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# MATHEMATICAL MODEL OF THE LD STEEL DEOXIDATION KINETICS WITH MANGANESE AND ALUMINIUM

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## ABSTRACT

*The paper presents the mathematical model of the kinetics of the electric arc furnace steel deoxidation with Mn and Al. Based on the solving of the kinetics model differential equations, the variation of the deoxidants solubility during the deoxidation process can be determined, as well as the kinetic constants of the reactions and the maximum durations which are necessary for the complete assimilation of the deoxidants.*

KEYWORDS: mathematical model, steel deoxidation kinetics

## 1. Introduction

The steel elaboration in electric arc furnace is a very complex process as a result of the fact that many technological parameters which interact among them and influence its progress are involved. The steels used for automobile industry are characterized by high grades of cupping and can be obtained only by an advanced deoxidation of the ferrous metallic bath using manganese and aluminum [1-3]. The efficiency of the deoxidation with manganese and aluminum depends to a great extent on the speed of the dissolving and assimilation processes of the two deoxidants, Mn and Al [4-7]. During the deoxidation process into the casting tank successive processes of Mn and Al pieces dissolving in iron are taking place, forming a liquid solution Fe-Mn-Al according to the scheme:

$$\begin{array}{ccccc} Fe & \xrightarrow{k_1} & Mn & \xrightarrow{k_2} & Al \\ 100-z & & y & & x \end{array}$$

Where $k_1$ and $k_2$ are the speed constants of the reactions. At the initial moment *t=0*, when the entire refined slag is removed, the iron concentration is 100% and those of the Mn and Al are zero. After a time *t*, the iron concentration becomes *100-z* and those of the Mn and Al are *y* and *x*, respectively. It results that:

$$x+y=z \tag{1}$$

With the aid of the relation (1) it can be determined the concentration of a certain element if the concentrations of the two others are known.

If we derived the relation (1) with the deoxidation time, we obtain the following kinetic relation of the deoxidation and alloying with Mn and Al:

$$\frac{dx}{dt}+\frac{dy}{dt}=\frac{dz}{dt} \tag{2}$$

The relation (2) expresses the fact that the speed of the iron content diminution is equal to the sum of the two deoxidants assimilation speeds.

## 2. Mathematical model of the kinetics of the steel deoxidation with Mn and Al

The kinetic equations of the deoxidation reactions are:

$$\frac{dz}{dt}=k_1\,(100-z) \tag{3}$$

$$\frac{dy}{dt}=k_1\,(100-z)-k_2\,y \tag{4}$$

$$\frac{dx}{dt}=k_2\,y \tag{5}$$

By integrating the relation (3) we obtain the solution:

$$100-z=100\,\exp(-k_1 t) \tag{6}$$

from which it results:

$$z = 100\ [1-\exp(-k_1 t)] \quad (7)$$

Replacing the relation (6) in (4) we obtain:

$$\frac{dy}{dt} + k_2 y = k_1\ \{100 - 100\ [1-\exp(-k_1 t)]\} \quad (8)$$

or:

$$\frac{dy}{dt} + k_2 y = 100\, k_1\ \exp(-k_1 t) \quad (8')$$

Solving this inhomogeneous differential equation, we obtain the solution having the form:

$$y = C_1 \exp(-k_1 t) + C_2 \exp(-k_2 t) \quad (9)$$

The constants $C_1$ and $C_2$ are calculated by deriving the equation (9) and replacing the obtained expression together with relation (9) in (8'):

$$\frac{dy}{dt} = -k_1\ C_1 \exp(-k_1 t) - k_2\ C_2 \exp(-k_2 t) \quad (10)$$

$$-k_1 C_1 \exp(-k_1 t) - k_2 C_2 \exp(-k_2 t) + k_2 C_1 \exp(-k_1 t) + k_2 C_2 \exp(-k_2 t) = 100\, k_1 \exp(-k_1 t) \quad (11)$$

It results:

$$C_1 = \frac{100\, k_1}{k_2 - k_1} \quad (12)$$

Replacing (12) in (9) we obtain:

$$y_{Mn} = \frac{100\, k_1}{k_2 - k_1} \exp(-k_1 t) + C_2 \exp(-k_2 t) \quad (13)$$

