STUDING OF OPPORTUNITIES PRODUCTION FERROALUMINUM SILICON FROM NEPHELINE ORE

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ABSTRACT

Has been studied thermodynamic peculiarities metallurgical system "metal - slag" in reducing melting of nepheline ore. Also has been researched influence additions of lime on the slog viscosity properties and reducing silicon and aluminum oxides. Is offered technological scheme receiving ferroaluminum silicon with nepheline ore.

KEYWORDS

Heat, slag, silicon, aluminium, reduction, thermodynamic characteristics, fraction, alumina.

There are considerable resources of nepheline syenit (the aluminum containing ore) on the territory of Ukraine. But those resources mostly remain unclaimed by the domestic metallurgical industry in present.

The aim of this research work is clearing-up the possibility in principle to involve nepheline ore from Mazurovsky deposit into aluminum-silicon ferroalloys production.

Existing technology of thermal-electric reducing melt of alumina-silicate alloys sets up number of limiting claims for the charge materials [1]. One of them is low content of potassium and sodium oxides in a charge. Nepheline, obtained by enrichment of ore from the Mazurovsky ore deposit, contains upon the average $Al_2O_3 - 30$ %, $SiO_2 - 45$ %, $Fe_2O_3 - 4$ %, $Na_2O - 15$ %, $K_2O - 6$ %. It does not meet mentioned condition. In addition, ratio between silica and alumina in the nepheline is higher than 2:1. It does not allow smelling alloy with high aluminum containing in the frames of existing technology.

It is obviously that solving of the problem of nepheline utilization for alumina-silicate ferroalloy production can be found in the creation of new technology process.

Carbothermic recovery of silica and alumina may run according to such reactions: [1,2,3]

$$SiO_{2TB} + 2C_{TB} = Si_{TB} + 2CO_{\Gamma}, \Delta G^{o}_{(298-1686)} = 658160 + 12,56T lgT - 394,05T;$$
 (1)

$$SiO_{2 \text{ TB}} + 2C_{\text{TB}} = Si_{\text{TK}} + 2CO_{\text{T}}, \Delta G^{o}_{(1686-1986)} = 708826 + 12,77T \text{ lgT} - 425,67T;$$
 (2)

$$SiO_{2 \text{ TB}} + C_{\text{TB}} = SiO_{\Gamma} + CO_{\Gamma}, \Delta G^{o}_{(298-1686)} = 673 654 + 12,56 \text{T lgT} - 384,63 \text{T};$$
 (4)

$$SiO_{2 \text{ **}} + C_{TB} = SiO_{\Gamma} + CO_{\Gamma}, \Delta G^{o}_{(>1986)} = 658 \ 165 + 17,38T \ lgT - 392,80T;$$
 (5)

$$2/3$$
Al₂O_{3 TB} + 2C _{TB}= $4/3$ Al _ж + 2CO _г, Δ G^o(298-2303)=908 990+10,46TlgT-432,82T; (6)

$$2/3$$
Al₂O_{3 \times} + 2C _{TB}= $4/3$ Al \times + 2CO _T, Δ G°₍₂₃₀₃₋₂₆₈₀₎= 830 824+10,46TlgT-398,92T;(7)

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Taking into account thermodynamic characteristics of these reactions two temperature intervals can be singled out:

- 1) 1830 1900K favorable for silica reduction with liquid silicon formation;
- 2) >1950K favorable for alumina reduction with liquid aluminum formation.

The intermediate reactions of the silicon carbide formation are possible up to 2850 K, however SiC which is being produced, inevitably reacts with silica:

$$SiO_{2x}+2SiC_{TB}=3Si_{x}+2CO_{r},\Delta G^{o}_{(>1986)}=901497+17,37TlgT-505,86T;$$
 (8)

$$SiO_{2x}+0.5SiC_{TB}=1.5SiO_{r}+0.5CO_{r},\Delta G^{o}_{(>1986)}=693250+17.37TlgT-391.41T;$$
 (9)

For the prevention of carbide silicon formation in the temperature range 1830-1900K the silicon reduction must be conducted with dissolving of silicon into the iron melt. With lower temperatures (1799-1820K) and accurate dosage of the reducing material the chemical reaction (4) is possible. All of these reactions products are in the gas condition The reaction (4) and under the more higher temperatures the reaction (5) allows to correct silicon oxides content in the slag during a heat and create favorable conditions for production of alloy with a given ratio Si/Al. The presence of iron in the system improves the conditions of the reduction process according the reactions (4) and (5).

