EXTRACTION OF MANGANESE FROM THE SLAG OF SILICOTHERMAL REDUCTION OF METALLIC MANGANESE

V.Ya. Dashevskiy, A.A. Aleksandrov, A.G. Kanevskiy, L.I. Leontiev

Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences,
Leninskiy prosp., 49, Moscow – 119991, Russia. e-mail: vdashev@imet.ac.ru

ABSTRACT

The reduction of manganese from the waste slag of silicothermal production of metal manganese in the course of its interaction with the melts of iron, high-carbon ferromanganese, and ferrosilicon manganese has been thermodynamically analyzed. It was shown that, in the case of iron melt, carbon containing in melt reacts with manganese oxide of slag and the reduced manganese passes into this melt. As for high-carbon ferromanganese and ferrosilicon manganese, in spite of high contents of carbon and silicon, no interaction of carbon or silicon with manganese oxide is observed because of very strong bonds of carbon and silicon with the base of melt. The interaction of the melts of iron, high-carbon ferromanganese, and ferrosilicon manganese with the slag of silicothermal production of metal manganese was experimentally studied. It was observed that the manganese reduction from the slag by carbon dissolved in iron occurs appreciably. The reduction of manganese from the slag by carbon and silicon dissolved in high-carbon ferromanganese or in ferrosilicon manganese does not develop. Therefore, the extraction of manganese can be increased using the waste slag of silicothermal production of metal manganese to alloy iron with manganese upon treatment of metal melt by slag. In this case, the consumption of manganese-containing raw materials for ironmaking can be decreased or completely excluded.

KEYWORDS: *High-carbon ferromanganese, ferrosilicomanganese, iron, extraction of manganese, slag, thermodynamic analysis, experimental study, manganese, carbon, sulfur, silicon.*

1. INTRODUCTION

A considerable amount of manganese is lost with waste slag upon production of manganese ferroalloys. One of the processes of production of manganese ferroalloys that is characterized by appreciable losses of manganese (up to 40%) is the silicothermal method [1]. In this case, the manganese extraction is no more than 60–65% since the considerable amount of manganese is lost with the waste slag and because of evaporation. The slag ratio for this process is 3.5–4.0, i.e., for one ton of metallic manganese, 3.5–4 t of waste slag with 20–22% MnO is formed [2]. It is promising to develop a reasonable method of manganese extraction from such a slag.

The waste slag of silicothermal method of production of metallic manganese has the following chemical composition (mass %): 13–16 Mn; 0.003–0.005 P; 27–29 SiO_2; 43–46 CaO; 2–4 Al_2O_3; 2–4 MgO; 0.1–0.2 FeO; 0.1–0.2 S [1, 2]. The increased content of manganese and very low phosphorus concentration allow one to consider this slag as a promising manganese-containing material. A possible method of extraction of manganese from this slag is the reduction of manganese in the course of interaction of this slag with metal melt containing the elements characterized by the higher affinity to oxygen in comparison with manganese. In this case, reduced manganese passes to the metal melt.

Iron, high-carbon ferromanganese and ferrosilicomanganese can be considered as metal melts that are the most convenient for such a process. These melts contain carbon and silicon, which are characterized by the higher affinity to oxygen as compared to manganese and, therefore, can reduce manganese from the waste slag. However, it appears that carbon and silicon being components of iron, high-carbon ferromanganese and ferrosilicomanganese can have the lower reducing ability in comparison with pure components because of presence of binding forces with the melt matrix (iron, manganese). For this reason, the supposition that carbon and silicon being in iron, high-carbon ferromanganese and ferrosilicomanganese can reduce manganese from the above slag requires the thermodynamic analysis and experimental verification.

