RESEARCH PAPER

THEORY AND TECHNOLOGY OF MANUFACTURING A FERROALLOY FROM CARBON FERROCHROME DUSTS

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ABSTRACT

The article contains the research results of obtaining a ferroalloy from a carbon ferrochrome dust containing 30.2% of Cr2O3, 23.4% of SiO2, 32.7% of MgO, 5.0% of FeO, 1.6% of CaO, 4.5% of Al2O3, 2.3% of C, and 0.3% - others. The studies were carried out by a thermodynamic modeling method using the HSC-6.0 software package (Outokumpu) based on the principle of the Gibbs energy minimum, the Box-Hunter rotatable planning technique and electric melting of the dust in an arc furnace. It was found that the interaction of the dust with carbon under equilibrium conditions and in the presence of iron leads to formation of Cr4C (T>1000°C), Cr3C2, Cr7C3, Cr (T>1100°C), FeSi (T>1300°C), SiC (T>1400°C), SiO2 and Si (T>1500°C). In the temperature range of 1745-1900°C and in the presence of 18-34% of carbon and 8% of iron of the dust mass, the resulting ferroalloy contained 18.5-25.2% of Si and 46.8-49.4% of Cr (in this case the silicon extraction degree into the alloy was 60.0-64.4%, the chromium one – 99.8%). When the electrosmelting the granulated dust together with coke and steel shavings, the chromium extraction degree into the alloy was 95.0-99.4%, the silicon one – 53.7-57.0%; the obtained ferroalloys containing 18.3-21.9% of silicon and 45.6-53.6% of chromium meet the requirements to FeCrSi23-grade ferrosilicochromium.

Keywords: ferroalloy, dust, carbon ferrochrome, electrosmelting, ferrosilicochromium, thermodynamic

INTRODUCTION

Kazakhstan is one of the largest producers of ferrochrome in the world (13% of world production) [1]. The share of ferrochrome in Kazakhstan accounts for 86.8% (2019) of the total production of ferroalloys in the country [2].

The ferroalloy production is characterized by dust formation [3]. The quantity and chemical composition of the dust depend on the alloy type, its production technology, the electric furnace design and power, the furnace bath temperature, pressure in the under-roof furnace space, the electrode arrangement, the electrical regime (in particular, for each ferroalloy, there is a limit value for the phase voltage, the excess of which leads to a sharp increase in the dust content in the furnace gases), as well as on the heat resistance of the ore and reducing [4]. Dust in the ferroalloy furnaces is formed as a result of mechanical entrainment of raw material components and due to sublimation of metals, their oxides and sulfides. The specific dust yield also depends on the furnace design [4,5]. The dust yield at the smelting carbon ferrochrome ranges from 12 kg to 150 kg [5-8] per 1 tonne of the alloy. The dust contains 10-15% of SiO2, 15-43.6% of Cr2O3, 13-33% of MgO, 3-8% of Al2O3, 0.2-4.5% of CaO, 4-6% of FeO, 1-1.2% of S, up to 6.2% of C.

The dust formed during the producing ferrochrome in electric arc furnaces contains various metals, such as chromium, zinc, iron, aluminum and magnesium. Some of these metals, for example chromium (VI), pose a threat to the environment and human life because of their toxicity [9]. Various studies have been conducted on the extraction of metals from dust, for example, the possibility of using vermiculite to remove Cr(VI) from fine-dispersed ferrochrome dust after its leaching in an aqueous solution [10], as well as the separation of chromium from industrial dusts by water ozonation [11]. To extract zinc from the ferrochrome dust collected in bag filters, a two-stage leaching procedure is proposed, which allows extracting zinc by 71.2% [12]. A hydrometallurgical method on the processing of carbon ferrochrome dust was suggested, which allows to obtain a chromium concentrate, followed by obtaining chromium metal by aluminothermic reduction [6]. The paper [13] describes the results of electric melting of high-carbon ferrochrome dusts (Aktobe Ferroalloy Plant, Aktobe, Kazakhstan) in a direct current arc furnace (DCAF-1). The recovery of chromium to chromium metal was 89.5%. The resulting alloy contained (wt.,%): Cr – 70.98; Fe-20.27; C – 8.09; Si – 0.61; S – 0.03; P – 0.02.

