

REOXIDATION OF STEEL BY ADDING AN OVERCRITICAL CONCENTRATION OF DEOXIDIZER

PONOVNA OKSIDACIJA JEKLA Z DODATKOM NADKRITIČNE VSEBNOSTI DEOKSIDANTA

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At deoxidation of molten steel using silicon or aluminium appears an paradox. Namely, increasing concentration of deoxidizer in the melt over some critical value results in increase of dissolved oxygen. Thermodynamical conditions for appearance of this phenomenon has been discussed in detail.

Key words: deoxidation, reoxidation, deoxidiser content

Dezoksidacija staljenega jekla s silicijem ali aluminijem lahko privede do paradoksa. S povečanjem vsebnosti dezoksidanta nad neko kritično mejo se opaža povečanje vsebnosti raztopljenega kisika. Analizirani so termodinamični pogoji, ki privedejo do tega pojava.

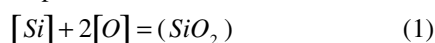
Ključne besede: dezoksidacija, reoksidacija, vsebnost dezoksidanta

1 INTRODUCTION

Deoxidation is the removal of excess oxygen from molten metal. The procedure involves adding materials with a high affinity for oxygen, the oxides of which are either gaseous or readily form slags¹. The deoxidation of steel is usually performed by adding Mn, Si and Al, or rarely by adding Cr, V, Ti, Zr and B. The deoxidation of molten steel exhibits a paradox. By increasing the concentration of deoxidizer in the melt over some critical value reoxidation of steel takes place. A few examples of the reoxidation of steel by adding the usual deoxidizers (Si and Al) are examined in this paper.

2 REOXIDATION OF STEEL BY ADDING SILICON

Silicon is a strong deoxidizer. If $[\%Si] \geq 0.2$, $[\%C] \leq 0.15$, and the temperature of the melt is 1873 K the allowing reaction is possible:



The equilibrium constant of the reaction (1) is

$$K_{Si-O} = \frac{a_{SiO_2}}{[\%Si][\%O]^2 f_{Si} f_O^2} \quad (2)$$

If the standard state is solid silica, then in the thermodynamic calculation for the deoxidation of steel by means of silicon a_{SiO_2} is taken as being equal to one. According to Kramarov² if the slag is saturated with silica then:

$$\log K_{Si-O} = \log \frac{1}{[\%Si][\%O]^2 f_{Si} f_O^2} = \frac{31000}{T} - 12.15 \quad (3)$$

So the deoxidation ability of silicon depends on its concentration and the temperature of the metal, but also on the activity a_{SiO_2} . At high temperature and the some value of $[\%Si]$, $[\%Mn]$ and $[\%C]$, its deoxidation ability is something smaller than that of carbon, but considerably higher than manganese.

At some point during the increase in the concentration of silicon in the Fe-Si melt the minimum concentration of oxygen $[\%O]_{min}$ is obtained, any further increase in $[\%Si]$ results in an increase of $[\%O]$. At first sight this suggests that the product of the activity coefficients $(f_O^{Si})^2 f_{Si}^{Si}$ decrease faster than the increase of $[\%Si]$. The result of that is that, in agreement with the expression for the equilibrium constant (2), the extreme value for the concentration of silicon $[\%Si]_{extr.}$ corresponds to the minimum concentration of $[\%O]_{min.}$

When calculating the critical value of $[\%O]_{min.}$ and $[\%Si]_{extr.}$ it is necessary to express equation (2) in the following way

$$\ln[\%O] = \frac{1}{2} \ln a_{SiO_2} - \frac{1}{2} \ln K_{Si-O} - \frac{1}{2} \ln[\%Si] - \frac{1}{2} \ln f_{Si}^{Si} - \ln f_O^{Si} \quad (4)$$

The logarithms of the coefficients of activity are:

$$\ln f_O^{Si} = 2.3 \log f_O^{Si} = 2.3 e_O^{Si} [\%Si] \quad (5)$$

$$\ln f_{Si}^{Si} = 2.3 \log f_{Si}^{Si} = 2.3 e_{Si}^{Si} [\%Si] \quad (6)$$

and the interaction parameters are $e_O^{Si} = -0.133$ and $e_{Si}^{Si} = 0.098$. The interaction parameters e_O^O and e_{Si}^O are neglected because the concentration of oxygen is relatively small ($\log f_O^O \approx 0$, $\log f_{Si}^O = e_{Si}^O [\%O] \approx 0$,

and follows $f_O^O \approx 1$ and $f_{Si}^O \approx 1$), and the activity $a_{SiO_2}=1$.