In general, the reduction of manganese from slag by an element R with the higher affinity to oxygen in comparison with manganese can be imagined as

$$n(\mathrm{MnO})(\mathrm{l}) + m[\mathrm{R}]_{1\%(\mathrm{Me})} = n[\mathrm{Mn}]_{1\%(\mathrm{Me})} + (\mathrm{R}_m\mathrm{O}_n)(\mathrm{s, l, g}) \quad (1)$$

$$K_{(1)} = \frac{([\%\mathrm{Mn}]\cdot f_{\mathrm{Mn}})^n \cdot a_{\mathrm{R}_m\mathrm{O}_n}}{a_{\mathrm{MnO}} \cdot ([\%\mathrm{R}]\cdot f_{\mathrm{R}})^m}$$

where f_i denotes to the activity coefficient when concentration is expressed as mass percent.

Liquid melts tapped from furnaces upon production of iron, high-carbon ferromanganese, and ferrosilicomanganese have a temperature of about 1500–1550°C. The slag formed in the course of silicothermal production of metallic manganese is liquid at this temperature [1]. Since the slag is melted by the heat of molten metal, then this heat is not taken into account in the further thermodynamic calculations.

When carbon in iron is the reducer, reaction (1)

$$(\mathrm{MnO}) + [\mathrm{C}]_{1\%(\mathrm{Fe})} = [\mathrm{Mn}]_{1\%(\mathrm{Fe})} + \mathrm{CO(g)} \quad (1a)$$

can be represented as the sum of reactions

$$\mathrm{MnO(s)} = \mathrm{Mn(l)} + {}^1/_2\mathrm{O_2(g)} \quad (2)$$

$$\Delta G^{\circ}_{(2)} = 406\,873 + 88.05T, \text{ J/mole [3]}$$

$$\mathrm{C(s)} + {}^1/_2\mathrm{O_2(g)} = \mathrm{CO(g)} \quad (3)$$

$$\Delta G^{\circ}_{(3)} = -114\,598 - 86.12T, \text{ J/mole [3]}$$

$$\mathrm{Mn\ (l)} = [\mathrm{Mn}]_{1\%(\mathrm{Fe})} \quad (4)$$

$$\Delta G^{\circ}_{(4)} = RT\ln\left(\frac{\gamma^{\circ}_{\mathrm{Mn(Fe)}}\cdot M_{\mathrm{Fe}}}{M_{\mathrm{Mn}}\cdot 100}\right)$$

$$\mathrm{C(s)} = [\mathrm{C}]_{1\%(\mathrm{Fe})} \quad (5)$$

$$\Delta G^{\circ}_{(5)} = RT\ln\left(\frac{\gamma^{\circ}_{\mathrm{C(Fe)}}\cdot M_{\mathrm{Fe}}}{M_{\mathrm{C}}\cdot 100}\right)$$

where $\gamma^{\circ}_{i(\mathrm{Fe})}$ denotes to the coefficient of oxygen activity in melt at infinite dilution; M_i denotes to molecular mass.

The Gibbs energy for reaction (1a) can be calculated as

$$\Delta G^{\circ}_{(1)} = \Delta G^{\circ}_{(2)} + \Delta G^{\circ}_{(3)} + \Delta G^{\circ}_{(4)} - \Delta G^{\circ}_{(5)}$$

For the iron-based solutions $\gamma^{\circ}_{Mn} = 1.44$; $\gamma^{\circ}_{C} = 0.538$ [4]. Iron contains 4% C on average; in this case, the activity coefficient $\gamma_{C} = 3.3$ [5].

At 1773 K, $\Delta G^{\circ}_{(2)}$ = 250 760 J/mole, $\Delta G^{\circ}_{(3)}$ = –267 289 J/mole, $\Delta G^{\circ}_{(4)}$ = –62 286 J/mole, $\Delta G^{\circ}_{(5)}$ = –27 639 J/mole, whence it follows that $\Delta G^{\circ}_{(1a)}$ = –51 176 J/mole. Therefore, under these conditions, the reduction of manganese from the slag of silicothermal process using carbon dissolved in iron must occur considerably.

