

High-Quality Low - Phosphorous Manganese Alloys for Production of Steel of Low-Temperature Reliability

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Abstract. The problem of enrichment and dephosphorization of poor manganese ores for receiving the low-phosphorous alloys necessary for smelting of steel of low-temperature reliability is considered.

Introduction

Development of the progressive technologies providing improvement in quality and increase in production volume of steel products and reduction in consumption of materials are the priority directions of steel production development in modern conditions.

It is difficult to expect high efficiency from the improvement traditional materials properties without the use of new technologies. The main ways to enhance strength and operational characteristics of steel products are based on a deep and effective influence on the structure of the crystallizing metal by ladle treatment of the melt with intensifying and modifying agents which influence at the nanoscale level. There is much tension today around the issue of the development and use of special steels for working in extreme conditions at maximum loads, therefore, the development of technologies improving steel quality and operating characteristics is of current interest.

The alloying materials bringing the greatest number of phosphorus in steel are manganese alloys. Manganese ores of the vast majority of domestic fields at a big variety of mineral structure are characterized by low quality at the low content of manganese and high specific content of phosphorus (the relation P/Mn more than 0.006). They contain the increased amount of iron and silicon dioxide and belong to rebellious ore. About 90% of balance reserves of manganese ores are the share of carbonate ores therefore efforts of researches of the last years also were directed to enrichment of these ores.

The most large-scale deposits of manganese ores in Russia – Usinsk in the Kemerovo region (92 million tons of carbonate ores) and fields of the North Ural region of manganese ores (41 million t of carbonate ores). Ores of these fields are practically not enriched with traditional methods [1].

Manganese concentrates with manganese content to 32% allow to receive use of methods of radiometric enrichment, but they also have the increased content of phosphorus [2]. It is connected mainly with the fact that phosphorus is a part of manganese ores in the form of difficult polymorphic connections. Therefore several researchers developed various options of the chemical and hydrometallurgical enrichment allowing to receive high-quality manganese concentrates from carbonate ores with manganese content – 55 – 65% and the relation P/Mn less than 0.0005 [1].

The calcium-chloride way of enrichment is the most perspective that is connected first of all with use of not scarce raw materials: chloride of calcium which solution is used for autoclave leaching on reaction



Sedimentation of manganese is made by limy milk on reaction



Thus, calcium chloride almost completely is returned to a production cycle.

Hydroxide of manganese is exposed to heat treatment. In result the concentrate of chemical enrichment (CCE) which contains 59 – 62% of Mn, 0.1 - 0.3% of SiO₂, P₂O₅, S-traces [3] turns out. Results of the X-ray phase analysis showed that manganese in KHO contains in the basic in the form of Mn₃O₄ (table 1).

Table 1 - Results of the X-ray phase analysis of CCE

Material	Main phase	A little
Concentrate of chemical enrichment (CCE)	Mn ₃ O ₄	α-manganese manganosit MnO calcium chloride CaCl ₂

As a result of the researches of the last years conducted at the Siberian state industrial university processing methods and parameters calcium - a chloride method of enrichment, allowing to increase extraction of manganese from carbonate raw materials in a concentrate from 80% to 93.0 - 93.5% were defined. Application of this method allows to enrich and also to carry out dephosphorization of oxidic manganese raw materials and to extract manganese from production wastes. Extraction at the same time makes more than 90% [4, 5].

It is expedient to use the received high-quality raw materials for direct alloying, or for smelting of high-quality manganese alloys, in particular metal manganese. The complex of researches with participation of authors showed high efficiency of technology of direct alloying of steel with application as a part of mixes of a concentrate of chemical enrichment [6]. Also the complex of works on development of technology of smelting of manganese metal by extra oven process with use of a concentrate of the chemical enrichment received at enrichment of carbonate manganese ores of the Usinsk field was carried out [7].

