Current situation on the production market of FeMn and FeCr

M. Karbowniczek*, J. Gladysz, W. Ślęzak
Department of Ferrous Metallurgy, AGH-University of Science and Technology, Al. A. Mickiewicza 30, 30-059 Kraków, Poland
* Corresponding e-mail address: mkarbow@agh.edu.pl
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ABSTRACT

Purpose: Ferroalloys are mainly used in steelmaking processes in order to obtain an appropriate chemical composition of metal. Main producers include China, South Africa, India, Kazakhstan and Russia. These countries in total constitute 83% of the global production. In 2009 nearly 30 million tons of ferroalloys were produced, mainly ferrochromium, ferromanganese and ferrosilicon.

Design/methodology/approach: It is presented a review of current methods in the production of chromium and manganese alloys, chemical reaction which take place, advantages and disadvantages of technologies.

Findings: Paper shows a situation in the production of ferroalloys based on FeMn and FeCr.

Research limitations/implications: This paper presents currently used methods in the production of ferromanganese and ferrochromium.

Originality/value: The article presents the share of production of ferroalloys in the world, major manufacturers and used methods.

Keywords: Ferromanganese; Ferrochromium; Metallothermic reduction

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1. Introduction

Most chromite ores are excavated in South Africa, India and Kazakhstan. 95% of ores are melted in electric arc furnaces to produce ferrochromium. Main producers include China, Kazakhstan and South Africa. The majority of the produced ferrochromium is used to make stainless steel. Ferrochromium is more and more commonly produced using environmentally friendly methods. These methods are energy efficient, involve the use of waste materials as well as the initial reduction and closed furnaces.

Ferroalloys are mainly used in steelmaking processes in order to obtain an appropriate chemical composition of metal. Main producers include China, South Africa, India, Kazakhstan and Russia. These countries in total constitute 83% of the global production. In 2009 nearly 30 million tons of ferroalloys were produced, mainly ferrochromium, ferromanganese and ferrosilicon. In this case China is the main producer - Chinese production constitutes 190% of the production of 3 other main producers: India, Japan and Ukraine in total.

Table 1 and 2 present an average percentage share when it comes to the total global production of ferroalloys, ferrochromium and ferromanganese in 2000-2009 [4,5].

Table 1. Average percentage share in the production of ferroalloys

<table>
<thead>
<tr>
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<th>EAF</th>
<th>BF</th>
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<tbody>
<tr>
<td>FeMn</td>
<td>14.23</td>
<td>90.03</td>
</tr>
<tr>
<td>FeCr</td>
<td>25.46</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>60.31</td>
<td>9.97</td>
</tr>
</tbody>
</table>

Fig. 1 presents the production of FeMn and FeCr in particular years. Ferroalloys are mainly produced in arc furnaces, whereas ferromanganese in blast furnaces - it constitutes 90% of the production. Five times as much of this ferroalloy can be produced...
in the electric arc furnace. FeCr constitutes 25% of the total ferroalloy production in the electric arc furnace.

Table 2. Average ferroalloy production in thousands of tons

<table>
<thead>
<tr>
<th></th>
<th>EAF</th>
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<tbody>
<tr>
<td>FeMn</td>
<td>3754.0</td>
<td>806.0</td>
</tr>
<tr>
<td>FeCr</td>
<td>6653.0</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td>26800.0</td>
<td>896.9</td>
</tr>
</tbody>
</table>

Fig. 1. Global production of FeMn and FeCr in tons

2. Production of manganese alloys

2.1. Production of high carbon ferromanganese

Carbon ferromanganese is produced by reducing manganese ores with carbon. Both the blast furnace melting process and the electrometallurgical process are used.

The melting process of carbon ferromanganese in the blast furnace has a number of shortcomings in comparison to the electric furnace process. These shortcomings include a high use of coke and high losses of manganese with slag and with blast furnace gases. The use of coke in the blast furnace process during the production of carbon ferromanganese amounts to 2 tons per ton of alloy and is 5-6 times as high as in the case of electric furnace processes. The production costs of carbon ferromanganese in both these processes depend on the relation between the prices of coke and electric energy. Nowadays approximately three fourths of carbon ferromanganese is produced in electric furnaces, whereas the remaining part comes from blast furnaces. The technology of melting carbon ferromanganese in the blast furnace is similar to the technology of melting the conversion pig iron.

Melting ferromanganese in the electrometallurgical process has a number of benefits in comparison to the blast furnace process. These benefits include higher total extraction of manganese from ores, lower use of carbon reducers, the possibility of using lower quality reducers and higher flexibility, i.e. it is easier to switch to the production of a different alloy.