When carbon dissolved in high-carbon ferromanganese is the reducer, reaction (1)

$$(MnO) + [C]_{1\%(Mn)} = Mn(l) + CO(g) \tag{1b}$$

can be represented as the sum of reactions (2), (3) and the reaction

$$C(s) = [C]_{1\%(Mn)} \tag{6}$$

$$\Delta G^{\circ}_{(6)} = RT \ln\left(\frac{\gamma^{\circ}_{C(Mn)} \cdot M_{Mn}}{M_{C} \cdot 100}\right)$$

The Gibbs energy of reaction (1b) can be calculated using the equation

$$\Delta G^{\circ}_{(1b)} = \Delta G^{\circ}_{(2)} + \Delta G^{\circ}_{(3)} - \Delta G^{\circ}_{(6)}$$

For the manganese-based solutions

$$\gamma^{\circ}_{C} = -1.5966 + 1{,}0735 \cdot 10^{-3} T \text{ [6]}$$

at 1773 K $\gamma^{\circ}_{C} = 0.307$. High-carbon ferromanganese contains 6% C on average; in this case, the activity coefficient $\gamma_{C} = 2.3$ [5].

At 1773 K $\Delta G^{\circ}_{(2)}$ = 250 760 J/mole, $\Delta G^{\circ}_{(3)}$ = –267 289 J/mole, $\Delta G^{\circ}_{(6)}$ = –33 191 J/mole; whence it follows that $\Delta G^{\circ}_{(1b)}$ = 16 662 J/mole. Therefore, under these conditions, the reduction of manganese from the slag of silicothermal process using carbon dissolved in ferromanganese must not develop. This is due to the high mutual affinity of carbon and manganese in the Mn-C melts.

When silicon of ferrosilicomanganese is the reducer, reaction (1)

$$2(MnO) + [Si]_{1\%(Si\text{-}Mn)} = 2Mn(l) + (SiO_2) \tag{1c}$$

can be represented as the sum of reaction (2) and the reactions

$$Si + O_2(g) = SiO_2 \tag{7}$$

$$\Delta G^{\circ}_{(7)} = -949\ 709 + 198.87T,\ \text{J/mole [3]}$$

$$\text{Si(l)} = [\text{Si}]_{1\%(\text{Si-Mn})} \qquad (8)$$

$$\Delta G^{\circ}_{(8)} = RT \ln\left(\frac{\gamma^{\circ}_{\text{Si(Si-Mn)}} \cdot M_{\text{Si-Mn}}}{M_{\text{Si}} \cdot 100}\right)$$

The Gibbs energy of reaction (1c) can be calculated as

$$\Delta G^{\circ}_{(1c)} = 2\Delta G^{\circ}_{(2)} + \Delta G^{\circ}_{(7)} - \Delta G^{\circ}_{(8)}$$

For the manganese-based solutions [7]

$$\ln \gamma^{\circ}_{\text{Si}} = -13\ 206/T - \ln[\exp(7693.6/T - 1{,}242) + 1]$$

whence it follows that at 1773 K $\gamma^{\circ}_{\text{Si}} = 2.518 \cdot 10^{-5}$. On average, ferrosilicomanganese contains 18% Si; in this case, $\gamma_{\text{Si}} = 0.0127$ [7].

At 1773 K $\Delta G^{\circ}_{(2)}$ = 250 760 J/mole, $\Delta G^{\circ}_{(7)}$ = –597 112 J/mole, $\Delta G^{\circ}_{(8)}$ = –124 730 J/mole, whence it follows that $\Delta G^{\circ}_{(1ñ)}$ = 29 074 J/mole. Therefore, under these conditions, the reduction of manganese from the slag of silicothermal process by silicon of ferrosilicomanganese must not develop. This is due to the high mutual affinity of silicon and manganese in the Mn-Si melts.

The interaction of the slag of silicothermal reduction of metallic manganese with molten iron, high-carbon ferromanganese, and ferrosilicomanganese was experimentally studied.

The experiments were carried out in an induction furnace fed by a CEIA Power Cube 180/50 high-frequency generator with a power of 12 kWt. Metal with a mass of 400 g was melted in an alumina crucible, heated to 1500°C, and sampled. Then slag was added on the surface of melt. This slag was melted and held during five minutes in a contact with metal before the next sampling. Then the same slag portion was added and after a 5-min holding the sample was taken again, etc.

