**A. ABDIRASHIT, YE. MAKHAMBETOV, T. TUSHIYEV, A. NURUMGALIYEV S. SMAILOV**

ISSN 0543-5846
METABK 61(3-4) 819-821 (2022)
UDC – UDK 669.14:669.715.782.74:66.067.7:536.45:537.7 = 111

# THERMODYNAMICS OF INTEGRATED DEOXIDATION OF STEEL WITH A NEW ALLOY OF ALUMINUM-SILICUM--MANGANESE (Al - Si - Mn)

Received – Primljeno: 2022-01-26
Accepted – Prihvaćeno: 2022-03-10
Preliminary Note – Prethodno priopćenje

The article considers the issue of using a complex alloy of aluminosilicomanganese as a deoxidizer. The value of the Wagner parameter of steel interaction - silicon, aluminum, manganese and concentration in the liquid, were associated with their activity in the metal. A certain consumption of the deoxidizer - aluminosilicomanganese per ton of liquid steel to improve the residual oxygen content in the metal. Possible generators of non-metallic inclusions are established.

*Keywords:* steel, Al-Si-Mn, deoxidation, thermodynamic analysis, quality.

## INTRODUCTION

The technology of steel deoxidation largely determines its quality, operational characteristics, which depend not only on the residual oxygen concentration, but also on the nature, quantity, size and distribution of nonmetallic inclusions in the metal matrix. The problem of oxide non-metallic inclusions and the rational organization of the steel deoxidation process remains one of the most important in metallurgy [1]. Therefore, one of the promising ways to obtain steel with a reduced content of nonmetallic inclusions (NI) is the use of complex deoxidation technology. The idea of complex deoxidation of steel is that the products of deoxidation of steel are obtained in liquid form due to the fact that oxides of deoxidizers form a more low-melting phase, and NI as deoxidation products are more easily enlarged and removed from the liquid metal. In the practice of steelmaking, complex deoxidizers are widely used, which are alloys of two or more components (silicocalcium, silicomanganese and silicon) [2, 3].

The advantages associated with the use of complex deoxidizers are due to two circumstances: a significant improvement in the thermodynamic conditions for the nucleation, enlargement and removal of nonmetallic inclusions. For example, at 1 600 °C in liquid iron with 0,2 % Si, 0,012 % of dissolved oxygen is in equilibrium. At the same time, with the addition of 0,5 % Mn to the 0,2 % Si content, there corresponds a lower equilibrium oxygen concentration: 0,008 %. Thus, the addition of manganese leads to an increase in the deoxidizing ability of silicon. Manganese and silicon together increase the deoxidizing ability of aluminum. The considered effect of increasing the deoxidizing ability under the influence of the second component is explained by a decrease in the thermodynamic activity of the formed oxide in complex products with separate deoxidation. Therefore, the complex aluminosilicomanganese alloy (AlSiMn), to date, has been little tested and studied as a deoxidizing agent in steel smelting [4, 5].

Calcium has a high affinity for oxygen and sulfur, favorably affects the morphology, type and distribution of non-metallic inclusions (NI). However, the low density (1,54 g / $cm^3$) and low boiling point, as well as the insignificant mutual solubility of calcium and iron, make it difficult to use it in its elementary form. In this regard, it is advisable to use calcium in the composition of complex ligatures, in particular with silicon and aluminum, due to the significant affinity of the latter to it, their favorable effect on the solubility of calcium in liquid iron and narrowing the region of immiscibility at high pressures [6]. Therefore, complex deoxidation of steel with a new alloy of aluminosilicomanganese is considered more effective.

## RESEARCH METHODOLOGY

The purpose of this research is to conduct a thermodynamic analysis of the complex deoxidation process of steel with a new AlSiMn alloy at a temperature of 1 600 °C. Thermodynamic analysis of a new complex aluminum-silico-manganese alloy (AlSiMn) as a steel deoxidizer consists in calculating the equilibria of the processes of interaction of oxygen dissolved in the met-

A. Abdirshit (asik_942017@mail.ru), A. Nurumgaliyev, T. Tushiyev, S. Smailov Karaganda Industrial University, Temirtau, Kazakhstan.
Ye. Makhambetov, Chemical and metallurgical institute named after J.Abishev, Karaganda, Kazakhstan.

al with a deoxidizer in order to determine the following parameters:

- nature and composition of deoxidation products (non-metallic inclusions);
- residual concentrations of oxygen and deoxidizing agent in steel;
- rational composition of deoxidizing alloys.