Ores of the Usinsk field have manganese content at the level of 19 – 22% and the increased phosphorus content therefore smelting of manganese alloys requires their preliminary enrichment. The concentrate received as a result of chlorcalcic enrichment (CCE) contains 59 – 62% of Mn, 0.1 - 0.3% of SiO₂ 0.1 – 0.2% of Fe, 0.004 - 0.009% P, S are traces.

The complexity of use of the received concentrate for extra oven process of smelting of manganese metal is in the aluminothermic way that heat generated during reaction of restoration is not enough for ensuring effective division of metal and slag.

It is connected with the fact that manganese in a concentrate of chemical enrichment according to the X-ray phase analysis is presented in the form by Mn₃O₄ (table 1). Aluminothermic process of restoration of Mn₃O₄ can be described reaction



For receiving liquid are mobile slag and decrease in temperature of melting of slag it is necessary to enter flux into furnace charge. As flux it is expedient to use lime, then process can be presented in a general view reaction



Thermal calculations showed that the specific thermal effect does not exceed 1900 kJ/kg of furnace charge.

For increase in a thermal stability of process it is necessary or to bring heat, using the electrooven unit or preliminary heating of furnace charge, or to enter the highest oxides of Mn_2O_3 and MnO_2 manganese into furnace charge.

At the Siberian state industrial university the technology of smelting of manganese metal, including preliminary preparation of burdening materials was developed.

The stablest oxide of manganese is Mn_3O_4 . In literature there are no data on a possibility of oxidation of Mn_3O_4 to Mn_2O_3 or MnO_2 . It is possible to receive higher okslennost of manganese when receiving the synthetic materials CaMnO_3 or CaMn_2O_4 [8]. The technology of synthesis of the containing manganese monophase material CaMn_2O_4 from a concentrate of chemical enrichment is known [9].

However, at extra oven melting for providing thermal conditions of process it is expedient to use CaMnO_3 connection in which manganese has the highest degree of oxidation. The researches conducted on a derivatograph allowed to determine technical parameters of receiving monophase synthetic material CaMnO_3 : temperature, synthesis time, ratio of a concentrate of chemical enrichment and lime. Thermochemical synthesis received material which X-ray phase composition is presented in table 2.

Table 2 - Results of the X-ray phase analysis synthesized material

Test	Material	Phase structure
1	Lime	Much: lime (CaO) Is present: portland Ca (OH) ₂ Calcite CaCO_3
2	Concentrate of chemical enrichment	Much: gausmanit Mn_3O_4
3	Synthesized material	Much: CaMnO_3 Is present: a little marokit CaMn_2O_4

Manganese restoration by aluminum from the synthesized material is followed by considerable allocation of heat and it is presented by reaction



the formed Al_2O_3 interacts with CaO with formation of fusible aluminate. Therefore, during restoration of loss of manganese can be theoretically reduced to minimum.

An attempt to analytically define frequency rate of slag and optimum structure of a slag phase at aluminothermic smelting of manganese alloy of the set structure is made. Other characteristics of process can be defined on the basis of these magnitudes. At the same time the equations received by processing of empirical data on extra oven alyuminotermic melting of complex alloys with manganese and titanium were used:

$$c[\text{Me}'] = \frac{c[\text{Me}']^{\frac{n}{x}} \cdot c(\text{Me}'_x\text{O}_y)^{\frac{1}{x}} \cdot \gamma[\text{Me}']^{\frac{2n}{x}} \cdot \gamma(\text{Me}'_x\text{O}_y)^{\frac{2}{x}}}{c(\text{Me}''_n\text{O}_y)^{\frac{1}{x}} \cdot \gamma[\text{Me}']^2 \cdot \gamma(\text{Me}''_n\text{O}_y)^{\frac{2}{x}} \cdot \exp\left(\frac{\Delta G_T^0}{x \cdot R \cdot T}\right)}, \quad (6)$$

where, $c[\text{Me}']$ and $c[\text{Me}'']$ – mole fraction of the restored metal and metal - reducer in metal fusion respectively;

