Thermodynamic Simulation of Reduction Processes at the Production of Ferrochrome

V A Salina, V I Zhuchkov and O V Zayakin

Laboratory of Steel and Ferroalloys, Institute of Metallurgy of the Ural Branch of the Russian Academy of Sciences, 101, Amundsen str., Ekaterinburg 620016, Russia

E-mail: valentina_salina@mail.ru

Abstract. The possibility of reduction process of chromium from the Cr₂O₃–FeO–CaO–SiO₂–MgO–Al₂O₃ system by carbon using the method of thermodynamic simulation was showed in the article. The compositions of chromium ore of the deposit Rai-Iz and dust of cyclones of the low-carbon ferrochrome in an amount of 0; 5; 10; 20% were used as a components of the system. The carbon was used a reducing agent. The thermodynamic simulation was performed using the HSC Chemistry 6.12 software package developed from Outokumpu, Finland. The thermodynamic characteristics of CrO (II) compound were entered into the software package’s database. The thermochemical data of compounds CaCr₂O₄, Fe₃C, Cr₃C₂, Cr₇C₃, Cr₂3C₆, SiC were refined. The calculations were performed using the “Equilibrium Compositions” module in the temperature range 1500–1700°C at a temperature increment of 100°C, at a total pressure of 0.1 MPa in the system and 2.24 m³ of N₂. It was determined that the increase in the dust amount from 5 to 20% did not affect practically at the reduction degree of chromium which is equal 90.2; 93.4; 94.6% respectively at the temperatures of 1500, 1600 and 1700°C. The chemical composition of the metal is, %: 65.6–65.1 Cr; 22.7–23.2 Fe; 11.5–11.6 C; 0.2–0.26 Si at the temperature of 1700°C. The thermodynamic simulation results can be used to develop technology for producing ferrochrome using wastes of metallurgical production.

1. Introduction

Significant volumes of industrial wastes (slag, dust, sludge, scale, gas) containing iron, manganese, chromium, nickel, calcium and magnesium are formed during various types of metal products (cast iron, steel, ferroalloys). The consumption of mineral raw materials, production costs, environmental pollution will be decrease at involving of wastes in the metallurgical processing [1–4].

The literature contains data about thermodynamic simulation of the reduction process of elements [5–8], a kinetic model of the process [9], using of chromium-containing slags, dusts in the metallurgical process to obtain commercial product are given [10–14].

The authors of [5] were determined possibly products of the reduction carbothermal process elements of the Fe–Cr–O system thermodynamically. It was found that more Fe–Cr–C solution and less residual carbon content are obtained at high temperatures and low nC: nO ratios (the initial molar ratio of C to O in the sample). Metal carbides are formed at the initial stage of the reduction process and Fe–Cr–C solution at the degree of reduction is quite high.

The results of the thermodynamic analysis of the reduction reactions of Cr from Cr₂O₃ (cored wire filler) by carbon in the standard state and under conditions different from the standard ones were carried out in [6]. It was determined that the products of the reduction reactions are carbides
chromium and chromium is formed as a component of the melt in furnace at the temperature of 2227 °C. Chromium oxide Cr₂O₃ has the highest reactivity in the liquid state. Most feasibly direct reduction process by carbon.

The thermodynamics of the interaction of the dust components of the gas purification electric furnace with carbon was studied by the authors of [7] using the Terra software package. It was determined that the metals Fe, Zn, Pb, Na, K, Cu, Cd reduced to the temperature of 1200 °C. Iron has been interacted with carbon at temperatures above 650 °C, forming cementite, and at higher temperatures is in the solid phase in the form of a metal.

In [8], the results of thermodynamic simulation of the reduction process of elements of the composition system, is %: 40 Cr₂O₃; 21 FeO; 15 Al₂O₃; 6 SiO₂; 16 MgO; 2 CaO; 0.006 P₂O₅, silicon ferrosiliconnickel (28% Fe, 65% Si, 7% Ni) are given. The HSC Chemistry 6.12 software package (Outokumpu, Finland) was used for simulation. It was found that the increase in the reduction degree of chromium by 31.1% (from 64 to 95.1%) at an increase in the basicity of slag from 0.07 to 1.86 and when the using degree of silicon at reduction of the elements is 94.5%. The study increasing in the reducing agent consumption from 0.5 to 1.05 m red. at the reduction degree of chromium. The obtained value of 95.1% is close to the industrial indicators of low-carbon ferrochrome production.

The kinetic model of the reduction carbothermal process of chromium oxide from slag during the production of stainless steel was developed and presented in [9]. The minimum values temperatures 1600–1645 °C were determined to obtain a final concentration of chromium oxide in the slag of 0.8–1.2 %. The model can be used to determine the treatment time and temperature.