For such a calculation, it is necessary to have information on the activities of the components of the metallic phases, as well as on their dependences on the composition of the corresponding phases.

The reactions of interaction of the components of the AlSiMn alloy with oxygen dissolved in the metal are as follows (1-11):

$$(FeO) = (Fe) + (O) \quad (1)$$

$$(SiO_2) = (Si) + 2\,(O) \quad (2)$$

$$(MnO) = (Mn) + (O) \quad (3)$$

$$(Al_2O_3) = 2\,(Al) + 3(O) \quad (4)$$

$$(FeAl_2O_4) = (Fe) + 2\,(Al) + 4\,(O) \quad (5)$$

$$(3Al_2O_3 \cdot 2\,SiO_2) = 6\,(Al) + 2\,(Si) + 13\,(O) \quad (6)$$

$$(CaO) = (Ca) + (O) \quad (7)$$

$$(2CaO \cdot SiO_2) = 2\,(Ca) + (Si) + 4\,(O) \quad (8)$$

$$(3CaO \cdot SiO_2) = 3\,(Ca) + (Si) + 5\,(O) \quad (9)$$

$$(CaO \cdot 2Al_2O_3) = (Ca) + 4\,(Al) + 7\,(O) \quad (10)$$

$$(CaO \cdot 6Al_2O_3) = (Ca) + 12\,(Al) + 19\,(O) \quad (11)$$

AlSiMn alloy contains several impurity elements. To consider the mutual influence of the solution components on their thermodynamic characteristics, the activities of the components in the metal were calculated using the Wagner interaction parameters ($e_i^j$), the numerical values of which are given in Table 1.

Table 1 **The Wagner interaction parameters ($e_j^i$) [7, 8]**

| Elements i | Elements j | | | | |
|---|---|---|---|---|---|
| | Al | Si | Ca | Mn | O |
| Al | 0,045 | 0,058 | -0,052 | 0,0065 | -1,62 |
| Si | 0,056 | 0,14 | -0,67 | 0,03 | -0,176 |
| Ca | 0,072 | -0,096 | -0,07 | 0 | -3,507 |
| Mn | 0,017 | 0,06 | 0 | 0 | -0,072 |
| O | -0,96 | -0,1 | -1,41 | -0,021 | -0,2 |

To determine the lg a (i) (activity) of the components, we used formulas (13-17) and the data in Table 1. The calculation results are shown in Table 2.

$$\lg a_{(O)} = \lg(O) + e_O^O(O) + e_O^{Si}(Si) + e_O^{Mn}(Mn) + e_O^{Ca}(Ca) + (Al), \quad (13)$$

$$\lg a_{(Mn)} = \lg(Mn) + e_{Mn}^O(O) + e_{Mn}^{Si}(Si) + e_{Mn}^{Mn}(Mn) + e_{Mn}^{Ca}(Ca) + e_{Mn}^{Al}(Al), \quad (14)$$

$$\lg a_{(Si)} = \lg(Si) + e_{Si}^O(O) + e_{Si}^{Si}(Si) + e_{Si}^{Mn}(Mn) + e_{Si}^{Ca}(Ca) + e_{Si}^{Al}(Al), \quad (15)$$

$$\lg a_{[Al]} = \lg(Al) + e_{Al}^O(O) + e_{Al}^{Si}(Si) + e_{Al}^{Mn}(Mn) + e_{Al}^{Ca}(Ca) + e_{Al}^{Al}(Al), \quad (16)$$

$$\lg a_{[Ca]} = \lg(Ca) + e_{Ca}^O(O) + e_{Ca}^{Si}(Si) + e_{Ca}^{Mn}(Mn) + e_{Ca}^{Ca}(Ca) + e_{Ca}^{Al}(Al). \quad (17)$$

where (Ca), (Mn), (Al), (Si), (O) - component concentration;

$e_i^j$ – interaction parameters.

