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Optimizing Technological Parameters of the Reduction Processes in Treating Steels in a Ladle Furnace

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Abstract. This work reports the possible development of reduction processes when treating the molten metal and slag using a ladle furnace under conditions of intensive stirring with an inert gas. The industrial data have been received, confirming the possibility of decreasing the concentration of ferrous and manganese oxides in the slag and stabilizing the contents of manganese and silicon in the metal.

Introduction

In modern metallurgy, much attention is paid to the problem of reducing the consumption of deoxidizing agents and alloying materials by developing efficient techniques employed for their adding to steel, with simultaneous improving steel properties by reducing concentrations of harmful impurities, as well as increasing a penetration coefficient for effective use of alloying elements. One of the solutions to this problem is increasing the extraction of an alloying element from slag by intensifying reduction processes while treating melts in modern ladle furnaces equipped with various systems for metal and slag mixing.

With the diffusion reaction to reduce metal oxides, a diffusion flux is determined by the known equation:

$$\Pi = \beta (C - C^*)$$

Where β is the mass transfer coefficient, m/s; C, C* are the concentration of substance in volume and at the boundary interface, mol/m³.

According to the surface renewal theory, the mass transfer coefficient β is defined as follows:

$$\beta = \sqrt{\frac{4\mathrm{DU}}{\pi \mathrm{l}}} \,, \tag{2}$$

Where D is the diffusion coefficient, m^2/s ; U is the rate of convective flow, m/s; l is the characteristic dimension of convective flow, m.

1. Отношение скоростей потоков металла и шлака обратно пропорционально динамической вязкости

When calculating a mass transfer coefficient, two assumptions have been made:

1. The ratio of metal and slag flow rates is inversely proportional to the dynamic viscosity

$$\frac{U_{Me}}{U_{slag}} = \frac{\eta_{slag}}{\eta_{Me}},$$
(3)

Where η_{Me} , η_{III} are the dynamic viscosity of metal and slag, Pa·s.

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2. The ratio of characteristic dimensions for metal and slag convective flows is directly proportional to the relative heights of metal (h_{Me}) and slag (h_{slag})

$$\frac{l_{Me}}{l_{slag}} = \frac{h_{Me}}{h_{slag}} = \frac{m_{Me}\rho_{slag}}{m_{slag}\rho_{Me}}, \qquad (4)$$

Where m_{Me} and m_{ui} are the masses of metal and slag, kg; ρ_{Me} and ρ_{slag} are the densities of metal and slag, kg/m³.

Due to these assumptions, such important conditions as viscosity of slag and its quantity affecting the process behavior can be taken into account.

The slag viscosity (η_{slag}) is defined by equations constraining the basicity and viscosity of slag. The constraint equations are derived from the data given by the author in [2]. Slag becomes heterogeneous when its basicity exceeds 2.5 causing constrained diffusion processes. The dependencies for 1500 and 1600 ° C temperatures are received (Figure 1).



Figure 1. The dependency of slag viscosity on the slag basicity

$$\eta_{\rm m} = 0.0062 {\rm B}^2 - 0.1069 {\rm B} + 0.511, \tag{5}$$

$$\eta_{\rm m} = 0.00664B^2 - 0.0893B + 0.3543, \tag{6}$$

Where B is the basicity of slag.

The oxidation rate for a reducing agent can be calculated according to the equations applicable to manganese and silicon, when the reducing agent is added to the surface of the molten slag, for the cases of limiting the process by diffusion of the reducing element to the metal/melt interface and oxides of interacting components in the molten slag:

$$V_{\rm Si} = -\frac{d[\%Si]}{d\tau} = \beta_{\rm [Si]} \{ [\%Si] - [Si\%]^* \} \frac{S}{V_{\rm slag}},$$
(7)

$$V_{Si} = \beta_{(SiO_2)} \frac{28}{60} \{ (\%SiO_2) - (SiO_2\%)^* \} \frac{S}{V_{slag}},$$
(8)

$$V_{Mn} = \beta_{(MnO)} \frac{28}{142} \{ (\%MnO) - (MnO\%)^* \} \frac{S}{V_{slag}},$$
(9)

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where $\beta_{[Si]}, \beta_{(SiO_2)}, \beta_{(MnO)}$ are the mass transfer coefficients, m/s; (% SiO2), (% MnO) are the concentrations of SiO2 and MnO in the slag, respectively, % by; [% Si] is the concentration of silicon in ferrosilicium, % by wt; (% SiO2) *, (% MnO) * are the equilibrium concentrations of SiO2 and MnO in the slag, respectively, % by wt; [Si] is the concentration of silicon in ferrosilicon, % by wt; [Si] * is the equilibrium concentration of silicon, % by wt; S is the area of phase interface, m²; Vslg is the volume of slag m³.

