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DEVELOPMENT OF A PYROMETALLURGICAL TECHNOLOGY FOR PROCESSING SYNTHETIC PYROLUSITE AND CHEMISORPTION MANGANESE OXIDE CONCENTRATE INTO METALLIC MANGANESE AND LOW-CARBON FERROALLOYS

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ABSTRACT

This paper describes a new pyrometallurgical technology for producing manganese ferroalloys from a new type of manganese materials — i.e. chemical concentrates, such as synthetic pyrolusite and chemisorption concentrate, which are produced from low-grade manganese material through pyrometallurgical processing. Two processes are described: a silicothermal process of producing low-carbon manganese in an electric furnace and an aluminothermic process of producing metallic manganese. A simple process, a high reaction rate, the possibility to set up a continuous process and feasibility in the current market environment all indicate that the aluminothermic process is likely to be adopted by the industry. Metallic manganese, the product of the aluminothermic process, is used in the production of alloyed steels and special-purpose manganese alloys. The possibility to use slag as clinker adds to the cost-effectiveness of this process.

Metallic manganese is mainly used as an alloying element for ultra high quality steels, as well as for the production of low-carbon manganese alloys. The output required to completely cover the demand of the national economy approximates 40 th tons per annum.

One of the most important tasks to ensure economic and environmental safety includes development of new techniques for producing manganese ferroalloys from a new type of manganese materials — i.e. chemical concentrates, such as synthetic pyrolusite (SPYR) and chemisorption concentrate (CSC), which are produced from low-grade manganese material through pyrometallurgical processing [1–4]. What differentiates the above mentioned chemical concentrates from the common types of manganese materials is a high concentration of manganese (more than 60%) in combination with a low concentration of iron, silica and phosphorus. A pyrometallurgical technology was developed with the purpose of finding application for this new type of raw materials [5–7]. Using the results of the research work and long-term experiments, the authors developed two processes for producing manganese alloys:

- a silicothermal process of producing low-carbon manganese in an electric furnace.
- an aluminothermic process of producing metallic manganese [8];

With the help of the above techniques, one can produce metallic manganese with the minimum Mn concentration of 95–97% (**Table 1**): grades “Mr 2”, ”Mr 1”, ”Mr A”.

Table 1. **Characteristics of metallic manganese produced through silicothermal and aluminothermic processes from SPYR and CSC**

Grade	Concentration, wt %				
	Mn	Si	C	Al	P
	Minimum	Maximum			
Mr 2	95.0	1.8	0.2	0.7	0.07
Mr 1	96.5	0.8	0.1	0.7	0.05
Mr A	97.0	0.5	0.05	2.0	0.02

Mr 2 and Mr 1 stand for the grades of metallic manganese that are well-known at the market, whereas the Mr A grade (i.e. aluminothermic manganese) is yet to be introduced to the market. It is not expected to be challenging considering the grade’s high quality and affordable price amid rising prices for high-quality manganese [9]. The affordability of aluminothermic manganese is due to its relatively low cost when using the proposed production process [10]. However, to minimize commercial risks the plan is to limit the initial production of Mr A to 20% of the total output [11].

Silicothermal Process

In terms of the main stages involved, the proposed silicothermal process for producing metallic manganese (low-carbon ferromanganese) is similar to the technology adopted by the Zaporozhye Ferroalloy Plant.

Two options are proposed for the silicothermal process of producing low-carbon ferromanganese in an electric furnace. Option 1 is when a mixture of ore and lime is melted in the furnace and a solid deoxidizer (ferrosilicium) is introduced to the melt at discharge.

It would be better to use Option 2, as it helps save electric power for melting ferrosilicium. What differentiates the proposed process is that we propose to blend the SPYR-lime melt with silicomanganese (ferrosilicium) in the ladle. This can help raise the manganese recovery to 80%. The main reaction describing the process is as follows:

$$MnO_2 + Si + CaO =$$

$$= Mn + SiO_2{\times}CaO \text{ or } Mn_2O_3 + Si + 2CaO =$$

$$= 2Mn + 2CaO{\times}SiO_2$$

Silicomanganese: Si: 20–28%, Mn: 65–72%, P: 0.05%, Fe: remainder up to 100%.

Slag: MnO: 12–16%, CaO: 43–45%, SiO_2: 32–36%.

A silicothermal process flow chart was developed for the production of low-carbon ferromanganese in an electric furnace. **Fig. 1** shows a process flow chart in which low-carbon ferromanganese is produced in and discharged from the electric furnace together with slag.

The resultant low-carbon ferromanganese is used in the production of super duty steels. The table below shows the chemical composition of the common grades of ferromanganese (extract from GOST 6008-90) (**Table 2**).