Table 2 **Results of calculating the activity of components (T = 1 600 °C)**

| № of metall | lg $a_{(O)}$ | lg $a_{(Si)}$ | lg $a_{(Al)}$ | lg $a_{(Ca)}$ | lg $a_{(Mn)}$ |
|---|---|---|---|---|---|
| 1 | -37,1068 | 2,4774 | 3,4520 | -0,8594 | 2,9851 |
| 2 | -40,1673 | 3,8776 | 4,2829 | -2,6147 | 4,0934 |
| 3 | -38,17847 | 2,9811 | 4,1448 | -3,7500 | 4,4209 |

For further analysis of the processes of interaction of the AlSiMn alloy with oxygen, an alternative assessment of their participation in the deoxidation process, it is necessary to establish a relationship between the additions of silicon, aluminum and manganese to steel, the deoxidation depth and the phase composition of the formed non-metallic inclusions, i.e. build the so-called table of consumption of refining components. The relationship between the composition of the metal, the compositions of non-metallic phases in equilibrium with it, and the composition of the alloy for deoxidation can be established by solving the balance equations. The calculation was carried out for 1 ton of the starting metal (before deoxidation). When steel is deoxidized with the AlSiMn alloy, liquid non-metallic inclusions (CaO, $Al_2O_3$, $SiO_2$, MnO) are in equilibrium with the metal [9]. To draw up balance equations, in addition, it is necessary to know the chemical composition of the metal before deoxidation, the composition of the metal after deoxidation and the composition of non-metallic inclusions. In our case, we assume that AlSiMn is completely consumed only for the deoxidation of steel, that is, it allows to reduce the oxygen content from the initial (O) initial oxygen content in the steel to the required (O). The equilibrium content of dissolved oxygen in steel at a temperature of 1 600 ° C is about 0,2 %. For each of the elements of the AlSiMn alloy under consideration, the following balance equations can be written to obtain an oxide melt during deoxidation (formulas 18 and 19):

$$\frac{1000(Fe)_{init}}{100} = \frac{(Fe)}{100} y_1 + \frac{(FeO/\%)M_{Fe}}{100M_{FeO}} y_2 \quad (18)$$

$$\frac{1000(O)_{init}}{100} = \frac{(O)}{100} y_1 + \left( \frac{(FeO/\%)}{M_{FeO}} + \frac{2(SiO_2/\%)}{M_{SiO_2}} + \frac{3(Al_2O_3/\%)}{M_{Al_2O_3}} + \frac{(CaO/\%)}{M_{CaO}} + \frac{(MnO/\%)}{M_{MnO}} \right) \frac{M_O}{100} y_2 \quad (19)$$

Table 3 **Consumption of elements for deoxidation of 1 ton of liquid steel alloy AlSiMn No. 1**

| Oxygen content in iron | | Deoxidizing elements | | | | | Sum / кg / t |
|---|---|---|---|---|---|---|---|
| $(O)_{init}$ | (O) | Mn | Si | Al | Ca | Fe | |
| 0,200 | 0,150 | 0,114 | 0,336 | 0,127 | 0,072 | 0,038 | 0,687 |
| 0,200 | 0,120 | 0,182 | 0,538 | 0,203 | 0,115 | 0,060 | 1,098 |
| 0,200 | 0,100 | 0,227 | 0,672 | 0,254 | 0,144 | 0,075 | 1,373 |
| 0,200 | 0,050 | 0,341 | 1,007 | 0,380 | 0,216 | 0,113 | 2,057 |
| 0,200 | 0,016 | 0,418 | 1,235 | 0,466 | 0,265 | 0,138 | 2,523 |