On the assumption that the system is balanced at the phase interface boundary, the equilibrium values of silicon, manganese, SiO2 and MnO concentrations are calculated using equilibrium constants.

This system of equations is solved together with the equilibrium constant expression using the method of successive approximations.

The equation below calculates a period required to transfer ferrosilicon drops

$$\tau = \frac{\mathbf{n}_{\text{slag}}}{\omega},\tag{10}$$

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where h_{μ} is the height of molten slag, m; ω is the velocity of moving particles, m/s.

The Hadamard–Rybczynski equation is used to estimate a velocity of moving the liquid drops through the molted slag [3]

$$V_{x} = \frac{2}{3}g \frac{\rho_{\text{slag}} - \rho_{\text{Me}}}{\eta_{\text{slag}}} r^{2} \frac{\eta_{\text{slag}} + \eta_{\text{Me}}}{2\eta_{\text{slag}} + 3\eta_{\text{Me}}},$$
(11)

where η_{M} is the dynamic viscosity of a molten ferrosilicon drop, Pa·s; η_{III} is the dynamic viscosity of molten manganese oxide, Pa·s; r is the radius of metal particles, m; g is the free fall acceleration, m/s; ρ_{M} is the drop density, kg/m³; ρ_{III} is the slag density, kg/m³.

Post reduction of oxides to metal in the molten slag occurs at the boundary interface of the steel - oxide melt. In this case, the oxidation rate of silicon can be described by the equation

$$V_{\rm Si} = -\frac{d[\%Si]}{d\tau} = \beta_{\rm [Si]} \left\{ [\%Si] - [Si]^* \right\} \frac{S}{V_{\rm slag}}, \qquad (12)$$

where β [Si] is the mass transfer coefficient for silicon, m/s; [% Si] is the concentration of silicon in steel, % by wt; [Si] * is the equilibrium concentration of silicon, % by wt.

The freshly burnt limestone is added to bind the resulting SiO_2 .

The dissolution rate of limestone dispersed particles is determined by the convection diffusion equation [4, 5]

$$\frac{d(CaO)}{d\tau} = \beta_{(CaO)} \left\{ (CaO) - (CaO) \right\} \frac{S}{V}, \qquad (13)$$

where $(CaO)_{Hac}$ and (CaO) are the concentrations of calcium oxide in the slag near the surface of limestone lumps (the concentration of saturation) and in the bulk of slag, respectively; S is the total surface area of limestone lumps, m^2 ; V is the volume of slag m^3 .

The total surface area of spherical particles can be expressed by the equation [5]

$$S = \frac{6M}{d\rho},$$
 (14)

where M is the total mass of particles, kg; $\rho_{\scriptscriptstyle TB}$ is the density of particles, kg/m³; d is the particle diameter, m.

For modeling a mixing process the pattern of successively located baths is applied [4]. Varying the concentration of substance C in a time for the successive baths is expressed by the equation

$$\frac{\partial C_{i}}{\partial t} = \frac{Q}{V_{m}} \left(\rho_{i-1} C_{i-1} - \rho_{i} C_{i} \right) \overline{\beta}_{i}, \qquad (15)$$

where ρ_i and ρ_{i-1} are the density of metal in the i-th and i-1 successive bath, kg/m³; Q is the metal flow between the baths, m³/s; Vm is the bath volume, m³; $\overline{\beta}_i$ is the mass transfer coefficient of sub-

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stance through the metal-slag boundary layer, $\overline{\beta}_i = \beta_i \cdot P$ (where P is the value to numerically characterize a power of melt mixing), m/s.

