Integrated Processing of Highly Phosphorus Containing Manganese Ore from the Novonikolayevka Deposit

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Abstract

A new approach is presented with respect to solving the problem of the complex processing of a low-grade manganese-containing raw material, based on deep reductive melting with the separation of metal and silicate parts of the melt and the amorphization of the latter by *via* cooling in a thermal shock mode. As the result of these processes, a XRD amorphous foamed silicate with wide application potentialities is formed as well as ferromanganese silicon segregation is observed.

Key words: manganese ore, ferroalloy, dephosphorization, Gibbs energy, deep reduction mode, melt separation, metastable foamed silicate, amorphization, porization

INTRODUCTION

Russian manganese ore species belong mainly to high fluorine-containing and poor ones [1, 2]. In the process of enriching them, the losses reach the value of 20 %, whereas a high content of phosphorus restricts to a considerable extent the scope of consumption thereof. This is connected with stringent requirements concerning the specific content of phosphorus in the concentrate those are made with respect to the quality of manganese ferroalloys. Known methods [3] for the ore purification from phosphorus (chemical, gravity ones), according to technical and economic indices, are not able of competing with the metallurgical method based on different levels of phosphorus, iron and manganese reduction. The entire experience in the separation melting the Mn-containing ore species both in the electrometallurgy and in the blast-furnace production concerns the manganese and phosphorus distribution between metal and slag (the processes of enriching with manganese and dephosphorization) [4, 5] to be char-

acterized by strong requirements for Mn content in ore species under processing (over 42 %).

Manganese belongs to the group of strategic minerals those are essential for normal functioning of the metallurgical complex of Russia. The source of shortfall compensation in manganese products and of profitability of the production could consist in reducing the losses of extracting the manganese in the course of manufacturing ferroalloys as well as integrated using the silicate component of the raw material.

At the present time, the enrichment of manganese ore species in Russia is performed to a very weak extent [6]. Increasing the level of manganese extraction into alloy rather than ore dressing is important for newly developed technologies of production manganese ferroalloys from the manganese ore feedstock available in Russia. When processing via the traditional technologies the silicate component is not used because of low chemical reactivity and variable phase composition and thus it is sent to waste. As the result, silicate dumps are formed with a high content of residual iron and

manganese. The presence of Fe, Mn impurities in different valence states causes the possibility of obtaining the products with high-performance operation properties (dielectric, mechanical, thermal) from silicate-based components to be excluded.

The relevance of the research work aimed at optimizing the cost-efficient schemes for processing the manganese ore and its complex use is of no doubt. At the same time, involving the silicate component in the processing for obtaining high-tech products would allow simultaneously solving the other urgent problems: eliminating a negative impact of silicate metallurgical wastes on the environment, obtaining a novel product such as foamed silicate almost free from hazardous iron and manganese impurities that offers a wide range of applications, as well as increasing the depth of manganese reduction. At the present time, in the ferroalloy industry there is mainly dephosphorization used that represents a method [7, 8], based on difference in the chemical affinity of manganese and phosphorus with respect to oxygen.

EXPERIMENTAL

For the investigations we used substandard ore species taken from the Novonikolayevka deposit with a low content of manganese and a high content of phosphorus, mainly in the form of graphonite $(Fe,Mn,Ca)_3(PO_4)_2$, stewartite $Mn_3(PO_4)_2 \cdot 4H_2O$, kurskite $(PO_4)_4(CO_3)P$ and a number of other phosphorus-containing minerals. The chemical composition of the starting manganese ore (mass %): MnO 18.04, Fe_2O_3 20.6, MgO 0.7, Al_2O_3 8.3, SiO_2 43.5, P_2O_5 1.3, K_2O 2.62, CaO 2.9, SrO 0.03, BaO 2.01. Melting the silicomanganese was performed in a two-stage process: at the first stage we separated phosphoric iron and low phosphorus containing Mn-slag in a weakly reducing atmosphere using a graphite crucible, with no adding a reducing agent. The second stage consisted in a deep reduction of the oxides of manganese and iron from the residual low-phosphorus Mn-slag (with adding a reducing agent) with the segregation of the melt into Fe–Si–Mn alloy and a silicate component that contains silicon carbide (SiC) formed uniformly distributed throughout the

bulk of the component. Cooling the silicate part of the melt in water was carried out in a thermal shock mode for the formation of a porous product (silica foam) that is almost free of hazardous iron impurities [9–11].