It is known that nepheline melts under the temperatures 1620-1670K. Therefore the reduction processes of aluminum and silicon oxides will proceed in the liquid phase.

Thermodynamic calculations have been done in order to analyze of lime additions influence on thermodynamic activities of components of the slag phase. The thermodynamic model for acid slag suggested by V. Kozheurov was used in calculations [4].

The expression of activity coefficient of the component l in the melt shall be written as following:

$$RT \ln \gamma_{t} = \sum_{i=1}^{l-1} x_{i} Q_{il} + \sum_{i=l+1}^{k} x_{i} Q_{li} - \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} x_{i} x_{ij}$$
 (1)

Where x_i – cation ionic fraction of the element i in the slag;

R – gas molar constant, $G/(K \cdot mole)$;

T –temperature, K;

 Q_{ij} – mixing energy of components.

To evaluate mixing energy for the two-components liquid regular solution by the help of constitution diagrams Me_IO - $Me_{II}O$ we can use the following equation :

$$Q_{12} = -\frac{\left[\Delta H_{\Pi(1)}(1 - \frac{T}{T_{\Pi(1)}}) - RT \ln x_1\right]}{(1 - x_1)^2}$$
(2)

 $\Delta H_{\pi(1)}$ - enthalpy

 $T_{\Pi(1)}$ -Temperature of melting

Reference data for enthalpy and temperature of melting for some pure oxides are given in the table 1.

Oxide	$\Delta H_{melt} \pm (\Delta H_{melt}), kj/kg$	$T_{melt}\pm\Delta T_{melt}$, K
Al_2O_3	$113,0 \pm 8$	2319 ± 20
SiO_2	$8,54 \pm 0,5$	1993 ± 20
Fe_2O_3	$34,0 \pm 0,5$	1838 ± 5
Na ₂ O	$36,0 \pm 0,5$	1405 ± 20
K ₂ O	$27,2 \pm 0,5$	1013 ± 20
CaO	$75,4 \pm 8$	2860 ± 20

Table 1. Enthalpy and temperature of melting for pure oxides

For the systems as $MeO\text{--}SiO_2$ the following equations have been obtained for calculation of Q_{12} parameter

$$Q_{12} = -\frac{\Delta H_{\Pi(1)}(T - T_{\Pi(1)})}{v_1 T_{\Pi(1)x_2^2}} - \frac{RT \ln x_1}{x_2^2}$$
(3)

 $\Delta H_{\Pi(1)}$ - enthalpy

 $T_{\Pi(1)}$ -Temperature of melting

The slag comvponent activity a_i can be determined with the help of activity coefficient y_i values

$$a_i = (y_i \cdot x_i)^{v_i}$$

The equations for calculation of the particular component activity can be written as follows

$$a_{AL_2O_3} = e^{\frac{4208}{RT}} \cdot x_{AL_2O_3}; \tag{4}$$

$$a_{CaO} = e^{\frac{-66458}{RT}} \cdot x_{CaO}; (5)$$

$$a_{FeO} = e^{\frac{-22568}{RT}} \cdot x_{Feo};$$
 (6)

$$a_{Na_2O} = e^{\frac{-5093}{RT}} \cdot x_{Na_2O}; \tag{7}$$

$$a_{K_2O} = e^{\frac{-5808}{RT}} \cdot x_{K_2O}; \tag{8}$$

$$a_{SiO_{3}} = e^{\frac{-66458}{RT}} \cdot x_{SiO_{3}}; (9)$$

The given equations (4-9) allow evaluate the influence of chemical composition of slag and temperature on the activity of the particular slag components.

The picture 1 shows the calculated dependence between activities of the slag components and CaO concentration in the slag phase.

