The thermodynamic studies of silication processes and manganese and silicon carbothermic reduction using system tetraedration method MnO-SiO$_2$-CaO-MgO

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ABSTRACT

Based on the calculations and analysis of MnO-SiO$_2$-CaO-MgO system, it was found that magnesium oxide addition in the charge for ferrosilicon manganese melting (as compared to CaO) contributes to the thermodynamic characteristics of carbothermic process, allows to improve physicochemical properties of molten slag and kinetics of manganese and silicon co-reduction from it.

INTRODUCTION

It is known [1, 5] that manganese and silicon are reduced from silicate melts under electric melting conditions. Thermodynamic calculations show that both magnesium oxide and calcium oxide addition in the ferrosilicon manganese charge results in silication; however, magnesium silicates are characterized by lower thermodynamic strength compared to the calcium silicates so that silicon reduction and its recovery in the alloy is simplified. As such, necessity for determination and comparison of Gibbs energy values of carbothermic reduction reactions in the charge containing magnesium and calcium oxides becomes apparent.

1. Studies

The most probable reactions during ferrosilicon manganese melting were studied using the data on thermodynamic preferability of compounds formation in binary and ternary systems that were obtained by the studiers. In such a case, the ratio of MnO : SiO$_2$ = 1.5 in the initial mixture for all reactions remained constant, which was equivalent to their ratio in the charge for marketable ferrosilicon manganese melting, while MnO and CaO quantities were changed to obtain real basicity for industrial (0.2) and test (0.5) charge. The results of calculations performed for ferrosilicon manganese melting temperature range (1573-1873 K) demonstrate that minimal changes in Gibbs energy are observed for reaction 5 (Table 1), i.e. for manganese and silicon reduction by carbon in the presence of MnO, when the charge basicity is 0.2.

Table 1 Thermodynamic characteristics of MnO and SiO$_2$ mixtures reduction reactions in case of MgO and CaO additions

No.	Chemical equation	$\triangle G^0_T = H^0_{298} - T\triangle S^0_{298}$ kJ/mole	T,K at $\triangle G^0_T = 0$
1	0.75 Mn$_2$SiO$_4$ + 0.25 SiO$_2$, + 3.5C = 1.5 Mn +Si + 3.5CO	1148.69—0.615T	1868
2	0.75Mn$_2$SiO$_4$+ 0.25 Ca$_2$SiO$_4$ + 2.5 C = 1.5 Mn+ 0.5Si + 0.5CaSiO$_3$++1.5 CO	793.60—0.443T	1791
3	0.75 Mn$_2$SiO$_4$ + 0.1 Ca$_2$SiO$_4$ + 0.15 SiO2 +3.1C=1.5Mn + 0.8Si + +0.2CaSiO$_3$ + 3.1 CO	996.52—0.552T	1805
4	0.75 Mn$_3$SiO$_4$ + 0.25MgOSiO$_4$ + +2.5C=1.5Mn+ 0.5Si + 0.5MgSiO$_3$+ 2.5 CO	791.10—0.448T	1766
5	0.75 Mn$_2$SiO$_4$+ 0.1Mg$_2$SiO$_4$ + 0.15SiO$_2$ + 3.1 C = 1.5 Mn + 0.8Si + + + 0.2 MgSiO$_3$ + 3.1 CO	999.87—0.573T	1744

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Consequently, this reaction is predominant. Magnesium oxide addition decreases theoretical reduction start temperature (Table 1) by 124 K as compared to the reaction 1. For the reaction 2 (basicity is 0.5 as a result of CaO addition) theoretical reduction start temperature was 1791 K and 1766 K when CaO was replaced with MgO.

