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FEASIBILITY STUDY OF USING WITH HIGH BASICITY MANGANESE ORE FOR SMELTING REFINED FERROMANGANESE

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Modern production of the refined ferromanganese based on the use rich manganese concentrate. But reserve the rich manganese concentrate deficit every year. Therefore, it is necessary to involve the base manganese ores for smelting manganese alloys. The article presents the results of X-ray phase, microstructural, thermal analyses of studies of the high basicity manganese ore "Ushkatyn III" and smelting of refined ferromanganese from it. Reached high extraction of manganese from the charge blend (78 %) from ore (56 %) and lime consumption was reduced by 30 %.

Keywords: manganese ore, high basicity, extraction, refined ferromanganese, X-ray analysis

INTRODUCTION

Refined ferromanganese is melted mainly by the silicothermic method, where the basis is the process of recovery the manganese oxide by silicon in the presence of calcium oxide [1]. The essence of the technology is that the metal must contain a limited amount of harmful impurities P, S and C. Therefore, manganese concentrates are used, pure in phosphorus, sulfur and carbon. For smelting refined grades of ferromanganese, manganese ores must meet the following requirements [2]:

– $Mn_{general} \geq 45\%$;
– $Mn/Fe \geq 10\%$;
– $SiO_2 \leq 15\%$;
– $P_2O_5 \leq 0{,}2\%$;
– ore fraction – 0 - 20 mm.

Modern manufacturers of manganese ferroalloys are experiencing a shortage of high-quality manganese ores. In this regard, the use of cheap manganese raw materials becomes an inevitable factor and is relevant all over the world.

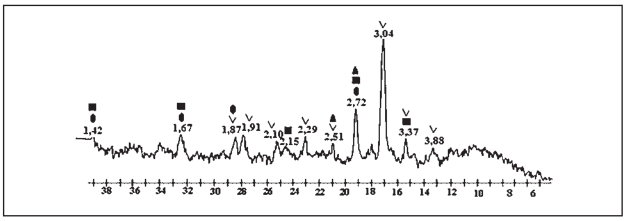
The object of the study is the use of high-base manganese ores Ushkatyn III (Karaganda, Kazakhstan). The high basicity manganese ore of the deposit Ushkatyn III are characterized by increased basicity (CaO/SiO_2 = 1,69), where the chemical composition of the ore is shown in table 1. For smelting most manganese ferroalloys, including refined ferromanganese, calcium oxide is introduced into the charge as a flux [3]. The relative high content of manganese and calcium with a simultaneous low content phosphorus in the high basicity manganese ore allows them to be considered as a complex raw material for the production of refined ferromanganese. The use of high basicity manganese ores should significantly reduce the consumption of the fluxing material - lime, as well as improve the technological parameters of the smelting of refined ferromanganese.

RESEARCH METHODOLOGY

The phase composition of the high-basictiy manganese concentrate of the Ushkatyn III deposit was studied, which was determined by roentgen phase analysis. As a result, it turned out that its main phase is represented by calcite ($CaCO_3$), brownite ($Mn_2O_3 \cdot MnSiO_3$) and bixbyite $(Mn,Fe)_2O_3$, and there is also a small amount of hematite phase (Fe_2O_3). The result of conducted X-ray phase analysis of a high basicity manganese ore is presented in the Figure 1.

In the course of the work, the textural and structural features of the mineralogical composition of ore and non-metallic components were studied. Mineralogical and petrographic analysis was carried out using a portable metallurgical microscope model «NYMCS-605».

As a result of microscopic analysis of the investigated manganese ore, it was found that the sample is



■ - brownit; ● - bixbyite; ∨ - calcite; ▲ - hematite

Figure 1 Result of X-ray phase analysis of a high basicity manganese ore of the Ushkatyn III

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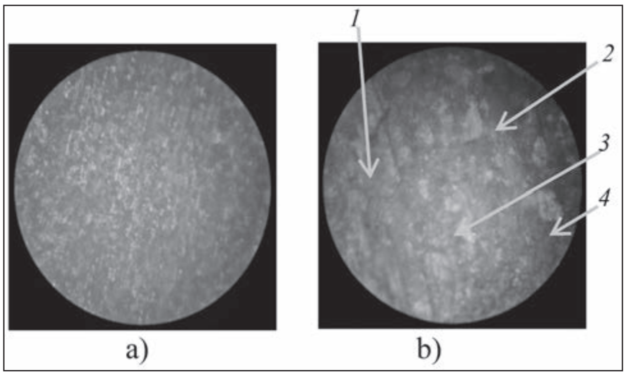


a) zoom x 100; b) zoom x 500:
1 – gausmanite; 2 – rhodochrosite; 3 – brownite;
4 – calcite

Figure 2 Microstructural analysis of the high basicity manganese ore of the Ushkatyn III

