

Manganese concentrate usage in steelmaking

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Abstract. The results of the research process of producing metalized products by solid-phase reduction of iron using solid carbonaceous reducing agents. Thermodynamic modeling was carried out on the model of the unit the Fe-C-O and system with iron ore and coal. As a result of modeling the thermodynamic boundary reducing, oxidizing, and transition areas and the value of the ratio of carbon and oxygen in the system. Simulation of real systems carried out with the gas phase obtained in the pyrolysis of coal. The simulation results allow to determine the optimal cost of coal required for complete reduction of iron ore from a given composition. The kinetics of the processes of solid-phase reduction of iron using coal of various technological brands.

Abstract. The paper describes experiments on effects of metal deoxidizer composition, component proportion, pelletizing mixture, particle size distribution of basic materials and flux on manganese recovering from oxides under direct melting.

Introduction.

Results of varied briquette usage for direct-ladle steel melting has shown that manganese recovery from briquettes is increased to 1,5-fold more than recovery from conventional ferroalloys, taking into account some losses due to melting and in-steel inclusions. Direct-alloyed steel satisfies standard specifications of gas and nonmetallic content and mechanical properties as well.

Analysis of modern steelmaking technology shows that costs of deoxidizing and alloying and the cost of consumed energy significantly affect the cost of the product; while the cost of energy consumption affects not only directly but also indirectly, through the price of ferroalloys. Besides, when alloying steel with manganese, Mn heavy losses are inevitable: up to 20 % of manganese is lost during extraction, 20 – 25 % – during ore concentration, 20 – 25 % – during smelting of ferroalloys, up to 25 % – during steel alloying, i.e. total recovery of manganese does not exceed 50 %. One way to improve the efficiency of deoxidizing and alloying of steel is modification of manufacturing of alloying agents, in some cases it is the use of direct steel alloying in the furnace or the ladle, using ores and concentrates [1 – 6].

Manganese can be reduced by aluminum, silicon or carbon. The simplest version of ladle steel deoxidizing and alloying is the use of melting briquettes composed of oxide materials and reducing agents [7]. Completeness of the reaction in the briquette depends on the size of the contact surface of



starting materials, fragmentation and concentration of major components, temperature, rate of reaction of products disengagement and forming of low-melting fluid slag at a given temperature.

Impact of various factors on metallothermic reduction of manganese with silicon has been examined in laboratory conditions. Conventional silicon-manganese alloy and unconventional alloys with different silicon and aluminum contents were used as reducing agents. Lime and dolomite were used as fluxes.

Use of aluminum-containing alloy as a reducing agent can improve the reduction of manganese. Table 1 shows the results of manganese reduction with various compositions of the reducing metal.

Briquettes were made from manganese ore, metal-reducing agent and flux. The briquettes were loaded into a graphite crucible which was put into a Tammann furnace and heated to 1500 °C. After a five-minute heating alloy and slag were poured and analyzed.

A fusible slag is formed when reducing with both aluminum and silicon in predetermined proportions; that increases the reaction rate in briquettes, allows more complete reduction of the major component and cuts flux consumption. Presence of 15 – 20 % of Al_2O_3 in the slag contributes to high speed of the process and good separation between the metal and the slag.

Mn-Si-Fe alloy-composition with a manganese content of 15 – 30 % and silicon content of 40 – 45 % used as a reducing agent (see Table 2) allows increasing of manganese-to-silicon ratio by 1.5 – 2-fold in the end metal. This enables the use of such briquettes for ladle deoxidizing and alloying of carbon steels, low-alloyed and alloyed steels of various grades.

Table 1. Results of manganese reduction with various reducing agents.