A schematic flow chart showing the model can be divided into several parts, including calculating the following indicators: a period of time for interacting a deoxidizer and oxides in the slag; an amount of the deoxidizer used for the reduction of metal oxides in the slag; a composition of metal in bulk and the molten oxide; activity of components of the metal and slag phases; a rate of reactions between de-oxidizers and oxides in the slag; mass transfer coefficients of interacting components in the metal and slag; a mass of slag and metal phases; a dissolution rate of limestone in the slag; compositions of metal and slag phases; slag basicity.

Below are the values for a specified calculation error relative to various parameters required for calculations (Table 1).

| Parameter | Specified calculation error |
|-------------------------------|-----------------------------|
| Metal mass, kg | 10 |
| Slag mass, kg | 10 |
| Manganese content in metal, % | 0.001 |
| Silicon content in metal, % | 0.001 |
| Manganese content in slag, % | 1.0 |
| Silicon content in slag, % | 1.0 |
| Ferrum content in slag, % | 0.1 |
| Basicity of slag | 0.1 |
| Mass of additives, kg | 1.0 |

Table 1. Specified calculation errors for parameters available from experiments

A prerequisite for constructing the mathematical model is the application of the law of conservation of mass, which is taken as a basis for instantaneous material balances.

The initial data to start working in the 'Advisor Wizard' system, are:

- Metal state parameters: a mass at a point in time τ_1 , kg; temperature, °C; composition, % by wt;

- Slag state parameters: a mass of oxidative slag at a point in time $\tau_1,\,kg;$ basicity, units; composition, % by wt;

- Chemical composition of coke;

- Ferrosilicon parameters: chemical composition, % by wt; mass, kg;

- Parameters of lining: a mass of lining washed out for a melt, kg; composition, % by wt;

- Parameters of limestone: a mass of lime, kg; time required for complete dissolution of lime in the slag min; composition, % by wt;

- Parameters of a ladle- furnace, a diameter of bath at the slag belt level, m; bath depth, m;

- Increments in calculations

Figure 2 depicts the schematic structure of the model

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Figure 2. Block flow chart of the mathematical model

Calculations are performed in the following way: knowing the metal and slag compositions, the compositions of these phases can be calculated after adding coke. These compositions are accepted as initial at a point in time τ_1 .

After adding ferrosilicon the metal and slag compositions can be determined at a point in time $\tau_2 = \tau_1 + \Delta \tau$, where $\Delta \tau$ is the increment in calculations (block 1, 2, 3).

In block 4, the activity coefficients of components in the metallic and slag phases [7] are calculated using the method proposed by the authors in [6]. In block 5, the oxidation rate of silicon in ferrosilicon is calculated using equation (12). Block 6 gives the calculation for an amount of silicon required for the reduction of oxides in the slag. In block 7, the compositions in the metallic and slag phases are determined; block 8 is for calculating a density of the metallic phase.

Block 9 - the density of the metallic phase and the density of the molten slag are compared. With the condition $\rho_{Me} > \rho_{o.p.}$, we proceed to calculate the time of the motion of a metal drop in the oxide melt (block 10).

Block 11 is used to calculate the mass of silicon used for the reduction of oxides in the slag to form metals and the mass of the reduced element (block 12). The metal and slag masses are then determined by solving a system of three balance equations: the total material balance, the balance of the reduced element, the balance of silicon (block 13), with further calculating the metal and slag compositions (block 14) and the basicity and viscosity of slag (block 15).

In blocks 17, 18, the mass, rate and dissolution time for limestone are calculated.

Then, the activity coefficients of components of the metallic and slag phases and the composition of the slag phase are calculated in blocks 19, 20. Activities of components of the metallic phase are determined using parameters of first-order interactions, and activities of components of the slag phase are determined using the method developed by the authors [7], with calculating the reaction rate for reducing oxides dissolved in the steel.

After block 20, the reaction rates are calculated used for the reduction of slag oxides to metals with silicon dissolved in the steel (block 21). Further, the masses and compositions of the metallic and slag phases are determined (block 22, 23, 24).

Calculations are made as long as the content of a metal in oxides in the slag phase is less than an estimated value of calculation accuracy as to this component.

