Kinetics of Desulfurization and Resulfurization when Low-Sulfur Steel Making at the Stage of Oxidizing Refining

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There are presented the results of theoretical investigation on determination of primary parameters and stages of desulfurization and resulfurization processes at metal and slag interaction when low-sulfur steel making with application of desulfurized pig-iron without and with ladle slag in the steelmaking bath.

Keywords: STEEL, SLAG, REFINING, SULFUR, DESULFURIZATION, RESULFURIZATION, DIFFUSION, SLAG-METALLIC EMULSION

Results and Discussion

According to Fick's first law it is possible to present the stable process of sulfur diffusion in metal and slag as following equations [1]:

$$\upsilon_{Sm} = -d[\%S]/d\tau = \beta_{[S]} \cdot F_{m\text{-}s} \cdot V_m^{-1} \cdot \{[\%S]-[\%S]_{m\text{-}s}\} \quad \text{(Eq. 1)}$$

$$\upsilon_{Ss} = -d[\%S]/d\tau = \beta_{(S)} \cdot F_{m\text{-}s} \cdot \rho_s^{-1} \, V_m^{-1} \, \rho_m^{-1} \cdot \{[\%S]_{m\text{-}s} \cdot \eta_s - (\%S)\} \quad \text{(Eq.2)}$$

where $\beta_{[S]}$ and $\beta_{(S)}$ - mass-transfer coefficients of sulfur in metal and slag, m/s; $F_{m\text{-}s}$ - phase interface metal - slag, m^2; V - metal volume, m^3; ρ_s and ρ_m - slag and metal density, kg/m^3; $[\%S]_{m\text{-}s}$ - sulfur content in boundary diffusion layer.

Mass-transfer coefficient β depends on Sherwood number (Sh) [1]:

$$\beta_S = Sh \cdot D_S/d \quad \text{(Eq.3)}$$

It is known from theory of similarity that in case of forced convection Sherwood number Sh is a function of Reynolds (Re) and Prandtl (Pr) numbers:

$$Sh = f(Re, Pr) = f(U \cdot d/v, v/D) \quad \text{(Eq. 4)}$$

According to investigations [2] taking into account equation (4) we obtain:

$$\beta_S = 0.55U^{0.5} \cdot D_S^{0.65} \cdot v^{-0.15} \cdot d_n^{-0.5} \quad \text{(Eq.5)}$$

where D_S - molecular diffusion coefficient of sulfur in melts, m^2/s; d_n - typical size (diameter of gas blowhole is accepted in this work), m; U - linear motion speed of fluid or gas stream, m/s; $v = \eta/\rho$ - kinematic viscosity of medium, m^2/s.

In equations (1) and (2) phase interface is composed of:

$$F_{m\text{-}s} = \Sigma F_{s\text{-}md} + \Sigma F_{s\text{-}mf} \quad \text{(Eq. 6)}$$

where $\Sigma F_{s\text{-}md}$ - total surface of metal drops in slag, m^2; $\Sigma F_{s\text{-}mf}$ - total surface of contact of metal film and blowholes with slag, m^2.

Taking into account fractional composition of metal drops in slag, $\Sigma F_{s\text{-}md}$ is defined from the following equation according to [3]:

$$\Sigma F_{s\text{-}md} = 4 \cdot 10^{-2} \, M_s \cdot C_{d\text{-}gs} \cdot \pi \cdot \Sigma(n_i \cdot r_i^2) \quad \text{(Eq. 7)}$$

where M_s - slag weight, t; $C_{d\text{-}gs}$ - amount of globules in slag, %; n_i - quantity of *i*-sized globules; r_i - radius of *i*-globule.

The total interface surface of contact of metal films and gas blowholes with slag is defined also taking into account carbon oxidation rate. With account of data [4] and amount of blowholes with i – radius, we defined $\Sigma F_{m\text{-}sf}$ as follows:

$$\Sigma F_{m\text{-}sf} = 2.355 \cdot \Sigma[(H_{se} - H_{sl}) \cdot D_c^2 \cdot C_{irb}/r_{ib}] \quad \text{(Eq. 8)}$$

where H_{se} - thickness of emulsified slag layer, m; H_{sl} - calculated thickness of not emulsified slag layer, m; D_c - diameter of basic-oxygen converter, m; C_{irb} - amount of blowholes with i - radius in slag; r_{ib} - average radius of i-blowholes, m.