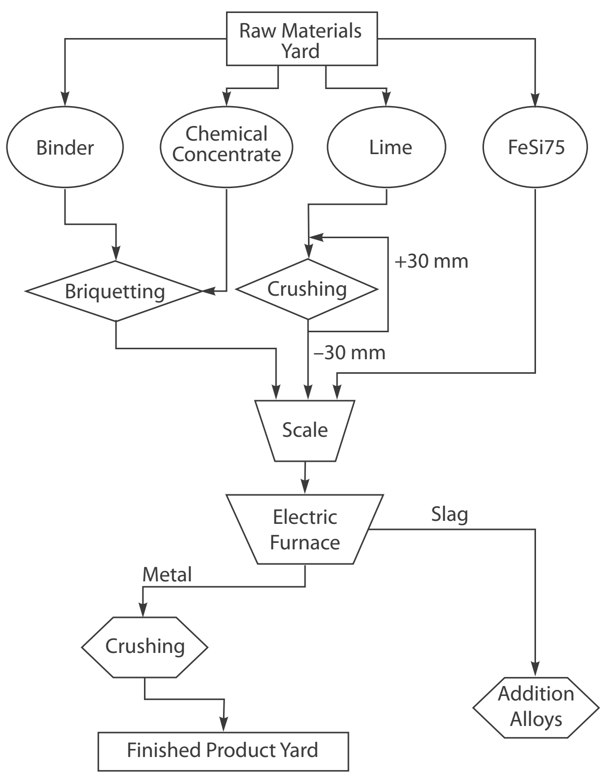

Fig. 1. Melting Process Flow Chart

Compared with the commonly used melting technology, the developed process helps reduce the power consumed per ton of the product and increase the yield. Due to the use of high-quality material — i.e. SPYR — one can significantly lower the phosphorus content in the final manganese alloys and, hence, make them more competitive versus their international counterparts.

The following burden materials are used in low-carbon ferromanganese production: chemical concentrate (SPYR or CSC), FeSi 75 and lime.

Recommended burden mixture: CSC — 100 kg; FeSi 75 — 23-30 kg; lime — 40-50 kg (**Table 3**).

Standard ferrosilicium and lime are used. Well-burned lime is fed in the furnace with the minimum concentration of CaO of 96.5% and the maximum concentration of C of 0.2%.

Because the process reaction does not produce enough heat to support a spontaneous process, the rest of the required heat is introduced by electric arcs when manganese concentrate is melted in the furnace together with lime.

Table 2. **Chemical composition of ferromanganese**

No	Grade	Concentration, wt%				
		Mn, minimum	Si, maximum	C, minimum	Al, maximum	P, maximum
1	FMn 88	85.0	3.0	2.0	0.5	0.1–0.3
2	FMn 90	85.0	1.8	0.5	0.5	0.1–0.3

Table 3. **Burden materials**

Mn concentrates used for the production of ferromanganese			
Grade	Composition	SPYR	CSC
Concentration, wt %	Mn	62.6	67
	MnO_2	98.8	–
	P	0.005	no
	S	0.02	0.05 (0.3)
	SiO_2	0.2	–
	$Na_2O + K_2O$	0.25	–
Ferrosilicium lumps (5–30 mm), FeSi 75 per GOST			
Grade		FeSi 75	
Concentration, wt %	Si	75	
	Fe	24	
	C	0.1	
	P	0.05	
Burned lime (TU 141-24-83)			
Grade		Quality 1	
Concentration, wt %	CaO	96.5	
	MgO	0.6	
	Al_2O_3	0.4	
	SiO_2	0.5	
	C	0.2	
	P	0.02	

Preparation and smelting. A double-electrode furnace with a 100 kVA transformer had a magnesite brick lining, and the seams were filled with grain magnesite. The lining was heated up for 6-8 hours under current load using coke. Once the furnace shell temperature reached 150–170 °C, the current was disabled, the furnace — tilted, and all the unburnt coke — removed from the furnace; after that the furnace was returned in the working position, the electrodes — lowered, and the burden materials — charged in.

The smelting process takes place in a tilting furnace. First, the appropriate amounts of lime and chemical concentrate are charged in the furnace, the electrodes are lowered and the current load is enabled. Once all the burden has melted, the full amount of ferrosilicium is charged within 3-5 minutes. After 10–12 minutes of maintaining the furnace under load the metal is discharged together with slag. At the beginning of the smelting process the secondary voltage is maintained at maximum, and when long electric arcs appear the furnace is switched over to lower voltage.