Indicators	FS45 (44 % Si, 1,36 % Al)	FS65 (66,2 % Si, 1,7 % Al)	FS75 (75,65 % Si, 2,1 % Al)	Alloy composition Al-Mn-Si-Fe (6,5 % Al, 22,1 % Mn, 32,47 % Si)
Briquettes composition, %				
Ferro-Silicium	50	42	41,5	42
Ore	35	42	41,5	35
CHPP ash	5	5	5	5
Dolomite	10	11	12	11
Alloy Composition,%				
Mn	36,30	38,29	38,21	46,95
Si	17,43	28,34	34,65	18,29
Mn Removing ,%	84,9	80,4	75,6	94,0
MnO content in the slag,%	10,9	12,2	12,9	6,0

Table 2. Results of manganese recovery from briquettes.

	Standard FS45	FS45Mn25
Briquette composition, mass. %:		
FerroSilicium	50,0	50,0
Roasted ore	35,0	35,0
Hearth slag	5,0	5,0
Dolomite	10,0	10,0
Metal Yield,%		
Consumption of FS 45	133	130
Alloy composition: %		
Mn	32,3	52,7
Si	22,1	24,1

	Standard FS45	FS45Mn25
P	0,09	0,12
Recovering:		
Mn	84,9	90,6
Si	65,3	69,6

Ratio between roasted concentrate consumption and reducing agent consumption should be $(0.7 - 0.8) / 1.0$ in briquettes. With such a ratio between components, manganese recovery is 90 – 95 %; recovery from the briquette concentrate is 85 – 90 %. The manganese content in the slag, which is formed in the briquette, is reduced to 7 – 10 % and below, with silicon residual content of 15 – 20 % in metal droplets. Slag multiplicity in the briquettes, after process completion, is only 0.70 – 0.75 when compared with the slag multiplicity of 2.0 – 2.5 at conventional low-carbon ferromanganese smelting.

For increased recovery of manganese from carbonate manganese ore, a product of manganese-carbonate ore thermal treatment was proposed as the oxidizer obtained by longer roasting of the ore in oxidizing environment.

Chemical composition of the product of carbonate ore thermal treatment is shown in Table 3, and its phase composition – in Table 4.

Table 3. Chemical composition of the product of carbonate ore thermal treatment.

Manganese Carbonate ore	Yield after roasting, %	Chemical composition, %							
		Mn	MnO	CaO	MgO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Fe ₂ O ₃
Usinskaya 26 % Mn	72,50	35,86	28,36	13,24	4,83	17,93	1,38	0,51	7,60
Usinskaya 30 % Mn	70,27	42,69	33,77	14,94	1,42	11,38	1,42	0,53	6,70

Table 4. Phase composition of the product of carbonate ore thermal treatment.

Manganese Carbonate ore	Phase composition %		
	(Ca, Mg)Mn ₂ O ₄ + (Ca, Mg) Fe ₂ O ₄	Mn ₂ O ₃ + Fe ₂ O ₃	Silica and other oxides
Usinskaya 26 % Mn	75,0	5,5	19,5
Usinskaya 30 % Mn	64,2	23,0	12,8

The best results are obtained by roasting of manganese carbonate ore, containing 26 – 31 % of Mn, 8 – 11 % of calcium oxide and 1 – 3 % of MgO, 2-7% of Fe₂O₃, 8-17% of SiO₂, in oxidizing environment.

The product of thermal treatment, which can be used for production of water-resistant exothermic briquettes for direct steel alloying, should be roasted in oxidizing environment for 1 hr at 850 – 950 °C. Cooling to 500 – 600 °C should be performed in oxidizing environment. Fusible manganese oxides which accelerate formation of ferrites and calcium manganites are formed in the ore.

Thus, the product of carbonate ore thermal treatment does not contain free bases and is presented by following, compounds, mass. %:

(Ca, Mg) (Mn, Fe) ₂ O ₄	55 – 75;
Mn ₂ O ₃ + Fe ₂ O ₃	5 – 25;
Silica and other oxides	10 – 30.

