrome from chromite ore [17]. The technology involves three stages: sintering, pre-reduction, and smelting. Energy reduction is as observed in the Outokumpu process. Energy reduction is achieved in the pre-reduction stage of the process. As can be seen in Figure 1.4, chromite pellets from the sintering stage are pre-reduced in a rotary kiln by a roasting operation before being charged in the closed submerged arc furnace for final smelting. The pre-reduction process results in the reduction of energy required for closed submerged arc furnace during final smelting of ore to ferrochromium. It is worth noting that the energy used in the pre-reduction stage is obtained from hot gas generated in the closed submerged arc furnace and also from coal pulverization, and thus is not paid for. With this technology, Lion ferrochromium is now in the forefront of chromite smelting in South Africa.

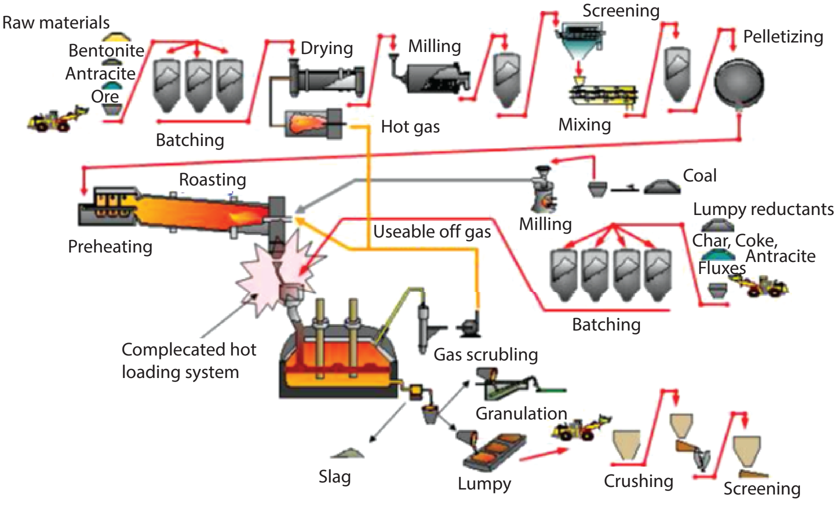

Figure 1.4 Schematic illustration of Premus process [13].

Premus technology is the least expensive and most energy-efficient ferrochrome technology. The technology also uses low-cost reductant material (anthracite), and thus coke consumption is low in Premus technology.

Another important feature of this technology, which is also a part of the DC-arc process and Outokumpu process, is that it is designed for smelting fine chromite ore. The conventional smelting process is designed to handle only lumpy ores. This is ideal for production of ferrochromium as the fine ores tend to form a sintered layer at the top of the charge. Thus, using fine ores sometimes causes a technical problem, such as preventing gas from escaping, thus posing operating difficulties [12]. Due to this problem, fine chromite ores have low economic value. However, with the development of Premus technology, DC-arc process, and Outokumpu process, fine chromite ores can now be smelted. These technologies have been designed to convert the fine ores into pellets during the pre-reduction stage. These technologies can therefore be used to generate more revenue in localities having a large amount of fine chromite ore.

1.3 Ferrochrome Production

Ferrochrome is produced by carbothermic reduction of iron magnesium chromium oxide at high temperature. Coke and coal are used as reducing agents. The reduction process is carried out in an electric arc furnace. The arc generates temperature around 2800 °C. For this purpose, the electricity consumed is high and consequently cost increases [20].

1.4 Chemical and Physical Properties of Ferrochrome

Ferrochrome or ferrochromium (FeCr) is a type of ferroalloy. Usually, such alloys contain chromium (50 to 70% by weight) and iron [22, 23]. Physical and chemical properties of ferrochrome are listed in Table 1.1.

Globally, large quantities of domestic chromite resources are available in South Africa, Kazakhstan and India. Stainless steel manufacturers are the largest consumer of chromium and ferrochrome. FeCr production (High Carbon FeCr, 52% Cr) has now reached the level of 5 M ton/year [24].

Chromite ore is ferrous chromic oxide ($FeCr_2O_4$). It belongs to spinel group with a generic formula of $R^{+2}O.R^{+3}O_4$. FeCr alloy is produced from chromite ore. Because of its high heat stability, it is used as a refractory liner of an arc furnace vessel.

Table 1.1 Physical and chemical properties of ferrochrome [21].

S.no.	Physical properties	Physical property value
1	Atomic Mass	52.0
2	Density	7.15 g/cm^3
3	Melting Point	1900 °C
4	Boiling Point	2642 °C
5	Appearance	Ferrochrome is available in a variety of forms, including small crystals, lumps and granules as well as in powder form.
6	Color	Color varies from dark gray to light gray.
7	Odor	Odorless; can be dangerous when inhaled.
8	Solubility	The alloy is not soluble in water.
9	Combustibility	The dust particles of this chemical alloy are combustible.