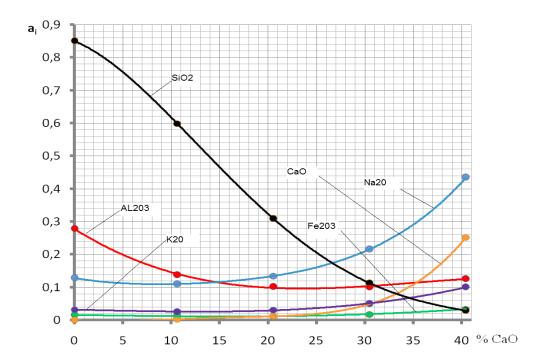


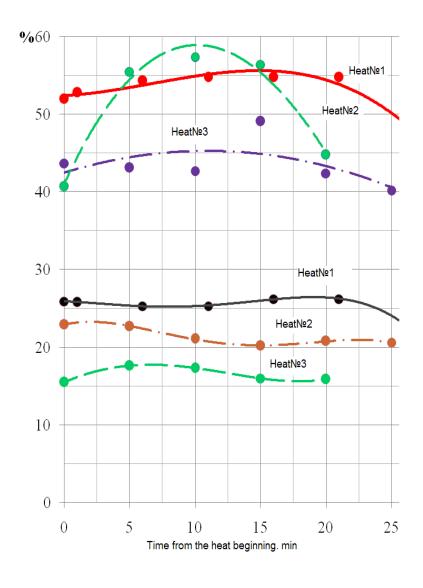
Figure 1 – The calculated dependence of components activity from CaO concentration in the slag.

The results of calculations show that SiO_2 activity slumps with the increase of lime concentration. It must have negative influence on the reduction process of silicon. At the same time Al_2O_3 activity decreases too. But not so considerably like SiO_2 activity. At calcium oxide concentrations more then 20-25%, the Al_2O_3 activity begins to grow again.

The research of the kinetics of silicon oxide reduction from the oxide melt obtained by melting nephelin ore have been conducted with a laboratory resistance furnace. Charge materials have been melted in graphite crucible of 25 cm height and 5 cm diameter. Graphite has been used as a reducing agent in all heats. Chemical composition of samples of metal and slag was investigated on the ARL 0806 device in the chemical laboratory of Ilych Iron & Steelworks of Moriupol (analysis method – RSFA).

The chemical analysis shows that degree of silicon reduction from slag into the metal phase is higher (15%) when pure nephelin concentrate was reduced. The lime additions to nephline suppress the silicon reduction process, but at the metal phase presence that negative influence decreases and the reduction degree is 15%. Carbide phase appeared when metal phase was absent.

Picture 4 shows the diagrams of SiO_2 and Al_2O_3 content change in the slag during the laboratory heats. The time account started when the temperature reaches 1850K. Heretofore easy reducible oxides in the slag (K_2O , Na_2O , Fe_2O_3) reacted partly with reducing material, and the chemical composition of the slag does not correspond exactly to chemical composition of nepheline concentrate.



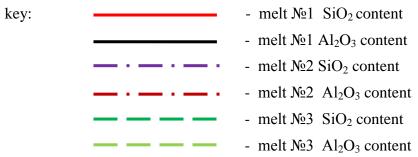


Figure 2 – Diagrams of chemical slag composition change during the laboratory heats

 SiO_2 and Al_2O_3 content increases during the first 10 minutes in the first heat. It can be explained by the iron, potassium and sodium reduction process finishing in the slag and by the silicon and aluminium carbides formation. The SiO_2 and Al_2O_3 concentration falls from the 15^{th} minute. However according to the chemical analysis silicon moved into the gas phase with formation its gaseous oxide SiO. Aluminum could not reduce and transit into the metal phase, therefore Al_2O_3 content in the slag decreased as a result of carbides formation.

The character of SiO₂ and Al₂O₃ content change in the second heat is similar to the first. All metal was accumulated in the slag layer as spherical inclusions. Degree of silicon reduction was 4%.

Presence of metal bath positively influences on the silicon reduction process during the third heat. Aluminum transition into the metal phase is also observed. The fast growth of SiO_2 content, in the beginning of the heat is supposedly connected with the acceleration of K_2O , Na_2O and Fe_2O_3 reduction processes due to the positive influence of metal phase presence in the charge.

According to the results of laboratory experiments the general conclusions can be made

-the lime presence in the charge materials negatively influences on the silicon reduction process. However lime addition can positively influence on the aluminum reduction process. So some lime additions are possible after the silicon reduction process finishing in order to slag dilution.

- the metallic iron presence in the charge positively influences the silicon, stimulates acceleration of the potassium and sodium oxide reduction processes and prevents carbides formation.

Thereby technological process for silicon-aluminum ferroalloys production with nepheline ore may be built in two stages. On the first stage it need reduce content of silicon in the slag phase and then arrange the aluminum reduction process to get alloy with required ratio Si/Al.

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