Furthermore, theoretical reduction start temperature of manganese and silicon is markedly affected by active concentration of oxides in the molten slag. The studiers examined compositions of ferrosilicon manganese molten slag, the basicity of which varied in the range of 0.22-1 using the method described in paper [3] to evaluate the activity. According to the data provided in the paper [2], activity of slag component is expressed by formula $á_{(i)} = C_{(i)}\psi_{(i)}$, where $C_{(i)}$ is complete analytic element concentration in slag expressed in atomic fractions: $\psi_{(i)} = (\Sigma\, C_{(i)}\, e^{\varepsilon ij/RT})^{-1}$ is atomic activity coefficient, where K is total number of slag components (number of atom qualities); $\varepsilon_{ij} = {}^{1}/2(H_{ij}^{1/2} - H_{j}^{1/2})$ is exchange energy; H_iH_j are atomic parameters of i and j elements [2].
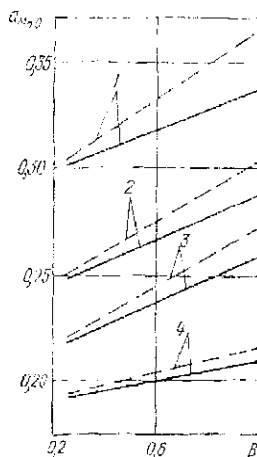

Fig. 1. Relation between activity a_{MnO} and basicity **B** *of molten slag of* MnO-SiO$_2$-MgO (CaO) system at **N** $_{MgO}$ / **N**$_{SiO2}$ (————) *and* **N**$_{CaO}$/**N**$_{SiO2}$(----------) *and* MnO *molar fractions of* 0.25 (1); 0.20 (2); 0.17 *(3)* and 0.11 *(4)*
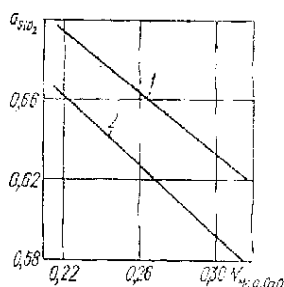

Fig. 2. Relation between silica activity $á_{SiO2}$ and molar fractions of magnesium oxide N_{MgO} (1) and calcium oxide N_{CaO} (2) in molten slag of system MnO-SiO$_2$-MgO (CaO).

2. RESULTS

The obtained calculated data on changes in the molten slag activity at addition of magnesium and calcium oxides (Fig. 1) demonstrate that when the basicity grows within the range of 0.2-1, MnO activity increases by 0.11 and 0.15 respectively, when MgO and CaO are added.

As can be seen from Fig. 2, when **N$_{CaO}$** increases from 0.22 to 0.32, the silica activity decreases from 0.665 to 0.580, i.e. by 0.085, and at the same changes from 0.695 to 0.620, i.e. only by 0.075.

Therefore, it can be assumed that during ferrosilicon manganese melting from charges containing magnesium oxide, the silica reduction conditions will be more preferable.

It is reasonable to consider the results of thermodynamic calculations together with equilibrium diagram patterns. The melts formed as a result of ferrosilicon manganese melting can be described based on MnO-SiO$_2$-CaO-MgO quaternary system study. The above mentioned system was studied with thermodynamic and diagram method [4] using the data on thermodynamic stability of compounds formed in the oxide mixtures. The Gibbs-Roozeboom triangle was plotted with imaging points of MnO-SiO$_2$-MgO, MnO-SiO$_2$-CaO, SiO$_2$-CaO-MgO compounds existing in the ternary systems and stable at the temperatures of the process being discussed. Negative change in Gibbs energy for reactions, in the equations of which equality sign uncouples the substances, defines stable co-existing phases. On diagram they are connected with conoid, so called line of co-existing phases.
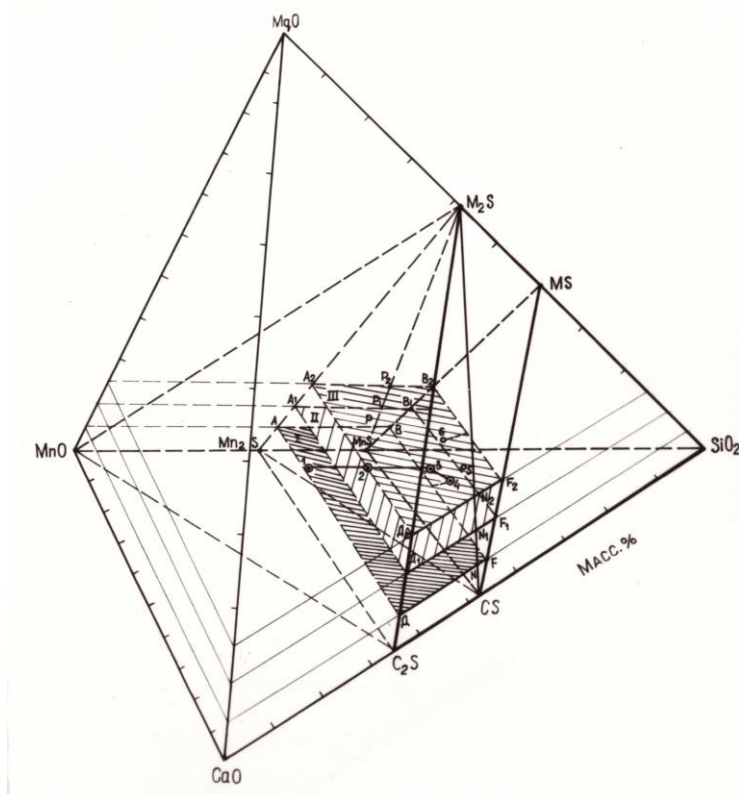
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Fig. 3. Compounds coexistence regions in MnO-SiO_2-CaO-MgO system:

I-III are sectional planes, when MgO content in slag is 5, 10 and 15% respectively; 1-3 are points corresponding to the compositions of intermediate manganese melts during ferrosilicon manganese melting; 4-6 are points corresponding to the final slag compositions, when MgO content in slag is 5, 10 and 15%.
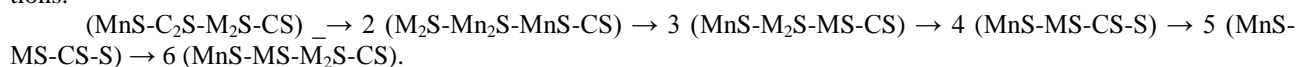
As can be seen from the above, the quaternary system under study was split into 7 tetrahedron compounds coexisting in the equilibrium (Fig. 3): C-Mn-C_2S-M; C_2S-Mn-M-M_2S; C_2S-Mn-M_2S-Mn_2S; C_2S-Mn_2S-CS-M_2S; CS-Mn_2S-MnS-M_2S; CS-MnS-M_2S-MS; CS-MnS-MS-S (generally accepted identification of oxides: MnO-Mn; SiO_2-S; CaO-C; MgO-M).

Table 2 Chemical composition of slag being studied, % wt

Slag No.	MnO	SiO$_2$	CaO	MgO	Al$_2$O$_3$
1	52.0	34.0	6.0	2.0	3.3
2	40,4	38.6	8.1	2.9	3.8
3	27.6	48,4	9.4	3,4	4.9
4	20.1	49.2	15.7	4.5	6.4
5	16.0	48.0	17.0	9.0	6.3
6	15.5	45.0	16.0	13.5	6.0

The intermediate slag (Table 2, slag 1-4) taken by the furnace horizons [5, 1] and magnesia slag (Table 2, slag 5-6) collected during the test campaign was used to describe the reduction process mechanism.

Using the relevant scaling method, the compositions of studied slag were plotted on the quaternary system and the direction of changes in its chemical composition during reduction (Fig. 4) was determined for the following reactions:

$(MnS$-C_2S-M_2S-$CS) \to 2 (M_2S$-Mn_2S-MnS-$CS) \to 3 (MnS$-M_2S-MS-$CS) \to 4 (MnS$-MS-CS-$S) \to 5 (MnS$-MS-CS-$S) \to 6 (MnS$-MS-M_2S-$CS)$.

The analysis of Mn-S-C-M system tetraedration show that points corresponding to the compositions of intermediate manganese and ore melts (1-3, Fig. 4) during ferrosilicon manganese melting are located in the space limited by planes Mn_2S-C_2S-M_2S on the side of line MnO-CaO and MnS-CS-MS on the side of angle SiO_2.