The technology of durable complex chromium pellets with specified physicochemical characteristics for the smelting of chromium ferroalloys has been developed by the authors of [10]. Charge materials is chrome ore, fine concentrate, slags of refined ferrochrome, coke. The content of 3 % coke in the composition of the charge decrease the firing temperature of pellets from 1350 to 1200 °C for receiving non-metallized pellets without significantly changing the hardware and technological design of the firing process. The chemical composition of the pellets, %: 44 Cr₂O₃; 6.08 Al₂O₃; 18.65 SiO₂; 12.48 FeO; 1.57 CaO; 9.95 MgO; 7.27 – rest. Average strength of the pellets at the firing temperature 1200 °C is 5325 N/pellet.

The technology producing high-carbon ferrochrome using up to 30-70 % of anthracite in the composition of charge materials (P₄=0.016%, S₃=0.15%) as a partial replacement for traditional coke was developed by authors of [11]. Charge materials is chrome ore, metal concentrate, ferrosilicon slag, chrome waste, quartzite fines, chrome briquettes. The extraction coefficient of chromium is 84.4% when using coke and anthracite (30–50 % per serving portion) and 84.7% when using coke and coal.

The manufacture of flux-cored wires based on dust of gas purification of ferrochrome production was considered by authors of [12]. Powders of silicon, aluminum and dust of gas purification aluminum production are used as reducing agents in an amount of at least 27 %. It was determined that the absorption of chromium in the melt is completely dependent on the fill factor of the cored wire.

A overview of solutions for the implementation resource-saving technologies and utilizing technogenic raw materials is given of [13, 14]. The technologies for processing waste of ferroalloy production and substandard raw materials at developments of Russia were described by authors.

The data on measuring the slag viscosity of the CaO–SiO₂–CrO system are presented by authors of [15]; extracting chromium from high-carbon ferrochrome slag by magnetic separation is in [16]; it is using in the preparation of refractory materials, ceramics, and construction is in [17-19], as well as the effect of boron-containing additives on the slag composition of low-carbon ferrochrome is in [20].

The scope of wastes of chrome production at the production of metal products (pellets, ferrochrome, wire) was described in the literature overview and insufficient knowledge of reduction
physicochemical processes of chromium in the \( \text{Cr}_2\text{O}_3–\text{FeO}–\text{CaO}–\text{SiO}_2–\text{MgO}–\text{Al}_2\text{O}_3 \) system was showed.

2. Materials and method

Existing methods of processing waste of the metallurgical industry can reduce the consumption of mineral raw materials, decrease the cost of finished products and improve the environment. Thermodynamic simulation can be to determine the possibility of using waste during obtaining products.

This work is aimed at studying the influence of the cyclone dust additives from the production of low-carbon ferrochrome to chrome ore on the reduction degree of chromium (\( \eta_{\text{Cr}} \)) from the \( \text{Cr}_2\text{O}_3–\text{FeO}–\text{CaO}–\text{SiO}_2–\text{MgO}–\text{Al}_2\text{O}_3 \) system within the temperature range of 1500–1700 °C by the method of thermodynamic simulation.

The chemical oxide compositions of the deposit Rai-Iz and dust cyclones of production low-carbon ferrochrome were used as the initial oxide system for thermodynamic simulation from at various ratios of system components (Table 1). The carbon was used as a reducing agent; its consumption was increased by 10 % of the stoichiometrically necessary for the complete reduction of iron and chromium for the formation of iron and chromium carbides.

| Component of system | \( \text{Cr}_2\text{O}_3 \) | \( \text{FeO} \) | \( \text{CaO} \) | \( \text{SiO}_2 \) | \( \text{MgO} \) | \( \text{Al}_2\text{O}_3 \) | \((\text{CaO+MgO})/(\text{SiO}_2)\) |
|---------------------|----------------|---------|---------|---------|---------|---------|----------------|
| Chrome ore          | 38.0           | 11.0    | 0.2     | 15.0    | 29.8    | 6.0     | 2.0            |
| Dust of cyclones    | 26.5           | 9.1     | 21.2    | 16.5    | 19.2    | 7.5     | 2.5            |
| Ratio ore : dust    |                |         |         |         |         |         |                |
| 95 : 5              | 37.3           | 11.0    | 1.3     | 15.1    | 29.3    | 6.0     | 2.0            |
| 90 : 10             | 36.9           | 10.9    | 2.3     | 15.2    | 28.6    | 6.1     | 2.0            |
| 80 : 20             | 35.7           | 10.6    | 4.4     | 15.3    | 27.7    | 6.3     | 2.1            |