Value D_S is defined by Stokes-Einstein`s formula:

$$D_S = kT/6\,\pi \cdot \eta \cdot r \qquad (Eq.\ 9)$$

It is accepted that sulfur in iron-carbon and oxide melts is in the form of groups $Fe^{2+} \cdot S^{2-}$ with predominating ionic bond and relation $n_{Fe^{2+}}/n_{S^{2-}} = 1$, and the total radius of group is $r = 1.801 \cdot 10^{-10}$ m.

Increase of melt level was defined depending on carbon oxidation rate in view of experimental data [4]:

$$(H - H_0) / H_0 = f\,(\upsilon_C) \qquad (Eq.\ 10)$$

where H_0, H - initial depth of liquid bath and its depth at blowing, m.

Rate of floating-up of gas blowholes in basic-oxygen bath depends on average speed of gas $\overline{\upsilon}_g$ in cross-section of bath, its initial (H_0) and final level (H) [5]:

$$U = \overline{\upsilon}_g\ (1 + \Delta H / H_0) / (\Delta H / H_0) \quad (Eq.\ 11)$$

where $\Delta H = (H - H_0)$ - increase of liquid bath level, m. According to [6], thickness of boundary diffusion layers on the surface of blowholes and metal drops in slag in gas-agitated liquid fluid are defined from the following equation:

$$\delta_a = k_1 \sqrt{D_S r_a / U_{blowhole}} \qquad (Eq.\ 12)$$

The average size of blowholes in basic-oxygen bath usually does not exceed 0.02 m [7].

Sulfur content in boundary diffusion layer on phase interface metal-slag was determined from equation (14):

$$[S]_{m-s} = (M_m \cdot [S]_m + M_s \cdot (S)_s) \cdot M_m + \eta_S \cdot M_s)^{-1} \qquad (Eq.\ 14)$$

where M_m and M_s - weight of molten metal and slag, t; $[S]_m$ and $(S)_s$ - actually observable sulfur content in metal and slag, %; η_S - sulfur partition ratio in system metal-slag.

The sulfur partition ratio is defined from equations (8, 9).

$$\eta_S = (S) / [S] = 32.06\ K_S \cdot f_{[S]} \cdot \Sigma\ n^- a_{(Fe^{2+})}^{-1} \gamma_{(S^{2-})} \qquad (Eq.\ 15)$$

We determined reaction equilibrium constant $[S]+[Fe] = (S^{2-})+(Fe^{2+})$ according to data by A. M. Samarin, L. A. Shvartsman and M. I. Temkin [10]:

$$lgK_S = -3160\ T^{-1} + 0.46 \qquad (Eq.\ 16)$$

Data of more than 150 smelting operations carried out in 350-ton units of integrated works Azovstal by two technologies were processed to estimate usability of equations obtained earlier to the real conditions of smelting. Design parameters of experimental smelting operations are introduced in **Table 1**.

Nature of liquid or gas motion at forced convection is defined by Reynolds number ($Re = U \cdot d / v$) which values at motion of gas blowholes in metal and slag melts in the beginning of blowing are $3.32 \cdot 10^5$ for metal and $1.0 \cdot 10^3$ for slag (**Table 1**). This proves that gas-slag-metal emulsion motion pattern is turbulent in basic oxygen bath.

Physical properties of medium (metal and slag), in which mass exchange takes place, are characterized by Prandtl (Schmidt) number ($Pr = v/D$) which values are 89.9 for metal and $1.01 \cdot 10^6$ for slag in early blowing (**Table 1**). These values show that mass exchange processes are carried out in a diffusion way, and sulfur transfer in slag is defining.

Sherwood number $Sh = f\ (Re,\ Pr)$ of diffusion considers motion mode of reacting phases in converter, viscosity of medium and sulfur molecular diffusion factors. Sherwood number values for metal 1452 and slag 3555 (**Table 1**) once again confirm that sulfur transfer process in system slag-metal is accomplished in diffusion mode.

