The Influence of Adsorbed Al₂O₃ Inclusions on the Viscosity Behavior of Mould Slag

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Abstract

The role of slag in the process of continuous casting of steel (CCS) is reduced to the thermal and chemical insulation of the liquid steel surface, and additionally to refining. The ability to adsorb non-metallic inclusions flowing off from the crystallizer, mainly Al₂O₃, determines its physicochemical properties. As a result of adsorption and dissolution of inclusions in the liquid layer the viscosity and thickness of mould flux change, which eventually affects the technological parameters and behavior of slag in the crystallizer. The influence of aluminum oxide on the viscosity of slag was empirically investigated with a structural viscosity model worked out by Nakamoto. The results of the simulation are presented in the form of plots. Authors observed a significant influence of Al₂O₃ on the slag viscosity, which suggests that this effect should be taken into account when selecting chemical composition of mould flux for definite types of steel. The results of calculations also show that the disturbances in casting caused by the use of the mould slag may be connected with the content of non-metallic inclusions in steel.

Keywords: Mould flux, Viscosity, Non-metallic inclusion Al₂O₃

1. Introduction

Mould slags contain about 70% (CaO and SiO₂), 0-6% MgO, 2-6% Al₂O₃, 2-10% Na₂O (+K₂O), 0-10% F with varying content of TiO₂, ZrO₂, B₂O₃, Li₂O and MnO. The CaO%/SiO₂% ratio is 0.7 to 1.3. The mould flux is additionally enriched in 2 to 20% carbon in the form of coke, soot and graphite which should control the rate of flux melting [1]. The chemical composition of slags which are applied for casting specific kinds of steel may considerably vary because of [2,3]:

- absorption of non-metallic inclusions from liquid steel (mainly Al₂O₃),
- reactions of the metal/slag interface during continuous casting.

The thin layer of slag may absorb and dissolve the approaching inclusions, but this ability largely depends on the chemical composition of the mould flux. The tendency to adsorb non-metallic inclusion lowers with the decreasing size of the non-metallic particles, lowering wettability between slag and particle, and the increasing non-metallic tension and viscosity of slag [4].

When liquid slag contacts solid Al₂O₃ a new phase can be formed on the interface, and its composition depends on the slag composition (fig.1) [5]. Ja-Yong Choi et al. [6] conducted experiments on the kinetics of Al₂O₃ dissolving in CaO-SiO₂-Al₂O₃ slag at T=1873 K. Authors stated that the dissolving rate increased with temperature and CaO content, and the decrease of Al₂O₃ for a given CaO/SiO₂ ratio. Viscosity had a negative impact on the dissolution of the Al₂O₃ particle, and the latter process was controlled by mass transfer in the slag phase. Analogously, X. Yu, R.J. Pomfret, and K.S. Colley
[7] analyzed the solubility of aluminum oxide in typical mould slags and stated that it equaled to 38% for analyzed slags, regardless their composition. They also observed that after addition CaF$_2$ and Na$_2$O to the basic system CaO-Al$_2$O$_3$-SiO$_2$ it had a very small influence on the solubility of aluminum oxide.

The problem of chemical composition of mould slag, and so the viscosity, can be problematic especially when steel containing Al admixture is cast. In the case of high-strength steel AHSS or TRIP with aluminum content, it is difficult to obtain an ingot with a high quality surface. This is directly connected with changing physicochemical parameters and reactions taking place in slag. TRIP steels contain C, Mn and Si, where C and Mn are used for stabilizing austenite. A similar role is played by Al. Accordingly, the required amount of Al in liquid metal ranges between 0.5 and 3%. In the case of continuous steel casting, the presence of dissolved Al in steel is problematic, especially in reference to classic slags based on SiO$_2$. In this situation the chemical composition of slag changes, which is directly connected with the chemical reaction between Al and SiO$_2$ [8-9]:

$$3 (SiO_2) + 4[Al] = 3[Si] + 2 (Al_2O_3)$$ (1)

$$3(MnO) + 2[Al] = 3[Mn] + (Al_2O_3)$$ (2)

Additionally, the following reactions should be taken into account:

$$3 (CaF_2) + (Al_2O_3) = 2[AlF_3] + 3 (CaO)$$ (3)

$$(CaF_2) + (Al_2O_3) = 2[AlOF] + (CaO)$$ (4)

In the course of these reactions the viscosity drastically changes and lubrication conditions in the crystallizer deteriorate. Hence mould fluxes low in SiO$_2$ should be analyzed and respective recipes worked out. This is caused by the fact that these slags are less reactive with Al and the formation of Al$_2$O$_3$ phase is limited [10]. After adding Al to steel, the control of the casting process may bring about problems and consequently generate a considerable increase of Al$_2$O$_3$ mass as compared to SiO$_2$ (mAl$_2$O$_3$ / mSiO$_2$) in metallurgic slag over the CCS process duration. Experiments performed during continuous casting of TRIP steel revealed that the chemical composition considerably changed after about 10 to 15 minutes from the beginning of the process, when the index of aluminum oxide absorption was high and SiO$_2$ content dropped [11].

