

Conference Paper

Recycling of Waste Slag Upon Production of Manganese Ferroalloys

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Abstract

The mineral resources base of manganese ores is sufficiently large in Russia. However, their mining capacity is almost absent. This is due to the low quality of domestic manganese ores and the high content of phosphorus. To date, Russia has been obliged to import the commercial manganese ore, manganese-containing ferroalloys, metallic manganese, and manganese dioxide. To produce the high-carbon ferromanganese the composition of charge was developed. The optimum variant was that where 10–15% of manganese-containing raw materials were changed for waste slag. In this case, the phosphorus content in the high-carbon ferromanganese is lower by approximately 20 rel. % in comparison with the production of ferromanganese only from the manganese-containing raw materials. About 50–60 rel. % of manganese can be extracted from the waste slag of silicon-thermal production. To produce the hot metal, the composition of iron-bearing burden material was developed. The optimum variant was that where 100% of manganese raw materials were changed for the waste slag. In this case, upon production of hot metal, the specific consumptions of manganese raw materials and limestone were decreased by 100 and 20%, respectively. The phosphorus concentration in metal was lower by about 10 rel. % as compared to the production of hot metal only from the manganese raw materials. Up to 55% of manganese can be extracted from the waste slag of silicothermic production, which is irretrievably lost at present.

Keywords: manganese ferroalloys, manganese-containing raw materials, waste slag, hot metal.

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Published: 31 December 2020

Publishing services provided by
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Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

Manganese is one of the most important strategic materials. The main consumer of manganese is ferrous metallurgy. No grade of steel can be produced without manganese. In metallurgy, manganese is used in the following forms: high-, medium-, and low-carbon ferromanganese, ferrosilicomanganese, metallic manganese. The production of manganese ferroalloys depends directly on the demand of steelmaking production.

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There is almost no mining of manganese ores in Russia [1]. This connected with a low quality of Russian ores and high price for the development of deposits. The acceleration of implementation of domestic manganese ores is of great importance from the view point of economic security. In spite of the fact that manganese belongs to the mineral resources having the strategic importance, Russia has to import currently the commercial manganese ore, manganese ferroalloys, metallic manganese, and manganese dioxide.

The provision of domestic industry with commercial raw manganese-containing materials is realized by import. In 2016, the import of commercial manganese ores and concentrates was 989 kt, including 93% of this amount from the South Africa (516 kt), Kazakhstan (203 kt), and Gabon (138 kt). In 2017, Russia imported more than 1 million tons manganese-containing raw materials [2].

In Russia, only four enterprises produce manganese ferroalloys, namely: Kosogorsk Iron Works (city of Tula) and Satka Iron-Making Plant (city of Satka, Chelyabinsk Region) produce the high-carbon ferromanganese; Chelyabinsk Electrometallurgical Works and (in small amount) West-Siberian Electrometallurgical Plant (city of Novokuznetsk) produce ferrosilicomanganese. In Russia, the total output of manganese alloys was 366 kt in 2016. In 2017, it increased to about 380 kt [2]. On the other hand, the Russian import of manganese alloys is considerable. It was 248 kt in 2016, where ferromanganese dominated (89%). The main suppliers of manganese-based alloys are four countries. These are Ukraine (83 kt), Kazakhstan (75 kt), Georgia (47 kt), and Norway (35 kt). The consumption of manganese alloys in 2016 was slightly less than 0.6 mln tons, 57% of which was provided by domestic materials. In 2017, this portion increased to about 60% [2]. Russia also imports metallic manganese. Annual buying is 40–50 kt; in 2016, 43 kt was imported, including 36 kt from China and 6 kt from Ukraine [2]. No domestic production of metallic manganese takes place in Russia.

It is necessary not only to increase the production of high-carbon ferromanganese and ferrosilicomanganese, partly owing to using the domestic manganese ores, but also to organize the production of refined manganese alloys, namely: medium- and low-carbon ferromanganese and metallic manganese. The production of refined manganese ferroalloys by the silicothermic method is characterized by a considerable loss of manganese with waste slags. The recovery of manganese in these processes is 55–65%, since the considerable amount of manganese is lost with the waste slag, which contains 18–22% MnO [3]. The slag ratio is 3–4, i.e., upon production of 1 t of metal, 3–4 t of waste slag is formed. For this reason, 15–20% of manganese being in the initial charge is irretrievably lost. To increase the beneficial use of manganese, the method should be found to reduce its losses with the waste slag upon the silicothermic production of medium- and low-carbon ferromanganese and metallic manganese.

The waste slag of these processes contains 40–45% CaO and 25–30% SiO₂. In the course of cooling of such a slag the transformation of calcium orthosilicate occurs ($\beta\text{-}2\text{CaO}\cdot\text{SiO}_2 \rightarrow \gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$), which is accompanied by the increase in the volume by 12%; this results in the slag slaking. The wastes containing this slag are an environment pollution source because the powdered slag is spread by wind. This substantially deteriorates the ecological situation in the region of the plants making the refined manganese ferroalloys.