$c[\text{Me}'_x\text{O}_y]$ and $c[\text{Me}''_n\text{O}_y]$ – mole fraction of oxides of the restored metal and metal-reducer in slag fusion respectively;

$\gamma[\text{Me}']$ and $\gamma[\text{Me}'']$ – coefficients of activity of the restored metal and metal - reducer in metal fusion respectively;

$\gamma(\text{Me}'_x\text{O}_y)$, $\gamma(\text{Me}''_n\text{O}_y)$ – coefficients of activity of oxides of the restored metal and metal-reducer in slag fusion respectively;

ΔG_T^0 – standard change of energy of Gibbs of reaction of metalthermal restoration, J;

R – universal gas constant, J / (mol · K);

T – process temperature, K.

For manganese monoxide restoration reaction by aluminum coefficients x and n will be respectively equal in the equation (6) to 1 and 2. The process temperature taken directly in laboratory at restoration of 1 kg a concentrate of manganese ore was about 2300 K. Standard change of energy of Gibbs of reaction of aluminothermic restoration of monoxide of manganese at this temperature paid off according to literary data.

Thus, the equation (6) takes the following form:

$$c[\text{Mn}] = \frac{c[\text{Al}]^2 \cdot c(\text{MnO}) \cdot \gamma[\text{Al}]^4 \cdot \gamma(\text{MnO})^2 \cdot 10^6}{1,016 \cdot c(\text{Al}_2\text{O}_3) \cdot \gamma[\text{Mn}]^2 \cdot \gamma(\text{Al}_2\text{O}_3)^2}. \quad (7)$$

The equations for reactions of aluminothermic restoration of monoxide of iron and dioxide of silicon were similarly received. They respectively have the following appearance:

$$c[\text{Fe}] = \frac{c[\text{Al}]^2 \cdot c(\text{FeO}) \cdot \gamma[\text{Al}]^4 \cdot \gamma(\text{FeO})^2 \cdot 10^{17}}{4,265 \cdot c(\text{Al}_2\text{O}_3) \cdot \gamma[\text{Fe}]^2 \cdot \gamma(\text{Al}_2\text{O}_3)^2}, \quad (8)$$

$$c[\text{Si}] = \frac{c[\text{Al}]^4 \cdot c(\text{SiO}_2) \cdot \gamma[\text{Al}]^8 \cdot \gamma(\text{SiO}_2)^2 \cdot 10^9}{3 \cdot c(\text{Al}_2\text{O}_3) \cdot \gamma[\text{Si}]^2 \cdot \gamma(\text{Al}_2\text{O}_3)^2}. \quad (9)$$

The high-percentage manganese alloy received in the aluminothermic way can be as a first approximation described by the Mn-Fe-Al-Si system. At the same time the slag phase represents a system MnO-Al₂O₃-SiO₂-FeO-CaO-MgO-Na₂O-K₂O-BaO. Coefficients in the equations were received as a result of statistical processing of these skilled swimming trunks of metal manganese:

$$\ln \gamma[\text{Mn}] = -0,033 \cdot \frac{c[\text{Fe}]}{c[\text{Mn}]} + 1,058 \cdot \frac{c[\text{Al}]}{c[\text{Mn}]} + 0,171 \cdot \frac{c[\text{Si}]}{c[\text{Mn}]}, \quad (10)$$

$$\ln \gamma[\text{Fe}] = -0,424 \cdot \frac{c[\text{Mn}]}{c[\text{Fe}]} + 5,252 \cdot \frac{c[\text{Al}]}{c[\text{Fe}]} - 2,278 \cdot \frac{c[\text{Si}]}{c[\text{Fe}]}, \quad (11)$$

$$\ln \gamma[\text{Al}] = 0,11 \cdot \frac{c[\text{Fe}]}{c[\text{Al}]} - 0,112 \cdot \frac{c[\text{Mn}]}{c[\text{Al}]} + 0,105 \cdot \frac{c[\text{Si}]}{c[\text{Al}]}, \quad (12)$$