The melting of carbon ferromanganese in electric furnaces can be performed using two methods - the flux method (with waste slag) or the fluxless method [1].

The flux method consists in reducing manganese with carbon by adding a basic flux to the charge (limestone, bitter spar). Slag in this process has a basic character (CaO/SiO2=1.3-1.6 and even higher). Slag from the flux process contains 15-20% of MnO and is a waste material. The extraction of manganese from ores in the flux process amounted to 80%.

The fluxless method consists in reducing manganese ores with carbon without adding any or at least very little of basic flux to the charge. Slag in this method has the basicity below one unit and contains 30-50% of MnO. This slag is then used to produce other manganese alloys, mostly ferromanganese. Total extraction of manganese from ores (including the production of FeSiMn) amounts to 85-90%.

Nowadays in order to produce manganese alloys it is common to install furnaces whose power of transformers is 75-90MVA.

2.2. Production of high and low carbon ferro-manganese

High carbon ferromanganese contains approximately 7% by weight of carbon. In case of the production of low carbon steel it is preferred to use low carbon ferroalloys melted using special technologies.

For many decades, up until the end of 1970’s, the silicothermic process was a basic method used to produce low carbon and medium carbon ferromanganese. This process involved reducing manganese ore or manganese slag with silicon. From 1976 centres in the US and Norway started to produce low and medium carbon ferromanganese by refining high carbon ferromanganese with gaseous oxygen - this process is similar to steel melting in oxygen converters. By 2003 this method had been used to produce 840000 tons of low and medium carbon ferromanganese [2].

2.3. Obtaining low and medium carbon ferro-manganese by means of silicothermic method

Ferro silicon manganese is the source of silicon which is needed to reduce manganese oxides from the ore or manganese slag in the silicothermic process. Sometimes a small amount of ferrosilicon is used (75%). The production process of medium and low carbon refined types of ferromanganese can be performed in electric furnaces operating in the arc regime or by means of mixing liquid metal rich in silicon with liquid lime and manganese slag in special types of ladles. Nowadays it is more common to use the method of mixing liquid solutions in ladles.

While the liquid solutions are being mixed in the ladle in the temperature of 1450-1600ºC, a reaction takes place between silicon from metal phase and MnO from slag phase:

\[ 2(MnO)_i + [Si]_i = 2[Mn]_i + (SiO_2)_i \] (1)
The equilibrium constant of this reaction increases when temperature drops (an exothermic reaction). The increase in temperature is beneficial from the point of view of kinetic conditioning of its course.

The content of carbon in low carbon ferromanganese depends on the content of carbon in ferro-silicon manganese that is used for its production. The solubility of carbon in alloys of FeMnSi (Mn/Si = 8) was shown in Fig. 2.

\[
[Mn] + \frac{1}{2}[O_2]_g = (MnO),
\]

(2)

If the process is conducted without using slag, then the activity of the produced solid MnO amounts to a unit. MnO, which was produced in the first stage, reacts with carbon diluted in ferromanganese:

\[
(MnO)_s + [C] = [Mn] + [CO]_g
\]

(3)

Equilibrium content of carbon for reaction (3) is set by the partial pressure of CO and the activity of manganese in the solution (the activity of MnO is equal to a unit):

\[
a_c = \frac{1}{K_T} p_{CO} a_{Mn}
\]

(4)

where: \(K_T\) - equilibrium constant of reaction (3) in temperature T.

The partial pressure of CO can be modified by diluting the inserted oxygen with argon or nitrogen. Fig. 4 presents the calculation results concerning equilibrium content of carbon in an
ally (with initial content: Fe15% - C) in the function of partial pressure of CO and temperature.

As can be seen in Fig. 4 it is possible to obtain in the alloy a carbon content which is slightly higher than 1.1% for partial pressure of CO equal to 1 atmosphere and in temperature 1800°C. Further increase in temperature leads to a serious increase in Mn losses by evaporation. As a result, obtaining lower content of carbon is possible by diluting oxygen with argon or nitrogen, i.e. by decreasing partial pressure of CO. The use of nitrogen leads to a rise in its content in the produced ferromanganese.

