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Impurities removal from high carbon ferrochromium by treatment with slag mixtures

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The purpose of the given research was to investigate the possibility of high-carbon ferrochromium refining to remove harmful impurities as a result of metal treatment by slag mixtures on the basis of the CaO-MgO-SiO_2 system. The final conclusions were drawn from experimental results.

It was shown that the treatment of high-carbon ferrochromium by SiO_2-MgO-CaO slag mixtures with additions of chromium sinter or iron-ore concentrate removes carbon, sulphur and phosphorus from the metal. A mechanism of phosphorus removal from a melt to a gas phase is proposed.

Introduction

Productions of high-carbon ferrochrome take place in submit arc furnaces and can be represented as a reduction of ores materials by coke. As a result of the reduction process the metal contains about 8% of carbon and 1–4% of silicon. Besides depending on the quality of initial materials, the metal can have heightened impurity levels: titanium, phosphorus, sulphur, etc. Some customers require very low concentrations of impurities. However, there is no industrial technology for removing these elements from metal. For that reason a possibility of metal refining is of great importance from theoretical and practical points of view.

The purpose of the given research is the experimental investigation of the possible refining of high-carbon ferrochromium from harmful impurities as a result of metal treatment by slag mixtures on the basis of the CaO-MgO-SiO_2 system.

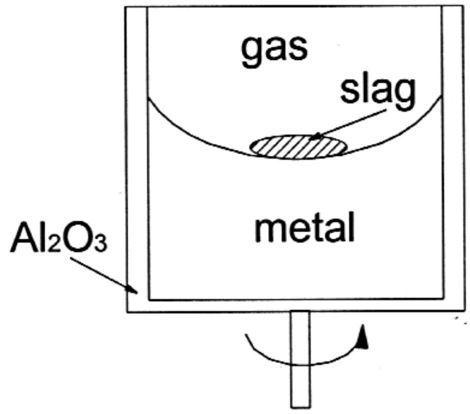

Figure 1. Scheme of the experiments

Experimental technique

Experiments to study metal refining by slag were carried out in a resistance furnace with a graphite heating element. Rotation (about 180–200 rev/min) of the crucible with the metal and slag was applied to accelerate the equilibrium between different phases. A flowing argon atmosphere was created inside the furnace. Expenditure of argon was about 0.5 *l*/min. 180 g of metal and 12.6 g (without the ore component) of slag was equilibrated in each test. Experiments were carried out in alumina crucibles.

Metal was supplied by Elkem Rana (chemical composition presented in Table I). The treatment of metal was carried out by synthetic master slag ($CaO(30\%)$-$MgO(30\%)$-$SiO_2(40\%)$) with the addition of 2.52 g of chromium sinter (Table II) or pellets made from iron-ore concentrate (Table III). Master slag was premelted from pure components (CaO, MgO and SiO_2) in an alumina crucible and quenched in air by spilling it on a massive metal plate. Initial oxide reagents were preheated in an air at 1273 K before premelting of the master slag. Obtained slag was crushed into pieces the size of 0.5 -1.0 cm. These were used as additions in the experiments.

The initial metal was placed in an alumina crucible and heated up to 1620–1650°C. The temperature was measured by a W/W-Re thermocouple immersed in a melt in an alumina protective cap. After reaching the required temperature the thermocouple was taken out from the melt and the rotation of crucible was started. The metal melt was kept at the temperature of the experiment for 20 minutes with simultaneous rotation. Further master slag and ores components were placed in a crucible. Metal and slag were equilibrated at 1600°C for 10, 20, 30 or 40 minutes. After the furnace was switched off, it was cooled down in an argon atmosphere. After cooling, the slag and metal were carefully separated from each other and from the material of the crucible and their samples were chemically analysed.