Ferrochrome is collected from the furnace at regular intervals. Usually, slag and molten metal are tapped where molten metal is separated in molten condition and is chilled in a metal mold. The molten ferrochrome is then solidified in large castings and is processed further.

On the basis of carbon content, ferrochrome alloy is classified into two categories: low carbon ferrochrome alloy and high carbon ferrochrome alloy.

1.4.1 Characteristics of Ferrochrome

- It is a steel-gray and hard metal.
- Chromite ore minerals belong to the spinel group.
- Cr is a carbide-forming element and forms $Cr_4C_3/Cr_{23}C_6$ in stainless steel.
- Cr is a ferrite stabilizer and makes the alloy stable at high temperature.
- Cr in stainless steel improves corrosion-oxidation resistance.
- Cr improves stress corrosion property in stainless steel.
- Metallic chrome products or super alloys or other special melting metallic products are produced using chrome alloy.

1.5 Ferrochrome Uses

Most of the ferrochrome produced worldwide is used in manufacturing of stainless steel. Chromium content stainless steel varies between 8 to 29% FeCr. Chromium content stainless steel provides resistance to corrosion. Ferrochrome is indispensable in manufacturing of ball-bearing steels, tool steels and other alloy steels [25]. Apart from making stainless steel, low-carbon ferrochrome is also used in the manufacturing of acid-resistant steels [26].

Ferrochromium alloy picks up carbon during carbothermal reduction. Since Cr and Fe have affinity for carbon, they pick up carbon. The amount of carbon in alloy depends on operating conditions, i.e., oxygen potential and temperature. Two types of ferrochrome alloy are produced [27, 28];

1. Low-carbon ferrochrome alloy
2. High-carbon ferrochrome alloy.

1.5.1 Low-Carbon Ferrochrome Alloy

An optical photograph of low-carbon ferrochrome is shown in Figure 1.5. Low-carbon ferrochrome is a ferrochrome having carbon content below 0.25. This is used as raw materials for producing silicon chromium alloy,

Figure 1.5 Optical photograph of low-carbon ferrochrome [29].

chromite and lime. Low-carbon ferrochrome chromium (LC FeCr) is used in austenitic stainless steel and superalloy. Due to high quality, it is a reliable and economical alternative to metallic alloy chromium for superalloy production [29].

1.5.1.1 Low-Carbon Ferrochrome – Chemical Analysis

Ferrochrome is an alloy of chromium and iron containing 50–70% chromium by weight. Addition of chromium improves the strength and yield point of steel and reduces elongation insignificantly. The presence of chromium in carbon steels improves hardness and wear resistance. The chemical composition of low-carbon ferrochrome is indicated in Table 1.2.

1.5.2 Problems of Carbon in FeCr

Ferrochrome production is done by chromite reduction with carbon (coke) in a submerged arc furnace. Ferrochrome product is basically carbon-saturated iron-chromium alloy with 6–8 wt% carbon. Carbon forms solid chromium carbide and complex iron-chromium carbides. The higher percentage of carbon in ferrochrome creates several problems.

Low-carbon alloy for making austenitic stainless steel, carbon contains less than 0.1% (0.02–0.05%). Excess carbon causes "sensitization" problems at about 810 K. At sensitization temperature, excess carbon combines with chromium to form chromium carbide ($Cr_{23}C_6$). At this temperature, carbide is insoluble and precipitates at the grain boundaries. At grain

Table 1.2 Chemical composition of low-carbon ferrochrome (LCFeCr) [30].

LCFeCr	Low-carbon ferrochrome (60%)	Low-carbon ferrochrome (70%)
Cr	65% Min	70% Min
C	0.03, 0.06, 0.10, 0.15	0.03, 0.05, 0.06, 0.08, 0.10, 0.15
Si	1% Max	1% Max
S	0.03% Max	0.03% Max
P	0.035% Max	0.035% Max
Size	10–50 mm – Min 90% or as required by end user	

boundaries, chromium has inadequate corrosion resistance. Thus, carbon is indirectly responsible for corrosion, and hence weakens the material. A similar problem is observed in welded structures [28, 31].

In austenitic stainless steels, the chromium to carbon ratio is more than 150, whereas in high-carbon ferrochrome steel it is about 10. High-carbon ferrochrome stainless steel inadvertently increases carbon content. Hence, it is essential to remove carbon from the parent source (i.e., high-carbon ferrochrome). To improve the chemical and mechanical properties of steels, minimizing the concentration of the detrimental and undesirable element (i.e., carbon) from steel is necessary.

Chromium metal is reactive towards carbon by simple oxidation to form chromium oxide. Such practice cannot be used for removing carbon. This is a major problem in the case of most ferroalloys [32].

Conventional decarburization techniques are used to remove carbon from FeCr. There are many disadvantages to these techniques such as high refractory consumption, poor metal recovery due to losses of chromium in slag, etc. However, nonconventional decarburization techniques are not used. Conventional decarburization methods are described below.

