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Optimization of technological parameters of manganese metal aluminothermic smelting

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Abstract. In the paper using the mathematical model, the technology parameters of manganese metal smelting by aluminothermic method from manganese concentrate of chemical enrichment with the use of synthesized monophase material CaMnO3 are predicted. Based on thermal analysis and mathematical modeling data, the technology of manganese metal smelting was developed, including the preliminary preparation of charge materials to produce a synthetic material that contains the highest manganese oxide MnO_2 and at the same time is an effective flux. With optimum proportions in the charge of monophasic material $CaMnO_3$ and concentrate of chemical enrichment, it is possible to completely eliminate the use of fluorspar. The developed optimal technological regimes for out-of-furnace aluminothermic smelting of metallic manganese using monophase material $CaMnO_3$ and concentrate of chemical enrichment made it possible to obtain a through-rate manganese recovery factor at the level 75-80%, which is almost twice as high as the through-extraction coefficient of manganese by the known technologies of manganese metal smelting.

1. Introduction

For the smelting of manganese metal by aluminothermic method, it is necessary to use high-quality manganese raw materials [1]. To ensure the required GOST 6008-80 chemical composition of manganese metal, such raw materials are peroxide manganese ores [2] or low-phosphorous manganese slags [3].

Concentrate of chemical enrichment, having in its composition the minimum content of impurities (Fe_2O_3 up to 0.1%, P up to 0.009%, 0.5-1.2% SiO_2, S – traces, less than 2% $CaCl_2$), can be an appropriate base material for the production of metallic manganese by an aluminothermic process [4,5].

When manganese metal is smelted by aluminothermic metallurgy, the problem of the most efficient use of scarce and expensive high-quality manganese ores and secondary aluminum powder appears. The main characteristics of the efficiency of the out-of-furnace process are undoubtedly the degree of extraction of components into the alloy, the chemical composition of the alloy and the associated slag, the multiplicity of slag. In the present work, an attempt was made to analytically determine the slag multiplicity and the optimal composition of the slag phase in the aluminothermic smelting of a manganese alloy of the given composition. The remaining characteristics of the process can be determined on the basis of these quantities.

2. Calculation procedure

To solve the problem, we used equations obtained by processing empirical data on out-of-furnace aluminothermic melting of complex alloys with manganese and titanium [6]:

$$c\left[Me^{/}\right]=\frac{c\left[Me^{//}\right]^{\frac{n}{x}}\cdot c\left(Me^{/}_{x}O_{y}\right)^{\frac{1}{x}}\cdot\gamma\left[Me^{//}\right]^{\frac{2n}{x}}\cdot\gamma\left(Me^{/}_{x}O_{y}\right)^{\frac{2}{x}}}{c\left(Me^{//}_{n}O_{y}\right)^{\frac{1}{x}}\cdot\gamma\left[Me^{/}\right]^{2}\cdot\gamma\left(Me^{//}_{n}O_{y}\right)^{\frac{2}{x}}\cdot\exp\left(\frac{\Delta G^{0}_{T}}{x\cdot R\cdot T}\right)}, \quad (1)$$

where $c[Me^{/}]$ and $c[Me^{//}]$ – the molar fraction of the metal to be reduced and the reducing metal in the metallic melt, respectively;
$c[Me^{/}_{x}O_{y}]$ and $c[Me^{//}_{n}O_{y}]$ – the molar fraction of oxides of the metal to be reduced and the reducing metal in the slag melt, respectively;
$\gamma[Me^{/}]$ and $\gamma[Me^{//}]$ – the activity coefficients of the metal to be reduced and the reducing metal in the metallic melt, respectively;
$\gamma(Me^{/}_{x}O_{y})$, $\gamma(Me^{//}_{n}O_{y})$ – the activity coefficients of oxides of the metal to be reduced and the reducing metal in the slag melt, respectively;
ΔG^{0}_{T} – standard change in the Gibbs energy of the metal-thermal reduction reaction, J;
R – the universal gas constant, J/(mol · K);
T – the process temperature, K.