To obtain $[\%Si]_{extr.}$ it is necessary to take the first derivative of the concentration of oxygen divided by the concentration of silicon and set the equation equal to zero under specific conditions:

$$\frac{\partial \ln[\%O]}{\partial [\%Si]} = -\frac{1}{2[\%Si]} - 2,3 \frac{e_{Si}^{Si}}{2} - 2,3e_o^{Si} = 0 \quad (7)$$

The second derivative is greater than zero:

$$\frac{\partial^2 \ln[\%O]}{\partial [\%Si]^2} = -\frac{1}{2[\%Si]^2} > 0 \quad (8)$$

Consequently, the function has a minimum. The concentration of silicon at which $[\%O]$ is a minimum:

$$[\%Si]_{ekstr.} = \frac{1}{-2,3e_{Si}^{Si} - 4,6e_o^{Si}} \quad (9)$$

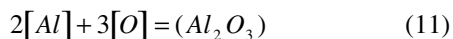
On the basis of the quoted value of the interaction parameters for $T=1873$ K and $a_{SiO_2}=1$ $[\%Si]_{extr.}$ a value of 2.59% is obtained. In that case $f_{Si}^{Si} = 1.794$ and $f_o^{Si} = 0.452$. For steel melts there is also the influence of the other elements on f_{Si} and f_o . At 1873 K the equilibrium constant $K_{Si-O} = 25099$. The minimum concentration of oxygen in the melt is:

$$[\%Si]_{min} = \frac{1}{\sqrt{K_{Si} [\%Si] f_{Si}^{Si} (f_o^{Si})^2}} \quad (10)$$

By inserting reasonable values into equation (10) a minimum concentration of oxygen $[\%O]_{min} = 6.5 \times 10^{-3}$ % is obtained.

3 REOXIDATION OF STEEL BY ADDING ALUMINIUM

The deoxidation of steel by aluminum proceeds according to the reaction:



The equilibrium constant may be determined from:

$$\log K_{Al-O} = \log \frac{a_{Al_2O_3}}{[\%Al]^2 [\%O]^3 f_{Al}^2 f_o^3} \quad (12)$$

At 1873 K the equilibrium constant $K_{Al-O} = 4.9 \times 10^{13}$. In the calculation it is assumed that $a_{Al_2O_3} = 1$, because at a small value of $[\%Al]$ (0.001-0.01) the equilibrium concentration ($\%FeO$) in the slag is neglected, so the products of deoxidation are solid Al_2O_3 or an oxide phase saturated with alumina. The coefficient of activity of aluminum $f_{Al} = f_{Al}^{Al} f_{Al}^O \approx 1$, and the coefficient of oxygen $f_o = f_o^O f_o^{Al} \approx f_o^{Al}$, which is an approximation, because the influence of the other elements present on f_o

is very strong, and f_o is <1 . The equilibrium concentration of oxygen in the melt may be expressed with:

$$[\%O] = \frac{1}{\sqrt[3]{[\%Al]^2 (f_o^{Al})^3 K_{Al}}} \quad (13)$$

An analysis of the equation (13) shows that at some increment of the concentration of aluminium the activity factor f_o^{Al} decreases faster than $[\%Al]^{2/3}$ increases. The result is that at some value of $[\%Al]$ the $[\%O]_{min.}$ is obtained. A further increase in $[\%Al]$ results in an increase of $[\%O]$.

To obtain $[\%Al]_{extr.}$, the first derivative of the logarithm of the concentration of oxygen divided by the concentration of aluminum must be set equal to zero:

$$\frac{\partial^2 \ln[\%O]}{\partial [\%Al]} = -\frac{1}{3[\%Al]} - 2.3e_o^{Al} = 0 \quad (14)$$

$$[\%Al]_{ekstr.} = -\frac{0.29}{e_o^{Al}} \quad (15)$$

According to Kulikov ³, interaction parameter $e_o^{Al} = -1.17$, which corresponds to $[\%Al]_{extr.} = 0.248$. According to formula (13) the minimum concentration of oxygen $[\%O]_{min} = 1.35 \times 10^{-4}$ % is obtained.

4 CONCLUSION

During the deoxidation of steel with common deoxidizers, Si and Al, a paradox occurs. For a particular concentration of deoxidizer there exists a minimum concentration of oxygen dissolved in the steel which increases with an increase in the concentration of the deoxidizers. This is explained by the fact that in the equation for the equilibrium constant the factor of activity decreases faster than the increment of the value of the concentration of dissolved deoxidizer. For the deoxidation of steel with silicon the critical concentration of Si is 2.59%, which corresponds to a minimum concentration of oxygen of 6.5×10^{-3} %. In the case of aluminum, the critical concentration of Al dissolved in the steel is 0.248%, which corresponds to a minimum concentration of oxygen of 1.35×10^{-4} %, under the defined conditions ($T=1873$ K, $a_{SiO_2}=1$, $a_{Al_2O_3}=1$, neglected influence of other elements present in the melt).

5 REFERENCES

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