Table I
Chemical composition of ferrochromium (Elkem Rana)

Si	Mn	P	S	C	Cr	Ni	Ti	V	Fe	Total
0,95	0,17	0,016	0,055	7,6	58,08	0,32	0,085	0,15	34,2	101,626
0,93	0,17	0,016	0,054	7,48	57,15	0,31	0,084	0,15	33,65	100

Table II
Chemical composition of chromium sinter

Cr_2O_3	FeO	SiO_2	MgO	Al_2O_3	CaO	TiO_2	P_2O_5	Total
43,1	17,24	8,4	16	10,7	1,14	0,27	0,02	96,87
44,49	17,80	8,67	16,52	11,05	1,18	0,28	0,02	100

Table III
Chemical composition of iron ore concentrate

Fe_2O_3	FeO	SiO_2	MgO	Al_2O_3	K_2O	Na_2O	P_2O_5	Total
97,64	1,04	1,07	0,04	0,05	0,06	0,05	0,005	100

Experimental results

The results of the metal and slag chemical analysis obtained in the experiments with chromium sinter and with iron ore concentrate pellets are graphically presented in Figure.2. As was expected from the results of preliminary calculations the given slag system promotes strong removal of sulphur and does not have any influence on the behaviour of titanium. The degree of desulphurization was about of 60%. On the other hand, the present conditions make it possible undoubtedly to decrease the concentration of phosphorus in a melt. For example, the concentration of phosphorus has decreased from 0.0166 to 0.0143% (degree of dephosphorization approximately 15%) after treatment of metal by slag with chromium sinter for 30 minutes. A similar treatment of metal by slag with an iron-ore concentrate decreases phosphorus by up to 0.0101% (degree of dephosphorization about 40%).

Discussion of phosphorus behaviour in the metal

Currently there is no scientifically justified theory and especially complete industrial technology that allows the removal of phosphorus from chromium containing melts. It is well known that phosphorus cannot be removed from metal to the slag. It is confirmed by the results of slag analysis after our experiments. The removal of phosphorus from a metal by vaporization process is theoretically impossible because it has a very low partial pressure above the melt.

From our point of view the removal of phosphorus is carried out in a gas phase by the following reactions:

$$[P] + 1/2O_2 = (PO)$$
$$(PO) = \{PO\}$$

or the total reaction is:

$$[P] + 1/2O_2 = \{PO\} \qquad [1]$$

$$K = \frac{P_{PO}}{[P] \cdot P_{O_2}^{1/2}} \qquad [2]$$

The P_{O_2} of a system on the metal-slag interface for a carbon saturated metal is strictly defined and fixed by equilibrium with carbon. Then at a given temperature:

$$K_P = K \cdot P_{O_2}^{1/2} = \frac{P_{PO}}{[P]} = \frac{0,0018}{0,0166} = 0,1084 \qquad [3]$$

P_{PO}=0,0018—obtained by simulation of the process with the use of the computer program 'Terra'.

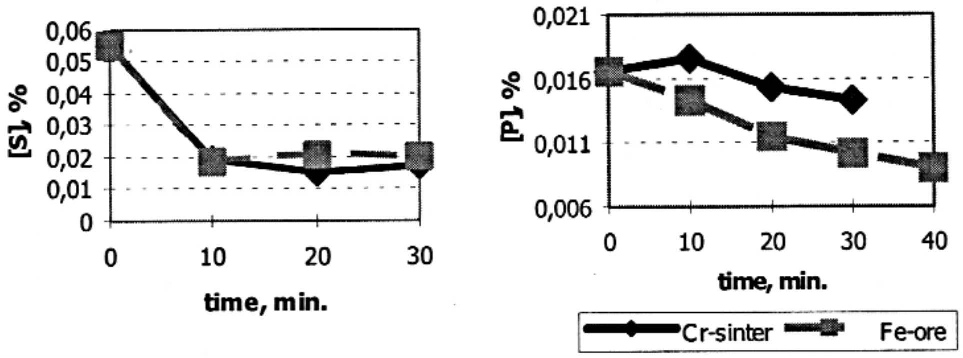

Figure 2. Kinetic curves of changing the metal composition

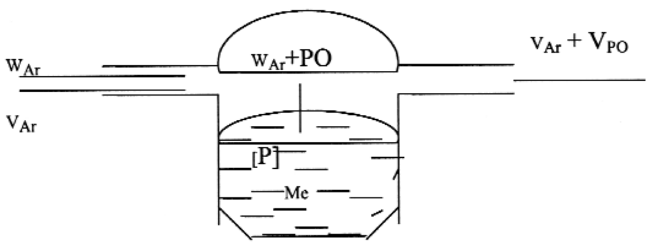

Figure 4. Scheme of phosphorus removal from a metal

The principal scheme of phosphorus removal is presented in Figure 4.