1.5.2.1 Refining of Ferrochrome by Chromium Ore

Elyutin [32] assumed that liquid high-carbon ferrochrome is a solution of chromium and carbon which exists in the form of carbide (i.e., Cr_7C_3). This process is used to determine the thermodynamic characteristic. Decarburization reaction is written as (Eq. 1.1):

$$\begin{aligned} &\langle Cr_2O_3\rangle + \langle FeCr_2O_4\rangle \rightarrow \langle Cr\rangle + \langle Fe\rangle + CO \\ &\Delta G^o = 612 - 0.323T \quad kJ \end{aligned} \tag{1.1}$$

Difficulties encountered in the decarburization process are due to the high melting point and viscosity of the high-chromium refining slag. This prevents the growth of chromic oxide in the slag. Hence, there is a limited possibility of increasing the oxidizing capacity of slag. Decarburization process is conducted at a temperature of 2175 K; 2% of the carbon in the alloy is decarburized. Decarburization of low carbon grade material is feasible at a temperature higher than 2375 K. Thus, production of low-carbon ferrochrome by this process is very difficult.

1.5.2.2 Refining of Ferrochrome by Blowing Oxygen

In this process, carbon is removed by blowing O_2 through molten ferrochrome in a converter. It is a more expensive process. Elyutin [32] brought carbon below 1% using air as an oxidizer. This method did not give satisfactory results because of insufficient bath temperature (i.e., 1935–1985 K).

1.5.2.3 Refining of Ferrochrome in Presence of Silicon

The process consists of refining ferrochrome by oxygen in the presence of silica under high vacuum. Since the reaction is carried out, gaseous product is formed. The disadvantages of the process are contamination of alloy with unreacted silica, high silicon content of product and lengthy production time.

1.5.2.4 Silicothermic Process (Production of Low-Carbon Ferrochrome)

Increasing silicon content in an alloy decreases solubility of carbon. Low-carbon ferrochrome is prepared by reduction of chromite using silicon as reducing agent and silico-chrome is formed. Smelting is done in a shaft type of electric furnace lined with magnesia [33]. Size of chromite ore should be less than 50 mm and size of ferrochrome should be less than 10 to 15 mm. Also, chromite ore contains less phosphorus and sulfur. Ferrosilicon chrome is free from slag inclusions. This is because slag contains entrapped carbon in silicon carbide particles. Use of higher voltage minimizes carbon pick up from the electrodes. The main advantage of the process is that it can produce an alloy with carbon less than 0.03%.

1.5.2.5 Production of Carbon-Free Ferrochrome (Aluminothermic Process)

In this technique, carbon-free ferrochrome is produced on a small scale. The reduction reaction (Eq. 1.2) proceeds as follows;

$$\begin{aligned}&\frac{2}{3}\langle Cr_2O_3\rangle+\frac{1}{2}\langle Al\rangle=\frac{4}{3}\langle Cr\rangle+\frac{2}{3}\langle Al_2O_3\rangle\\&\Delta G^o=-309+0.004\,T\quad kJ\end{aligned}\tag{1.2}$$

The amount of heat produced per unit mass of reactants is 2649 kJ/kg, which is sufficiently higher [34]. Aluminothermic reduction will be easier in comparison to the silicothermic process.

1.5.3 Non-Conventional Techniques

Non-conventional techniques (AOD and VOD) have been adopted for the stainless-steel manufacturing process since several difficulties are encountered by conventional decarburization methods.

1.5.3.1 Decarburization of Solid Ferrochrome

0.01 to 0.03 % carbon content ferrochrome is obtained from high-carbon ferrochrome (6–8% carbon) by vacuum heat treatment process with an oxidant (e.g., iron oxide). A distinctive composition of ferrochrome of 60–70% Cr, 0.01–0.03% C is obtained by this process.

1.5.3.2 Decarburization Using Oxidizing Gas Mixture

(a) Water Vapor
Oxidation of carbon from ferrochrome takes place according to the reaction shown in Eq. 1.3. Shimizu [35] carried out the experiment using water and calcium compound to form dense ferrochrome. Actual mechanism of decarburization is still not clear. This is because of the endothermic nature of the reaction (Eq. 1.3) and requirement of high vacuum.

$$\begin{aligned}&\langle Cr_{23}C_6\rangle + 6\left(H_2O\right) = 23\langle Cr\rangle + 6H_2 + 6\left(CO\right)\\&\Delta G^o = 1890 - 0.296\,T \quad kJ\end{aligned} \tag{1.3}$$

(b) Carbon Dioxide
In this method, decarburization is carried out by subjecting ferrochrome pallet to carbon dioxide flow. Decarburization proceeds by the following reaction (Eq. 1.4):

$$\begin{aligned}&\langle Cr_{23}C_6\rangle + 6\left(CO_2\right) = 23\langle Cr\rangle + 6H_2 + 12\left(CO\right).\\&\Delta G^o = 1436 - 1.012\,T \quad kJ\end{aligned} \tag{1.4}$$