To prove the model adequacy, a number of experimental melts were made using a ladle-furnace at Novokuznetsk Iron and Steel Plant. The melting process and oxidation time were observed according to the plant's production process instruction. After pouring the molten steel from the furnace, the ladle with steel was moved to the 'ladle-furnace' unit, where an amount of slag in the ladle was measured. Then, coke breeze in quantity of 50 - 100 kg was added onto the slag surface, with the holding time 10 - 20 min. After that, ferrosilicon FS65, FS75 was added in amounts to ensure the silicon content in the steel closer to the upper limit. Simultaneously with the silicon mixing, limestone was added in an amount to obtain the free running slag. The additives were introduced while stirring the steel with an inert gas. The treatment time was 40-70 min. In the course of experiments, samples of the metal and slag were taken to monitor the chemical composition of the steel, with the exact timing of all technological operations.

The initial data on each melt were entered into the program 'Advisor Wizard' for calculating. The results of changes in the content of manganese and silicon in reference points in time in the samples taken to identify melts, and the content of silicon and manganese estimated for the same points in time are shown in Table 2.

The residual content is 0.01 - 0.04% for manganese, and 0.01 - 0.08% for silicon. The relative error is 2 - 4% for manganese and 6 - 8% for silicon; the errors are within acceptable limits (less than 10%).

| ~~~~~, , , , | | | | | | | | | | |
|--------------|--------|--------------------|------|----------------|------|----------|------|--|--|--|
| No. melt | No.* | Experimental melts | | Estimated data | | Residual | | | | |
| | sample | Mn | Si | Mn | Si | Mn | Si | | | |
| 1 | 1 | 0.98 | 0.85 | 1.01 | 0.90 | 0.02 | 0.05 | | | |
| | 2 | 1.11 | 0.75 | 1.15 | 0.70 | 0.04 | 0.04 | | | |
| | 3 | 1.35 | 0.69 | 1.36 | 0.74 | 0.01 | 0.05 | | | |

Table 2. Change in the contents of manganese and silicon during the melting process, Steel 25G2S %

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| No. melt | No.* | Experimental melts | | Estimated data | | Residual | | |
|--|--------|--------------------|------|----------------|------|----------|------|--|
| | sample | Mn | Si | Mn | Si | Mn | Si | |
| | 4 | 1.45 | 0.66 | 1.46 | 0.70 | 0.01 | 0.04 | |
| | 5 | 1.47 | 0.64 | 1.46 | 0.70 | 0.01 | 0.06 | |
| 2 | 1 | 0.94 | 0.86 | 0.98 | 0.92 | 0.04 | 0.06 | |
| | 2 | 1.07 | 0.77 | 1.12 | 0.80 | 0.05 | 0.03 | |
| | 3 | 1.31 | 0.63 | 1.33 | 0.70 | 0.02 | 0.06 | |
| | 4 | 1.39 | 0.61 | 1.41 | 0.68 | 0.02 | 0.07 | |
| | 5 | 1.42 | 0.60 | 1.41 | 0.68 | 0.02 | 0.08 | |
| 3 | 1 | 1.22 | 1.10 | 1.18 | 0.72 | 0.04 | 0.03 | |
| | 2 | 1.29 | 0.89 | 1.25 | 0.82 | 0.04 | 0.07 | |
| | 3 | 1.37 | 0.79 | 1.33 | 0.77 | 0.02 | 0.02 | |
| | 4 | 1.47 | 0.70 | 1.48 | 0.75 | 0.01 | 0.05 | |
| | 5 | 1.47 | 0.70 | 1.48 | 0.75 | 0.01 | 0.05 | |
| 4 | 1 | 0.91 | 0.89 | 0.94 | 0.90 | 0.03 | 0.01 | |
| | 2 | 1.10 | 0.81 | 1.12 | 0.82 | 0.02 | 0.01 | |
| | 3 | 1.34 | 0.78 | 1.35 | 0.75 | 0.01 | 0.02 | |
| | 4 | 1.37 | 0.64 | 1.42 | 0.72 | 0.05 | 0.08 | |
| | 5 | 1.42 | 0.64 | 1.42 | 0.72 | 0.01 | 0.08 | |
| * - samples 1, 2, 3, 4, 5 are refinery samples taken in a 10, 20, 30, 40 and 60 minute interval after adding ferrosilicon. | | | | | | | | |

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Conclusion

Thus, it can be claimed that the model adequately exhibits the main features of the process under investigation and allows you to predict the reduction process of oxides to metals and evaluate the slag oxidation.

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