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A MODEL OF FERROUS OXIDE REDUCTION IN STEELMAKING SLAG VOLUME

MODEL REDUKCJI TLENKU ŻELAZA W OBJĘTOŚCI ŻUŻLA STALOWNICZEGO

Ferrous oxide reduction in steelmaking slag is related to the formation of carbon oxide gas bubbles resulting from the reaction of a carbon reducer upon the ferrous oxides contained in slag. The formation and surfacing of carbon oxide bubbles from liquid slag volume causes slag foaming. Changes in the FeO content in slag are described on the basis of Fick's first law.

No models describing the mathematical dependence between the slag chemical constitution, process temperature and the size of injected reducer particles versus the volume of carbon oxide gas bubbles formed in the slag are presented in previous studies. The above-mentioned dependencies can be partially described by the model presented in the paper [1], which allows the variability of the foregoing parameters to be examined, assuming the equilibrium FeO content in the reduced phase is 0.

As it is assumed that a non-metallic phase of the FeO content higher than 0 is obtained in the industrial conditions, it has been decided to develop the solution of Fick's equation in a broader scope than in the paper [1].

Redukcja tlenków żelaza w żużlu stalowniczym związana jest z tworzeniem się gazowych pęcherzyków tlenku węgla, które powstają w wyniku reakcji reduktora węglowego z tlenkami żelaza zawartymi w żużlu. Tworzenie się i wypływanie pęcherzyków tlenku węgla z objętości ciekłego żużla powoduje jego pienienie. Zmiany zawartości FeO w żużlu opisuje się w oparciu o pierwsze prawo Ficka.

W dotychczasowych opracowaniach brak jest modeli opisujących matematyczną zależność pomiędzy składem chemicznym żużla, temperaturą procesu oraz wielkością wdmuchiwanym cząsteczek reduktora a objętością tworzących się w żużlu pęcherzyków gazowych tlenku węgla. Częściowy opis wymienionych zależności umożliwia model przedstawiony w pracy [1], który pozwala na badanie zmienności wymienionych parametrów przy założeniu, że równowagowa zawartość FeO w zredukowanej fazie wynosi 0.

Ze względu na to, że zakłada się otrzymywanie w warunkach przemysłowych fazy niemetalicznej o zawartości FeO wyższej od 0 postanowiono dokonać rozwinięcia rozwiązania równania Ficka w szerszym zakresie niż przyjęty w pracy [1].

1. Introduction

The slag reduction process in the EAF is one of the developed methods of utilizing the continuously growing mass of converter slag, yet the results of previous research do not allow for the implementation of the process into industrial practice [2-5]. This is due to the current state of knowledge, which does not allow a clear-cut determination of the reduction reaction mechanism, while the kinetics of the process are only partially known.

The occurrence of slag foaming during the reduction process is related to the formation of carbon oxide gas bubbles, which is itself the results of the reaction of a carbon reducing agent with ferrous oxides contained in the slag. The flow rate and ability to precipitate depend

on the physico-chemical characteristics of slag and the size of the CO gas bubbles.

The reduction process rate depends on the speeds of the consecutive process stages. The slowest stage dictates the course of the process. Deliberations on the process kinetics of ferrous oxide reduction in a liquid phase assume that Fe^{+2} and O^{-2} ion diffusion in the foamed slag phase is the slowest stage of the process. The temperature and physico-chemical characteristics of liquid slag also influence the process rate. Dynamic viscosity is the basic characteristic of the liquid slag phase. It decreases as the temperature increases and depends on the slag chemical constitution. A decrease in viscosity improves the conditions of Fe^{+2} ions and O^{-2} ions movements

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within the liquid phase, increasing the reduction process rate.

No models describing the mathematical dependence between the slag chemical constitution, process temperature and the size of injected reducer particles versus the volume of carbon oxide gas bubbles forming in the slag are presented in the previous studies. The above-mentioned dependences can be partially described by the model presented in the paper [1], which allows the variability of the foregoing parameters to be examined, assuming the equilibrium FeO content in the reduced phase is 0.

Previous research on the reduction process indicates that the resulting non-metallic phase can be utilised as Portland clinker, calcium-magnesium fertilizer or slag-forming material in secondary steelmaking. In any case the FeO content in the obtained phase may be higher than 0. Different equilibrium conditions, i.e. a different reducer share and process temperature than for the process which assumes the complete reduction of FeO, should be determined. The model presented in the paper [1] does not allow these conditions to be determined. Therefore it has been decided that additional calculations be performed, aiming at the development of a model allowing the variability of the process parameters for various equilibrium conditions to be examined.

