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

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\textsubscript{general} ≥ 45 %;
- Mn/Fe ≥ 10 %;
- SiO\textsubscript{2} ≤ 15 %;
- P\textsubscript{2}O\textsubscript{5} ≤ 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\textsubscript{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-basicity 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\textsubscript{3}), brownite (Mn\textsubscript{2}O\textsubscript{3} \cdot MnSiO\textsubscript{3}) and bixbyite (Mn,Fe)\textsubscript{2}O\textsubscript{3}, and there is also a small amount of hematite phase (Fe\textsubscript{2}O\textsubscript{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...
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 (Mn₃O₄) 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 (SiO₂) and in places crystalline tephroite (Mn₂SiO₄).

The carbonate is mainly represented by fine-crystalline calcite, rhodochrosite (MnCO₃) is present, including in places with barites (BaCO₃) 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 shell 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.

$\text{MnCO}_3 \rightarrow \text{MnO} + \text{CO}_2$

$\text{MnCO}_3 \rightarrow \text{Mn}_3\text{O}_4 + \text{CO} + \text{CO}_2$

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, Mn₃O₄.

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Then at 730 - 765 °C follows a slight exothermic effect of oxidation of the formed oxides to β-kurnakite (β-Mn₃O₄). 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 tem-
pecture of a weak exothermic effect of 480 °C corre-
sponds to the processes of hygroscopic moisture release
and 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 tem-
perature 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 thermographies information can
be used to study the processes of pyrometallurgical pro-
cessing of manganese raw materials. The dynamics of
phase transformations in the concentrate is clearly dem-
onstrated 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 as-
sert 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 melt-
ing 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 fur-
cace 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 provid-
ed by the discharge of an arc in two graphite electrodes
with a diameter of 100 mm. The calculation of the
charge materials per batch load, kg:
- Manganese ore – 10;
- Fe-Si-Mn alloy – 3 - 4,3;
- Lime - 2 - 2,5.

Table 1 Composition of materials / %

<table>
<thead>
<tr>
<th>Material</th>
<th>Mn</th>
<th>CaO</th>
<th>SiO₂</th>
<th>FeO</th>
<th>P</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese ore</td>
<td>35,0</td>
<td>17,3</td>
<td>10,2</td>
<td>6,2</td>
<td>0,02</td>
<td>0,02</td>
</tr>
<tr>
<td>Lime</td>
<td>-</td>
<td>89,1</td>
<td>1,6</td>
<td>0,6</td>
<td>0,01</td>
<td></td>
</tr>
<tr>
<td>FeSiMn</td>
<td>65,1</td>
<td>29,2</td>
<td>3,5</td>
<td>0,4</td>
<td>0,04</td>
<td></td>
</tr>
</tbody>
</table>

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 signifi-
cantly facilitated, while when lime is introduced together
with ore in accordance with traditional technology, a re-
fractory 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 dis-
stributed 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; SiO₂ – 28,6; CaO – 45,3; Al₂O₃
– 1,8; P₂O₅ – 0,0002. The chemical composition of
the resulting metal corresponded to medium-carbon ferro-
manganese as required by ISO 5446-80.

CONCLUSIONS

Thus, based on studies of the technology of processing
high-basic 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 high-
basicity 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,
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