As the reducing agent we used lignite with the following composition (mass %): humidity (W) 29.7, ash content (A) 6.5, volatile matter (V) 46, carbon 31.5, sulphur 0.3.

The thermoanalytical measurements were carried out at the Multiaccess Center (the MAC of the KSC, SB RAS) employing Netzsch equipment (Germany) with the use of differential scanning calorimetry (DSC) including simultaneous sample mass measurement of the, heat flow determination and registering the results of mass spectroscopy for gases evolved (CO_2, O_2, H_2O), software combined with thermal analysis data. The measurements were performed in a dynamic atmosphere of argon. The oven heating rate in the course of thermal analysis amounted to 10 °C/min.

In order to determine the phase and elemental composition of the materials under investigation we used the methods of XRD phase analysis and X-ray fluorescence spectral analysis.

The procedure of deep reductive induction melting was carried out using a KIT-25 induction unit. As a criterion for the potentiality of reductive reactions to occur we used changing the Gibbs energy (ΔG^o) calculated for different reducing agents (C_s, CO, H_2, CH_4) entering the reactions of higher manganese oxide conversion into lower manganese oxides with the help of an HSC 5-1 software. Burdening the ore was performed using limestone and sand till reaching a desired ratio between the concentration of calcium oxide and silicon oxide.

RESULTS AND DISCUSSION

Figure 1 demonstrates the results of analysis performed for the sample of manganese ore: mass change depending on the temperature (TG), heat flow (DSC) and the flow of ions for the mass number m/z, equal to 44 (CO_2), 32 (O_2), 18 (H_2O) (mass spectrometry investigation). It can be seen that with within the temperature range of 272.6 °C the DSC curve exhibits an endothermic effect, whereas the TG
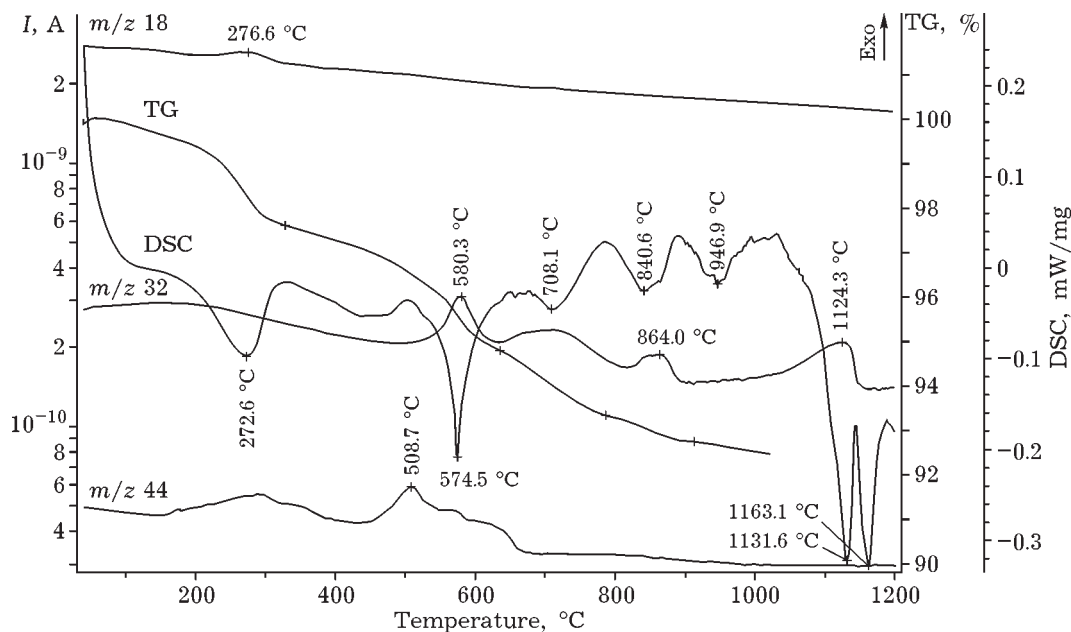
Fig. 1. Mass (TG), heat flow (DSC) and ion current for m/z 44 (CO_2), 32 (O_2), 18 (H_2O) for a manganese ore sample depending on temperature.

curve demonstrates a maximum change in the mass loss rate, and the ionic flow curve the ion mass number m/z 18 (H_2O), exhibits a peak of water evolution insignificant in the intensity. All the effects observed within the mentioned temperature range are inherent the dissociation of iron hydroxides.