2. The reference model of ferrous oxide reduction

The paper [1] assumes the FeO content in the slag and its ability to move in the slag controls the course of the reaction of the gas CO forming in the slag. Changes in the ferrous oxide content are described on the basis of Fick's first law as follows:

$$\frac{d(\%FeO)}{dt} = \beta [(\%FeO) - (\%FeO)_r], \quad (1)$$

where: $\%FeO$ – the percentage of FeO in the slag [%],

$(\%FeO)_r$ – the content of FeO in the slag in a stationary state [%],

β – the mass transport coefficient on the assumption of unit thickness of diffusion value [s^{-1}],

$\frac{d(\%FeO)}{dt}$ – the change in the FeO content vs time [% / s],

t – the time [s].

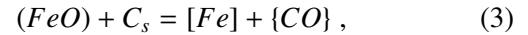
The value of the mass transport coefficient β is described by the dependence:

$$\beta = 2 \sqrt{\frac{D}{\pi t_{co}}}, \quad (2)$$

where: D – the diffusion coefficient [m^2/s],

t_{co} – the time of CO bubble forming at the interface [s].

In the process of converter slag reduction, the reaction occurs at the interface and is written in a simplified way:



The time of CO bubble forming at the interface is determined by the formula:

$$t_{co} = \frac{V_{co_k}}{u_{co}} = \frac{\frac{4}{3}\pi r_k^3}{u_{co}} \cong 3,67 \cdot 10^8 \frac{r_k^3}{T W_z \left[-\frac{d(\%FeO)}{dt} \right]} \quad (4)$$

where: u_{co} – the rate of CO bubble forming in the slag [m^3/s],

V_{co_k} – the critical volume of a CO bubble capable of existing on its own [m^3]

r_k – the critical radius of a CO bubble [m],

T – the temperature [K],

W_z – the slag mass [kg]

The diffusion coefficient D depending on the temperature and chemical constitution of the liquid in which the process takes place is expressed by the formula:

$$D = D_0 e^{-\frac{E}{RT}}, \quad (5)$$

where: D_0 – the diffusion coefficient in normal conditions [m^2/s],

E – the diffusion activation energy [J/mol],

R – the universal gas constant 8.31 [$J/molK$]

T – the temperature [K].

The D_0 value is described by the Stokes-Einstein equation:

$$D_0 = \frac{kT}{6\pi r \eta}, \quad (6)$$

where: k – the Boltzman constant equal to $1.38 \cdot 10^{-23}$ [J/K],

T – the temperature [K],

r – the radius of a CO diffusing molecule [m],

η – the viscosity of medium [$Pa \cdot s$].

Using the equations (4), (5) and (6) the formula (2) is written in the form:

$$\beta = XY \sqrt{\left[-\frac{d(\%FeO)}{dt} \right]}, \quad (7)$$

where: $X = 5,04 \cdot 10^{-17}T$,

$$Y = \sqrt{\frac{W_z e^{-\frac{E}{RT}}}{\eta r r_k^3}},$$

In further considerations in the paper [1] the equilibrium content of FeO in the liquid phase is assumed to be zero and the equation (1) assumes the form:

$$\frac{d(\%FeO)}{dt} = \beta (\%FeO) \quad (8)$$

The solution to the foregoing problem is the function in the form:

$$(\%FeO) = \frac{(\%FeO)_0}{1 + X^2 Y^2 (\%FeO)_0 t}, \quad (9)$$

where: $(\%FeO)_0$ – the precondition of the equation (1) at the time $t = 0$ %].

The paper [6] presents computer simulations of the reduction process of converter slag of chemical constitution: CaO – 44.50%, SiO₂ – 16.64%, MgO – 5.26%, FeO – 23.25%, MnO – 5.40%, Cr₂O₃ – 0.16%, Al₂O₃ – 1.68%, P₂O₅ – 1.24% i Σ S – 0.11%. Elementary carbon is used as the reducing agent. Equilibrium chemical compositions of the forming phases are determined with FactSage software. The results of the calculations of the equilibrium FeO content in the reduced non-metallic phase are presented in Fig. 1.