At the beginning of the deoxidation (*t=0*) y=0 and it results:

$$C_2 = \frac{100\, k_1}{k_1 - k_2} \quad (14)$$

Replacing $C_1$ and $C_2$ in expression (9) we obtain the manganese concentration as a function of the speed constants $k_1$ and $k_2$ and of the deoxidation duration:

$$y_{Mn} = \frac{100\, k_1}{k_2 - k_1} \exp(-k_1 t) + \frac{100\, k_1}{k_1 - k_2} \exp(-k_2 t) \quad (15)$$

The aluminum concentration is obtained from the relations (1) and (15):

$$x_{Al} = z - y_{Mn} = 100[1-\exp(-k_1 t)] - \frac{100\, k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \quad (16)$$

or

$$x_{Al} = 100\left[1 - \frac{k_2}{k_2 - k_1}\exp(-k_1 t) + \frac{k_1}{k_2 - k_1}\exp(-k_2 t)\right] \quad (16')$$

In figure 1 are represented the variations of the concentrations *100-z*, *y* and *x* respectively, as functions of the elapsed time from the moment of adding of the deoxidants Mn and Al in the iron metallic bath.

The maximum value of manganese concentration, $y_{max}$, depends on the speed constants $k_1$ and $k_2$, which in turn, depend on the temperature, according to Arrhenius law.

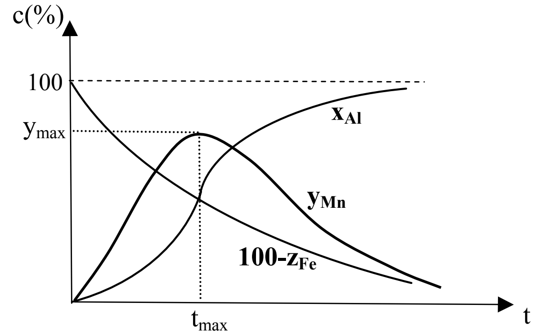


***Fig. 1.*** *The variations of the Mn and Al concentrations (c) as functions of the deoxidation time (t)*

In order to obtain the maximum duration necessary to achieve the maximum concentration of manganese, we put the derivate $\frac{dy}{dt}$ from relation (15) equal to zero for $t = t_{\max}$:

$$\frac{dy}{dt} - \frac{100\, k_1}{k_2 - k_1}[k_1 \exp(-k_1 t) - k_2 \exp(-k_2 t)] = 0 \quad (17)$$

resulting

$$k_1 \exp(-k_1 t_{\max}) = k_2 \exp(-k_2 t_{\max}) \quad (18)$$

from which we obtain:

$$t_{\max} = \frac{\ln k_2 - \ln k_1}{k_2 - k_1} \quad (19)$$

If we put the ratio $\frac{k_2}{k_1} = p$, we obtain:

$$t_{\max} = \frac{\ln p}{(p-1)\ k_1} \quad (20)$$

From the relation (20) we can conclude that the necessary time for manganese to reach the maximum concentration depends only on the speed constants of the deoxidation reactions i. e. on the nature of the reactants Mn and Al, and not on their concentrations. Replacing the relation (20) in (15) we obtain the maximum manganese concentration from the liquid solution Fe-Mn-Al:

$$y_{\max Mn} = \frac{100}{1-p}\left[\exp\left(-\frac{p\ \ln p}{p-1}\right) - \exp\left(-\frac{\ln p}{p-1}\right)\right] \quad (21)$$

It can be observed that the value of the manganese maximum concentration does not depend on the absolute values of the speed constants of the two reactions, but only on their ratio.

The greater $k_1$ and smaller $k_2$, the greater the manganese concentration at $t = t_{\max}$.

The aluminum concentration variation curve presents an inflexion point which coincides with the duration of the maximum manganese assimilation. If we put the derivate of the relation (16') with the deoxidation time equal to zero, we obtain the minimum duration of aluminum deoxidation, $t_{\inf}$:

$$\frac{d^2x}{dt^2} = k_2 \frac{d}{dt}\left(\frac{100\,k_1}{k_2-k_1}[\exp(-k_1 t) - \exp(-k_2 t)]\right) = 0 \quad (22)$$

or

$$-k_1 \exp(-k_1 t_{\inf}) + k_2 \exp(-k_2 t_{\inf}) = 0 \quad (23)$$

By logarithmation of the last expression it results:

$$t_{\inf} = \frac{\ln k_1 - \ln k_2}{k_1 - k_2} = \frac{\ln p}{(p-1)\,k_1} = t_{\max Mn} \quad (24)$$

