High-temperature rheometry of blast furnace synthetic slags doped with TiO₂ and TiN

Wysokotemperaturowe badania reometryczne wielkopiecowych żużli syntetycznych domieszkowanych TiO₂ oraz TiN

Abstract
Development has been conducted regarding the methodology of rotational measurements with a high temperature rheometer using Searle's method. The rheological analysis of liquid systems CaO-SiO₂-Al₂O₃-MgO-TiO₂ slags, and solid particles of titanium nitride TiN are presented (within a range of 0.1–0.7 of the volume fraction of TiN). The measurements were conducted at a range between 1310°C and 1500°C, which is typical for high-temperature zones in a blast furnace. The main objective of the study was to analyze the possibilities of viscosity measurements in homogenous and heterogenic systems (not standard systems within the industrial practice). The measurements were conducted for totally liquid blast furnace slags which show similarity to ideally viscous Newtonian bodies and also for heterogenic systems.

Keywords: slag viscosity, high-temperature rheometry, titanium nitride, rheology

Streszczenie
W pracy zaprezentowano wyniki badań przeprowadzonych z wykorzystaniem reometrii wysokotemperaturowej opartej na metodzie Searle’a. Przeprowadzono analizę reologiczną ciekłych systemów żużłowych CaO-SiO₂-Al₂O₃-MgO-TiO₂ domieszkowanych TiN, w zakresie 0,1–0,7 ułamka objętościowego. Badania przeprowadzono w temperaturze 1310–1500°C, która jest charakterystyczna dla strefy ściekania występującej w wielkim piecu. Głównym celem prowadzonych badań była analiza reologiczna współczynnika lepkości dynamicznej oraz możliwości wysokotemperaturowych pomiarów reometrycznych układów homogenicznych i heterogenicznych (rozszerzających zakresy przemysłowe). Badania przeprowadzono zarówno dla parametrów reologicznych dla całkowicie ciekłych systemów żużłowych, które wykazują podobieństwo do cieczy idealnej Newtona, jak i dla układów heterogenicznych.

Słowa kluczowe: lepkość żużła, reometria wysokotemperaturowa, azotek tytanu, reologia

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1. Introduction

Two non-mixing liquid phases are involved in the blast furnace process. These are liquid iron and liquid tapping silicate melts – along with metal oxides – which do not get reduced in a blast furnace at all (or only to a limited degree).

Blast furnace slag significantly influences the course of the thermo-chemical effects in the process of obtaining iron. It is an important factor in regards to the right mechanics of charge material movement in a blast furnace and the correct flow of reducing gases through the charge mass [1–3].

The addition of TiO\(_2\) to the system decreases its dynamic viscosity by depolymerization of the network structure. Results of an XPS analysis show that the bridged oxygen (O\(^0\)) content declines with the addition of TiO\(_2\), while the free oxygen content (O\(^{2-}\)) increases. The addition of over 5% TiO\(_2\) to the system (with constant basicity B\(_1\) = 0.8) has a comparably lesser effect on the share of the fraction O\(^0\), O\(^-\), and O\(^{2-}\), which appears to correlate well with the results of viscosity measurements. It seems that an increase in basicity will be more significant for viscosity reduction than the addition of TiO\(_2\) [4, 5].

The different authors [6–9] analyzed the viscosity of various slag grades; however, none of the known and applied theories of slag structure satisfactorily describe the influence of TiO\(_2\) on the structure of liquid silicates. The main reason for this is the fact that these theories have been developed in order to identify the physical properties of liquid silicate systems. However, the viscosity values and their changes with temperature changes for high concentrations of TiO\(_2\) in the system differ significantly from those values and changes for typical polymerised silicate liquids. This proves that slags with an addition of TiO\(_2\) have a substantially different structure [8]. It seems that this opinion is still valid, having arisen from the heterogeneous structure of the systems analyzed and the participation of solids in the system.

Continuous work and research [1–18] enable to apprise the influence of the addition of titanium compounds to a blast furnace on the ironmaking process and the hearth carbon refractory lining to be determined.

2. Research approches

Rheometric measurements of semi-solid slag systems of the blast-furnace type were performed within a temperature range of 1310–1500°C in an inert-reduction atmosphere. The base slag (sample 1-basis) with the chemical composition as presented in Table 1 had the addition of rutile-TiO\(_2\) within a range of 0.5–3% by weight and within a range of 6–30% TiO\(_2\). Solid TiN was also added, which was treated as a substance that had precipitated from the system.

The authors [14, 15] examined the possibilities of precipitation of titanium compounds from blast furnace slags with the addition of TiO\(_2\). On the basis of the chemical
stability of minerals, they found that within a temperature range of 1450–1100°C, titanium compounds precipitate in the following sequence: Ti(N,C), perovskite, spinel (Al₂O₃·MgO), Ti-rich diopside, and Ti-bearing diopside. The experimental results show that – apart from titanium carbonitrides – the perovskite phase is one of the first phases precipitating [15].