For the reduction reaction of manganese monoxide with aluminum, the coefficients x and n in equation (1) will be respectively equal to 1 and 2. The process temperature, measured directly in the laboratory conditions during reduction of 1 kg of manganese ore concentrate, was approximately 2300 K. The standard change in Gibbs energy of the aluminothermic reduction of monoxide manganese at the given temperature was calculated from the data in [6].

Thus, equation (1) takes the following form:

$$c[Mn]=\frac{c[Al]^{2}\cdot c(MnO)\cdot\gamma[Al]^{4}\cdot\gamma(MnO)^{2}\cdot10^{6}}{1.016\cdot c(Al_{2}O_{3})\cdot\gamma[Mn]^{2}\cdot\gamma(Al_{2}O_{3})^{2}}. \quad (2)$$

Similarly, equations for the reactions of aluminothermic reduction of iron monoxide and silicon dioxide were obtained. They have the following form:

$$c[Fe]=\frac{c[Al]^{2}\cdot c(FeO)\cdot\gamma[Al]^{4}\cdot\gamma(FeO)^{2}\cdot10^{17}}{4.265\cdot c(Al_{2}O_{3})\cdot\gamma[Fe]^{2}\cdot\gamma(Al_{2}O_{3})^{2}}, \quad (3)$$

$$c[Si]=\frac{c[Al]^{4}\cdot c(SiO_{2})\cdot\gamma[Al]^{8}\cdot\gamma(SiO_{2})^{2}\cdot10^{9}}{3\cdot c(Al_{2}O_{3})\cdot\gamma[Si]^{2}\cdot\gamma(Al_{2}O_{3})^{2}}. \quad (4)$$

The high-percent manganese alloy obtained by the aluminothermic method can be described in the first approximation by the Mn-Fe-Al-Si system. The slag phase is a system of MnO-Al_2O_3-SiO_2-FeO-CaO-MgO-Na_2O-K_2O-BaO. Th coefficients in the equations were obtained as a result of statistical processing of experimental melting data of metallic manganese:

$$\ln\gamma[Mn]=-0.033\cdot\frac{c[Fe]}{c[Mn]}+1.058\cdot\frac{c[Al]}{c[Mn]}+0.171\cdot\frac{c[Si]}{c[Mn]}, \quad (5)$$

$$\ln\gamma[Fe]=-0.424\cdot\frac{c[Mn]}{c[Fe]}+5.252\cdot\frac{c[Al]}{c[Fe]}-2.278\cdot\frac{c[Si]}{c[Fe]}, \quad (6)$$

$$\ln\gamma[\mathrm{Al}] = 0.11\cdot\frac{c[\mathrm{Fe}]}{c[\mathrm{Al}]} - 0.112\cdot\frac{c[\mathrm{Mn}]}{c[\mathrm{Al}]} + 0.105\cdot\frac{c[\mathrm{Si}]}{c[\mathrm{Al}]}, \quad (7)$$

$$\ln\gamma[\mathrm{Si}] = -2.845\cdot\frac{c[\mathrm{Fe}]}{c[\mathrm{Si}]} + 1.362\cdot\frac{c[\mathrm{Mn}]}{c[\mathrm{Si}]} + 28.135\cdot\frac{c[\mathrm{Al}]}{c[\mathrm{Si}]}, \quad (8)$$

$$\ln\gamma(\mathrm{MnO}) = 0.104\cdot\frac{c(\mathrm{Al_2O_3})}{c(\mathrm{MnO})} - 0.292\cdot\frac{c(\mathrm{SiO_2})}{c(\mathrm{MnO})} + 0.176\cdot\frac{c(\mathrm{FeO})}{c(\mathrm{MnO})} + 0.176\cdot\frac{\Sigma(c)}{c(\mathrm{MnO})}, \quad (9)$$

$$\ln\gamma(\mathrm{SiO_2}) = -0.802\cdot\frac{c(\mathrm{Al_2O_3})}{c(\mathrm{SiO_2})} + 0.465\cdot\frac{c(\mathrm{FeO})}{c(\mathrm{SiO_2})} + 0.465\cdot\frac{c(\mathrm{MnO})}{c(\mathrm{SiO_2})} + 0.465\frac{\Sigma(c)}{c(\mathrm{SiO_2})}, \quad (10)$$