2. INTERACTION OF SLAG WITH IRON MELT

The initial iron contained (mass %): 3.25 C; 0.26 Mn; 0.41 Si; 0.11 S. The waste slag of silicothermal production of metallic manganese contained (mass %): 15.7 Mn; 0.2 FeO; 0.005 P; 27.9 SiO_2; 45.4 CaO; 3.5 Al_2O_3; 3.3 MgO; 0.19 S.

Four experiments were carried out. The slag portion in experiments 1 and 2 was 5% of the mass of iron (20 g); in experiment 3, it was 3% (12 g); in experiment 4, it was 10% (40 g). The results obtained are demonstrated in table 1 and figure 1. These data show that the manganese content in metal melt increases with the holding time as a result of interaction of manganese oxide in the slag with carbon in the metal melt (table 1, figure 1a). The carbon content in metal melt decreased correspondingly (table 1, figure 1b).

In experiments 1–3, the carbon content in metal was decreased by a more value than it was required for the manganese reduction. In experiment 1, the manganese reduction required 0.122% C and the carbon content in metal decreased by 0.53%; in experiment 2, these values were 0.12% and 0.51% and, in experiment 3, 0.08% and 0.40%, respectively. This is connected with the fact that, in these experiments, slag did not cover completely a surface of molten metal and carbon was also oxidized by air. (As was mentioned above, metal was melted by the induction method and, therefore, the melt surface was cupola-shaped). In experiment 4, the slag wholly covered the surface of metal melt and carbon was not oxidized by air; for this reason, the manganese reduction required 0.205% C and the carbon content in metal was decreased by 0.23%.

Table 1: Change in the concentrations of manganese, carbon, and sulfur in iron (%)

Exp. number	Sample 1			Sample 2			Sample 3			Sample 4		
	Mn	C	S	Mn	C	S	Mn	C	S	Mn	C	S
1	0.26	3.25	0.11	0.58	3.07	0.076	0.70	2.87	0.077	0.82	2.72	0.077
2	0.26	3.25	0.11	0.75	3.10	0.082	0.79	2.95	0.078	0.81	2.74	0.082
3	0.26	3.25	0.11	0.51	3.13	0.092	0.56	2.99	0.087	0.61	2.85	0.087
4	0.26	3.25	0.11	1.0	3.23	0.061	1.1	3.13	0.056	1.2	3.02	0.059