A research related to studying the possibility of using ferrochrome dust for production of concrete (partial replacement for conventional Portland cement) show that the addition of up to 40% of the dust and 7% of lime does not affect the properties of concrete (does not worsen or improve it) [14]. Due to its high fire resistance, the ferrochrome production dust can be used for manufacture of refractory materials [16], such as refractory bricks [17]. In order to recycle the waste formed at the production of high-carbon ferrochrome at the Aktobe Ferroalloy Plant, Kazakhstan, it is proposed to conduct a study on the possibility of using the dust in the production of concrete.
Plant, it is proposed to apply the bag filter dust to produce refractory materials for furnace lining [18]. The carbon ferrochrome dust is also used as a binder for the pelletizing chromium-containing ores (50% of the dust and 12% of a commonly used binder) [4, 19, 20] as well as at the manufacturing a refractory chromium oxide containing concentrate (95.8% of Cr₂O₃) [8]. In contrast to the well-known works, we suggest to use the carbon ferrochrome dust to produce high-quality ferroalloys containing Cr, Si and Fe.

MATERIAL AND METHODS

Subtitle of material and methods

The research was carried out using a thermodynamic modeling technique and experimental electric melting of the dust in a laboratory ore-thermal arc furnace. The thermodynamic modeling was performed using the HSC-6.0 software package (Outokumpu) [21], based on the minimum Gibbs energy principle. To calculate the equilibrium distribution degree of the dust elements (\( α_{el} \)), we developed an algorithm [22]. According to the algorithm, using the data about the quantitative distribution of substances obtained by means of an Equilibrium Composition module of the HSC-6.0 software package, the equilibrium distribution degree of elements (\( α_{el} \)) is determined as a ratio of the mass of an element (kg) in the product (\( G_{el(pr)} \)) to the mass of the element (kg) in the initial system (\( G_{el(init)} \)) under the formula:

\[
α_{el} = \frac{G_{el(pr)}}{G_{el(init)}} \times 100
\]  
(1)

The mass of an element in the initial mixture (\( G_{el(init)} \), kg) was calculated by the following way:

\[
G_{el} = \frac{x \times A_{el} \times G_{i}}{M_{j}}
\]  
(2)

where \( A_{el} \) — atomic mass of an element; \( M_{j} \) — molecular weight of the initial substance; \( G_{i} \) — mass of the initial substance, kg; \( x \) — the number of kilo-atoms of an element in the initial substance.

The mass of an element in the products (\( G_{el(pr)} \), kg) was calculated using the formula:

\[
G_{el(pr)} = \frac{n \times A_{el} \times G_{i}}{M_{j} \times r}
\]  
(3)

where \( A_{el} \) — atomic mass of an element; \( M_{j} \) — molecular weight of the product; \( G_{i} \) — mass of the product, kg; \( n \) — the number of kilo-atoms of an element in the product.

After determination of \( G_{el(pr)} \) and \( G_{el(init)} \) the elements’ equilibrium distribution degree was calculated under the formula (3). In addition, the effect of temperature and carbon amount on the formation of a ferroalloy and the silicon and chromium content in the resulting ferroalloy were determined.

The experimental installation is shown in figure 1. Electric melting of a charge was carried out in a single-electrode arc furnace lined with chrome-magnesite bricks. The hearth electrode was made of a graphite block. A graphite crucible (\( d = 6 \) cm, \( h = 12 \) cm) was placed on the hearth. The space between the crucible and the lining was filled with graphite chips. The upper part of the furnace was closed with a removable cover with holes for the graphite electrode (\( d = 3 \) cm) and the gas outlet.