The measurements of slag viscosity performed by M. Persson et al. [12] for slags containing 2.5-5 wt. % Al$_2$O$_3$ at temperature 1373-1673K confirmed the increase of viscosity, which was caused by the formation and development of network of silicates. An inverse phenomenon was observed for slags with elevated participation of alkali oxides and CaF$_2$. In the course of experiments authors observed that the increased viscosity of slag caused by the presence of Al$_2$O$_3$ was particularly visible at lower temperatures. This relatively high increase of viscosity has influence on the thickness of the slag layer, changes heat transfer conditions and evokes the operation of friction forces on the solidified cover [10].

After adding Al to steel the control of the casting process may bring about problems with the control of the casting process owing to the chemical reactions between SiO$_2$ in slag and Al dissolved in steel. As a consequence, a considerable increase of the mAl$_2$O$_3$ / mSiO$_2$ ratio in metallurgical slag was observed over the progressing continuous steel casting process. Experiments performed during continuous casting of TRIP steel are indicative of a considerable change of chemical composition after about 10 to 15 minutes from the beginning of the process, when the index of aluminum oxide absorption was high and SiO$_2$ content lowered [11].

Gi-HyunKim et al. [13] analyzed the effect of Al$_2$O$_3$ on viscosity in a system based on calcium silicate alloy containing Na$_2$O and CaF$_2$. It was correlated with the structure of the alloy with the use of the Fourier Transform Infrared spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy. The substitution of SiO$_2$ with the use of Al$_2$O$_3$ modified the dominating silicate network into a strongly structured aluminosilicate structure, where the latter was especially at 20% and higher Al$_2$O$_3$ mass. With the gradual polymerization of oxides the participation of symmetrical stretching vibrations Al-O$^n$ considerably increased. Analogously the viscosity increased too. XPS showed to the decrease of the amount of unbridged oxygen (O$^-$), and increase of bridged oxygen (O$^+$) and free oxygen (O$^{2-}$) with higher Al$_2$O$_3$. Though the changes in the structure and viscosity with higher CaO / SiO$_2$ + Al$_2$O$_3$ were not big, the symmetrical stretching of Al-O$^n$ in tetrahedric units [AlO$_4$]$^{2-}$ decreased. The apparent activation energy for viscous flow ranged from 118 to 190 kJ / mol. Hence, the substitution of Al$_2$O$_3$ for SiO$_2$ increased the viscosity [12].

2. Calculation models

The main assumption of the model is the analysis of the slag structure. The basic element of the structure are silicate chains composed of SiO$_4$$^4-$, interconnected with 'bridging' oxygen atoms (O$^-$). Upon adding oxides of metals belonging to group 1 and 2 the silicate chains get disrupted. Apart from O$^{2-}$ ions located between Si$^{4+}$ ions (‘bridging’ ions O$^{2-}$ BO) there are also ions placed at the ends of chain fragments (‘non-bridging’ ions O$-$...
NBO and free O\(^2^-\) ions (FO) coming from the dissociation of oxides. Al\(_2\)O\(_3\) plays an interesting role in the system. At small amounts of oxides of metals belonging to 1 and 2 group, Al\(_2\)O\(_3\) dissociate into Al\(^{3+}\) cations and oxide anions, which disrupt silicate chains. When the participation of oxides of metals belonging to 1 and 2 group is considerable, Al\(_2\)O\(_3\) forms tetrahedral structures AlO\(_4\)^{3-}, similar to the silicate ones. The oxygen ion in this group is denoted as AlO. M. Nakamoto et al. [14] assumed that a deformation of the structure under the influence of shear stress evoked by the speed gradient is possible only for all four positions of the oxygen ion. However in the case of FO and NBO the deformation tendency is higher than for BO and AlO.