$$\ln\gamma(\mathrm{FeO}) = -1.733\cdot\frac{c(\mathrm{Al_2O_3})}{c(\mathrm{FeO})} + 3.262\cdot\frac{c(\mathrm{SiO_2})}{c(\mathrm{FeO})} - 0.668\cdot\frac{c(\mathrm{MnO})}{c(\mathrm{FeO})} - 0.668\cdot\frac{\Sigma(c)}{c(\mathrm{FeO})}, \quad (11)$$

$$\ln\gamma(\mathrm{Al_2O_3}) = -0.071\cdot\frac{c(\mathrm{SiO_2})}{c(\mathrm{Al_2O_3})} + 0.052\cdot\frac{c(\mathrm{FeO})}{c(\mathrm{Al_2O_3})} + 0.052\cdot\frac{c(\mathrm{MnO})}{c(\mathrm{Al_2O_3})} + 0.052\cdot\frac{\Sigma(c)}{c(\mathrm{Al_2O_3})}, \quad (12)$$

where Σ(c) – is the total molar concentration of CaO, MgO, BaO, Na_2O and K_2O in the slag.

Since the molar composition of the alloy is usually known or can be calculated, equations (2) - (12) can be reduced to a system containing thirteen unknowns. Such a system can not be uniquely solved. To obtain a single-valued solution, the following additional equations are proposed:

$$\sum c \approx 1 - c(Al_2O_3) - c(SiO_2) - c(MnO) - c(FeO), \quad (13)$$

$$K_{sl} = \frac{N_{sl}\cdot[102\cdot c(Al_2O_3) + 60\cdot c(SiO_2) + 71\cdot c(MnO) + 72\cdot c(FeO) + 81\cdot\sum(c)]}{55\cdot c[Mn] + 56\cdot c[Fe] + 27\cdot c[Al] + 28\cdot c[Si]}, \quad (14)$$

where K_{SL} – slag multiplicity;
N_{SL} – amount of slag, mole.

$$1 = c[\mathrm{Al}] + c[\mathrm{Si}] + c[\mathrm{Mn}] + c[\mathrm{Fe}]. \quad (15)$$

Thus, a system of fourteen equations (including nonlinear ones) with fifteen unknowns can be obtained. The missing equation can be obtained either on the basis of any additional technological requirements, or similarly to equations (2) - (4) for any of the following reactions:

$$2FeO + Si = 2Fe + SiO_2, \quad (16)$$

$$2MnO + Si = 2Mn + SiO_2, \quad (17)$$

$$FeO + Mn = Fe + MnO. \quad (18)$$

This system of equations was solved using the MathCAD program under the following conditions:

- composition of CEC,%: 87 Mn_3O_4, 7 CaO, 4.0 $CaCl_2$, 0.3 SiO_2, 0.1 Fe_2O_3, S – traces, P_2O_5 – traces;

- monophasic material $CaMnO_3$: ~ 40% CaO, ~ 60% MnO_2;
- 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 Al_2O_3, 0.5 – 1.5 SiO_2, 2.8 – 4.8 $CaCl_2$, 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 ($CaMnO_3$) – $\frac{CEC}{CaMnO_3} = \frac{6.5-7.5}{2.5-3.5}$. The slag multiplicity is 2.2 – 2.7.

3. Results and discussion

Based on thermal analysis and mathematical modeling data, the technology of manganese metal smelting was developed, including the preliminary preparation of charge materials to produce a synthetic material that contains the highest manganese oxide MnO_2 and which is also an effective flux.

Previously, optimal conditions for the preparation of solid solutions of calcium and manganese oxides, including $CaMnO_3$ [7], were established.

The use of monophase material $CaMnO_3$ as a charge component for aluminumothermal smelting of manganese metal makes it possible to increase the thermal character of the process, and, consequently, to increase the manganese extraction from the concentrate to an average of 90%.

The charge contained CEC, a synthesis product 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% [8]. The extraction of manganese from the concentrate amounted to an average of 90%.

Table 1. 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

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).

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 [2. 3].

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 Al_2O_3, 0.6-1.3 SiO_2, 3.2-6.4 $CaCl_2$, 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%.

4. Conclusion

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.

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