1 – furnace casing; 2 – chrome-magnesite lining; 3 – carbon graphite plate; 4 – graphite crucible; 5 – fine-crushed graphite; 6 – TAFH-1002 transformer; 7 – graphite electrode; 8 – lower current supply; 9-12 – ammeters and voltmeters; 13 – electrode movement mechanism; 14 – flexible part of a short network; 15 – furnace cover; 1 – general view; II – scheme of the furnace

Fig. 1 A laboratory single-electrode arc furnace

Before the melting, the crucible was heated with electric arc for 20-25 minutes at amperage of 250-300A and voltage of 45-55V. A part of a charge (200-230 g) was loaded in the heated crucible. It was melted for 3-5 minutes, and then the remaining part of the charge (200-250 g) was loaded in the crucible and melted for the required time. The current during the melting was 350-450A and the voltage was 25-30V. Electricity to the furnace was supplied through a TAFH-1002 transformer. The required power was maintained by means of a thyristor regulator. The amperage was monitored by a Tangen 42L6 ammeter (the accuracy class is 1.5), and the voltage by a Chint 42L6 voltmeter (the accuracy class is 1.5). After termination of the electric melting, the furnace was cooled for 6 hours. Then the graphite crucible was taken out of the furnace and broken. The alloy was weighed and analyzed using a scanning electron microscope to determine the metals and carbon content. The coke before the charging was crushed to a fraction of 0.5-1.5 cm and dried at 120°C. The dried components were pelletized in a plate-type granulator in the presence of a binder (bentonite clay). The pellets (\( d = 1 \) cm), dried at 120-140°C, had the strength of 5-7 kg per a pellet and withstood 5 drops from a height of 1 m.

According to the data of the test chemical laboratory of the Aktove Ferroalloy Plant (a branch of JSC “TNC Kazchrome”), the ferroalloy dust contains 21-35% of Cr₂O₃, 6-20% of SiO₂, 14-31% of MgO, 3.7-5.7% of Al₂O₃, 7-9% of FeO, 0.6-7.4% of CaO, 3-6% of C, 0.3-1% of S. During the experiments we used the dust containing 30.2% of Cr₂O₃, 23.4% of SiO₂, 32.7% of MgO, 5.0% of FeO, 1.6% of CaO, 4.5% of Al₂O₃, 2.3% of C, 0.3% of others, as well as coke (85.7% of C, 5.2% of SiO₂, 2.1% of FeO, 2.0% of Al₂O₃, 1.6% of CaO, 0.4% of MgO, 0.8% of H₂O, 5.0% of FeO) and steel shavings (2.1% of C, 0.4% of S, 97.1% of Fe, 0.4% of others).

RESULTS AND DISCUSSION

Subtitle of results and discussion

The effect of carbon and temperature on the quantitative (kg) distribution of substances containing chromium and silicon at the interaction of the dust formed at the manufacturing ferrochromium (hereinafter referred to as dust) with carbon (18%) of the dust mass in the presence of iron (8%) of the dust mass is represented in figure 2.

As follows from the figure, the reduction products in the system under consideration are chromium carbide, chromium, iron silicide, iron monoxide, silicon and calcium carbide, which begin to form at the following temperatures: C – 1000°C, Cr₂C₃, CrC₂ and Cr – 1100°C, FeSi – 1300°C, SiC – 1400°C, SiO₂

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and Si – 1500 °C. Chromium is completely reduced at 1400 °C, and silicon at 2100 °C.

Figure 3 shows the effect of temperature (from 1400 to 1900 °C) and amount of carbon (18% and 34% of the dust mass) on the equilibrium silicon transition degree (αSi) and chromium and silicon content in the resulting alloy (CαSi, Crα, %). It can be seen that a high αSi (>55%) is at the temperature of more than 1700-1800 °C. An increase in the carbon amount from 18 to 34% increases αSi from 55 to 61% (at 1800 °C). At the constant carbon quantity (18 or 34%) an increase in the temperature from 1400 to 1800 °C leads to an increase in the silicon extraction degree into the alloy and the silicon concentration in it. In this case, the chromium concentration in the alloy decreases.