The relations between viscosity \(\eta\) and temperature is given with formula [1, 14-16]:

\[
\eta = A \cdot \exp \left( \frac{E_v}{R \cdot T} \right)
\]

where \(A = 4.80 \cdot 10^8\) Pa·s, \(T\) - temperature K, \(R = 8.314\) J/mol·K, \(E_v\) denotes activation energy of viscous flow, which can be determined with:

\[
E_v = \frac{E}{1 + \left( \sum \alpha_i \cdot N_{(NBO+FO)} + \sum \alpha_{j/Al} \cdot N_{(Al-BO)} \right)^{1/3}}
\]

where:
\(E\) - viscosity activation energy for pure SiO\(_2\), defined as \(E = 5.21 \cdot 10^3\) J.
\(\alpha_i\) - index of components of liquid solution, except for SiO\(_2\), \(\alpha_j\) - index of cation (Ca\(^{2+}\), Mg\(^{2+}\), Fe\(^{2+}\), Na\(^+\), K\(^+\)).

All kinds of oxide ions are determined from the chemical composition of slag. In a two-component system SiO\(_2\) – Al\(_2\)O\(_3\) composed of (aSiO\(_2\)-cAl\(_2\)O\(_3\)), aluminum oxide modifies the network. After introducing c Al\(_2\)O\(_3\) moles, the number of bonds formed by oxygen (except for bonds with Si) is 6c. The total number of oxygen bonds in the system equals to \((4a+6c)\).

\[
N_{(NBO+FO)} = \frac{n_{(O-M)}}{n_{(Calk-O)}} = \frac{3 \cdot c}{2 \cdot a + 3 \cdot c}
\]

\[
N_{(Al-BO)} = 0
\]

In a three-component system SiO\(_2\) – M\(_2\)O\(_3\) – Al\(_2\)O\(_3\) composed of (aSiO\(_2\)-bM\(_2\)O\(_3\)-cAl\(_2\)O\(_3\)), two variants are possible: \(b>c\) (variant I) or \(b<c\) (variant II). In the first case it is assumed that Al\(_2\)O\(_3\) plays the role of a network element. The number of oxygen bonds with an Al cation for tetrahedron is \(n_{(AlO)} = 8c\). The number of the remaining oxygen bonds except Si is \(n_{(O-M)} = 2(b_i - c)\), and the total number of oxygen bonds in such the system equals to \(n_{Total-O} = 4a + 2b_i + 6c\) moles. The proportion of oxygen bonds in a tetrahedron containing Al, i.e. \(n_{(Al,O)}\) to total number of oxygen bonds in the system \(n_{(Calk-O)}\) constitutes the amount of bonding oxygen ions in Al tetrahedrons, i.e. \(N_{(Al-BO)}\). Hence:

\[
N_{(Al-BO)} = \frac{n_{(O-Al)}}{n_{(Calk-O)}} = \frac{4 \cdot c}{2 \cdot a + b_i + 3 \cdot c}
\]

\[
N_{(NBO+FO)} = \frac{n_{(O-M)}}{n_{(Calk-O)}} = \frac{b_i - c}{2 \cdot a + b_i + 3 \cdot c}
\]

For: \(b_i<c\) assumption was made that ions from an alkaline oxide predominantly react with Al-O tetrahedrons. The number of oxygen bonds in Al-O tetrahedrons is \(n_{(O-Al)} = 8 \cdot b_i\), the number of the remaining oxygen bonds not connected with z Si, i.e. \(n_{(O-M)}\), equals to \((4a+6c)\): Hence:

\[
N_{(Al-BO)} = \frac{n_{(O-Al)}}{n_{(Calk-O)}} = \frac{4 \cdot b_i}{2 \cdot a + b_i + 3 \cdot c}
\]

\[
N_{(NBO+FO)} = \frac{n_{(O-M)}}{n_{(Calk-O)}} = \frac{3 \cdot (c - b_i)}{2 \cdot a + b_i + 3 \cdot c}
\]

For multicomponent systems containing at least two oxides of metals belonging to 1 and 2 group (except for SiO\(_2\) and Al\(_2\)O\(_3\)) aSiO\(_2\) + \(\Sigma b_i(M\(_2\)O\(_3\)) + cAl\(_2\)O\(_3\). If: \(a + \Sigma b_i + c = 1 \) and \(\Sigma b_i > c\), then aluminum oxide is a component of the structural network.