The study shows that the product of thermal treatment of carbonate ore in the oxidizing environment is not hygroscopic. Moisture content does not increase during storage for 3 – 4 weeks in air. X-ray phase study shows that all lime and magnesia in the products are fixed isomorphous mixtures of ferrites and manganites of Ca and Mg.

Briquettes, having compositions as shown in Table 5, are manufactured from the material obtained and the reducing metal (Mn 30,13 %; Si 30 %; Al 7 %). Results of manganese reduction from the briquettes are given in Table 6.

Table 5. Composition of briquettes.

Components	Compositions, mass %				
	1	2	3	4	5
Alloy of Aluminum, manganese, silicon and iron	56,5	47,5	43,0	60,0	40,0
Product of carbonate manganese ore thermal processing	39,5	47,5	51,5	36,0	45,5
Liquid glass	4,0	5,0	5,5	4,0	5,5

During sintering of the briquettes of the proposed composition, manganese reduction from aluminum oxide and silicon occurs at high speed as well as inter-reacting of Al_2O_3 and SiO_2 which are resulted from the reaction.

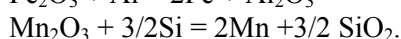
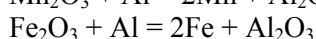
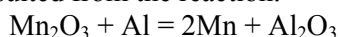


Table 6. Results of manganese reduction from products of thermal treatment.

Characteristics	Compositions of exothermic briquettes				
	1	2	3	4	5
Alloy compositions, %					
Mn	49,52	52,37	52,9	The metal is not completely separated from the slag	54,9
Si	19,11	17,11	17,42		13,4
Al	0,22	0,24	0,20		0,20
Slag compositions, %					
MnO	4,36	6,68	6,03	The metal is not completely separated from the slag	15,0
SiO ₂	43,0	43,78	43,62		47,0
Al ₂ O ₃	24,16	20,28	20,93		not found
CaO	19,7	17,7	21,2		
Slag multiplicity	0,48	0,52	0,53	0,6	0,7
Recovery of Manganese to alloy, %	87,2	82,97	80,14	75,0	70,0

At the first process stage, when aluminum is being oxidized, silica ore is an active flux; whereby products of thermal treatment of high-grade ore (Mn 30 – 35 %; SiO_2 8 – 10 %; CaO 8 – 11 %; MgO 1 – 3 %) and of relatively low-grade ore (Mn 25 – 27 %; SiO_2 13 – 17 %; CaO 6 – 10 %; MgO 1 – 3 %; Fe_2O_3 3 – 7 %) can be successfully used.

In laboratory conditions, the main technological parameters of mixtures for direct steel alloying were investigated as well as their impact on volume of manganese reduction from oxides. These parameters include value of component mixing, particle size distribution (PSD) of oxidant, reductant and flux, type of coupling agent and a mixture pelletizing technology.

It is established experimentally that grinding of ore fines together with reductant powder ensures total contact between the particles of metal reducing agent and ore. This increases (by 5 %

approximately) the amount of recovered manganese in comparison with briquettes made by conventional techniques. Besides, in briquettes with the charge subjected to co-grinding, recovery of silicon increased by about 3 %. Investigation of effect of starting material PSD on rates of manganese reduction from oxides by direct alloying showed that quantity of particles larger than 1 mm should be limited in mixtures.

It is established experimentally that during pelletizing of mixtures for ladle direct steel alloying with manganese, lignosulfonate concentrates and liquid glass can be used as coupling agents. Particularly effective is the use of boric oxide as a coupling agent. In this case, even briquettes with lime content retain strength in air for two weeks. When utilizing TPP ash as a flux (8.88 % Al_2O_3 , 23.98 % SiO_2 , 0.56 % TiO_2 , 45.85 % CaO , 4.98 % MgO , 6.32 % FeO , 8.18 % Fe_2O_3 , 1.82 % other impurities) it is practical to use water for moistening the mixture. Oxides of CaO , SiO_2 , Al_2O_3 presenting in the ash, react with water to form stable compounds: $2\text{CaO}\cdot\text{SiO}_2\cdot 4\text{H}_2\text{O}$, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$, $\text{SiO}_2\cdot 2\text{H}_2\text{O}$ having astringent properties. It is found that pelletizing of mixtures for direct steel alloying can be performed by pelletizing or briquetting at a disk granulator; wherein, pelletizing method does not significantly affect the parameters of manganese reduction from oxides. The briquettes and pellets have a sufficient strength for transportation.