A broad maximum observed on the curve of the ion flux for the mass number equal to m/z 44 (CO_2) within the temperature range of 300 °C is caused by burning out the organic substances, as indicated by decreasing the amount of oxygen on the curve m/z 32 (O_2) within this temperature region, and the mass loss on the TG curve. The maximum temperature equal to 508.7 °C is inherent in the dissociation of manganese carbonate being accompanied by the mass loss on the TG curve. Four peaks on the curve of m/z 32 (O_2) correspond to the dissociation of higher manganese oxides into the lower manganese oxides, which is accompanied by the evolution of oxygen. The endothermic effect within the temperature range of 574.5 °C could be caused by the decomposition reaction of pyrolusite (MnO_2) with the evolution of oxygen and the formation of β-kurnakite (β-Mn_2O_3). An insignificant mismatch of peaks reflecting the endothermic effects and oxygen evolution on the temperature scale could be caused, to all appearance, by impurities, however the shape of the peak of the endothermic effect indicates the fact that there observed a possible influence of a "quartz effect" [12] which is observed at the temperature equal to 573 °C. A broad maximum of endothermic effect within the temperature range of 708 °C indicates the fact that there occurs a diffusion mechanism of oxygen evolution in the course of the dissociation of pyrolusite. The endothermic effect on the DSC curve within the temperature range of 840 °C are caused by the transition from Mn_2O_3 to α-Mn_3O_4 with oxygen evolution, whereas those observed at 946.9 °C can be attributed to α-Mn_3O_4 transition into β-Mn_3O_4 (hausmannite). The peak splitting observed for the DSC curve could be associated with the decomposition of β-Mn_2O_3 and the formation of β-Mn_3O_4 with oxygen evolution and the reversible polymorphic transformation from β-Mn_3O_4 to γ-Mn_3O_4 at 1163 °C.

Insignificant discrepancies in the dissociation temperature for converting higher manganese oxides into to the lower ones (see Fig. 1) as to compare with pure oxides [13, 14] could be, to all appearance, caused by impurities. Burdening the ore by quartzite and limestone up to the ratio between the oxides in the mixture equal to $CaO/SiO_2 = 1.1$ eliminates the dissociation of manganese oxides within the temperature range 600−900 °C, which could be con-
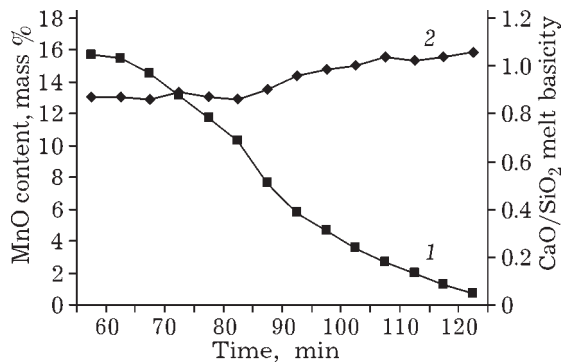
Fig. 2. Changing the manganese content in the melt (*1*) and its basicity thereof (*2*) depending on the reduction time.

nected with endothermic decomposition of limestone within the mentioned temperature range. The process of burden mixture dephosphorization at the first stage of melting was carried out in the course of heating up to 1400 °C to hold at this temperature for 30 min. Then, a high phosphorus- containing metal with the following composition (mass %): Al 0.67, Si 2.9, P 3.6, Cr 0.07, Mn 5.4, Fe 86.12, Co 0.4, Ni 0.15, was poured in a chill mold, whereas a lingot was poured with a charge manganese-containing slag of the following composition (mass %): Na_2O 0.79, MgO 0.82, Al_2O_3 4.86, SiO_2 39.5, P_2O_5 0.02, SO_3 0.06, K_2O 1.88, CaO 34.44, TiO_2 0.21, MnO 15.7, Fe_2O_3 0.25, ZrO_2 0.01, BaO 1.46.

The charge Mn-slag was burdened by lignite in the amount of 20 mass % to be subjected to deep reductive melting in a graphite crucible. Every 5 min since the melting the slag and reaching the melt temperature equal to 1600 °C, sampling was performed in order to determine the basicity dynamics and changing the manganese content in the course of the melting process.