$$\ln \gamma[\text{Si}] = -2,845 \cdot \frac{c[\text{Fe}]}{c[\text{Si}]} + 1,362 \cdot \frac{c[\text{Mn}]}{c[\text{Si}]} + 28,135 \cdot \frac{c[\text{Al}]}{c[\text{Si}]}, \quad (13)$$

$$\ln \gamma(\text{MnO}) = 0,104 \cdot \frac{c(\text{Al}_2\text{O}_3)}{c(\text{MnO})} - 0,292 \cdot \frac{c(\text{SiO}_2)}{c(\text{MnO})} + 0,176 \cdot \frac{c(\text{FeO})}{c(\text{MnO})} + 0,176 \cdot \frac{\Sigma(c)}{c(\text{MnO})}, \quad (14)$$

$$\ln \gamma(\text{SiO}_2) = -0,802 \cdot \frac{c(\text{Al}_2\text{O}_3)}{c(\text{SiO}_2)} + 0,465 \cdot \frac{c(\text{FeO})}{c(\text{SiO}_2)} + 0,465 \cdot \frac{c(\text{MnO})}{c(\text{SiO}_2)} + 0,465 \cdot \frac{\Sigma(c)}{c(\text{SiO}_2)}, \quad (15)$$

$$\ln \gamma(\text{FeO}) = -1,733 \cdot \frac{c(\text{Al}_2\text{O}_3)}{c(\text{FeO})} + 3,262 \cdot \frac{c(\text{SiO}_2)}{c(\text{FeO})} - 0,668 \cdot \frac{c(\text{MnO})}{c(\text{FeO})} - 0,668 \cdot \frac{\Sigma(c)}{c(\text{FeO})}, \quad (16)$$

$$\ln \gamma(\text{Al}_2\text{O}_3) = -0,071 \cdot \frac{c(\text{SiO}_2)}{c(\text{Al}_2\text{O}_3)} + 0,052 \cdot \frac{c(\text{FeO})}{c(\text{Al}_2\text{O}_3)} + 0,052 \cdot \frac{c(\text{MnO})}{c(\text{Al}_2\text{O}_3)} + 0,052 \cdot \frac{\Sigma(c)}{c(\text{Al}_2\text{O}_3)}, \quad (17)$$

where, $\Sigma(c)$ – total molar concentration CaO, MgO, BaO, Na₂O and K₂O in slag.

As the molar composition of alloy is usually known or can be calculated, the equations (6) - (17) can be reduced in the system supporting thirteen unknown. Such system cannot be unambiguously solved. For obtaining the unambiguous decision the following additional equations are offered:

$$\sum c \approx 1 - c(\text{Al}_2\text{O}_3) - c(\text{SiO}_2) - c(\text{MnO}) - c(\text{FeO}), \quad (18)$$

$$K_{sl} = \frac{N_{sl} [102 \cdot c(\text{Al}_2\text{O}_3) + 60 \cdot c(\text{SiO}_2) + 71 \cdot c(\text{MnO}) + 72 \cdot c(\text{FeO}) + 81 \cdot \Sigma(c)]}{55 \cdot c[\text{Mn}] + 56 \cdot c[\text{Fe}] + 27 \cdot c[\text{Al}] + 28 \cdot c[\text{Si}]} \quad (19)$$

where, K_{sl} – frequency rate of slag;

N_{sl} – amount of slag, mole.

$$1 = c[\text{Al}] + c[\text{Si}] + c[\text{Mn}] + c[\text{Fe}]. \quad (20)$$

Thus, it is possible to receive a system from fourteen equations (including nonlinear) with fifteen unknown. The missing equation can be received or on the basis of any additional production requirements, or similar to the equations (6) - (8) for any of the following reactions:



This system of the equations was solved with use of the MATHCAD program under following conditions:

- composition of chemical enrichment concentrate, %: 87 Mn₃O₄, 7 CaO, 4.0 CaCl₂, 0.3 SiO₂, 0.1 Fe₂O₃, S are traces, P₂O₅ – traces;
- monophasic material CaMnO₃: ~ 40 % CaO, ~ 60 % MnO₂;
- aluminum powder;
- composition of manganese metal.