Based on the table data and using [23], the following adequate regression equations were obtained:

\[ \text{αSi}=1197.08+1.274\text{T}+4.245\text{C}-3.2\times10^{-4}\text{T}^2+1.539\times10^{-5}\text{C}^2-2.56\times10^{-8}\text{T}\text{C} \] (4.)

\[ \text{C}_{\text{αSi}}=477.76+0.56\text{T}-1.957\text{C}-1.59\times10^{-4}\text{T}^2+1.17\times10^{-7}\text{C}^2+1.24\times10^{-3}\text{T}\text{C} \] (5.)

\[ \text{C}_{\text{Cr}}=60.608+1.49\times10^{-3}\text{T}-0.993\text{C}-6.76\times10^{-6}\text{T}^2+1.77\times10^{-5}\text{C}^2-1.24\times10^{-7}\text{T}\text{C} \] (6.)

On the basis of the regression equations and according to the method [24], three-dimensional and planar images of the temperature and carbon effect on αSi, CαSi, CCr were constructed (figure 5).

The pattern of temperature and carbon amount effect on αSi, CαSi and CCr (table 1) was obtained on the basis of the data of figure 3 and the results of the additional study conducted by a planning method [23].

| № | Code kind | Natural kind | T, °C | CαSi, % | CCr, % | CCr, % |
|---|---|---|---|---|---|---|
| 1 | +1 | +1 | 31.7 | 1856 | 62.6 | 21.0 |
| 2 | -1 | +1 | 20.3 | 1856 | 59.1 | 20.8 |
| 3 | +1 | -1 | 31.7 | 1644 | 48.0 | 15.9 |
| 4 | -1 | -1 | 20.3 | 1644 | 38.3 | 13.0 |
| 5 | +1.41 | 0 | 34 | 1750 | 60.2 | 22.0 |
| 6 | -1.41 | 0 | 18 | 1750 | 51.6 | 17.4 |
| 7 | 0 | +1.41 | 26 | 1900 | 60.9 | 20.8 |
| 8 | 0 | -1.41 | 26 | 1600 | 34.5 | 11.1 |
| 9 | 0 | 0 | 26 | 1750 | 55.0 | 19.9 |
| 10 | 0 | 0 | 26 | 1750 | 54.2 | 20.3 |
| 11 | 0 | 0 | 26 | 1750 | 55.6 | 19.5 |
| 12 | 0 | 0 | 26 | 1750 | 54.8 | 19.7 |
| 13 | 0 | 0 | 26 | 1750 | 55.4 | 20.1 |

Fig. 2 Temperature effect on the quantitative distribution of chromium (I) and silicon (II) containing substances in a system of dust – C – Fe

I – 18% of carbon; II – 34% of carbon

Fig. 3 The temperature and carbon amount effect on αSi, CαSi and CCr

The chromium concentration achieves its maximum value of 59.8% at 1400 °C and 18-34% of carbon; the maximum silicon content is 16.4-23.0% at 1800-1900 °C and 34% of carbon. The change in the concentration of elemental chromium and its carbides is shown in figure 4. As follows from figure 4, an increase in the temperature from 1400 to 1900 °C changes the concentration of chromium-containing substances. So, if at 1400 °C and 18% of carbon C_{Cr} < C_{Cr} < C_{Cr} > C_{Cr} > C_{Cr} > C_{Cr}, then at 1800 °C C_{Cr} > C_{Cr} > C_{Cr} > C_{Cr} > C_{Cr} > C_{Cr}. At 34% of carbon and 1800 °C the sequence of changes in the concentrations is different – C_{Cr} > C_{Cr} > C_{Cr} > C_{Cr} > C_{Cr}.

Fig. 4 The temperature and carbon amount effect on the concentration of chromium and its carbides in the ferroalloy

I – 18% of carbon; II – 34% of carbon

Fig. 5 A planning matrix and indicators of temperature (T, °C) and carbon (C, %) influence on the silicon transition degree and the silicon and chromium concentrations in the alloy
Judging by the figures, aSi is from 60 to 63.0% for the temperature range of 1745-1900 °C and the carbon amount of 18-34% (the shaded area of figure 5 I, B). C is from 20 to 23.2% at 1710-1900 °C and 19.8-34% of carbon. As follows from figure 5 (II, B), the chromium concentration of ≥50% in the alloy is at 18-24.3% of carbon in the temperature interval of 1600-1830 °C. At the higher temperature (1900 °C) and 34% carbon content, the chromium concentration in the alloy decreases to 46.6%.