Aluminothermic Process

The aluminothermic process is basically a reaction of reducing manganese oxides (MnO_2 or Mn_2O_3) to obtain manganese:

$$MnO_2 + Al + CaO = Mn + Al_2O_3{*}CaO$$

Materials consumed per 1 ton of metallic manganese (97% Mn): SPYR — 1,920 kg, aluminium — 770 kg, lime — 385 kg.

Slag: MnO — 8-12 %, Al_2O_3 — 65-72 %, CaO — 15-22 %.

The thermal characteristic of the aluminothermic smelting process includes specific heat. This parameter indicates how much heat is released during the process per unit weight of the burden. According to the calculations, a spontaneous manganese reduction process can take place if the specific heat has reached and is maintained at around 550 Cal/kg of burden. Manganese reduction from the chemical concentrate, in which manganese is mainly present as manganese dioxide (MnO_2), produces more than 4,615 MJ of heat per ton of burden. To decrease heat generation when reducing manganese dioxides it is proposed to use the in-house waste product (i.e. slag) and lime.

Fig. 2 shows an aluminothermic process flow chart.

Metallic manganese produced from manganese oxides (SPYR, CSC) through aluminothermic process is used in the production of alloyed steels and special-purpose manganese alloys.

The burden used in the process consists of manganese oxides, aluminium powder (deoxidizer for manganese), lime (slag quality enhancer) and return slag added for decreasing the process heat generation.

The following burden composition was defined through calculations and experiments, kg: manganese concentrate — 100 kg; aluminium — 35–40 kg; lime — 10–20 kg; return slag — 10–25 kg.

The chemical concentrates of SPYR and CSC are used in the production of metallic manganese. Their compositions are given in **Table 4**. The size is smaller than 1 mm.

Aluminium powder is used in the aluminothermic process. It is produced by atomization of liquid primary aluminium with air. **Table 5** shows the composition of aluminium powder. Its size distribution is as follows: 0–0.1 — 30% max; 0.1–1.0 — 60% min; 1.0–3.0 — 2% max.

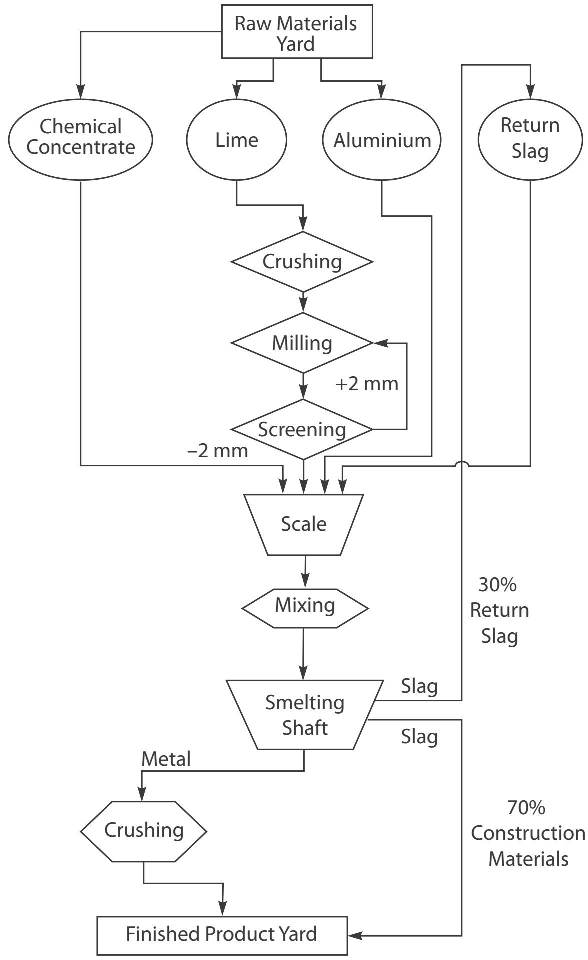

Fig. 2. Aluminothermic Process Flow Chart

Table 4. **Compositions of the manganese concentrates used in the aluminothermic process**

Grade	Concentration,% min				
	Mn	MnO_2	P	S	W
SPYR	62.6	98.8	0.005	0.02	0.03
CSC	67.0	–	–	0.05	3

Table 5. **Aluminium powder composition**

Grade	Al, minimum	Additional elements, maximum				
		Fe	Si	Fe + Si	Cu	Total
A-1	99.5	0.30	0.30	0.45	0.015	0.50

Table 6. **Lime composition**

Material	Concentration,%				
	CaO	MgO	Al_2O_3	P	S
Lime	>96.5	<1.5	<0.9	0.02	0.02

Freshly burned lime containing no CO_2 should be used. The lime composition is shown in **Table 6**.