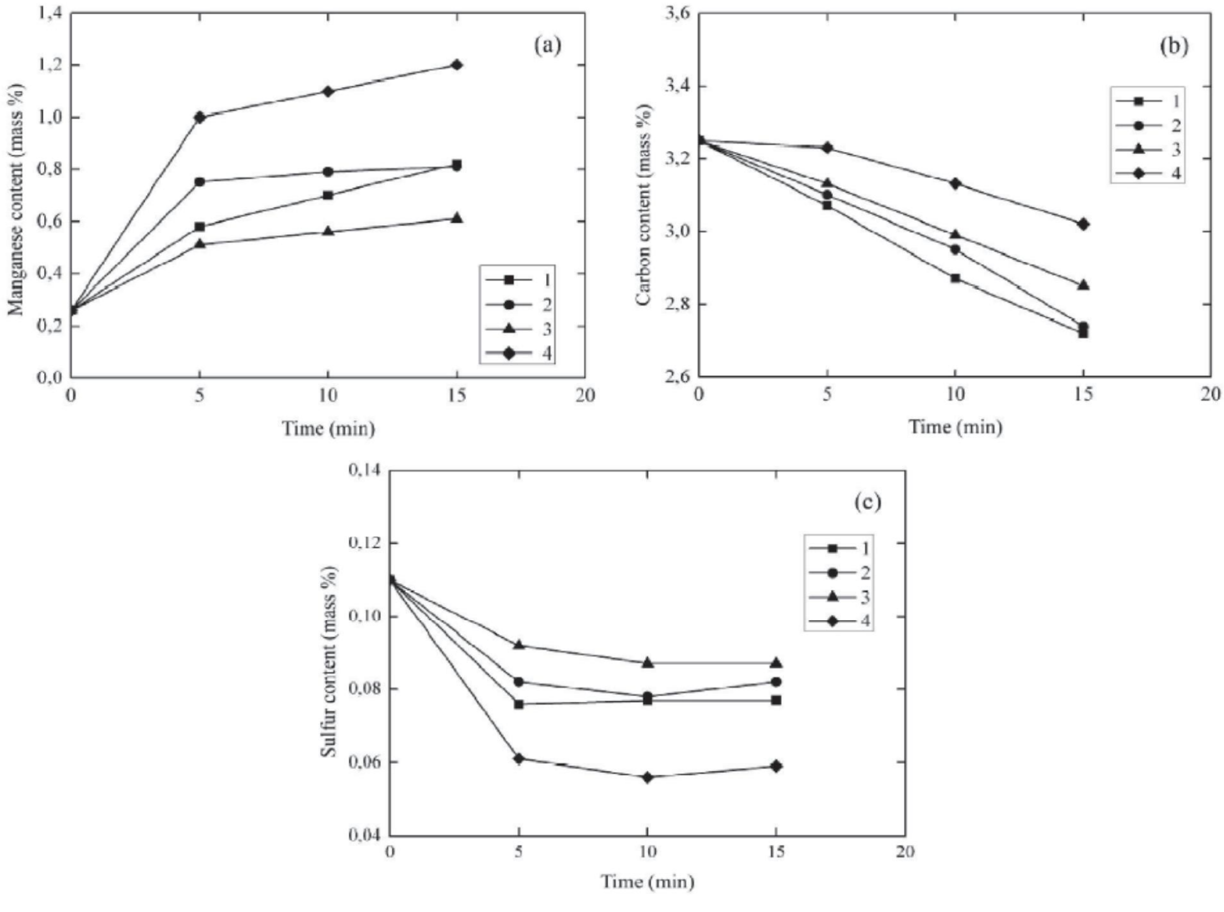

Figure 1: Concentrations of (a) manganese, (b) carbon, and (c) sulfur in iron depending on the time of holding of metal melt in a contact with the slag of silicothermal process (1–4 are the numbers of experiments)

The more the mass of slag added onto the melt surface, the higher the content of manganese in metal. When the mass of the slag added was 10% of the mass of the metal, the manganese concentration in melt increased by a factor of about five. According to our calculations, when iron melt is treated by the waste slag of silicothermal reduction of metallic manganese, 60–75 rel. % of manganese is reduced (table 2).

Table 2: Reduction of manganese in slag by carbon dissolved in iron

Exp. number	Manganese amount in slag added, g	Passed into iron, g	Manganese reduction, rel. %
1	3.14	2.24	71.34
2	3.14	2.20	70.06
3	1.88	1.40	74.31
4	6.28	3.76	59.87

Thus, upon ironmaking, it is possible to decrease (or exclude) the consumption of manganese-containing charge. In this case, the required manganese concentration in iron (0.5–1.5% and more) can be reached by treatment of liquid metal with the waste slag of silicothermal production of metallic manganese.

It is interesting that the sulfur content in iron decreased by 30–45 rel. % (depending on the slag mass) in the course of interaction of metal melt with slag (table 1, figure 1c). Since the initial slag contains 0.19 % S, it is important to understand the mechanism of desulfurization. This process can develop in two directions, i.e., either because of interaction of calcium oxide (45.4% CaO in slag) with sulfur dissolved in metal with the formation of calcium sulfide (CaS) in slag or due to the interaction of manganese reduced from slag with sulfur dissolved in metal with the formation of manganese sulfide passing into slag.

