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Modelling of conditions of manganese reduction with carbon, silicon and aluminum

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Abstract. The paper contains the research results of the process of manganese oxides reduction by various types of reducers - carbon, silicon and aluminum, the purpose of which is definition of a possibility of the use of carbon-bearing material (coke, silicon carbide), ferrosilicon and aluminum by production of alloys of manganese and direct alloying of steel in a ladle by manganese and definition of optimal conditions of implementation of these processes.

1. Introduction

Metallurgy is one of the resource-intensive industries. The need to reduce the energy and material intensity of metallurgical products and increase their operational properties requires both the improvement of traditional metal production schemes and the development of new technologies.

The solution to the problems of improvement of the existing and development of new metallurgical technologies is connected, first of all, with studies of high-temperature processes in complex thermodynamic systems with physicochemical transformations in the equilibrium and nonequilibrium conditions. Since experimental studies, as a rule, are quite expensive, and often difficult to implement, in these conditions a computational experiment is of great importance, which allows the states and processes to be analyzed and conclusions about the behavior of the objects under study based on model concepts to be drawn. In this regard, it is urgent to create methods and instrumental modeling systems that allow for multivariate calculations, research and solve optimization problems, which will open up new opportunities for the development and design of advanced metallurgical technologies.

2. Methods of research

The solution to the problem of determining the conditions for the reduction of metals from oxides was carried out using thermodynamic modeling methods based on the calculation of equilibrium states in model thermodynamic systems [1-3]. The advantage of these methods is the possibility of calculating the equilibrium state of any process based on only the fundamental laws of thermodynamics. The calculation of thermodynamic equilibrium allows the fundamental possibility of obtaining certain substances to be found out, the isolation of which is the main one when solving the problem of assessing the ultimate limit state, and to determine the range of permissible parameter values.

When implementing thermodynamic modeling, we used the Terra software package developed at Moscow State Technical University, which allows, on the basis of the maximum entropy principle, the equilibrium composition of a multicomponent, heterogeneous thermodynamic system for high-

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temperature conditions [1,2] to be determined, as well as an instrumental system in the form of a set of programs and databases data allowing multivariate calculations created by the author [4]. The thermodynamic modeling technique was successfully applied to solve the problems of studying the reduction processes of iron, nickel, vanadium, barium, and strontium [5–9].

An elementary system is formed by setting the moles numbers of its constituent components. If necessary, the compositions of condensed solutions are formed. When two thermodynamic parameters are selected, multivariate calculations of equilibrium compositions are carried out depending on the thermodynamic parameters or the flow rates of the initial materials.

The study of the metal reduction process was carried out by calculating the equilibrium compositions in systems, the input stream of which consists of a combination of Me - O - C - Fe - Si - Al elements and is represented by a set of substances lMeO - nC - mSi - kAl - pFe. Depending on the values of the parameters l, k, n, m and p, one or another initial composition of the system was formed.

The set of substances that can be formed at a given elemental composition of the mixture was determined as a result of numerical simulation for a selected temperature range and various thermodynamic states. From the complete list of possible substances, only those substances were selected the concentrations of which exceeded the value of 10^{-4} mol/kg of the mixture.

3. Results of the research

The study of the carbon-thermal reduction of manganese in the $MnO_2 - C$ system in the absence of iron showed that the reduction of manganese begins at temperatures above 1723 K with a carbon consumption of more than 1.5 moles (figure 1). At the same time, the process of evaporation of manganese begins. At a temperature of 1723 K with an excess of carbon, Mn_7C_3 manganese carbide is present in the system, which disappears with the increase in the temperature. Complete reduction of manganese occurs at a carbon consumption of 2 moles.

Calculations in the $MnO_2 - Si$ system showed that the reduction of manganese by silicon is feasible over the entire specified temperature range. The research results are presented in figure 2, from which it follows that the complete reduction of manganese occurs at a silicon molar rate of 1 mol. This value corresponds to a maximum content of manganese in the system of 47%, which decreases with an increase in the consumption of reducing agent due to dilution with excess silicon.

The results of calculations of the joint reduction of manganese with carbon and silicon in the MnO_2 – C - Si system revealed the predominant effect of carbon on the reduction process, which occurs at temperatures above 1773 K (figure 3). The dependences of the process parameters on the carbon consumption at various silicon consumption at a temperature of 1823 K are shown in figure 4, from which it follows that the maximum content of reduced manganese corresponds to a carbon consumption of 1 mol with a minimum silicon content in the system.