The technology of ladle deoxidizing and alloying of steel with manganese using mixtures of different composition passed industrial tests in 25-ton electric arc furnaces. Mixtures of the following compositions were used:

I – friable alloy [8] Al–Mn–Si–Fe–C (7 % Al, 25.5 % Si, 27 % Mn) – 39.2 %, manganese ore – 39.2 %, dolomite – 19.6 %, a coupling agent – 2 %.

II – FS45 – 42 %, manganese ore – 42 %, dolomite – 12 %, a coupling agent – 4 %.

III – FS75 – 17.4 %, manganese ore – 43 %, dolomite – 11.5 %, CHP ash – 23.2 %, water – 4.9 %. Steel grades St40, St45, St20 (briquettes, composition I and II) and St45L, St35L (composition III, pellets) were smelted by direct alloying. Technological characteristics of certain melts, using briquettes of composition I, are shown in Table 7.

The mixtures were fed into the ladle during tapping. The temperature of the steel before the tapping was 1883 – 1893°K, that is close to the upper limit recommended by technological instruction. Briquettes dissolved completely at the period of tapping. Use of briquettes and pellets containing manganese oxide materials gave rise to manganese recovery by 78 – 88 % compared with 70.5 % at conventional smelting.

It is known that, when melting ferromanganese and silicomanganese, about 80 % of manganese is recovered from the ore; and the coefficient of manganese total recovery does not exceed 60 %. Obviously, the above-described technology increases total recovery of manganese and eliminates the use of conventional manganese ferroalloys which contain 1 % of manganese. The use of oxide manganese materials for ladle deoxidizing and alloying of steel reduces the cost of deoxidizing by 276 rubles per ton for the steel with 0.35 – 0.65 % manganese content.

Table 7. Technological characteristics of some experimental melts

Characteristics	conventional (average for 10 melts)	melt № and steel grade						
		1	2	3	4	5	6	7
		St35	St45	St35	St40	St40	St40	St40
Before deoxidizing, %								
C	0,26	0,37	0,44	0,37	0,39	0,41	0,38	0,38
Mn	0,19	0,17	0,18	0,16	0,22	0,22	0,23	0,23
In finished steel, %								
C	0,35	0,35	0,35	0,36	0,42	0,44	0,38	0,39
Mn	0,63	0,70	0,68	0,68	0,68	0,69	0,70	0,68
Si	0,22	0,21	0,25	0,27	0,22	0,22	0,24	0,22
S	0,030	0,034	0,032	0,031	0,032	0,032	0,031	0,030
P	0,019	0,017	0,014	0,018	0,014	0,022	0,018	0,018

Consumption of deoxidizer, kg								
To furnace: FMn70	123	-	-	-	-	-	-	-
SMn17	150	-	-	-	-	-	-	-
FS65	-	-	-	-	-	-	-	-
FS25	-	150	150	150	100	100	100	100
To ladle: FS65	150	70	60	60	60	60	60	60
Briquettes	-	800	750	750	700	700	700	700
Melt weight, t	30,4	31	30,4	30,4	31	31	30,4	30,4
Recovery of Mn, %	70,5	78,08	77,05	75,5	77,5	79,1	77,6	75,5
Total recovery of Mn %	57,5	74,64	73,65	76,57	74,1	75,6	74,1	72,2

Quality tests of steel, produced by direct alloying with oxide manganese-containing materials in the ladle have shown that macrostructure, gas content, nonmetallic inclusions and mechanical properties of the resulting metal satisfy all requirements and are identical to the steel produced by the conventional technique (see Figures 1 and 2).