Hence the number of oxygen bonds in Al-O tetrahedrons, i.e. \(n_{(AlO)}\) per given type of cation equals to:

\[
n_{(Al-O)} = 8 \cdot c \cdot \sum b_i
\]

The number of oxygen bonds not associated with Si equals to:

\[
2 \cdot b_i - 2 \cdot c \cdot \sum b_i
\]

Hence:

\[
N_{(Al-BO)} = \frac{n_{(O-Al)}}{n_{(Calk-O)}} = \frac{4 \cdot \sum b_i}{2 \cdot a + \sum b_i + 3 \cdot c}
\]

\[
N_{(NBO+FO)} = \frac{n_{(O-M)}}{n_{(Calk-O)}} = \frac{b_i - c \cdot \sum b_i}{2 \cdot a + \sum b_i + 3 \cdot c}
\]
3. Results of calculations

The values of parameters used in calculations are presented in table 1. They were determined by Authors of the model on the basis of available experimental data for two-, three- and four-component oxidic solutions.

<table>
<thead>
<tr>
<th>Parameters used for calculating viscosity of oxidic solutions after Nakamoto</th>
<th>αi</th>
<th>j</th>
<th>αi/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>4.00</td>
<td>Ca2+</td>
<td>1.46</td>
</tr>
<tr>
<td>Na2O</td>
<td>7.35</td>
<td>Na+</td>
<td>0.27</td>
</tr>
<tr>
<td>Al2O3</td>
<td>1.14</td>
<td></td>
<td></td>
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</tbody>
</table>

Calculations based on Nakamoto model were performed for a four-component system SiO2-CaO-Na2O-Al2O3 for given quantities of Al2O3: X(Al2O3) = 0.1 and 0.2.

The viscosity of the basic phase system Al2O3-CaO-SiO2 was broadly discussed in literature [13-15]. Authors [4] calculated viscosity values and compared with calculations by Kozakevitch and Urbain. The Al2O3-CaO-SiO2 system and isocoms for 1873 K have been presented in fig. 2.

Viscosity increases with the increment of SiO2 due to the higher participation of slag polymerization. The presented isocoms assume a U form, i.e. at constant XSiO2 the initial viscosity increases with the growth of CaO/Al2O3, and then decreases. When the mass ratio CaO/Al2O3 exceeds unity, the excessive CaO plays the role of an oxide modifying the network. Therefore the increase of CaO in the system leads to the lowering of polymerization level, and so the viscosity of slag lowers.

Fig. 2. Two-phase (Al2O3-CaO-SiO2) diagram and isocoms defined at 1873 K [4]

First the effect of alkaline oxides content in slag on viscosity under the influence aluminum oxide adsorption was analyzed using Ribound model for temperatures 1673 and 1973 K. Viscosity can be defined with [1, 13-15]:

\[ \eta = A \cdot T \cdot e^{B/T} \] (17)

Coefficients A and B are functions of liquid slag composition in molar fractions:

\[ \ln A = -20.81 - 35.75 \cdot X_{Al2O3} + 1.73 \cdot X_{CaO} + 5.82 \cdot X_{CaF2} + 7.02 \cdot X_{Na2O} \] (18)

\[ B = 31140 + 68833 \cdot X_{Al2O3} - 23896 \cdot X_{CaO} - 46351 \cdot X_{CaF2} - 39519 \cdot X_{Na2O} \] (19)

The influence of alkaline oxides at various participations of Al2O3 on the viscosity of four-component systems for temperatures 1673 and 1973 K in the Riboud model has been presented in figures 3-8.

Fig. 3. Effect of slag CaO-SiO2-Na2O viscosity on XCaO and XNa2O content for XAl2O3=0 at temperature 1673 K