Data concerning the change in the content of manganese in the melt and its basicity depending on the reduction time are demonstrated in Fig. 2. The first point of the curve *1* corresponds to the content of MnO in the original slag, whereas the first point of the curve *2* corresponds to the ratio between the initial content of the components CaO/SiO_2. The distance between the first and the second points of curves *1* and *2* corresponds to the transition time for the burden mixture transition from the solid to the liquid state. It can be seen that the

manganese oxide is partially reduced in the solid phase, but preferably this process occurs in the melt. It should be noted that the maximum rate of manganese reduction was observed after the exposure of the melt at 1600 °C for 20 min. With increasing the exposure time, an increase in the basicity of the melt is observed.

This is caused not only by decreasing the amount of manganese in the melt, but also by the reduction of silica. The maximum rate of manganese reduction calculated using a technique proposed by the authors of [15], is equal to 0.3 g/min. Subsequent decreasing the rate of manganese reduction is caused by a decrease of the reactivity and concentration of manganese oxide in the melt. The reduction of manganese oxides from ore occurs in accordance with the Baykov principle, from higher oxides to lower oxides:

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO \rightarrow Mn.$$

Basing on thermodynamic calculations we assessed the possibility of reducing the oxides of manganese in different temperature zones by different reducing agents (C_s, CO, H_2, and CH_4) and of the dissociation of higher manganese oxides to convert into lower manganese oxides. It is demonstrated that within all the temperature zones, methane and its decomposition products are most efficient as reducing agents for higher manganese oxides only in the course of reductive conversion into monoxide (MnO), which is confirmed by the data obtained
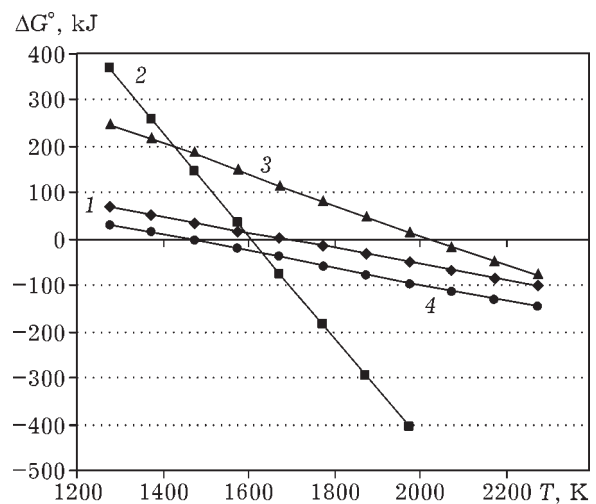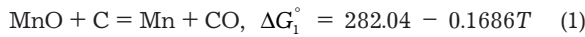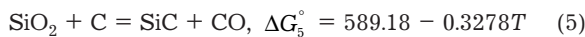

Fig. 3. Changing the Gibbs energy ($\Delta G°$) depending on the temperature in the course of reducing MnO into Mn *via* reactions (1)−(4): *1−4* − reactions (1)−(4), respectively.

the authors of [16−19]. Among all the manganese oxides, manganese monoxide can be reduced in the most difficult manner. The thermodynamic calculations demonstrate that the mentioned process is possible only in the presence of solid carbon. The change in Gibbs energy depending on the temperature for reactions of reducing MnO with different reducing agents are presented as it follows:

$$MnO + C = Mn + CO, \quad \Delta G_1^\circ = 282.04 - 0.1686T \quad (1)$$

$$7MnO + 10C = Mn_7C_3 + 7CO, \quad \Delta G_2^\circ = 1782.2 - 1.0985T \quad (2)$$

$$3MnO + CH_4 = 3Mn + CO + 2H_2O, \quad \Delta G_3^\circ = 667.69 - 0.3307T \quad (3)$$

$$3MnO + SiC = 3Mn + CO + SiO_2, \quad \Delta G_4^\circ = 256.95 - 0.1781T \quad (4)$$

It can be seen that *via* using various reducing agents the manganese oxide can be reduced into manganese carbide as well as into manganese. Most likely that there occurs reducing MnO into manganese carbide Mn_7C_3 (whose beginning reduction temperature is 100 K lower than that for the former) rather than into manganese (Fig. 3, curve 2). Besides the carbon, the reduction of manganese is participated by silicon carbide (see Fig. 3, curve 4) formed at the last stage of deep reductive melting according to the reaction

$$SiO_2 + C = SiC + CO, \quad \Delta G_5^\circ = 589.18 - 0.3278T \quad (5)$$

$$3FeO + SiC = 3Fe + SiO_2 + CO, \quad \Delta G_6^\circ = -160.44 - 0.112T \quad (6)$$