$$[S] + (CaO) \rightarrow (CaS), [S] + [Mn] \rightarrow (MnS)$$

It is possible to clarify the mechanism of this phenomenon if to study the desulfurization of sulfur-containing carbon-free iron melt in the course of its treatment by the waste slag of silicothermal reduction of metallic manganese. Three experiments were carried out. Carbonyl iron with a mass of 400 g was melted in an alumina crucible and heated to 1600°C. Then, the Fe-S alloy (25.5% S) was charged onto the melt surface in amounts that are sufficient to reach 0.1% S in the melt. After a 5-min holding, the initial sample was taken. Further, the slag of silicothermal reduction of metallic manganese was added onto the melt surface in amounts of 5% of the mass of metal (20 g) and the samples were taken after holdings of 5, 10, and 15 min. Experimental results are represented in table 3.

Table 3: Sulfur concentration in iron melt, %

Exp. number	Sample 1	Sample 2	Sample 3	Sample 4
1	0.09	0.09	0.09	0.10
2	0.15	0.15	0.15	0.14
3	0.13	0.13	0.13	0.13

As illustrated by the data in table 3, when iron melt with 0.09–0.15% S is treated by this slag, no decrease in the sulfur concentration occurs despite the high content of calcium oxide in slag (45.4% CaO). This is appearingly connected with the fact that this slag already contains sulfur (0.19%). Therefore, when liquid iron was treated by the slag of production of metallic manganese, it is most probable that the desulfurization occurred because of the formation of manganese sulfide, which passed into the slag. The degree of desulfurization depends both on the manganese content in melt and on the carbon concentration, since carbon not only reduces manganese from slag but also appreciably increases the sulfur activity in the iron-based melts ($\varepsilon^{C}_{S(Fe)} = 6.24$ [4]), which promotes the more complete desulfurization.

Thus, the experimental results are in good agreement with the thermodynamic data. Carbon dissolved in liquid iron appreciably reduces manganese from the slag of its silicothermal reduction. Therefore, the manganese extraction can be increased because of an additional extraction of manganese from the waste slag of silicothermal production of metallic manganese.

Based on the investigation performed, the method of alloying of iron with manganese was developed, which is protected by the patent [8]. In the course of production, liquid iron is tapped from a blast furnace into a ladle where the waste slag of silicothermal reduction of metallic manganese is preliminary placed on the bottom in amounts that are required to produce a given manganese concentration in iron; in this case, manganese-containing raw materials are wholly or partially excluded from charge.

3. INTERACTION OF SLAG WITH THE HIGH-CARBON FERROMANGANESE MELT

The initial high-carbon ferromanganese contained (mass %): 16.3 Fe; 6.36 C; 1.09 Si; 0.01 S; 0.12 P. Three experiments were carried out according to the technique described above. The amount of slag was 5% of the mass of ferromanganese (20 g). Results obtained are represented in table 4.

As these data show, the contents of manganese, carbon, and silicon in the metal melt are almost unchangeable in time. Therefore, there was no interaction of carbon dissolved in the melt with manganese oxide being in the slag. These results are in good agreement with the data of thermodynamic analysis.

Table 4: Change in the concentrations of carbon and silicon in ferromanganese (%)

Exp. number	Sample 1			Sample 2			Sample 3			Sample 4		
	Mn	**C**	**Si**	**Mn**	**C**	**Si**	**Mn**	**C**	**Si**	**Mn**	**C**	**Si**
1	75.61	6.28	1.06	75.69	6.28	1.09	73.81	6.21	1.02	73.31	6.31	1.07
2	76.39	6.27	1.12	74.52	6.39	1.01	72.38	6.30	0.72	70.06	6.40	0.64
3	74.06	6.44	0.92	73.41	6.49	1.08	73.53	6.47	1.00	72.91	6.50	0.88

4. INTERACTION OF SLAG WITH THE FERROSILICOMANGANESE MELT

The initial ferrosilicomanganese contained (mass %): 73.8 Mn; 20.3 Si; 1.05 C; 0.32 P. Three experiments were carried out according to the technique described above. The amount of slag was 5% of the mass of ferrosilicomanganese (20 g). Results obtained are represented in table 5. As is seen, the contents of silicon and manganese in the metal melt are almost unchangeable in time. Therefore, there was no interaction of silicon dissolved in the melt with manganese oxide being in the slag. These results are in good agreement with the data of thermodynamic analysis.