The decarburization of ferromanganese with the use of oxygen proceeds in three stages. During the first stage the temperature of ferromanganese increases from approx. 1350°C to approx. 1550°C. This increase takes place mainly at the expense of the oxidation of manganese to MnO. The share of carbon oxidation in the heat transfer at this stage is minimal. The decarburization process at this stage is controlled by the course of carbon oxidation at the border of gas phase and metal bath. During the second stage the reaction rate of the carbon oxidation increases significantly. The temperature of the metal bath increases steadily from 1550°C up to 1650°C. The rate at which oxygen is inserted into the border layers near the metal bath is now a controlling factor when it comes to the decarburization rate. During the third stage (in temperature above 1650°C) the decarburization rate decreases while both the amount of oxidized manganese and temperature rise. The diffusion of carbon in metal bath is now the controlling factor as far as the decarburization process is concerned.

As a result of decarburization of ferromanganese using the above method it is possible to obtain approx. 92% of medium carbon ferromanganese. The losses include vapour and dust - approx. 3% as well as slag, spatters and skulls. 2% in relation to the initial mass of the decarburized ferromanganese.

3. Production of chromium alloys

3.1. Production of high carbon ferrochromium

High carbon ferrochromium is produced by reducing chromium ores with carbon in electric low shaft furnaces. The melting is conducted in a continuous way. The melting of carbon ferrochromium is based on the process of simultaneous carbon reduction of chromium and iron oxides from the chromium ore. The reduction of Cr₂O₃ with carbon can be described by the following equations:

\[
\frac{2}{3} \text{Cr}_2\text{O}_3 + \frac{18}{7} \text{C} = \frac{4}{21} \text{Cr}_7\text{C}_3 + 2\text{CO}
\]  

\[
\frac{2}{3} \text{Cr}_2\text{O}_3 + 2\text{C} = \frac{4}{3} \text{Cr} + 2\text{CO}
\]  

The temperature at the beginning of the reaction (5) amounts to 1130°C, and in case of reaction (6) to 1140°C. The temperature of reducing Cr₂O₃ to chromium carbide is lower than that of reducing it to metallic chrome. As a result, the ferrochromium obtained using the carbothermic method is always a high carbon alloy. While Cr₂O₃ is being reduced with carbon, iron oxides and partially silicon oxides are being reduced from the chromium ore, too.

Fig. 4. Equilibrium content of carbon in refined ferromanganese

The charge used in melting carbon ferrochromium consists of a chromium ore, a carbon reducer and fluxes. A mixture of metallurgical coke and coal are most commonly used as carbon reducers. Fluxes used in melting carbon ferrochromium include: quartz, slag from melting ferro silicon chromium and sometimes also bauxite. Ferrochromium containing 65-70% of Cr and 6-8% of C has the melting temperature of approx. 1550°C. The temperature of the alloy tapping from the furnace amounts to 1580-1620°C. The slag melting temperature in the process of melting high carbon ferrochromium, which allows to ensure the above mentioned temperature of the alloy, should amount to approx. 1650°C. The alloy and slag are tapped from the furnace into a ladle with a chamotte refractory lining every two hours. The alloy from the ladle is then cast into iron ingot moulds and after cooling it is milled. Slag used in melting carbon ferrochromium can have the following chemical composition: 3-6% Cr₂O₃; 1.3-2.3% CaO; 38-41% MgO; 19-22% Al₂O₃; 27-34% SiO₂; 1% FeO; 0.002% P and 0.15-0.75% S. The relation between the amount of slag and the amount of alloy is 0.89-1.35 [3].

3.2. Production of low carbon ferrochromium

Low carbon types of ferrochromium are used mainly to produce stainless steel, acid-resistant and creep-resistant steel containing up to 0.07% of C.

Silicothermic method of low carbon ferrochromium production

The basic methods of low carbon ferrochromium production include, as in the case of low carbon manganese, silicothermic processes. These processes consist in reducing oxides present in
the chromium ore or high chromium slag by using silicon from ferro silicon chromium. These processes can be conducted in electric refining furnaces or using secondary metallurgy.

Refining furnaces used for low carbon ferrochromium production have transformers with the power of 3-7 MVA. Due to the risk of alloy carburization with the carbon from electrodes it is common to use increased voltage on the secondary side ranging from 260-300V. The furnaces have graphitized electrodes. Melts are conducted using the periodic method.

The charge used in low carbon ferrochromium melts consists of the chromium ore, ferro silicon chromium and calcined lime. The reduction of chromium oxide with silicon from ferro silicon chromium can be described in the following way:

\[
\frac{2}{3} (CrO_2) + [Si] + 2CaO = \frac{4}{5} (Cr) + \{2CaO - SiO_2\}
\]

During the melt samples of alloys are taken from the furnace and the silicon content is assessed. When the content of silicon falls below the level set by the norm for a particular type of alloy then tapping of alloy and slag is initiated. In case of the silicothermic method the content of Cr₂O₃ in slag from final ferrochromium melts usually amounts to 3.5-4%. An increased content of Cr₂O₃ in slag means that the process temperature was too low or that not enough lime was added or possibly that not enough ferro silicon chromium present in the charge.

