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VISCOUS BEHAVIOR OF ALUMINA AND TITANIA IN AMPHOTERIC SLAGS AND THEIR INFLUENCE ON REFRACTORY CORROSION

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Abstract

Recovering iron from bauxite residue (red mud) by carbothermic reduction creates, depending on the composition of bauxite, slag phases with high amounts of alumina and titania which are commonly known as amphoteric slag components. In this case the prediction of slag properties and even the calculation of basicity are very difficult since the slag consists of about 50 wt.-% amphoteric components. As a consequence the correct choice of refractory materials has to be taken into consideration as well. In this study synthetic slags similar to the compositions which occur during the reductive smelting of bauxite residue are mixed and melted. By the addition of CaO and Na_2O and SiO_2 the basicity is constantly adjusted to 1 [$(CaO+Na_2O)/SiO_2$] to monitor the influence of the addition of amphoteric compounds regarding the viscosity and refractory corrosion. In advance thermodynamic calculations concerning the liquidus temperature and viscosity of the examined slag are done by the software FactSage (vers. 6.4). The molten slags are qualitatively examined regarding the viscosity and later on exposed to three different types of refractory materials (MgO, Al_2O_3, mullite) in order to observe the refractory corrosion and infiltration behavior.

Introduction

Most commonly pyrometallurgically treated raw materials, minerals and ores are selected regarding their content of targeted metal and their gangue which will contribute to the composition of slag phase later on. Silica is a major compound of many minerals and therefore most widely spread are silica based slags like calcium silicate slag in ferrous metallurgy or fayalite slags in non-ferrous metallurgy. But in case of aluminum production, the hydro-metallurgical Bayer process is used with its special requirements of aluminum hydroxide rich and low silica containing feedstock. As a result the content of acidic acting silica is very low depending on the origin of the ore. Tropical bauxites which are preferred due to their low silica content and high content of easy digestible $Al(OH)_3$ phases usually contain less than 5 wt.-% SiO_2. In contrast karst bauxites from i.e. Europe, US or Australia contain up to 10 wt.-% SiO_2. [1] The typical range of composition for bauxite ores is given in Table . [2–4] After the Bayer process and the extraction of aluminum hydroxide, the bauxite residue varies in its composition which is also shown in Table . Today's common practice is the disposal of bauxite residue due to its high alkaline content. But the high amount of iron oxide offers potential for the production of iron.

Table I. Range of compositions of bauxite and the intermediates bauxite residue and slag after iron reduction

in wt.-%	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	CaO	Na_2O
Bauxite	40-60	10-20	2-10	1-3 (up to 10)	< 2	n.a.
Bauxite Residue	10-20	30-60	5-15	5-20	5-12	5-10
After Iron Reduction	30-50	0-1	20-30	10-30	10-15	5-10

With the intention to use bauxite residue as raw material for winning of iron via carbothermic smelting, two problems arise: What is actually the basicity of the generated slag and which refractory material can be used to treat this slag?

Usually basicity is an empiric indicator defined according to equation 1 as the ratio of network depolymerizing basic oxides like alkaline and divalent alkaline metal oxide (Na_2O, CaO, MgO, etc.) and network forming acidic oxides like SiO_2 or P_2O_5. [5]

$$B=\frac{\sum_{i=1}^{n} x_i(\text{basic oxides})}{\sum_{i=1}^{n} x_i(\text{acidic oxides})} \tag{1}$$

x_i: wt.-% of oxide component

Background is the structure of molten slags. Silica tends to polymerization and forms three-dimensional networks of corner linked tetrahedral units by bridging oxygens between the silicon cations. Basic oxides dissociate into metal cations and oxygen anions. Thus the addition of basic oxides provides free oxygen to the network which can be integrated in the structure by breaking the Si-O-Si bonds of the bridging oxygen and creating Si-O and O-Si endings of now non-bridging oxygens. As a result the degree of polymerization of the network decreases and the ratio of depolymerizing and polymerizing components is a rough indicator for the degree of polymerization in the liquid slag which strongly affects the viscosity of the melt. [6–8]

Table 1 also gives the expected slag composition after the carbothermic reduction of bauxite residue. The calculation of B according to equation 1 gives values of 0.75-1, a slightly acidic or even neutral slag after the iron reduction. But the acidic and basic oxides constitute to just 50 % of the overall slag composition. The remaining 50 % are alumina and titania which must not be neglected. These oxides are amphoteric oxides which means that they can either act as acidic or as basic oxides depending on the concentration of free oxygen, thus depending on the basicity of the matrix.