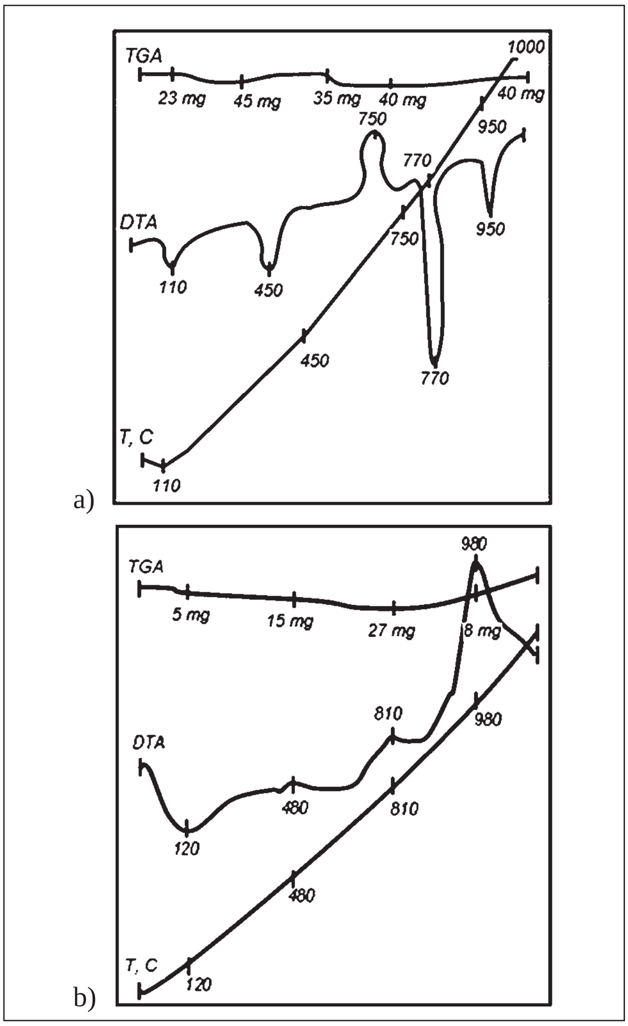
represented by sharp-angled fragments of 5,0 mm in size. The fragments are heterogeneous both in texture and structure. In some fragments there is a subtle rhythmic layering, there are areas with sooty and collomorphic texture. In some fragments there are nodules (inclusions) filled with calcite. The color of the debris is heterogeneous, from dark brown to black. Basically, the texture is close to massive (Figure 2).

For microscopic studies, there were made the polished slates from presented samples. Microscopic studies have established that samples of high-base manganese ores represent gausmanite ore (Mn_3O_4) of a banded structure due to the alternation of shiny dark interlayers of dense fine-crystalline gausmanite and lighter nonmetallic bands consisting of carbonate with a small amount of chalcedony (SiO_2) and in places crystalline tephroite (Mn_2SiO_4).

The carbonate is mainly represented by fine-crystalline calcite, rhodochrosite ($MnCO_3$) is present, including in places with barites ($BaCO_3$) and small amounts of tephroite. In some parts of the sample, gausmanite is impregnated with feldspar rock, highly modified, sericitized, largely replaced by carbonate, chalcedony and ore mineral. Brownite in the shelf is observed in the form of fine-crystalline formations, most often in accretion with calcite, forming a carbonate rock [4].

The method of Differential Thermal Analysis (DTA) was used for examination of chemical reactions and physical transformations, occurring under heat pressure in the alloy between its single compounds. DTA was conducted in the air oxidizing atmosphere, using derivatograph of F. Paulik, I. Paulik, L. Erdei system that allows to measure mass variation Termogravimetric Analysis (TGA) and rate of mass Differential Termogravimetric Analysis (DTGA) for the sample, as well as temperature difference between the examined and inert samples in the conditions of the continuous heating with preset rate. The heating rate made 10 grad per min. The temperature interval 25 - 1000 °C [5].

The Figure 3 presented the results of thermographic studies of the high basicity manganese ore Ushkatyn III and its mixture with ferrosilicon manganese.



a) the high basicity manganese ore;
b) high basicity manganese ore + FeSiMn;

Figure 3 Examples of derivatograms of the charge materials for smelting the refined ferromanganese

The processes occurring in the concentrate during heating (Figure 3 a) are accompanied by a weak endothermic effect at 107 - 120 °C, this is explained by the release of adsorbed moisture. Starting from 435 - 460 °C, the DTA curves show an endothermic effect caused by the dissociation of rhodochrosite with the formation of manganese oxides MnO, Mn_3O_4.

$$MnCO_3 \rightarrow MnO + CO_2$$

$$MnCO_3 \rightarrow Mn_3O_4 + CO + CO_2$$

Then at 730 - 765 ° C follows a slight exothermic effect of oxidation of the formed oxides to β-kurnakite (β-Mn_3O_4). At 770 °C on the differential curve appears a pronounced endothermic effect, which is the result of dissociation of calcium carbonate with the formation of CaO.