We calculated the total interphase surface of metal and slag contact during desulfurization and resulfurization. If accept for the first smelting (9-th minute of blowing) [%S] - [%S]$_{m-s}$ = 0.001 %, then $\upsilon_{res} = 7.071 \cdot 10^{-5}$ %/s. Observed resulfurization rate is $1.84 \cdot 10^{-6}$ %/s. For the second smelting carried out with converter slag in steel-smelting bath $\upsilon_{res} = 7.15 \cdot 10^{-5}$ %S/s. Observed $\upsilon_{res} = 3.22 \cdot 10^{-5}$ %S/c. Thus, kinetic possibilities of resulfurization are much higher than real parameters.

Table 1. Kinetic parameters of experimental smelting operations

No.	Values	Dimension	Smelting without converter slag		Smelting with converter slag	
			Start, 9-th minute	Finish	Start, 9-th minute	Finish
1	Reynolds number for metal	n/d	$3.32 \cdot 10^5$	$1.57 \cdot 10^5$	$4.44 \cdot 10^5$	$1.64 \cdot 10^4$
2	Reynolds number for slag	n/d	$1.0 \cdot 10^3$	$8.48 \cdot 10^3$	$1.43 \cdot 10^3$	$0.94 \cdot 10^5$
3	Prandtl number for metal	n/d	89.9	554.8	81.9	554.8
4	Prandtl number for slag	n/d	$1.01 \cdot 10^6$	$1.09 \cdot 10^6$	$1.01 \cdot 10^6$	$1.09 \cdot 10^6$
5	Sherwood number for metal	n/d	1452	1622	1452	1622
6	Sherwood number for slag	n/d	3555	8909	3555	8909
7	Mass-transfer coefficient of sulfur in metal, $\beta_{[S]}$	m/s	$2.67 \cdot 10^{-4}$	$1.55 \cdot 10^{-4}$	$3.15 \cdot 10^{-4}$	$1.21 \cdot 10^{-4}$
8	Mass-transfer coefficient of sulfur in slag, $\beta_{(S)}$	m/s	$5.62 \cdot 10^{-6}$	$1.18 \cdot 10^{-5}$	$6.74 \cdot 10^{-6}$	$1.2 \cdot 10^{-5}$
9	Ratio $\beta_{[S]} \cdot \rho_m / \beta_{(S)} \cdot \rho_s$	n/d	124.1	26.6	122.0	20.43
10	Experimental and calculation (numerator / denominator) rates of resulfurization: – metal	%/c	$\dfrac{-1.55 \cdot 10^{-5}}{2.03 \cdot 10^{-4}}$	$\dfrac{1.36 \cdot 10^{-5}}{2.82 \cdot 10^{-4}}$	$\dfrac{2.7 \cdot 10^{-4}}{-3.11 \cdot 10^{-3}}$	$\dfrac{7.99 \cdot 10^{-7}}{2.19 \cdot 10^{-5}}$
	– slag		$\dfrac{-6.53 \cdot 10^{-8}}{1.15 \cdot 10^{-6}}$	$\dfrac{3.4 \cdot 10^{-6}}{7.07 \cdot 10^{-5}}$	$\dfrac{1.44 \cdot 10^{-7}}{1.65 \cdot 10^{-6}}$	$\dfrac{2.01 \cdot 10^{-7}}{5.51 \cdot 10^{-6}}$

Relations $\beta_{[S]} \cdot \rho_m / \beta_{(S)} \cdot \rho_s = 20.17$ and $L = \eta_S + \sqrt{D_{[S]}/D_{(S)}} = 10.75$ show that resulfurization is in diffusion mode on the 9-th minute of blowing and is limited by sulfur diffusion in slag.

In the closing stage of converter bath oxygen-blowing, desulfurization process is steady and possible to consider as steady-flow process, thus $\upsilon_{Sm} = \upsilon_{Ss}$.