Table 1. Chemical compositions of the analyzed slag systems

<table>
<thead>
<tr>
<th>Sample description</th>
<th>CaO</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>TiO₂</th>
<th>TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[%]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 – basis</td>
<td>43.71</td>
<td>7.97</td>
<td>8.50</td>
<td>39.10</td>
<td>0.00</td>
<td>–</td>
</tr>
<tr>
<td>2 – low concentr. TiO₂</td>
<td>43.29</td>
<td>8.39</td>
<td>8.52</td>
<td>38.68</td>
<td>0.48</td>
<td>–</td>
</tr>
<tr>
<td>3 – low concentr. TiO₂</td>
<td>42.96</td>
<td>8.35</td>
<td>8.56</td>
<td>38.13</td>
<td>1.45</td>
<td>–</td>
</tr>
<tr>
<td>4 – low concentr. TiO₂</td>
<td>42.43</td>
<td>8.04</td>
<td>8.50</td>
<td>37.62</td>
<td>2.87</td>
<td>–</td>
</tr>
<tr>
<td>5 – high concentr TiO₂</td>
<td>42.54</td>
<td>7.22</td>
<td>9.86</td>
<td>32.98</td>
<td>5.81</td>
<td>–</td>
</tr>
<tr>
<td>6 – high concentr TiO₂</td>
<td>28.95</td>
<td>7.62</td>
<td>9.10</td>
<td>24.31</td>
<td>29.73</td>
<td>–</td>
</tr>
<tr>
<td>7 – TiN (min. 5.81% TiO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.44</td>
</tr>
<tr>
<td>8 – TiN (max. 5.81% TiO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.14</td>
</tr>
<tr>
<td>9 – TiN (min. 29.73% TiO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>17.67</td>
</tr>
<tr>
<td>10 – TiN (max. 1.45% TiO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.58</td>
</tr>
<tr>
<td>11 – TiN (max. 2.87% TiO₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.67</td>
</tr>
</tbody>
</table>

The shape and size of perovskite precipitates change depending on temperature (1300°C or 1370°C), chemical composition, and rate of cooling. Crystals of pervoskites are dendrites – long, not round; thus, they might have an influence on the rheological character of the system [15].

Due to the presence of solid particles in the systems (in the conditions of rheological experiments), a theoretical analysis of solids was performed. The amount of TiN particles in the system was calculated with the FactSage thermodynamic database – equilibrium module. Within the assumed conditions of temperatures, compositions, and pressures of gases (N₂ and CO), possible theoretical quantities of TiN precipitates in the equilibrium state were calculated. High temperature rheometrical measurements were performed for these conditions: these were for chemical compositions of slag doped with 1.45%, 2.87%, 5.81%, and 29.73% TiO₂ respectively in a sample of 50 g of the slag.
A high temperature FRS 1600 rheometer was used for the measurements, with the measuring systems presented in publications [12, 13]. Synthetic slags were prepared from chemical-reacting substances from the Merck and Aldrich companies. Pure oxides were melted to be synthesized under an inert atmosphere (5.0 Ar purity) at a temperature of 1500°C. This slag formed the base which subsequently was doped with TiO₂ and TiN. Solid particles did not exceed 3 μm and therefore remained unchanged. Chemical compositions of the slag systems that were analyzed are presented in Table 1. The analysis was performed with an XRF Twin-X spectrometer.

Samples 5 and 6 correspond to the possible theoretical amount of precipitated TiN (for 5.81% TiO₂). These values were calculated for two cases, based on the minimum and maximum amount of TiN and dependant on the pressures and concentrations of N₂, CO within the furnace tube. The samples 8 – 29.73% TiO₂, 10 – 1.44% TiO₂, and 11 – 2.87% TiO₂, correspond only to the maximum theoretical amount of TiN that was obtained by reduction and precipitation under specific conditions of pressure, temperature, and chemical composition.

3. Analysis of findings

High temperatures rheometry measurements have been performed, and additionally, an SEM analysis in a micro-area for the selected samples also has been done. Sample 1 – containing 5.81% TiO₂ – is presented in Figure 1. The analysis was performed at the liquid-crucible interface. High concentrations of titanium as well as carbon and nitrogen can be observed; titanium most likely occurs in the forms of TiC, Ti(C,N), and TiN. This confirms the hypothesis in that the titanium compounds are formed as a result of the reaction of carbon and nitrogen that are present in the system. These titanium compounds are solid within the specific conditions of the experiment, and affect the dynamic viscosity coefficient of the liquid. At high temperatures, titanium oxide may be reduced from the slag-liquid phase with the crucible carbon, and titanium carbonitrides may precipitate [12, 15] (Fig. 1). However, at lower temperatures, the perovskite phase may precipitate [15] (apart from the existing high-melting solid particles).

Figure 2 presents the flow curves for the base slag without the addition of titanium compounds. It can be concluded from the curves that the analyzed system shows similarities to a Newtonian viscous liquid.