Secondary metallurgy used to produce low carbon ferrochromium is linked to mixing liquid synthetic lime chromium slag with ferro silicon chromium (Perrin method). The chromium ore and lime are melted in electric furnaces whose transformers have the power of 10-15 MVA. The chemical composition of the synthetic lime chromium slag can be as follows: ~30% Cr₂O₃; 7-8% MgO; 7-8% Al₂O₃; 10-12% FeO; 1-3% SiO₂ and 40-45% CaO. The process of mixing this slag with ferro silicon chromium is conducted in special ladles with magnesite refractory lining. The ladles have a mechanism that allows them to rotate and tilt. Perrin method can be best presented if the process is divided into two phases:

- **Phase I.**
  A weighed amount of synthetic slag (slag I) is tapped into a ladle, then a weighed amount of ferro silicon chromium II with a known silicon content is added. After a short period of mixing, which is intensified due to the rotation of the ladle, low carbon ferrochromium and slag containing 10-12% of Cr₂O₃ (slag II) are obtained.

- **Phase II.**
  Ferro silicon chromium I (Si content: 40-45%) is added to slag II with a known Cr₂O₃ content. The slag remained in the ladle after the tapping of the alloy. As a result of mixing these solutions the following are produced: waste slag (Cr₂O₃ content: 0.5-1.0%) and ferro silicon chromium II (Si content: 20-23%).

The essence of this process consists in using an excessive amount of one reagent in relation to the other one during each of the process phases. In phase I there is an excess of Cr₂O₃ in slag in relation to the amount of silicon in ferro silicon chromium II. In phase II there is an excess of silicon from ferro silicon chromium I in relation to the amount of Cr₂O₃ in slag II. An excess of one of the reagents increases the reduction and oxidation process rates and makes it possible to obtain low silicon content in ferrochromium (<0.5%) and low chromium oxide content in waste slag (<1.0%).

### Production of low carbon ferrochromium using the aluminothermic method

Low carbon types of ferrochromium, including nitride ferrochromium and metallic ferrochromium, can be produced using aluminothermic method. The reduction process of Cr₂O₃ with aluminium takes place according to the following reaction (8):

\[
2 \left(\text{Cr}_2\text{O}_3\right) + \frac{4}{3} \text{Al} = \frac{4}{3} \text{Cr} + \frac{2}{3} \text{Al}_2\text{O}_3
\]

The heat of the reduction of metal oxides with aluminium constitutes the source of heat in case of aluminothermic processes. When it comes to melting chromium alloys using this method, heat deficiency is dealt with by introducing thermal admixtures into the charge, e.g. a mixture of sodium saltpeter and aluminium powder. Lime is used as a flux - adding lime decreases the melting temperature and viscosity of slag, improves kinetic conditions of the process and increases chromium share as a result of the activity of chromium oxide in slag.

### Production of low carbon ferrochromium using the vacuum method

The vacuum method of decarburizing ferrochromium in solid state allows to obtain an alloy with the carbon content of 0.01-0.03%. The process consists in oxidizing carbon from ferrochromium using the oxygen from oxidizers, metal oxides (chromium, silicon, iron and others) in temperatures ranging from 1250°C to 1400°C with pressure decreased to 0.5-1.0 mmHg. The decarburization process can be described by the following equation:

\[
\frac{1}{6} (Cr, Fe)_y + \frac{1}{y} Me, O_x = \frac{23}{6} (Cr, Fe) + \frac{x}{y} Me + CO
\]

Finely ground carbon ferrochromium and oxidizer are used to make briquettes. These briquettes are then dried and decarburized in a chamber vacuum furnace for 80-100 hours.

### 3.3. Production of medium carbon ferrochromium

The production methods of medium carbon ferrochromium can be divided into two groups. The first group includes oxidizing carbon from high carbon ferrochromium. The second group, on the other hand, includes variations on the silicothermic process.