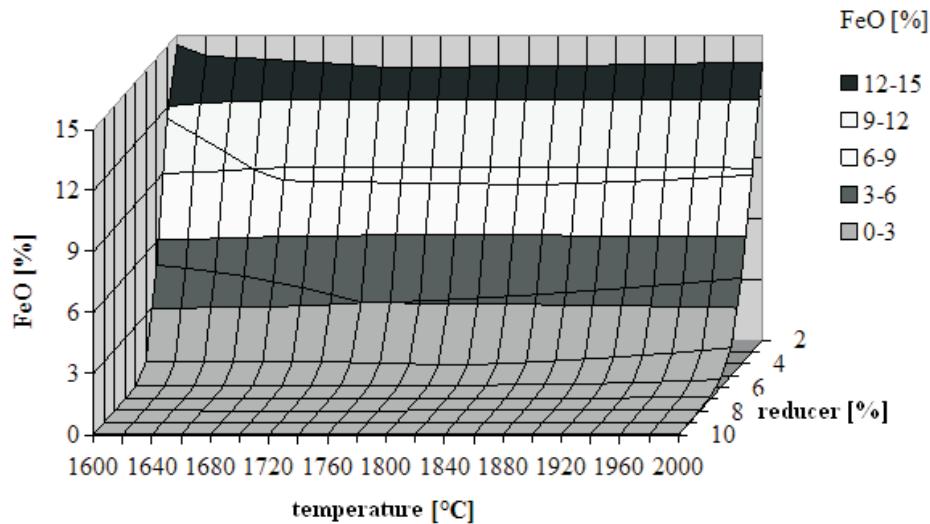


Fig. 1. The equilibrium FeO content in the non-metallic phase [6]

The scope of application of the equation (9) derived in the paper [1] can be determined by analysing the graph shown in Fig. 1. The equation allows the FeO content to be determined only if the reducing agent content is higher than about 8%. As it is assumed that a non-metallic phase of the FeO content higher than 0 is obtained in industrial conditions it has been decided to develop Fick's equation in a broader scope than in the paper [1].

3. The general form of Fick's equation solution in the ferrous oxide reduction process

The equation (9) allows changes in the FeO content in slag reduced to be determined only if the equilibrium content of ferrous oxide after completion of the reduction process equals 0. In a more general case, when the amount of the reducing agent available in the process is insufficient for a complete reduction of ferrous oxide, the

quantity $(\%FeO)_r$ must not be omitted from the calculations. Below, the method of solving the equation (1) with a mass transport coefficient β calculated for the initial temperature $iT_0 = 273K$ is presented. The formula (4) assumes the form:

$$t_{co} \cong 3,67 \cdot 10^5 \frac{r_k^3}{T W_z \left[-\frac{d(\%FeO)}{dt} \right]}, \quad (10)$$

whereas the coefficient X in the formula (7) is:

$$X \cong 15,95 \cdot 10^{-16} T \quad (11)$$

For any values $(\%FeO)_r$ meeting the condition:

$$(\%FeO)_r \leq (\%FeO)_0 \quad (12)$$

the equation (1) can be presented in the form:

$$\frac{d(\%FeO)}{dt} = X Y \sqrt{-\left[\frac{d(\%FeO)}{dt}\right] [(\%FeO) - (\%FeO)_r]} \quad (13)$$

$$z(t) = (\%FeO), \quad \dot{z}(t) = \frac{dz(t)}{dt} = \frac{d(\%FeO)}{dt}, \quad z_{ust} = (\%FeO)_r, \quad z_0 = (\%FeO)_0, \quad (14)$$

According to the foregoing denotations Fick's law can be written as:

$$\dot{z}(t) = X Y \sqrt{-\dot{z}(t)} [z(t) - z_{ust}]. \quad (15)$$

To ensure that the square root in the equation (15) is non-negative it is necessary to assume that the function $z(t)$ is non-growing throughout the entire time interval in which it is determined. The dependence is described by the formula:

$$\forall_{t \geq 0} (\dot{z}(t) \leq 0 \iff -\dot{z}(t) \geq 0). \quad (16)$$

In addition, it is assumed that the ferrous oxide reduction process occurs at a constant temperature so the functions X and Y assume constant values on the time axis.

By squaring both sides of the equation (15) and taking account of the assumption (16) we obtain:

$$(\dot{z}(t))^2 = X^2 Y^2 (-\dot{z}(t)) [z(t) - z_{ust}]^2. \quad (17)$$

Having moved the right hand side of the equation (17) to the left and taken the derivative (t) out of the bracket:

$$\dot{z}(t) [\dot{z}(t) + X^2 Y^2 (z(t) - z_{ust})^2] = 0. \quad (18)$$

hence:

$$\dot{z}(t) = 0 \implies z(t) = const, \quad (19)$$

or

$$\begin{aligned} L = \dot{z}(t) &= \frac{dz_1(t)}{dt} = \frac{dz_{ust}}{dt} = 0, \\ P &= -X^2 Y^2 (z_1^2(t) - 2z_1(t)z_{ust} + z_{ust}^2) = -X^2 Y^2 (2z_{ust}^2 - 2z_{ust}^2) = 0, \\ L = P &\implies z_1(t) = z_{ust} \text{ is the particular solution of the equation (20).} \end{aligned}$$