The acidic behavior of alumina is commonly explained by its ability to form tetrahedral units of $[AlO_4]^{5-}$ polyanions which fit perfectly in the network of $[SiO_4]^{4-}$ tetrahedrons. In order to compensate the charge balance in case of fivefold negatively charged alumino tetrahedrons, dissociated basic metal cations position themselves in proximity to the alumino tetrahedrons. But with increasing aluminum addition the network becomes instable and aluminum arranges in a sixfold octahedral structure which disturbs the network, breaks the network and reduces the viscosity. [6,9,10]

The effect of titania addition is commonly described as network modifying influence in calcium silicate slags. The amount of O^{2-} -ions is increased with increasing titania addition and as a consequence the viscosity generally lowered. But at higher titania amounts of more than 10 wt.-% the effect becomes less significant. In alumina bearing calcium silicate slags titania addition affects the depolymerization of the silica network without changing the aluminate order. [6, 11-12]

In literature many different authors made attempts to calculate the viscosity of several slag systems. One of the most famous viscosity models was created by Urbain and uses the Weymann relationship (equation 2) and was made for ternary systems SiO_2-Al_2O_3-MO with MgO, CaO or MnO as basic oxide MO. The examined range of concentration (in weight %) is roughly 30-60 % SiO_2, 10-40% Al_2O_3, 7-40% CaO that means rather high silica containing slags:

$$\eta=A_W\cdot T\cdot e^{(\frac{E_W}{RT})} \qquad (2)$$

Thereby all oxides are divided into three groups: network former (Si^{4+}, Ge^{4+}, P^{5+}), modifier (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cr^{3+}, Ti^{4+}) und and amphoterics (Al^{3+}, Fe^{3+}) and the basicity B is calculated as follows:

$$\ln(A_W)=-m\cdot B-n \qquad (3)$$

$$E_W=1000\cdot B \qquad (4)$$

$$B=B_0+B_1\cdot X+B_2\cdot X^2+B_3\cdot X^3 \qquad (5)$$

$$B_i=a_i+b_i\cdot\beta+c_i\cdot\beta^2 \quad , i = 0,1,2,3 \qquad (6)$$

$$\beta=\frac{\sum_{i=1}^{n} x_i(\text{modifier})}{\sum_{i=1}^{n} x_i(\text{modifier})+\sum_{i=1}^{n} x_i(\text{amphoteric})} \qquad (7)$$

X: molefraction of network former; x_i: mole fraction of component i; a_i, b_i, c_i are empirical constants

Kondratiev [13] adapted this model to the SiO_2-Al_2O_3-FeO-CaO system of coal ashes and calculated new parameters a_i, b_i, c_i and adapts the range of composition to 40-60 % SiO_2, 20-40 % Al_2O_3, 0-25 % CaO, 0-40 % FeO (as substitution for CaO), which means a silicon aluminate slag and is comparable to the red mud composition.

Another viscosity model was developed by Riboud and tailored for continuous casting powders of the SiO_2-Al_2O_3-CaO-CaF_2-Na_2O system. But it was found out that it works also well for other slags systems due to the similar character of MnO, MgO and FeO to CaO but it fails in cases like CaO-Fe_2O_3-SiO_2 and Fe_nO-MnO-SiO_2 [14]. Thereby the slag components are divided into five groups: SiO_2-group (SiO_2+P_2O_5+TiO_2+ZrO_2), CaO-group (CaO+MgO+FeO), Na_2O-group (Na_2O+K_2O), CaF_2 and Al_2O_3, which is treated as an acidic component. The studied range of slag compositions is 30-50 % SiO_2, 7-45 % CaO, 0-12 % Al_2O_3, 0-22 % Na_2O, 0-18 % CaF_2.