The increased content of manganese in the waste slag, the low phosphorus concentration (0.003–0.005%), and high concentration of calcium oxide allow one to consider this slag as a promising material for the production of high-carbon ferromanganese and hot metal in the blast furnace.

To produce the high-carbon ferromanganese, the charge is well-known, which consists of manganese-containing raw materials, coke, limestone, and iron-containing additions [4]. The charge composition was developed, which differs from the known one by the fact that for the production of high-carbon ferromanganese the charge, besides the above-mentioned components, also contains the waste slag of silicothermic processes. This charge has the following composition (mass. %): 1–85 of waste slag; 5–25 of coke; 0–20 of limestone; 0–10 of iron-containing additions; manganese-containing raw materials – the rest [5].

The addition of the slag from the production of silicothermic refined ferromanganese to the charge for the production of high-carbon ferromanganese allows one not only to extract a large portion of manganese from the slag, which would be irretrievably lost, but also to decrease the specific consumption of manganese-containing raw materials. The phosphorus concentration in these raw materials (ore, concentrates) is 0.2–0.3%. Since the portion of manganese-containing raw materials in the charge decreases, the phosphorus amount contributed by these raw materials also reduces and, as a consequence, the phosphorus concentration in ferromanganese diminishes too. The high content of calcium oxide (40–45%) in the waste slag allows one to decrease considerably the limestone consumption when this slag is added to the charge for the production of high-carbon ferromanganese.

Different variants of burden materials depending on the amount of waste slag of silicothermic production of refined manganese ferroalloys from 0 to 100% were studied.

The production of high-carbon ferromanganese using the above charge allows one to decrease the specific consumptions of manganese-containing burden materials and limestone, and also the phosphorus concentration in the high-carbon ferromanganese, to extract a large amount of manganese from the waste slag of silicothermic process,

which could be irretrievably lost. However, with an increase in the amount of this slag, the slag ratio upon production of high-carbon ferromanganese also increases.

The optimum variant is that where 10–15% of manganese raw materials were changed for the waste slag. Upon production of high-carbon ferromanganese according to this technology the limestone specific consumption also decreases to zero. The phosphorus concentration in the high-carbon ferromanganese is lower by about 20 rel. % in comparison with the production of ferromanganese only from the manganese raw materials. From the waste slag of silicothermic process, 50–60 rel. % Mn can be extracted.

The charge for the production of hot metal consisting of iron-containing and manganese-containing raw materials and also limestone is well-known [6]. The composition of burden material was developed that differs from the known one by the fact that the charge for the production of hot metal, besides iron- and manganese containing burden materials and limestone, also contains the waste slag of production of refined manganese ferroalloys. This charge has the following composition (mass. %): 0.1–5.0 of waste slag; 85–90 of iron-bearing burden materials; 5–10 of limestone; manganese-bearing burden materials is the rest [7].

The addition to the charge for the hot metal making of the waste slag of silicothermic production of refined manganese ferroalloys allows one not only to extract the most part of manganese from the slag, which would be irretrievably lost, but also to decrease or completely exclude the consumption of manganese-containing raw materials (ore or concentrate) upon hot-metal production. The phosphorus content in these materials (ore, concentrates) is 0.2–0.3% and more. Since the amount of manganese raw materials in the charge for the hot metal production decreases, the phosphorus amount introduced by them also diminishes. Therefore, the phosphorus concentration in the hot metal also decreases as the waste slag contains 0.002–0.005% P. The high content of calcium oxide (40–45%) in the waste slag allows one to decrease the limestone consumption when it is added to the charge for the hot metal production.

Different variants of composition of burden materials depending on the amount of waste slag of silicothermic production of refined manganese ferroalloys (0-100%) were studied. The hot metal production using this charge allows one to decrease the specific consumption of limestone and the phosphorus concentration in the hot metal, and also to extract manganese from the waste slag, which could be irretrievably lost.

The optimum variant of charge composition is that where 100% of manganese-bearing burden materials are changed for the waste slag. When the hot metal is produced according to this technology, the decrease in the specific consumption of manganese raw materials is 100% and that of limestone is 20%. The phosphorus concentration in the hot metal is lower by about 10 rel. % as compared to the production using only the

manganese raw materials. Up to 55% of manganese can be extracted from the waste slag of production of metallic manganese, which is currently irretrievably lost.

Upon production of high-carbon ferromanganese and hot metal in the blast furnace using the above compositions of charge, the conventional components are added in the blast-furnace mouth, the powder slag of silicothermic production of metallic manganese is blown through tuyeres. In some situations, upon production of refined manganese ferroalloys, the additions stabilizing the slag and preventing its slaking are introduced into the charge. In this case, the solid slag is broken and added into the blast-furnace mouth together with other components.

Thus, the recycling of waste slag of production of refined manganese ferroalloys by the silicothermic method allows one to increase the beneficial use of manganese because of its loss reduction with the waste slag and to improve the environmental situation in the regions of the plants producing this material.

Funding

This study was financially supported by the Program of Presidium of RAS No. 22P “Fundamental Foundations of Advanced Technologies in Interest of National Safety”

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