Using the formulas (22) one can write:

$$z(t) = z_{ust} + \frac{1}{u(t)}, \quad \dot{z}(t) = \frac{d(z_{ust} + \frac{1}{u(t)})}{dt} = -\frac{1}{u^2} \frac{du(t)}{dt} \quad (23)$$

By inserting (23) into (20) one obtains:

To simplify the notation of the equation (13) the following denotations are implemented:

$$\dot{z}(t) = -X^2 Y^2 (z^2(t) - 2z(t)z_{ust} + z_{ust}^2), \quad (20)$$

The equation (19) only means that the equilibrium point of the slag reduction process is a constant value (it follows from the equation (20) that this point is z_{ust}) and provides no information about the process dynamics. Therefore the further part of the paper concerns only the equation (20), which is a non-linear, differential Riccati equation in the form:

$$\dot{z}(t) = p(t)z^2(t) + q(t)z(t) + r(t), \quad (21)$$

$$\begin{aligned} \text{where: } p(t) &= -X^2 Y^2, \\ q(t) &= 2X^2 Y^2 z_{ust}, \\ r(t) &= -X^2 Y^2 z_{ust}^2. \end{aligned}$$

Knowing a certain particular solution $z_1(t)$ of the equation (21) one can reduce the Riccati equation to a linear form by substituting:

$$z(t) = z_1(t) + \frac{1}{u(t)}, \quad \dot{z}(t) = \frac{d(z_1(t) + \frac{1}{u(t)})}{dt} = \frac{d(z_1(t))}{dt} - \frac{1}{u^2} \frac{du(t)}{dt}, \quad (22)$$

$$\begin{aligned} \text{where: } u(t) &- \text{ the new dependent variable,} \\ z_1(t) &- \text{ the particular solution of the equation (21).} \end{aligned}$$

In the case considered functions $p(t)$, $q(t)$ and $r(t)$ are scalars, and the particular integral of the equation (20) is $z_1(t) = z_{ust}$, which can be proven by inserting this solution into the equation (20):

$$-\frac{1}{u^2} \dot{u}(t) = -X^2 Y^2 [(z_{ust} + \frac{1}{u(t)})^2 - 2z_{ust}(z_{ust} + \frac{1}{u(t)}) + z_{ust}^2] \quad (24)$$

By making necessary simplifications the equation (24) is reduced to a linear form:

$$\dot{u}(t) = X^2 Y^2. \quad (25)$$

By integrating the equation (25) on both sides one obtains the solution in the form:

$$u(t) = X^2 Y^2 t + C, \quad (26)$$

hence after taking account of the formulas (23), the solution of the equation (20) assumes the form:

$$z(t) = z_{ust} + \frac{1}{u(t)} = z_{ust} + \frac{1}{C + X^2 Y^2 t}. \quad (27)$$

The integration constant C can be calculated by inserting the precondition $z(0) = z_0$ into (27):

$$z(0) = z_0 = z_{ust} + \frac{1}{C} \Rightarrow C = \frac{1}{z_0 - z_{ust}}, \quad z_0 \neq z_{ust}. \quad (28)$$

Inserting the calculated value C into the formula (27) the final solution of the equation (20) is obtained in the form:

$$z(t) = z_{ust} + \frac{z_0 - z_{ust}}{1 + X^2 Y^2 t(z_0 - z_{ust})}. \quad (29)$$

Taking into account denotations (14), the equation (29) can be written in the form:

$$(\%FeO) = (\%FeO)_r + \frac{(\%FeO)_0 - (\%FeO)_r}{1 + X^2 Y^2 t[(\%FeO)_0 - (\%FeO)_r]}. \quad (30)$$

The equation (30) is a more general solution of Fick's equation for the reduction process of ferrous oxide in liquid slag. Assuming only that the state of equilibrium in the liquid slag reduction process with a solid carbon reducing agent is obtained for the value $(\%FeO)_r = 0$, the equation (30) assumes the form of equation (9).

4. Conclusion

The model presented in the paper [1] only allows for a partial description of the dependences between the slag chemical constitution, process temperature and the

size of injected reducer particles versus the volume of carbon oxide gas bubbles forming in the slag as when the model was derived it was assumed that the equilibrium content of FeO in the reduced phase is 0.

As it is assumed that a non-metallic phase of the FeO content higher than 0 is obtained in industrial conditions it has been decided to develop Fick's equation to a greater extent than in the paper [1]. Assuming the equilibrium FeO content in the reduced phase may be equal or higher than 0 a model of ferrous oxide reduction in the slag volume is proposed in the form:

$$(\%FeO) = (\%FeO)_r + \frac{(\%FeO)_0 - (\%FeO)_r}{1 + X^2 Y^2 t[(\%FeO)_0 - (\%FeO)_r]}$$

which allows a more general determination of changes in the FeO content.

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