Another famous model is made by Iida [15] and later been adapted by Xu [16] to the CaO-Al_2O_3-MgO-system. The range of compositions varies from 35-50 % SiO_2, 10-20 % Al_2O_3 and 25-50 % CaO (1-20 % MgO, respectively)

Calculations with FactSage

In order to represent the red mud slag system after the reduction of iron as good as possible the basic requirements are a fixed basicity of 1 created by the main constituents SiO_2, CaO and Na_2O with the ratio of 2:1:1. Then the addition of alumina and titania is calculated in the appropriate phase diagrams to understand the process temperature (affected by the liquidus temperature of the system) and the phases which precipitate at first. It was find out that an alumina content of more than 60 wt.-% will set the liquidus temperature to values higher than 1600 °C which is not useful for experimental verification and later on in the process. Therefore the addition of alumina is in this study limited to 50 wt.-% of the mixture. In case of the quaternary system TiO_2-SiO_2-CaO-Na_2O the liquidus temperature is moderate up to 70 wt.-% titania content. But a miscibility gap occurs at about 45 wt.-% titania and the considered range is therefore limited to 30 wt.-% TiO_2 content.

The calculated viscosities for both systems are shown in figure 1. FactSage© predicts in case of alumina addition a significant increase of the viscosity up to 30 wt.-% Al_2O_3. At higher alumina concentrations, the viscosity decreases again. In case of rising titania content, the viscosity continuously decreases, indicating that FactSage© treats titania as a basic, depolymerizing compound. It is remarkable that the viscosity is independent from the calculated liquidus temperature and thus independently treated from the superheat of the melt, explicitly shown by the plotted slag liquidus temperature in the viscosity diagrams of figure 1.

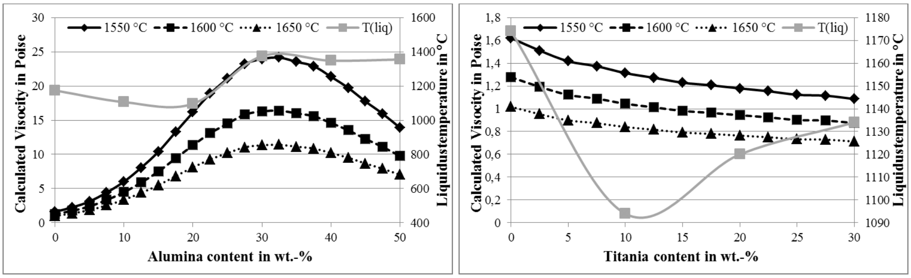

Figure 1. With FactSage© calculated course of viscosity dependent on the alumina content (left) and the titania content (right) of a CaO-Na_2O-SiO_2 slag (wt.- ratio 50/25/25) at different temperatures

For comparison also the introduced viscosity models are applied on the slag system at a temperature of 1550 °C and the results are shown in figure 2. Urbain's, Ribout's and Iida's models are created for slags with considerable higher silica contents and therefore the predicted viscosities are generally far too low. Only Kondratiev's modified model from Urbain predicts almost the same course of viscosity with increasing alumina content. The case of titania is more difficult since many models do not tolerate titania (Kondratiev) or only in low contents of << 5 wt.-% (Riboud, Iida). Thus only the Urbain's model, which is valid up to ~ 10 wt.-% TiO_2, gives the right tendency of decreasing viscosity with increasing titania content.

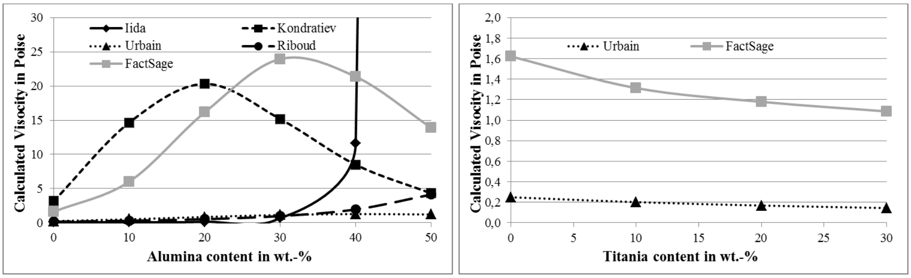

Figure 2. Calculated viscosities dependent on the alumina content (left) and the titania content (right) of a CaO-Na_2O-SiO_2 slag (wt.- ratio 50/25/25) using different viscosity models