Figure 6 represents the combined information about the temperature and carbon influence on the technological parameters of the dust processing, provided that aSi is more than 60%.

The process parameters for the boundary points of the abcd area, where aSi≥60%, are shown in table 2.

Table 2 The process technological parameters in the boundary points

| Point in fig. 5 | T, °C | Carbon, % | aSi, % | Cš, % | CCr, % | Alloy grade |
|----------------|------|-----------|--------|------|--------|-------------|
| a              | 1880 | 18        | 60.0   | 18.7 | 49.4   | FeCrSi23    |
| b              | 1745 | 34        | 60.0   | 21.9 | 47.4   |             |
| c              | 1900 | 34        | 64.4   | 25.2 | 46.8   |             |
| d              | 1900 | 18        | 60.6   | 18.5 | 49.2   |             |

The data of table 2 show that in the equilibrium conditions at 1745-1900 °C and 18-34% of carbon (aSi is 60-64, 4%), the resulting ferroalloy containing 18.7-25.2% of silicon and 46.8-49.4% of chromium corresponds to the FeCrSi23 grade ferrosilicochrome [25].

The results of electric melting of the charge consisting of the dust, coke and steel shavings (8% of the dust mass) are shown in table 3. Photos of several alloys and the content of elements in them are shown in figures 7-8.

Table 3 Resultsof electric melting of ferrochrome dusts

| Experiment # | Carbon, % of the dust mass | aSi, % | aCr, % | Cš, % | CCr, % |
|--------------|----------------------------|--------|--------|------|--------|
| 1            | 20                         | 53.7   | 96.8   | 22.6 | 41.26  |
| 2            | 24                         | 54.6   | 98.9   | 21.9 | 45.6   |
| 3            | 28                         | 53.9   | 99.3   | 19.5 | 49.9   |
| 4            | 32                         | 55.8   | 98.5   | 18.4 | 53.0   |
| 5            | 36                         | 57.0   | 99.4   | 18.3 | 53.6   |

Fig. 6 Temperature and carbon amount effect on the technological parameters of processing the ferrosilicochrome dusts

The process technological parameters in the boundary points

Fig. 7 Photographs of the resulting ferroalloys

Fig. 8 Energy-dispersion spectra and elemental composition of the alloys composition made by the scanning electron microscope

The ferroalloys produced (alloys 2-5) in accordance with [25] belong to ferrosilicochrome of the FeCrSi23 grade, for which the chromium concentration is ≥45%, and the silicon content is in the interval of 18-28%.

CONCLUSION

The results obtained at the processing of the dusts formed at the manufacturing carbon-containing ferrochrome allowed to draw the following conclusions:

1. In the equilibrium conditions:
   - interaction of the dusts with carbon in the presence of iron occurs with the formation of CrC (T>1000 °C), CrC2, CrC3, C (T>1100 °C), FeSi (T>1300 °C), SiC (T>1400 °C), SiO2 and Si (T>1500 °C);
   - an increase in the amount of carbon from 18 to 34% of the dust mass leads to an increase in the silicon and chromium transition degree into the alloy and the silicon concentration in the alloy;
   - in the temperature interval of 1745-1900 °C and in the presence of 18-34% of carbon and 8% of iron of the dust mass, a ferroalloy is produced, which contains 18.5-25.2% of Si and 46.8-49.4% of Cr (the silicon extraction degree in the alloy is 60.0-64.4%, one for Cr is 99.8% and more).

2. When the electro smelting the granulated dust together with coke and steel shavings, the extraction degrees of chromium and silicon were 98.5-99.4% and 53.7-57.0%, respectively; the resulting ferroalloys containing 18.3-21.9% of silicon and 45.6-53.6% of chromium corresponds to ferrosilicochrome of FeCrSi23 grade.
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