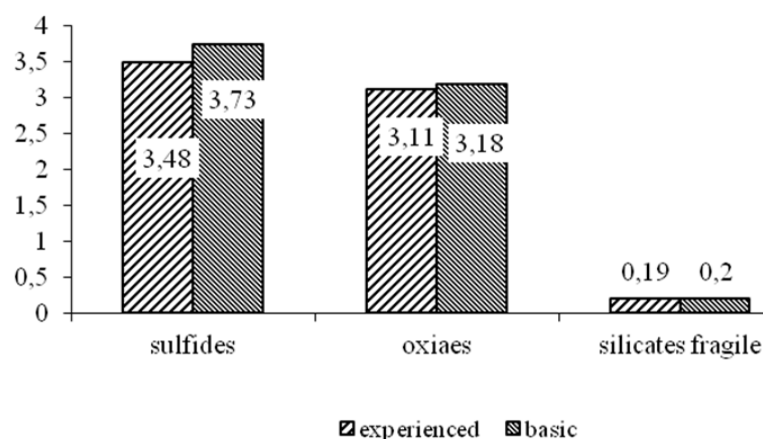
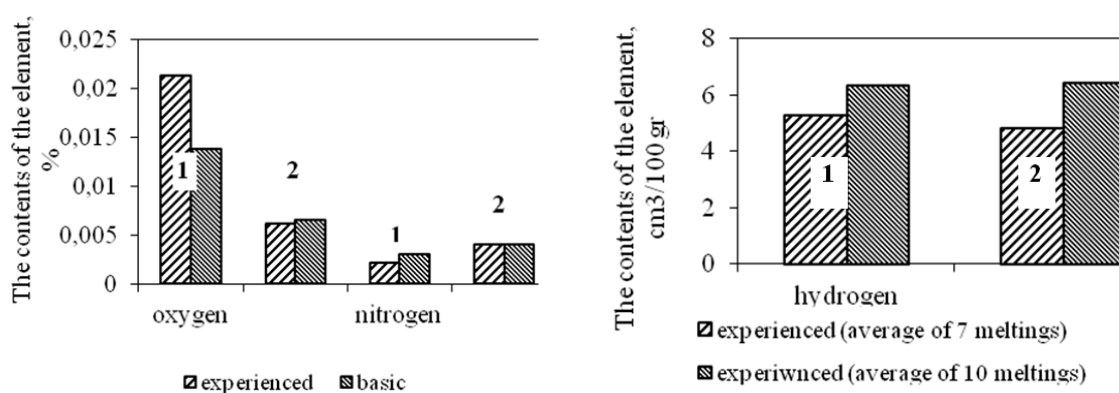


Figure 1 – Pollution of steel 40 with nonmetallic inclusions



1 – sample of metal from furnace before tapping; 2 – sample of metal from ladle after tapping

Figure 2 – Content of gases in steel

Findings

1. Mixtures for direct alloying, based on the Al–Mn–Si–Fe–C friable alloy and on the conventional ferrosilicium, were tested in industrial environments.
2. In direct steel deoxidizing and alloying with briquettes based on Al–Mn–Si alloy, manganese is recovered with high stability. Total recovery of manganese from briquettes exceeds the recovery using conventional ferroalloys by almost 1.5 times (taking into account all the collateral manufacturing losses).
3. The stable recovery of manganese is approximately 90 % in direct steel deoxidizing and alloying with briquettes and pellets in the ladle, using exhaust system dust as a reducing agent in fractionating of conventional ferrosilicium FS45 and FS75.
4. The metal from experimental melts satisfies standard specifications of macrostructure, gas content, nonmetallic inclusions and mechanical properties.

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