Sulfur transfer coefficients in metal and slag melts $\beta_{[S]} = 1.58 \cdot 10^{-4}$ km/s and $\beta_{(S)} = 1.33 \cdot 10^{-5}$ km/s differ approximately by one order, and metal density exceeds slag density approximately in 2 times, therefore $\beta_{[S]} \rho_m / \beta_{(S)} \cdot \rho_s = 23.93$. It specifies that desulfurization is limited by sulfur diffusion in the closing stage of blowing.

Desulfurization rate (in the closing stage of blowing) is $3.6 \cdot 10^{-4}$ and $1.0 \cdot 10^{-4}$ %S/s according to equations (1) and (2).

Observed desulfurization rate for the first smelting $\upsilon_{Sm} = 3.3 \cdot 10^{-6}$ %/s; second - $\upsilon_{Sm} = 5 \cdot 10^{-6}$ %/s which is much less than calculated. Such deviation is caused by relation of rate of sulfur removal from metal in slag to slag formation process.

Mass of sulfur passed from slag into metal drop and blowhole film (and vice versa) can be evaluated by solution of Fick's second law equation:

$$\frac{\partial C_S}{\partial \tau} = D_S \left(\frac{\partial^2 C_S}{\partial x^2} + \frac{\partial^2 C_S}{\partial y^2} + \frac{\partial^2 C_S}{\partial z^2} \right) \quad \text{(Eq. 17)}$$

or in spherical coordinates:

$$\frac{\partial C_S}{\partial \tau} = D_S \left(\frac{\partial^2 C_S}{\partial r^2} + \frac{2}{r} \frac{\partial C_S}{\partial r} \right) \quad \text{(Eq. 18)}$$

where r - distance from globule centre, m; x, y and z - coordinates; D_S - sulfur diffusion coefficient, m^2/s; C_S - sulfur concentration, %; τ - time, s.

We define degree of noncompletion of diffusion process by means of equation (4) at $C_{Ssuf} = $ const and $T_{suf} = $ const:

$$\overline{\theta} = (C_{Ssuf} - \overline{C}_{S(\tau)})/(C_{Ssuf} - C_{S0}) \quad \text{(Eq. 19)}$$

depending on Fourier diffusion criterion,

$$F_{0d} = D_S \tau / r^2 \quad \text{(Eq. 20)}$$

where C_{Ssuf} - concentration on drop surface, %; $C_{S\tau}$ - average concentration in drop volume at the moment τ, %; τ - stay period of drop in the liquid, s; C_{S0} and T_0 - initial concentration and temperature in drop volume, % and °C;

r - radius of spherical drop, m. Analysis shows that to make diffusion processes in drops complete at $\overline{\theta} = 0$ or $1 - \overline{\theta} = 1$, $\overline{C}_{S\,\tau} = C_{S\,suf,}$ it is necessary that $F_{0d} \geq 0.5$. Diffusion process came to the end in $\tau = 134$ seconds at $D_{[S]} = 1.55 \cdot 10^{-9}$ m/s in a drop with radius $0.644 \cdot 10^{-3}$ m.

Conclusions

It may be concluded that diffusion and sulfur transfer in metal and slag are the slowest stage during desulfurization and resulfurization. High rate of refining processes under conditions of oxygen-converter bath is caused by great interphase contact specific surface of gas-slag-metal emulsion which value is 46-106 m^2/t at carbon oxidation rate 0.15-0.20 % /min.

Having used the analytical solution of unsteady-state diffusion problem, we determined that diffusion processes on metal films of boundary diffusion layers and in metal drops with radius $1 \cdot 10^{-5}$ m cutoff completely, at $r_k = 1 \cdot 10^{-5} - 1 \cdot 10^{-4}$ m partially, and in drops $r_k > 1 \cdot 10^{-3}$ m - they are far from the end.

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Кинетика десульфурации и ресульфурации при выплавке низкосернистой стали на стадии окислительного рафинирования

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Представлены результаты теоретического исследования по определению главных параметров и стадий процессов десульфурации и ресульфурации при взаимодействии металла со шлаком при выплавке низкосернистой стали с применением обессеренного чугуна без и с наличием ковшового шлака в сталеплавильной ванне.