The thermodynamic simulation was performed using the HSC 6.12 Chemistry software package (Outokumpu, Finland). The software, based on minimization of the Gibbs energy and variation principles of thermodynamics [21]. The equilibrium composition of the \( \text{Cr}_2\text{O}_3–\text{FeO}–\text{CaO}–\text{SiO}_2–\text{MgO}–\text{Al}_2\text{O}_3 \) multicomponent oxide system was determined using the “Equilibrium Compositions” software. Initial parameters of thermodynamic simulation are temperature 1500–1700 °C, total pressure of 0.1 MPa and 2.24 m\(^3\) of N\(_2\)\(_{\text{gas}}\) as a neutral additive for the acceleration of the computational procedure of searching for the equilibrium composition. The thermodynamic characteristics of CrO (II) were entered into the database of the HSC Chemistry 6.12 software package and the thermochemical data of the compounds CaCrO\(_4\), Fe\(_3\)C, Cr\(_2\)C\(_2\), Cr\(_7\)C\(_3\), Cr\(_{23}\)C\(_6\), SiC were specified [22].

3. Result and discussion

The dependence of the reduction degree of chromium (\( \eta_{\text{Cr}} \)) on amount of dust cyclones at the temperatures of 1500–1700 °C is shown in figure 1. It was determined that increase the amount of dust in the system to 5% insignificantly decreases the reduction degree of chromium. For example, \( \eta_{\text{Cr}} \) at temperatures of 1500, 1600 and 1700 °C decreased by 0.4; 0.3 and 0.2 %, respectively. This is due to a decreasing in the total \( \text{Cr}_2\text{O}_3 \) content in the system from 38 to 37.3 %.

An increasing in the amount of dust from 5 to 20 % in the system had practically no effect on the reduction degree of chromium. It was amounted to 90.2; 93.4; 94.6 % for temperatures of 1500, 1600 and 1700 °C, respectively. The charge the reduction degree of chromium in the system is caused on the one hand by the increasing slag basicity of \((\text{CaO+MgO})/(\text{SiO}_2)\) from 2 to 2.1, and with another – decreasing concentration of \( \text{Cr}_2\text{O}_3 \) in the system.
The reduction degree of chromium was changed slightly (by 0.2–0.4%) at the decreasing of Cr$_2$O$_3$ by 2.3% in the system as a result of the combined effect of these oppositely influencing factors.

Figure 1. Dependence of the reduction degree of chromium ($\eta_{Cr}$) from the amount of dust at the temperatures of 1500, 1600 and 1700 °C.

The content of chromium in the metal [Cr] decreased slightly from 65.6 to 65.3 % at the temperature of 1700 °C and increasing the amount of dust to 5% (Table 2). Moreover, an increasing the temperature of reduction process of chromium from 1500 to 1700°C increases the chromium content in the metal by 1.4–1.6 % an average for all system compositions.

Table 2. The chemical composition of the metal, %.

| Element | Ratio ore : dust | 0   | 5   | 10  | 20  |
|---------|-----------------|-----|-----|-----|-----|
| Cr      |                 | 65.6| 65.3| 65.2| 65.1|
| Fe      |                 | 22.7| 23.1| 23.1| 23.2|
| C       |                 | 11.5| 11.4| 11.4| 11.6|
| Si      |                 | 0.26| 0.22| 0.21| 0.2 |

The values of the thermodynamic strength of iron and chromium oxides ($\Delta G^{0}_{298.15}$ (FeO) = −244.299 kJ/mol; $\Delta G^{0}_{298.15}$ (Cr$_2$O$_3$) = −1058.966 kJ/mol) [22] are shown that chromium reduction process after iron, that corresponds to the data obtained in of [23–25]. The amount of iron, silicon and carbon in the metal changes slightly.

The melt containing oxides of magnesium, silicon, aluminium, chromium, iron and calcium is formed during reduction carbothermal of chromium. Phases of calcium silicates are formed at an increasing the amount of dust in the system to 20% and its content increases. The amount of magnesium silicates in the system is decreased. The phase composition of the slag is also represented by magnesia spinel, oxides of chromium, magnesium, aluminium and silicon.

4. Conclusions

It was shown that adding to the chromium ore up to 20% more poorer dust Cr$_2$O$_3$ content slightly decreases the reduction degree and the content of chromium in ferrochrome. The results of
thermodynamic simulation can be used to develop a technology for producing ferrochrome from chrome ore using wastes of metallurgical production.

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