With the help of a material balance of conducted experiments we shall try to evaluate the dependence between run time and the degree of dephosphorization.

The total pressure in the system is 1 atm. It is the result of argon pressure (P_{Ar}) and PO pressure (P_{PO}).

$$P_{total} = P_{Ar} + P_{PO} \qquad [4]$$

$$P_{total} = 1 \ \ atm$$

The rate of argon flow:

$$dV_{Ar} = W_{Ar} \cdot dt \qquad [5]$$

Total rate of flow:

$$dV = dV_{Ar} + dV_{PO} \qquad [6]$$

where, dV_{Ar}—rate of argon flow; dV_{PO}—rate of PO flow.

Let us express the rate of argon flow, dV_{Ar}, through argon pressure, P_{Ar}:

$$dV_{Ar} = P_{Ar} \cdot dV \qquad [7]$$

Similarly for the rate of PO flow:

$$dV_{PO} = P_{PO} \cdot dV \qquad [8]$$

or

$$dV = dV_{PO} / P_{PO} \qquad [9]$$

So for 1 mole of any gas at normal conditions (1 atm and 293 K) with a volume of 22420 cm^3, the rate of PO flow can be presented as:

$$dV_{PO} = -\frac{m \cdot 22420}{100 \cdot n \cdot \mu_P} \cdot d[\%P] \qquad [10]$$

where, *m*—mass of metal, *m*=180 g; *n*—the number of atoms of a gas-making element (P) in a gas molecule (PO), *n*=1; μ_P—atomic weight of a gas-making element (P), μ_P=30.974.

The ‘minus’ in the right part of Equation [10] is an indication of the decrease of analyzed element in a substance at the transferred to the gas phase.

From Equations [5], [6] and [9]:

$$dV_{PO} / P_{PO} - dV_{PO} = W_{Ar} \cdot dt \qquad [11]$$

After substitution of [10] to [11]:

$$\begin{aligned} W_{Ar} \cdot dt &= -\left(\left(1 - P_{PO}\right) / P_{PO}\right) \\ &\cdot 22420 / 30.974 \cdot M_{Me} / 100 \cdot d[P] \end{aligned} \qquad [12]$$

From here:

$$\begin{aligned} -\left(\left(1 - P_{PO}\right) / P_{PO}\right) \cdot d[P] = (100 \cdot 30.974 \cdot W_{Ar}) / \\ \left(22420 \cdot M_{me}\right) \cdot dt \end{aligned} \qquad [13]$$

and after integration of the given expression:

$$\begin{aligned} \int_{[P]init.}^{[P]fin.} d\,[P] - \int_{[P]init.}^{[P]fin.} \frac{1}{K_P \cdot [P]} \cdot d[P] \\ = \int_0^t \frac{100 \cdot 30.974 \cdot W_{Ar}}{22420 \cdot M_{Me}} \cdot dt \end{aligned} \qquad [14]$$

will observe:

$$\begin{aligned} &-[P]_{init.} + [P]_{fin.} - 1\mathrm{n}[P]_{fin.} / Kp + 1\mathrm{n}[P]_{init.} \\ &Kp = \left(100 \cdot 30.974 \cdot W_{Ar}\right) / \left(22420 \cdot M_{Me}\right) \cdot t \end{aligned} \qquad [15]$$

From [15] the time necessary for reaching the final phosphorus concentration in the metal is as follows:

$$\begin{aligned} t = \left[[P]_{fin.} - \frac{1}{K_P} \cdot 1\mathrm{n}[P]_{fin.} - [P]_{init.} + \frac{1}{K_P} \cdot 1\mathrm{n}[P]_{init.}\right] \\ \cdot \frac{22420 \cdot M_{Me}}{30.974 \cdot 100 \cdot W_{Ar}} \end{aligned} \qquad [16]$$

Figures 5 and 6 show the experimental data. Concentration of phosphorus in a melt decreases as a result of metal treatment by slag mixtures with chromium sinter or iron-ore concentrate, accordingly. It is clear that increasing treatment time increases the degree of melt dephosphorization. The dotted lines represent the average experimental data.