With the increase in the carbon, the manganese content decreases due to an increase in the concentration of silicon carbide (figure 5). The content of gaseous manganese at this temperature is negligible and does not exceed 2.5%.

As a result of calculations of the process of manganese reduction by carbon in the $MnO_2 - SiO_2 - C$ system, it was revealed that the addition of 0.5 moles of silicon oxide does not change the qualitative nature of the dependences obtained for the $MnO_2 - C$ system, but only leads to a decrease in the reduced manganese content from 48 to 37.8% due to dilution with silicon oxide.



Figure 1. Relations of equilibrium compositions in the $1MnO_2 - nC$ system with temperature at n=0.5; 1.0; 1.5; 2.0 mole.



Figure 2. Relations of equilibrium compositions in the $MnO_2 - Si$ system with silicon consumption.

Similar results were obtained in the study of the $MnO_2 - SiO_2 - C - Si$ system. Manganese reduction also occurs at temperatures above 1773 K. The predominant reducing agent is carbon, the best results correspond to the consumption of carbon 1 mol and silicon 0.5 mol. The content of reduced manganese at these parameters is lower (30%) than in the $MnO_2 - C - Si$ system (47%) due to dilution with silicon oxide.

The addition of CaO to the $MnO_2 - SiO_2 - C - Si$ system also did not significantly affect the nature of the dependences. The maximum degree of reduction of manganese corresponds to the temperature of 1773 K and a consumption of 1 mol of carbon and 0.5 mol of silicon. An increase in the amount of



CaO in the system leads to a slight decrease in the amount of reduced manganese due to dilution (figure 6).

Figure 3. Relations of equilibrium compositions in the $1MnO_2 - 0.5Si - nC$ system with temperature at n = 0.5; 1.0; 1.5; 2.0 mole.



Figure 4. Dependence of reduced manganese content in the $MnO_2 - Si - C$ system on carbon consumption at different silicon consumption.



Figure 5. Dependence of silicon carbide content in the $MnO_2 - Si - C$ system on carbon consumption at different silicon consumption.



Figure 6. Dependence of reduced manganese content in the $1MnO_2 - 0$, $5SiO_2 - 1C - 0.5Si - nCaO$ system on temperature at different *CaO* flow rates.

The results of calculations of the processes in the $MnO_2 - Al$ system showed that manganese is reduced over the entire specified temperature range. The dependences of the equilibrium compositions on the consumption of aluminum are shown in figure 7.



Figure 7. Dependence of equilibrium compositions in the $MnO_2 - Al$ system on aluminium consumption.

The maximum degree of manganese reduction corresponds to the consumption of aluminum 1.5 mol. The results of studies in the $MnO_2 - Si - Al$ system using the Terra program showed that manganese is reduced over the entire specified temperature range. The optimal total consumption of reducing agents, providing a maximum content of reduced manganese of 43%, is 1.5 mol.

An increase in the expenditures of silicon and aluminum leads to their accumulation in the system and a decrease in the concentration of reduced manganese (figure 8).





Figure 8. Dependence of reduced manganese content in $MnO_2 - Si - Al$ system on silicon consumption at different amount of aluminum.

The addition of CaO to the $MnO_2 - Si - Al$ system did not change the nature of the dependences; the maximum content of reduced manganese also corresponds to the total consumption of reducing agents of 1.5 moles in a given temperature range. An increase in CaO consumption leads to a slight decrease in the concentration of manganese in the system due to dilution.

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The analysis of the results of studies in the $MnO_2 - SiC$ system showed that complete reduction of manganese is possible at any temperature in a given range with 1 mol of silicon carbide in the system. At higher flow rates, silicon carbide accumulates in the system, thereby reducing the concentration of reduced manganese. At temperatures below 1823 K, the reduced manganese is in the form of Mn_7C_3 carbide, and at higher temperatures, it is in its pure form in the condensed and gas phases.

4. Conclusion

Thus, it can be concluded that any of the described reducing agents or a combination thereof in certain ratios can be used as reducing agent when using oxide manganese containing alloy smelting and steel processing materials. Naturally, for the targeted use of silicon and aluminum in steel processing, a prior thorough deoxidation of the metal and slag is required to reduce the overall oxidation of the metal-slag system.

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