Table 5: Change in the concentrations of silicon and manganese in ferrosilicomanganese, %

Exp. number	Sample 1		Sample 2		Sample 3		Sample 4	
	Si	**Mn**	**Si**	**Mn**	**Si**	**Mn**	**Si**	**Mn**
1	21.2	74.8	20.7	72.8	20.3	73.9	19.6	75.0
2	19.6	73.6	19.4	72.3	21.1	75.4	21.1	74.2
3	21.8	73.2	20.0	74.4	19.2	76.8	19.5	73.6

5. CONCLUSIONS

1. Thermodynamic analysis of reduction of manganese from the waste slag of its silicothermal reduction upon interaction of this slag with liquid iron, high-carbon ferromanganese, and ferrosilicomanganese showed the following: in the case of iron, carbon dissolved in the metal has to interact with manganese oxide being in the slag, i.e., the reduction of manganese can occur; when high-carbon ferromanganese and ferrosilicomanganese are used, despite high contents of carbon (the former) and silicon (the latter), no interactions of carbon and silicon dissolved in metal melt with manganese oxide being in slag must develop because of strong bonds of carbon and silicon with the base of metal melt.

2. As was experimentally shown, the reduction of manganese from the slag of its silicothermal reduction develops considerably when carbon dissolved in iron melt is used. Therefore, the manganese extraction can be increased by using the waste slag of silicothermal production of metallic manganese to alloy iron with manganese upon treatment of liquid metal by slag. In this case, the consumption of manganese-containing raw materials for ironmaking is decreased (or wholly excluded).

3. The experiments showed that no reduction of manganese by carbon and silicon being in high-carbon ferromanganese and in ferrosilicomanganese occur when these melts interact with the slag of silicothermal reduction of metallic manganese.

6. REFERENCES

[1] Gasik M.I., Marganets (Manganese), Moscow, Metallurgiya, 1992. 608 p.
[2] Liakishev N.P., Gasik M.I., Dashevskiy V.Ya., Metallurgiya ferrosplavov (Metallurgy of Ferroalloys), Part 1, Moscow, Ucheba, 2006. 117 p.
[3] Kulikov I.S., Raskislenie metallov (Deoxidation of Metals),Moscow,Metallurgiya,1975. 504 p.
[4] Steelmaking Data Sourcebook. N.Y.-Tokyo: Gordon & Breach Science Publ., 1988. 325 p.
[5] Katsnelson A.V., Dashevskiy V.Ya., Kashin V.I. Carbon activity in Fe-, Co-, Ni- and Mn-based melts at 1873 K // Steel Research. 1993. V. 64. No 4. P. 197–202.
[6] Dashevskiy V.Ya., Termodinamika rastvorov ugleroda i kisloroda v rasplavakh margantsa (Thermodynamics of Carbon and Oxygen Solutions in Manganese Melts), Izv. Akad. Nauk, Ser. Metally. 2007. No 6. P. 13–17.
[7] Dashevskiy V.Ya., Katsnelson A.M., Krylov A.S., et al, Termodynamicheskie svoistva rasplavov marganets-fosfor i marganets-kremniy (Thermodynamic Properties of Manganese-Phosphorus and Manganese-Silicon Melts), Teoriya i praktika metallurgii margantsa (Theory and Practice of Manganese Metallurgy), Moscow, Nauka, 1990. P. 9–18.
[8] Dashevskiy V.Ya., Aleksandrov A.A., Yusfin Yu.S.,et al., Sposob legirovaniya chuguna margantsem (Method of Alloying of Iron with Manganese), Patent of Russian Federation, Izobreteniya, Poleznye modeli (Inventions, Useful Models), No. 23, 2012. RU 2458994 C1.