Analyzing the overall kinetic equation of the aluminium concentration variation during the deoxidation period, $x = \mathrm{f}(t)$, we can observe two limit cases:

a) $k_1 >> k_2$ and $x = 100[1-\exp(-k_2 t)]$ (25)

b) $k_1 << k_2$ and $x = 100[1-\exp(-k_1 t)]$ (26)

The overall kinetics in successive deoxidation processes is determined by the slowest stage which is, in the case of steel manufacture in electric arc furnace and deoxidation in the casting tank, the manganese dissolution, so that $k_1 << k_2$ and the kinetic equation has the form (26). On the curve of manganese concentration variation it can be observed that at the maximum reaching, the speed of passing into solution is zero:

$$\frac{dy}{dt} = 0 \Rightarrow k_1(100 - z) = k_2\, y \quad (27)$$

It results that:

$$y_{\max} = \frac{k_1}{k_2}(100 - z)_{\max} = p\,(100 - z)_{\max} \quad (28)$$

If the dependence of the temperature of the speed constants is taken into consideration, according to Arrhenius law, the equation (28) becomes:

$$y_{max} = \frac{A_1\, exp(-E_1/RT)}{A_2\, exp(-E2/RT)}(100 - z)_{max} \quad (29)$$

where $E_1$ is the activation energy of the deoxidation process with manganese and $E_2$ is the activation energy of the deoxidation process with aluminum.

Because the reactions of the manganese and aluminum dissolving into iron are of the first order, it can be admitted that the pre-exponential factors are approximately equal, $A_1 = A_2$.

It results that:

$$y_{\max} = \exp\left(-\frac{E_1 - E_2}{RT}\right)(100 - z)_{\max} \quad (30)$$

Because aluminum is a stronger deoxidant than manganese, $E_2 > E_1$ and the maximum manganese solubility increases exponentially with $E_2 - E_1$.

## 3. Experimental results

The aim of this experiment was the deoxidation of a alloyed steel with Mn (1.4/1.6%Mn) and minimum 0.025%Al.

On the bases of the relations (25), the constant $k_1$ was determined after logarithmation:

$\ln x = \ln 100 - k_1 t$

$$k_1 = \frac{1}{t} ln\frac{100}{x} = \frac{1}{2} ln\frac{100}{0,025} = 2.645\, min^{-1} \quad (31)$$

where: t- represents the duration resulted for an Al concentration, x=0,025, in the variation graph of Mn and Al deoxidation.

The $k_2$ constant is graphically determined at the intersection of the two curves $f(k_2)$ and $g(k_2)$

$f(k_2) = Y_{Mn} . k_2 - k_1 Y_{Mn}$

$g(k_2) = 100 k_1 e^{-k_1 t} - 100 k_2 e^{-k_2 t}$

$f(k_2) = g(k_2) \rightarrow k_2 = 2{,}61\ \mathrm{min}^{-1}$

The maximum duration of Mn dissolution in steel is determined with the relation:

$$t_{max\ \ Mn} = \frac{ln\, k_1 - ln\, k_2}{k_1 - k_2} = 3.55\, min \quad (32)$$

Considering the values of $k_1$ and $k_2$ we can calculate:

$Y_{max}$=1.6% Mn

$X_{max}$=0.07% Al

## 4. Conclusions

The speed of the making process of the Mn and Al tempered steel depends on the speed of the two deoxidants assimilation. During the manganese and aluminium deoxidation process the iron content decreasing speed is equal to the sum of the deoxidants dissolving speeds.

The necessary time for manganese to reach the maximum concentration depends only on the speed constants of the deoxidation reactions i.e. the nature of the reactants and not on their concentrations. The maximum value of the manganese concentration does not depend on the absolute values of the speed constants of the two reactions, but only on their ratio.

The variation curve of the aluminium concentration presents an inflexion point which coincides with the duration of the maximum assimilation of manganese.

The characteristics of the profound cupping steels in electric arc furnace co depend in a great extent on the assimilation grade of the deoxidants Mn and Al, at the steel temperature during the deoxidation process.

Based on the curves in Fig.1 it can be determined the concentrations of manganese and aluminum at different times and at known temperatures, and with their aid we can determine the speed constants $k_1$ and $k_2$ of the two reactions.

On their basis we can establish the maximum durations necessary for the complete dissolution of the two deoxidants.

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