Experimental studies

In order to confirm the tendency and test the basicity experiments with synthetic slag mixtures experiments have been conducted in an induction furnace, which is shown in figure 3. An aluminum crucible or graphite crucible with chromium corundum ramming mass inlet and an operation volume of 400 ml is used. The temperature is controlled by a type B thermocouple in an alumina sheath. For viscosity measurements a graphite shaft of 12 mm diameter and a flattened tip of 40 mm length is used. The revolutions per minute in idle mode are optically (contactless) measured. After melting of the blended raw material powders (purity Na_2CO_3, TiO_2, Al_2O_3, CaO > 99.5 %) the tip of the shaft is completely introduced in the melt and the decrease of the rotational speed due to the friction in the melt is recorded. The induction furnace is shut off for the duration of the measurement. After the viscosity measurement, four different types of refractory bricks [pure alumina, pure electro-fused alumina, mullite (71 wt.-% Al_2O_3, 27 wt.-% SiO_2) and pure MgO] are inserted in the melt for 60 min as shown in figure 3 (right side). The furnace is poured with argon during all experiments.

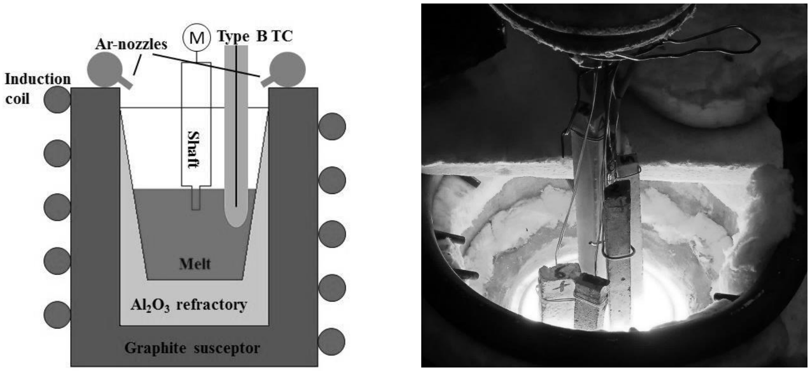

Figure 3. Experimental setup schematic for viscosity measurement (left) and picture of refractory test (right)

The induction furnace is switched on for this holding time and the induced bath convection leads to an increased refractory stress. All experiments are conducted at 1600 °C. The examined slag compositions and measured declines in rotation speed are shown in table 2.

Table II. Slag composition of experiments and decrease of rotation speed during dipping in melt (Δ rpm)

in wt.-%	Al_2O_3	SiO_2	CaO	Na_2O	Δ rpm
1	0	50	25	25	20
2	10	45	22.5	22.5	24
3	20	40	20	20	26
4	30	35	17.5	17.5	30
5	40	30	15	15	n.a.

In becomes obvious that the assumption of an increase in viscosity with higher amounts of alumina can be verified by the experiments. Although the viscosity apparatus is not calibrated, the qualitative evidence of the acidic and thus network forming acting of alumina in calcium sodium silicate slags of basicity of 1 can be provided.

The attack on the tested refractories is moderate. The MgO brick is completely infiltrated, partly in combination with a substantially loss of physical strength, but it is not dissolved. Thus it can be assumed that the basicity of the slag is neutral till slightly basic. All alumina bricks are infiltrated. The sintered alumina brick is even partly dissolved but the electro-fused alumina brick is though slightly infiltrated still rigid and without any superficial erosion. It is surprising to see, that the cheapest brick, the Al_2O_3/SiO_2 brick, still perform satisfactory. After 60 min the brick is slightly dissolved at it edges but only slightly infiltrated.

Conclusion

It has been shown that the addition of alumina to neutral (basicity=1) $CaO\text{-}Na_2O\text{-}SiO_2$ slags, as they appear in reductive smelting processes of red mud, increases the viscosity up to a Al_2O_3 content of about 30 wt.-%. Beside FactSage© even the viscosity model from Kondratiev suggests a similar course of slag viscosity with increasing alumina content. At higher contents of > 60 wt.-% the liquidus temperature increases dramatically due to the formation of corundum. The effect of titania is not experimentally verified yet but literature and all viscosity models show clearly a decrease of viscosity in case of rising titania concentrations, assigning titania a role as network modifier which depolymerizes the silicate structures.

Especially electro-fused corundum withstands this slag system. But even low cost mullite brick erodes slowly. The magnesia brick was infiltrated but not dissolved, indicating that the slag has a neutral till slightly basic character.

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