As it follows from formula (5), the temperature of starting the reaction of carbide formation amounts to 1797 K. Beginning from this temperature, manganese monoxide should be reduced into manganese by silicon carbide *via* reaction (4) with simultaneous reduction of iron oxides remaining in the slag after dephosphorization *via* reaction (6). The equilibrium of this reaction is entirely shifted to the right, so till the reduction of iron into the metallic state becoming complete, both free silicon and silicon carbide are almost not detected in the melt. However, with removing the iron and the most part of manganese from the silicate component of the melt the concentrations of silicon and silicon carbide in the melt exhibit an abrupt increase. Silicon, just as silicon carbide is involved in the additional reduction of manganese according to reaction

$$2MnO + Si = 2Mn + SiO_2, \quad \Delta G_7^\circ = -130.13 + 0.0225T \quad (7)$$
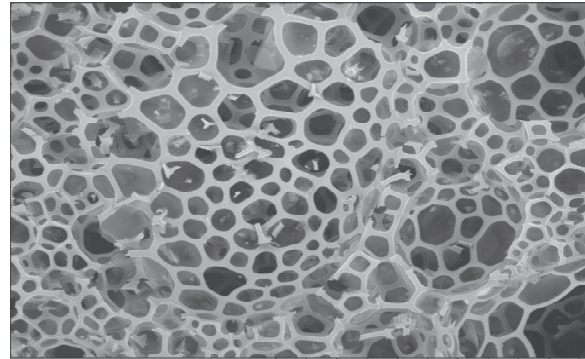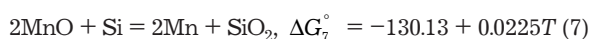
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Fig. 4. Electron microscope image of silica foam.

The silicate component of the melt containing silicon carbide uniformly distributed over the melt is cooled in water in a "thermal shock" mode with the formation of X-ray amorphous porous silica foam (Fig. 4). The porization of the melt could be caused by the interaction between water vapour and silicon carbide, whereas the destruction of some interpore partitions observed is connected with a high rate of the porization process.

The silica foam structure represents a set of porous layers with the pore size from 50 to 150 μm. The interlayer spacing is comparable with pore diameters. According to X-ray fluorescence and XRD phase analysis we obtained an X-ray amorphous foamed silicate with a stable chemical composition (mass %): Na_2O 0.53, MgO 1.23, Al_2O_3 6.81, SiO_2 44.22, P_2O_5 0.04, SO_3 0.06, K_2O 0.52, CaO 43.84, TiO_2 0.19, MnO 0.72, Fe_2O_3 0, ZrO_2 0.02, BaO 1.82. Owing to a low thermal conductivity (0.04 W/(m · K)), the material obtained could be used as a non-

TABLE 1

Chemical composition of the alloy (Fe−Si−Mn) obtained as compared with the requirements of the State Standard GOST 4756−91 ($FeMnSi_{18}$)

Elements	Composition, mass %	
	Fe−Si−Mn alloy	$FeMnSi_{18}$
Si	18.3	15.0−20.0
P	0.05	More than 0.35
S	Less than 0.03	More than 0.03
Mn	76.63	60.0−75.0
C	−	Less than 2.5
Fe	The rest	The rest

combustible heat-insulating backfill in the construction and building industry. The X-ray amorphous state and an almost complete absence of hazardous iron impurities determines the prospects of using silica foam for obtaining ceramics and ceramic foam with targeted functional properties.

The metal part of the melt is poured into a mold. According to the composition (mass %): Si 18.3, P 0.05, S 0.03, Mn 76.6, Fe 5.02, the metal almost meets the requirements for ferromanganese silicon (State Standard GOST 4756−91) which is used in the steel and foundry industries, as well as for the production of manganese alloys.

An evaluation of the characteristics for the resulting alloy composition of ferromanganese silicon (Fe−Si−Mn) based on the Novonikolayevsk ore deposit as compared to the requirements for the alloy characteristics according to the State Standard GOST 4756−91 is presented in Table 1.

CONCLUSION

An approach presented in the paper concerning a comprehensive utilization of highly phosphorus containing manganese ore species allows obtaining ferromanganese silicon with the best characteristics according to phosphorus and manganese content, whereas instead of the traditional slag discarded to a mouldboard the approach provides obtaining a porous material (foamed silicate) with a stable chemical composition, which is suitable for the use both in building, and in the construction industry. The industrial use of this approach would cause radically reducing the load on the environment.

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