Fig. 4. Effect of slag CaO-SiO2-Na2O-Al2O3 viscosity on XCaO and XNa2O content for XAl2O3=0.1 at temperature 1673 K
By introducing $X_{\text{Al}_2\text{O}_3}$=0.1 - 0.2 to the slag at temperature 1673 K its viscosity increases. The participation of aluminum oxide considerably increases the viscosity (for $X_{\text{Al}_2\text{O}_3}$=0.2). The lowest values were obtained for $X_{\text{CaO}}$=0.5 for $X_{\text{Na}_2\text{O}}$<0.3, regardless the amount of added $X_{\text{Al}_2\text{O}_3}$. In the analyzed case the low viscosity values are obtained for all analyzed $X_{\text{CaO}}$, a order smaller than for temperature 1673 K. Also in this case the lowest viscosity values were obtained for $X_{\text{Na}_2\text{O}}$=0.3-0.5. A high alkaline oxides content causes that the participation of $\text{Al}_2\text{O}_3$ is compensated by their presence. With the increasing $\text{SiO}_2$ content in slag, viscosity also increases reaching high values at high $X_{\text{SiO}_2}$. Authors observed that for $X_{\text{CaO}}+X_{\text{Na}_2\text{O}}>X_{\text{Al}_2\text{O}_3}+X_{\text{SiO}_2}$ the presence of aluminum oxide does not cause any rapid growth of viscosity. Upon adding $X_{\text{Al}_2\text{O}_3}$=0.2 at low $X_{\text{Na}_2\text{O}}$=0.1 and $X_{\text{CaO}}$=0.3, the viscosity was observed to increase to 5.5 Pa·s, whereas for the same values of alkaline oxides and $X_{\text{Al}_2\text{O}_3}$=0.1 it was 3 Pa·s. The results of calculations also clearly reveal that $\text{Na}_2\text{O}$ more easily counteracted the negative impact of $\text{Al}_2\text{O}_3$ than $\text{CaO}$, therefore $\text{Na}_2\text{O}$ participation in mould flux mixtures used for absorbing $\text{Al}_2\text{O}_3$ inclusions should be bigger. Attention should be paid to the fact that when the $\text{Al}^{3+}$ ion is balanced, $\text{Na}^+$ ion dominates $\text{Ca}^{2+}$. The presented slag compositions for which calculations were performed met the condition $X_{\text{CaO}}+X_{\text{Na}_2\text{O}}>X_{\text{Al}_2\text{O}_3}$. This means that there was a sufficient amount of $\text{Na}^+$ ions supplemented with $\text{Ca}^{2+}$ ions to outbalance the activity of $\text{Al}^{3+}$ ions.

The calculations following Nakamoto model were performed for $\text{SiO}_2$-$\text{CaO}$-$\text{Na}_2\text{O}$-$\text{Al}_2\text{O}_3$ system with the assumed constant contents $X_{\text{Al}_2\text{O}_3}$=0; $X_{\text{Al}_2\text{O}_3}$=0.1; $X_{\text{Al}_2\text{O}_3}$=0.2. The results were compared with the output of calculations performed for the same parameters as in Riboud model.
Fig. 9. Results of calculations of viscosity for (CaO-SiO\textsubscript{2}-Na\textsubscript{2}O) at temp. 1673 K in Nakamoto model (X\textsubscript{Al\textsubscript{2}O\textsubscript{3}}=0)

Fig. 10. Results of calculations of viscosity for (CaO-SiO\textsubscript{2}-Na\textsubscript{2}O) at temp. 1673 K in Riboud model (X\textsubscript{Al\textsubscript{2}O\textsubscript{3}}=0)

Fig. 11. Results of calculations of viscosity for (CaO-SiO\textsubscript{2}-Na\textsubscript{2}O-Al\textsubscript{2}O\textsubscript{3}) at temp. 1673 K in Nakamoto model (X\textsubscript{Al\textsubscript{2}O\textsubscript{3}}=0.1)

Fig. 12. Results of calculations of viscosity for (CaO-SiO\textsubscript{2}-Na\textsubscript{2}O-Al\textsubscript{2}O\textsubscript{3}) at temp. 1673 K in Riboud model (X\textsubscript{Al\textsubscript{2}O\textsubscript{3}}=0.1)
The comparison of the results of calculations performed with Nakamoto and Riboud models shows a great similarity of the obtained outputs only for X_{AlO3}=0. The obtained isocoactivity plots have nearly the same inclination angles [16]. The increase of Na₂O and CaO content results in a considerable drop of viscosity. Viscosity increases with the growing SiO₂ content because of the higher participation of slag polymerization. For the assumed X_{CaO}+X_{Na₂O}=1, system the alkaline oxides play the role of silicate network modifiers, decreasing the polymerization degree of silicate chains and lowering the viscosity of slag. After adding Al₂O₃, a difference can be observed in the results of obtained with Nakamoto and Riboud models, with higher viscosity values for Nakamoto model. The most interesting is the course of isocoms calculated with Nakamoto model for X_{AlO3}=0.2, where the inclination angle of isocoms changed. There is a considerable difference in the results of viscosity calculated with these two models.

4. Conclusions

Results of calculations of viscosity values with mathematical models proved the influence of aluminum oxide on the viscosity of mould slag. Viscosity was observed to significantly increase with the growing X_{SiO2} and X_{AlO3} content in slag. In all cases the viscosity values in Nakamoto model are higher than in Riboud model. The differences between values obtained with Nakamoto and Riboud models suggest that experimental verification should be performed to clearly determine the influence of particular oxides on the viscosity of the solution.

References