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Industrial ferrosilicon manganese slag (4, Fig. 4) crosses MnS-CS-MS plane, which is characterized by equilibrium between silicate melt and SiO_2. The presence of free silica in slag demonstrates that reduction process capabilities are not employed in fill under industrial conditions. This is probably connected with low kinetic conditions of reduction and unsatisfactory physical properties of melts.
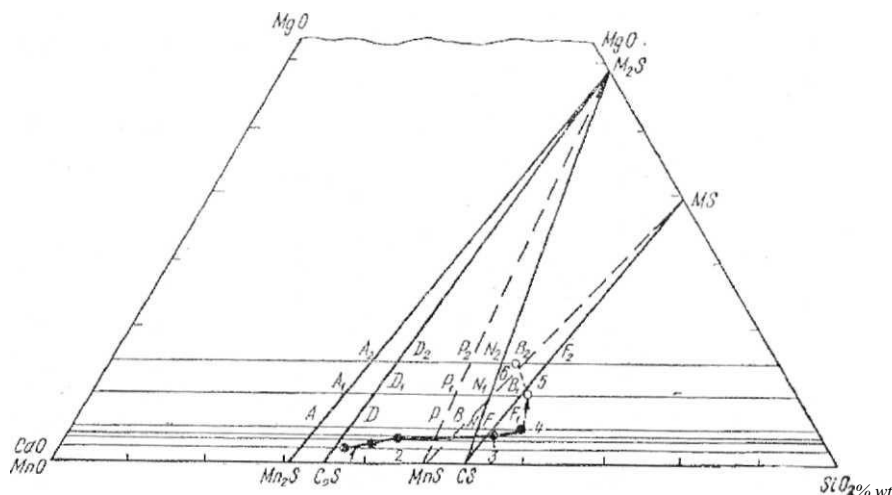

Fig. 4. Direction of changes in chemical composition of slag being studied during their carbothermic reduction.
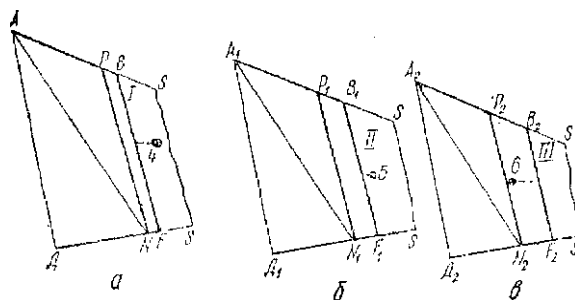

Fig. 5. Private sections of MnO-SiO_2-CaO-Mg0 diagram by lines *BF (a), B_1F_1 (b)* and *B_2F_2 (c)* (see Fig. 3) for various MgO content in slag.

The equilibrium state during SiO_2 reduction from magnesia melts (5, 6 Fig. 4) will be also defined by MтS-CS-MS plane, which shifts toward melts with leaner MnO content (inclination to SiO_2 top), when MgO content increases in the slag. Moreover, the reduction in thermodynamic strength of magnesium silicates as compared to the calcium silicates predetermines additional energetic preconditions for more complete silica reduction. When MgO content (10%) increases in the slag, its imaging point (5, Fig.5, b) shifts closer to the line (i.e. approaches the equilibrium line) and slag content is determined by ratio of MS-MnS-CS-S compounds. At the point 6, CS disappears completely, but C replacement with M allows changing profoundly the ratio of M_2S-MS phases towards M_2S formation that contributes to increase in the process temperature and disruption of silica oxygenic anions, which reduces the viscosity.

As can be seen from the above, the performed calculations and analysis of MnO-SiO_2-CaO-MgO system demonstrated that MgO additions (as compared to CaO) in the charge for ferrosilicon manganese melting contribute to the thermodynamic characteristics of carbothermic process, allow to improve physicochemical properties of molten slag and kinetics of manganese and silicon co-reduction from it.

SUMMARY

The thermodynamic calculations of carbothermic co-reduction of manganese and silicon from melts of MnO-SiO_2-CaO, MnO-SiO_2-MgO systems, considering the preferable formation of silicate compounds, showed that processes of manganese and silicon co-reduction by carbon from silicate melts containing MgO proceed significantly better at lower temperatures. If CaO and MgO are replaced in equal molar ratios, the silica activity is increased by 6-8%.

The thermodynamic and diagram method shows diagram space of MnO-SiO_2-CaO-MgO system corresponding to the compositions of initial oxide melts and final slag of ferrosilicon manganese production.

It was established that region of their coexistence is limited by planes formed by conoids Mn_2S-M_2S, M_2S-C_2S and C_2S-Mn_2Sc from the angle of MnO and MnS-MS, MS-CS, CS-MnS from the angle of SiO_2. The equilibrium during

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SiO_2 reduction from high magnesia slag is determined by MnS-CS-MS plane, which shifts toward lower MnO concentrations in silicate melts, when MgO increases.

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