The slag from the previous heat is used as return slag in the process. It contains up to 15% of manganese oxides, 55 — 70% of aluminium oxides and 20 — 25% of calcium oxides. Before use the return slag is crushed and milled to the size of 2 mm.

Principal Diagram of the Process. The following items of the main equipment are used to enable the process:

1. *Raw Materials Yard:* hoppers, dozing units, scale, overhead cranes, inter bay trolley.
2. *Comminution and Pyro Section:* hoppers, crusher, mill, vibrating screen, scale, mixer, container, kiln, cyclone, overhead crane.
3. *Smelting Section:* hoppers, crucible, moulds, ignition chamber, inter bay trolley.
4. *Slag Yard:* crushers, breaker, screen, scale, hoppers.
5. *Finished Product Yard:* scale, hoppers, packaging, crane, electric car.

Let's look at the smelting process. A crucible is a 1 m high steel pipe 1—1.2 m in diameter with a refractory lining on the inside (grain magnesite with a binder). The minimum wall thickness of the pipe is 20 mm. The crucible is put on a platform and rolled in the shaft.

Once the crucible is ready, 10—15% of conditioned burden is charged in its bottom. Burden is fed and the feed rate is adjusted from a hopper by opening and closing a feeder. The charge is evened, and dips are made on the surface, in which an ignition charge of saltpeter and magnesium turnings is placed. A hot metal core is used to ignite the charge.

After the process has spread through the shaft top, the rest of the burden material is gradually charged, and the smelting process is maintained in the way that there was always a thin layer of initial burden covering the surface of the melt. The burden feed rate is dictated by the rate of the reduction process and can be adjusted by closing the feeder.

The normal smelting process can take from 12 to 20 minutes per 200—250 kg of burden. After that the crucible with the melt is kept in the smelting shaft for 30 minutes until degasification has ended and all the reguli have precipitated. Slag can be discharged in the moulds, which will help the metal cool down faster. Samples of the metal and the slag are taken only after the melt has completely cooled down.

The final metal is transferred to the finished product yard, where it is crushed to a certain size and shipped off. A part of the slag is recycled in the process, while the rest of it goes to construction companies.

Aluminothermic process is also used in the production of metallic chromium and a broad range of iron-free chromium alloys, the latter are added to special-purpose steels and alloys [12—14].

Metallic manganese produced from manganese oxides (SPYR, CSC) through aluminothermic process can be used in the production of alloyed steels and special-purpose manganese alloys [15].

It should be noted that that slag is used to produce clinker contributes to the cost-effectiveness of the process [16].

The indicators see a considerable rise when smelting takes place in a furnace and when lower temperatures are used.

Processing Waste. Up to 1.5 tons of slag is produced with every ton of metallic manganese. The slag mainly contains aluminium oxides (Al_2O_3 — 50—60%; CaO — 25—30%; MnO — 15—20 %). These high-alumina slags can serve as alumina cement, a product for synthetic slags, crushed stone, abrasive materials.

Up to two tons of slag of the following composition are produced together with low-carbon ferromanganese: CaO — 39—44 %; SiO_2 — 29—35 %; MnO — 15—22 %. All highly basic slags are subject to slaking, and their further use can only be possible as the following materials:

- Liquid quick-hardening moulding sand mixtures;
- Material for casting ladles;
- For chalking of acidic soils;
- For neutralization of waste water.

Appropriately processed, such waste can be transformed in construction materials and other by-products.

Conclusions

1. The authors tested a pyrometallurgical technology of producing manganese ferroalloys from a completely new type of manganese materials — i.e. SPYR and CSC.
2. Two processes were developed: aluminothermic process — for producing metallic manganese from manganese alloys (SPYR and CSC); and silicothermal process — for producing low-carbon manganese in an electric furnace.
3. A simple process, a high reaction rate, a possibility to create a continuous process and feasibility in the current market environment all indicate that the aluminothermic process is likely to be adopted by the industry.
4. Metallic manganese produced from manganese oxides (SPYR, CSC) through aluminothermic process is used for the production of alloyed steels and special-purpose manganese alloys. The possibility to use slag as clinker adds to the cost-effectiveness of this process.
5. Aluminothermic manganese ("Mr A") with a high concentration of metallic manganese (97%) was produced.
6. Aluminothermic process may become an important sector of steel making industry, the products of

which will mainly be used in the production of high-alloy steels and specific alloys. Many alloys are currently produced on a non-commercial scale. A growing demand for low-carbon manganese alloys created the need for setting up new production lines. In this one should strive to scale up the introduction of machines and automation to streamline the most labour-intensive operations and to improve the quality of burden materials, which will benefit the quality of the end product and boost performance.

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