Table 4 **Consumption of elements for deoxidation of 1 ton of liquid steel with alloy AlSiMn No. 2**

| Oxygen content in iron | | Deoxidizing elements | | | | | Sum / кg / t |
|---|---|---|---|---|---|---|---|
| $(O)_{init}$ | (O) | Mn | Si | Al | Ca | Fe | |
| 0,200 | 0,150 | 0,101 | 0,300 | 0,113 | 0,064 | 0,034 | 0,612 |
| 0,200 | 0,120 | 0,162 | 0,480 | 0,181 | 0,103 | 0,054 | 0,98 |
| 0,200 | 0,100 | 0,203 | 0,600 | 0,226 | 0,129 | 0,067 | 1,225 |
| 0,200 | 0,050 | 0,304 | 0,899 | 0,339 | 0,193 | 0,101 | 1,836 |
| 0,200 | 0,016 | 0,373 | 1,103 | 0,416 | 0,237 | 0,123 | 2,252 |

Table 5 **Consumption of elements for deoxidation of 1 ton of liquid steel alloy AlSiMn No. 3**

| Oxygen content in iron | | Deoxidizing elements | | | | | Sum |
|---|---|---|---|---|---|---|---|
| $(O)_{init}$ | (O) | Mn | $(O)_{init}$ | (O) | Mn | $(O)_{init}$ | (O) |
| 0,20 | 0,15 | 0,100 | 0,296 | 0,112 | 0,063 | 0,033 | 0,604 |
| 0,20 | 0,12 | 0,160 | 0,473 | 0,178 | 0,101 | 0,053 | 0,965 |
| 0,20 | 0,10 | 0,200 | 0,591 | 0,223 | 0,127 | 0,066 | 1,207 |
| 0,20 | 0,05 | 0,300 | 0,886 | 0,334 | 0,190 | 0,099 | 1,809 |
| 0,20 | 0,016 | 0,367 | 1,086 | 0,410 | 0,233 | 0,122 | 2,218 |

where $(Fe)_{init}$ and (Fe) - concentration of components in the original and deoxidized metal / % wt.;

(FeO), $(SiO_2)$, (MnO), (CaO), $(Al_2O_3)$ – concentration of components in the oxide melt / % wt;

$y_1$ and $y_2$ – the amount of metal and oxide phases after deoxidation/ kg;

M – molar masses of compounds and elements.

The amount of an element introduced into the metal (silicon, aluminum, calcium, manganese) is spent directly on binding oxygen (deoxidation). The consumption of elements of the AlSiMn alloy required to reduce the oxygen content in steel to a given value was calculated using the following formulas (20 - 24):

$$z^{P}_{Si} = \frac{(SiO_2/\%)M_{Si}}{100M_{SiO_2}}y_2 \quad (20)$$

$$z^{P}_{Al} = \frac{2(Al_2O_3/\%)M_{Al}}{100M_{Al_2O_3}}y_2 \quad (21)$$

$$z^{P}_{Ca} = \frac{(CaO/\%)M_{Ca}}{100M_{CaO}}y_2 \quad (22)$$

$$z^{P}_{Mn} = \frac{(MnO/\%)M_{Mn}}{100M_{MnO}}y_2 \quad (23)$$

$$z^{P}_{Fe} = \frac{(FeO/\%)M_{Fe}}{100M_{FeO}}y_2 \quad (24)$$

$z_i$ – consumption of elements for deoxidation of 1 000 kg of initial liquid metal, kg.

(CaO), (FeO), (MnO), $(SiO_2)$, $(Al_2O_3)$ – concentrations of components in the oxide melt, % wt.

## RESULTS RESEARCH

Tables 3-5 show the results of calculating the consumption of elements for the deoxidation of steel for various final oxygen concentrations in steel.

## CONCLUSION

The carried out thermodynamic analysis of complex deoxidation of steel with a new alloy of aluminosilicomanganese with calcium made it possible to establish the activity of alloy elements in deoxidized steel at a temperature of 1 600 °C. According to the data obtained, calcium is a more active element in steel. The presence of elements such as manganese, silicon and aluminum increase the deoxidizing ability of the alloy. While calculating the consumption of elements directly for deoxidation, it was determined that to reduce the oxygen content in steel from [0,2] ref to [0,016], the total consumption of the alloy is from 0,6 to 2,25 kg / t. (depending on the composition of the AlSiMn alloy).

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**Note:** The responsible translator for English language is Yerekeeya Gaukhar, Temirtau, Kazakhstan