**Melting medium carbon ferrochromium by oxidizing carbon from carbon ferrochromium with oxides present in the chromium ore**

Refining carbon ferrochromium with oxides present in the chromium ore takes place according to the following reactions:
and makes it possible to obtain low silicon content in the process phases. In phase I there is an excess of Cr₂O₃ in slag amount of one reagent in relation to the other one during each of ferrochromium and slag containing 10-12% of Cr₂O₃ (slag II) are which is intensified due to the rotation of the ladle, low carbon a known silicon content is added. After a short period of mixing, a ladle, then a weighed amount of ferro silicon chromium II with x if the process is divided into two phases:

\[
\frac{1}{3}[\text{Cr}, \text{Fe}] + \frac{1}{3} \text{Cr}_2\text{O}_3 + \frac{2}{5} \text{Fe} + \frac{2}{3} \text{Cr} + \text{CO}
\]

(10)

This process ensures high chromium extraction (amounting to 87%) but it also requires a high use of electric energy (~9000 kWh/Mg). This method can be used to melt medium carbon types of ferrochromium with carbon content above 1.5%. The process is conducted in furnaces with low power (approx. 3MVA) and it consists of two stages. The first stage involves the production of high carbon ferrochromium as a result of chromium ore reduction with carbon. Slag containing 3-7% of Cr₂O₃ is removed from the furnace in its entirety. High carbon alloy is refined during the second stage - it is done using lump chromium ore. Refining slag containing 35-40% of Cr₂O₃ and 3-5% of FeO is left in the furnace after the refinement process is over. It is then reduced even further during the next melt.

Melting medium carbon ferrochromium using the converter method

Converter production process of medium carbon ferrochromium consists in oxidizing carbon from carbon ferrochromium using gaseous oxygen. In order to obtain a satisfactory process rate the temperature of the decarburized alloy should amount to 1700°C. The oxidation of carbon takes place both as a result of its reaction with gaseous oxygen and with Cr₂O₃. The latter is produced in the course of chromium oxidation which is taking place simultaneously to the above mentioned reaction. It can be best described by the following reactions:

\[
\frac{1}{3} \text{Cr}_2\text{O}_3 + \frac{1}{2} \text{O}_2 = \frac{7}{3} \text{Cr} + \text{CO}
\]

(12)

\[
\frac{1}{3} \text{Cr}_2\text{O}_3 + \frac{1}{3} \text{Cr} = 3\text{Cr} + \text{CO}
\]

(13)

Inserting gaseous oxygen, whose pressure is 7-9 MPa, into carbon ferrochromium makes it possible to obtain medium carbon ferrochromium with the following chemical composition: 65-69% Cr; 0.3-1.2% Si; 0.8-2.0% C; 0.02-0.04% S and 0.03-0.04% P. Final slag containing 70-80% of Cr₂O₃ is used in the process of melting high carbon ferrochromium. High costs of refractory materials as well as the possibility to replace medium carbon ferrochromium with high carbon one in currently used steel melting processes contributed to the fact that the converter production process of medium carbon ferrochromium is practically no longer used.

Silicothermic process of melting medium carbon ferrochromium

The silicothermic process is most commonly used in industrial practice when it comes to producing medium carbon ferrochromium. The melting process is conducted in two identical furnaces which are used in low carbon ferrochromium melting processes.

The simplest way to melt low carbon ferrochromium is to use the silicothermic process without adding fluxes to the charge. The charge consist of lump chromium ore (the size of the lumps is above 30mm) and ferrosilicon chromium with low silicon content (27-34%). This process is no longer used mainly due to the following reasons: the necessity of using lump chromium ore, low chromium extraction rate (55-62%) and difficulties in recycling slag containing 27-35% of Cr₂O₃.

It is possible to increase chromium extraction in the melting process of medium carbon ferrochromium by introducing lime into the charge (the flux method). Melting medium carbon ferrochromium by means of the flux method with the use of ferro silicon chromium with low silicon content poses certain difficulties. A decrease of Cr₂O₃ content in slag causes its melting temperature to drop and makes it impossible to reach the temperature necessary for the refinement process to be conducted properly. Refining ferro silicon chromium with low silicon content by using slag with low Cr₂O₃ content proceeds very slowly. It leads to extending the duration of the process, increasing the amount of electric energy used and sometimes even to alloy solidification in the furnace. That is why, ferro silicon chromium rich in silicon (47% Si) is used to melt medium carbon ferrochromium. Ferro silicon chromium with such a silicon content contains approx. 0.1% of carbon. In order to increase the carbon content in the alloy to an appropriate level for this particular type of medium carbon ferrochromium it is necessary to add an appropriate amount of high carbon ferrochromium (conversion ferrochromium). The silicothermic method of melting medium carbon ferrochromium differs from melting low carbon ferrochromium only because of the presence of carbon ferrochromium in the charge.

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References