Then, after substitution of experimental values (initial and final concentration of phosphorus, expenditure of argon, WAr=200 ñì^3/min, mass of metal) and equilibrium constant to Equation [16] we will observe the dependence of the final phosphorus concentration in the melt (or degree of dephosphorization) on the treatment time of metal by slag. The results of the calculations are presented in Figure 7.

From the calculated data introduced in a Figure 7, follows that the decreasing of phosphorus contents in metal by 40% is a result of metal treatment by slag with an iron-ore concentrate for about 30 minutes. The short treatment of metal by slag with chromium sinter results in some increasing of the phosphorus content. Probably it is connected to the high content of phosphorus in sinter. After 10 min the rate of metal dephosphorization is the same as treatment by slag with iron-ore concentrate. In other words, the dephosphorization of metal begins with a higher initial concentration of phosphorus.

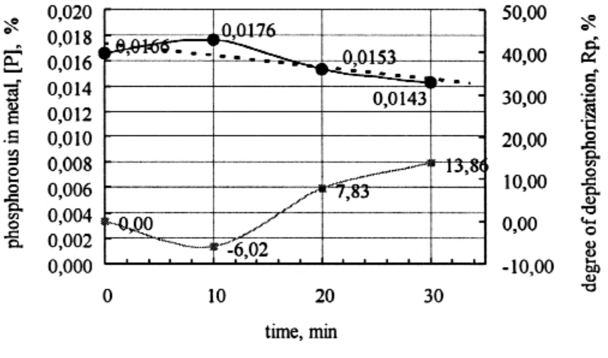

Figure 5. Concentration of phosphorus in metal and degree of dephosphorization depending on run time of melt treatment by slag mixture with chromium sinter

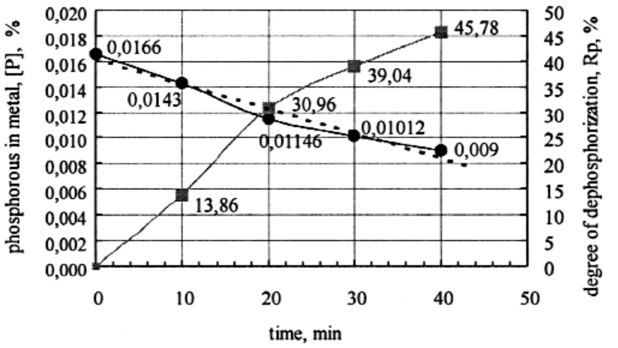

Figure 6. Concentration of phosphorus in metal and degree of dephosphorization depending on run time of melt treatment by slag mixture with iron-ore concentrate

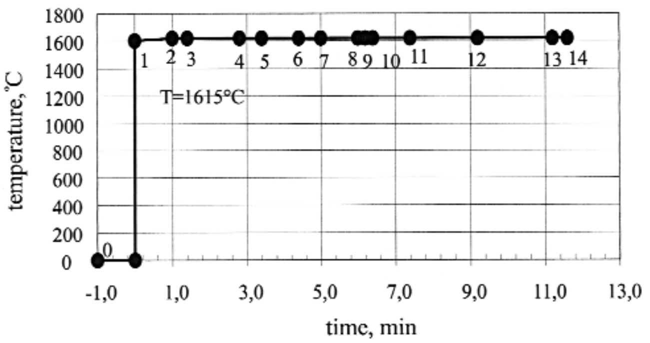

Figure 8. Procedures during the test in induction furnace

Legend:

0-1 Heating of metal in an argon
1. Blowing by argon
2. Sampling of initial metal
3. Sampling of a metal No 1
4. Addition of the first slag portion
5. Addition of the second slag portion
6. End of a slag additions
7. Liquid slag
8. Sampling of a metal No 2
9. Sampling of a metal No 3
10 Addition of a coke
11. Boiling of liquid slag
12. Sampling of a metal No 4
13. Sampling of a metal No 5
14. Tapping of a metal from the furnace

According to the proposed theory, phosphorus first leaves the metal to the slag. Further phosphorus leaves the slag to a gas phase. Thus removal of phosphorus from metal occurs in the two steps at the stable oxygen potential of the system. An additional experiment was executed for confirmation of the proposed scheme of phosphorus removal. 1 917 g of high carbon ferrochromium was melted down in an induction furnace. After the metal was melted, 102 g of slag of the CaO-MgO-SiO_2 system was added to the surface of the metal. The main purpose of the introduced slag is as a protection of metal from an oxidizing atmosphere inside the furnace. In addition, the surface of the melt was breezed by argon. The expenditure of argon was W_{Ar}=200 cm^3/min. In the given system PO_2 maintained fixed. For this purpose after reaching the necessary temperature, t=1615°C, a certain calculated amount of coke (15 g) was added to the slag. The procedures during the test are presented in a Figure 8.

The dependence of the degree of dephosphorization on the time of metal treatment by slag can be calculated from Equation [16]. The results of the calculations and experimental values are presented in Figure 9. Due to the insignificant changing of phosphorus during the test, in Figure 9 initial and final concentrations of phosphorous only are presented.

The phosphorus content in metal is reduced very poorly on 0.004% (from 0.0166% up to 0.0162%) at an expenditure of argon of 200 cm^3/min. The obtained experimental value completely coincides with the expected calculation. For more successful removal of phosphorus from metal it is necessary to have much more expenditure of argon. So for the removal of phosphorus by 40% from 1 917 g of metal for 11.6 min, the expenditure of argon must be 4 500 cm^3/min.

Conclusions

1. The preliminary experiments have shown that as a result of high-carbon ferrochromium treatment by SiO_2-MgO-CaO slag mixtures with additions of chromium sinter or iron-ore concentrate, the removal of carbon, sulphur and phosphorus from metal is possible.
2. The mechanism of phosphorus removal from a melt to a gas phase is proposed.

Acknowledgment

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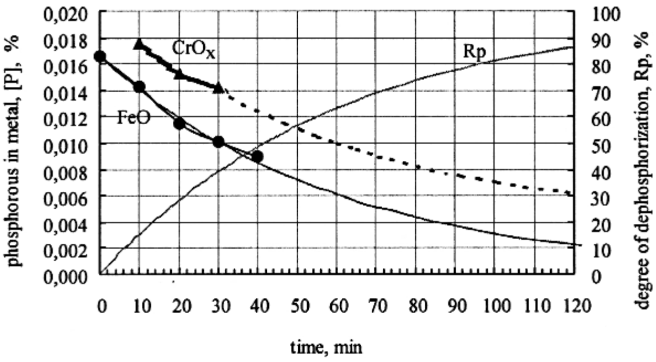

Figure 7. Degree of dephosphorization of high carbon ferrochromium by slag mixtures with chromium sinter or iron-ore concentrate (calculated values)

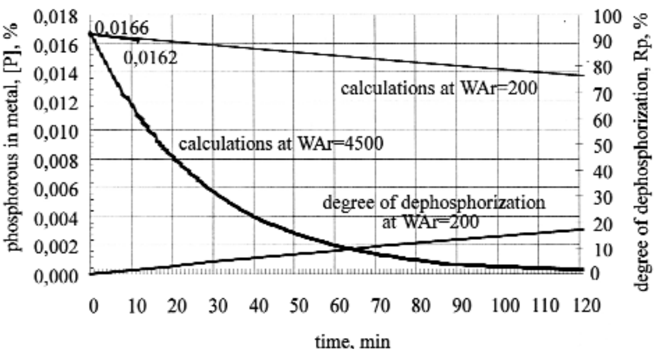

Figure 9. Changing of phosphorus concentration in the metal (experimental and calculated data for conditions in an induction furnace)