As a result of the calculation, the optimum slag phase composition was obtained, wt%: 6.0 – 8.2 MnO, 35.5 – 40.0 CaO, 50.0 – 58.0 Al₂O₃, 0.5 – 1.5 SiO₂, 2.8 – 4.8 CaCl₂, 0.08 – 0.20 FeO, traces P, 0.015 – 0.05 S, which corresponds to the optimum ratio of chemical enrichment concentrate (CEC) and monophase material (CaMnO₃) (ratio CEC to monophase material equal to (6.5 – 7.5) to (2.5 – 3.5).

Frequency rate of slag 2.2 – 2.7.

On the basis of the thermal analysis and data of mathematical modeling the technology of smelting of manganese metal, including preliminary preparation of burdening materials for the purpose of receiving synthetic material which contains the highest oxide of MnO₂ manganese and at the same time is effective gumboil was developed.

Use of monophase material CaMnO₃ as a burdening component at aluminotermichesky melting of metal manganese allows to increase a thermal character process, and, therefore, to increase extraction of manganese from a concentrate on average to 90%.

Furnace charge consisted of a concentrate of chemical enrichment, a product of synthesis and aluminum powder. The smelting was conducted in the hearth with an upper ignition. As a result of experimental meltings, a metal was obtained, the chemical composition of which is given in table 1.

From the results obtained it is clear that the chemical composition of the alloy meets the requirements.

It should be noted that manganese metal has a low content of harmful impurities – phosphorus and sulfur, and the iron content does not exceed 1%. The extraction of manganese from the concentrate amounted to an average of 90%.

Table 3 - Chemical composition of the test metal

Melting No.	Composition of metal, wt. %						Content of MnO in the slag, %	Extraction of Mn, %
	Mn	Al	Si	Fe	S	P		
1	96.89	0.81	0.45	0.88	0.004	0.006	7.24	90.70
2	97.00	0.75	0.38	0.83	0.002	0.006	6.15	90.11
3	97.12	0.73	0.40	0.74	0.003	0.005	6.01	91.16
4	96.78	0.68	0.58	0.97	0.004	0.004	8.15	87.68
5	96.84	0.83	0.64	0.91	0.004	0.006	7.35	89.89

Frequency rate of slag – 2,30 – 2,65.

Melt temperature, measured during the experiment, was from 2300 to 2373 K at the optimum ratio of CEC to monophase material equal to (6.5 – 7.5) to (2.5 – 3.5).

Conclusions

End-to-end manganese recovery in the smelting of manganese metal from the concentrate of chemical enrichment, obtained by the developed technology of enrichment of carbonate ores by calcium-chloride method was 85.3 – 89.3%, which significantly exceeds the extraction of manganese in the smelting of manganese by the aluminothermic out-of-furnace process from peroxide manganese ores, which is 69 – 72%, and is at the level of manganese extraction with the use of CEC in the production of manganese metal using electric heating.

As a result of experimental meltings, the slag of the composition was obtained, wt%: 6.1-8.15 MnO, 36.0-38.1 CaO, 51.2-56.8 Al₂O₃, 0.6-1.3 SiO₂, 3.2-6.4 CaCl₂, 0.1-0.4 FeO, 0.02-0.03 S, traces of P.

This slag practically does not contain harmful impurities. oxides of iron and silicon and can be used as a synthetic slag for processing steel in a ladle. and also this slag can be used in the construction industry to produce cements.

The useful use of aluminum is 94 – 96%.

The obtained results of laboratory aluminothermic meltings of manganese metal are consistent with the predicted data of technological parameters of aluminothermic melting of manganese metal, which allows us to conclude about the adequacy of the method used for parameters calculation.

Use of manganese metal, melted on the offered technology, for steel alloying with manganese allows to receive low-phosphorous became, suitable for use in the conditions of low temperatures.

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