In the temperature range of 930 - 950 °C, a slight endothermic effect of decomposition of the previously formed β - kurnakite with the formation of β - gausmanite is noticeable in the sample. Further temperature increase up to 1000 °C leads to weight loss in the amount of 40 mg.

The derivatogram of the charge mixture consisting of manganese concentrate and FeSiMn (ferrum-silicon-manganese) alloy is present in figure 3 b. The area on the DTA curve of the endothermic effect (120 °C) to the tempe-rature of a weak exothermic effect of 480 °C corresponds to the processes of hygroscopic moisture release and with a decrease in weight by 15 mg. The exothermic effect at a temperature of 810 °C is accompanied by a sharp decrease in the weight of the sample by 27 mg. Presumably, the appearance of these effects is associated with the beginning of the interaction of lower ore oxides and the reducing agent, since a similar picture was not reflected in the above derivatogram. Starting from a temperature of 890 °C, it is noticeable on the DTA curve that heat is released, accompanied by a large exothermic peak at 980 °C. The mass of the sample is reduced by 8 mg.

Thus, the obtained thermographics information can be used to study the processes of pyrometallurgical processing of manganese raw materials. The dynamics of phase transformations in the concentrate is clearly demonstrated in all derivatograms, and the interaction of the concentrate with reducing agents is not observed at the studied temperature ranges. This case allows us to assert that the reduction processes in the metallothermy of ferromanganese will occur at temperatures above 1300 - 1400 °C, which excludes earlier slag formation and the transition of the melt into the diffusion mode.

RESULTS RESEARCH

To assess the physicochemical properties of the high basicity manganese ore Ushkatyn III, there were melting experiments of the alloy refined ferromanganese. The chemical composition of the charge materials was given in Table 1.

Melting experiment was carried out in a refining furnace with total nominal capacity 0,1 MV with a tilting bathtub. Transformer operating voltage 49 V. The working layer of the lining is made of magnesite refractory bricks with backfilling of the seams with magnesite powder. The temperature in the reaction zone is provided by the discharge of an arc in two graphite electrodes with a diameter of 100 mm. The calculation of the charge was carried out to obtain standard refined ferromanganese and the amount of calcium oxide in the final slag should correspond to CaO/SiO_2 = 1,5 - 1,6.

The melting process is periodic, with an average duration of 2 hours. The order of loading the charge into the furnace: after the load was set, firstly - the entire bulk of the ore and, as it melted, a mixture of ferrosilicon manganese and lime [6]. The amount of the charge materials per batch load, kg:

- Manganese ore – 10;
- Fe-Si-Mn alloy – 3 - 4,3;
- Lime – 2 - 2,5.

Table 1 **Chemical composition of materials / %**

Material	Mn	CaO	SiO_2	Fe_2O_3	P_2O_5
Manganese ore	35,0	17,3	10,2	6,2	0,02
Lime	-	89,1	1,6	0,6	0,01
FeSiMn	Mn	Si	Fe	C	P
	65,1	29,2	3,5	0,4	0,04

Slag and metal at the end of melting were kept in the furnace for 20-30 minutes and released into cast iron mills. The specified procedure for loading the charge does not cause technological difficulties, since there is a sufficient amount of calcium oxide in the initial ore, which, forming strong silicates with silica, prevents the corrosion of the magnesite lining, as well as the formation of manganese silicates . At the same time, the melting process is significantly facilitated, while when lime is introduced together with ore in accordance with traditional technology, a refractory melt is formed in the furnace bath, which reduces the technical and economic indicators of the process.

During the melting process, the current load was distributed evenly. Metal and slag were well separated after cooling. The slag crumbled completely as it cooled down.

As a result of the conducted research, the average chemical composition of the melting products were as follows %:

Metal: Mn – 87,3; Si – 2,0; Fe – 8,2; C – 0,6; P – 0,001. Slag: MnO – 9,2; SiO_2 – 28,6; CaO – 45,3; Al_2O_3 – 1,8; P_2O_5 – 0,0002. The chemical composition of the resulting metal corresponded to medium-carbon ferromanganese as required by ISO 5446-80.

CONCLUSIONS

Thus, based on studies of the technology of processing high-base manganese deposits of Ushkatyn III for refined ferromanganese in semi-industrial conditions, the following conclusions can be drawn:

1 Refined ferromanganese was smelted from the highly basic manganese ores of the Ushkatyn III deposit.
2 The process is characterized by high technical and economic indicators. High extraction of manganese from the charge (78 %), from ore (56 %) was achieved. Cost-saving the flux materials ~ 30 %.

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Note: The responsible for England language is Aigerim Kaliollayeva, Aktobe, Kazakhstan