X.L. Tang et al. [16] reported measurements that were carried out at five different speeds of rotation, varying from 100 to 200 rpm at each temperature. The variation of viscosity values (due to the variable rotation speeds) is less than 2%, indicating that the melt behaves like a Newtonian liquid. However, the systems analyzed were CaO-SiO₂-Al₂O₃-MgO with different alumina concentrations of 5–20% [18].
The authors of this study have also applied the FactSage thermodynamic database to calculate the possibility of TiO$_2$ reduction in the particular conditions of a state of equilibrium. One can find that titanium oxide in the analyzed conditions will be slightly
reduced to lower oxides, and when the temperature decreases, solid particles will precipitate in the form of perovskite, TiN, and Ti(C,N). Based on the observations taken after the rheometric tests of the measurement tools (cup, bob), no changes in the linear dimensions of those tools in the area of cup-slag or bob-slag contact were observed. Significant changes in the linear dimensions could influence the rheometric measurement results.

In order to calculate the activation energy for viscous flow ($E_\eta$), the Arrhenius type relationship of equation (1) was used, and the slope from the plot of the natural logarithm of the viscosity ($\ln \eta$) with reciprocal temperature ($1/T$) provided $E_\eta$ [4].

\[ \eta = \eta_0 \exp\left(\frac{E_\eta}{RT}\right) \]  

(1)

Table 2 shows the calculated [4] activation energies for the various slag compositions, where values between 195 to 262 kJ/mol were calculated depending on the various slag compositions. These values are comparable to the results obtained by others authors between 150 to 210 kJ/mol for CaO-SiO$_2$-20% mass Al$_2$O$_3$ slags at constant CaO/SiO$_2$ of unity and containing either MgO or TiO$_2$ and published activation energy values of viscous flow from 200 to 240 kJ/mol for the CaO-SiO$_2$-20% mass Al$_2$O$_3$-10% mass MgO slags at CaO/SiO$_2$ from 0.8 to 1.2, which is also comparable to study of Sohn et al. [4].

<table>
<thead>
<tr>
<th>CaO/SiO$_2$</th>
<th>TiO$_2$</th>
<th>0% mass</th>
<th>5% mass</th>
<th>10% mass</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Activation energy $E_\eta$ [kJ/mol]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>206 ± 3</td>
<td>221 ± 7</td>
<td>195 ± 4</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>220 ± 7</td>
<td>199 ± 12</td>
<td>209 ± 18</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>225 ± 9</td>
<td>246 ± 1</td>
<td>262 ± 4</td>
<td></td>
</tr>
</tbody>
</table>

The authors of this study have performed rheometric measurements of a comparable slag system of CaO-SiO$_2$-Al$_2$O$_3$-MgO with TiO$_2$ additions. The values of activation energy for TiO$_2$ concentrations within the range of 0.5–3% TiO$_2$ were calculated based on the results of dynamic viscosity coefficient obtained by the authors.

Equation (2), determining the slag basicity under the molecular theory [17], was applied to calculate the hypothetical value of the dynamic viscosity coefficient for the shear rate approaching zero.

\[ B = \frac{\text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2} \]  

(2)
Next, the relationship of the dynamic viscosity coefficient $\eta_0$ as a function of system basicity $-B$ was plotted. The graph is presented in Figure 3. For samples 1, 2, 3, and 4, value $\eta_0$ was determined.

![Figure 3: Viscosity $\eta_0 = f(B)$](image)

The viscous flow activation energy values were calculated based on the Arhenius–Guzmann’s equation (1) and the rheometric measurement results. The findings are presented in Figure 4.

![Figure 4: Calculated activation energy for different temperatures and shear rates](image)
Changes of the activation energy values – which show a non-linear nature – can be seen in Figure 5. The values of activation energy depend not only on temperature values but also on shear rate values. For all temperatures analyzed, deviations from a straight line could be observed. It seems that the formation and precipitation of solid particles at these temperatures – carbonitrides, titanium oxides, perovskite, and others – do imply those deviations that were observed. Deviations from a straight line may also result from a change in the internal structure of the liquid remaining in the system; i.e., its polymerisation. It is similar to the case of the tests conducted by the authors [18]. An increase in viscous flow activation energy for a decreasing temperature can be observed. At high temperatures of 1500°C, a considerable influence of shear rate on the activation energy value can also be observed, while its changes maintain a similar nature. At a shear rate of 150 s⁻¹, the energy activation value is at its maximum. Also, the influence of TiO₂ concentration on the activation energy level can be observed. In each case, the energy is at its maximum for a concentration of 0.5% TiO₂, and it subsequently decreases as the TiO₂ content in the system increases. It indicates a significant influence of TiO₂ on the depolymerization of the internal structure of the whole system.

Figure 5 presents a change in the viscous flow activation energy depending on the TiO₂ concentration in slag. For liquids in which a constant change in structure occurs at a specific temperature (e.g., polymerisation or depolymerization), a change in the activation energy should be rectilinear. A change in the activation energy as a function of TiO₂ and Ti₂O₃ concentration is non-linear. Also, the Ti₂O₃ content more effectively reduces Eₜ than TiO₂.

![Fig. 5. Change in the activation energy as a function of TiO₂ addition to slag [17]](image)

For the addition of 20% Ti₂O₃, the activation energy falls by ca. 57% when compared to the initial value, whereas for TiO₂, this energy drop is about 27%. Both curves have irregular shapes Authors [17] have obtained similar irregularities for the same type of slag. Slags of this type do not meet the Arrhenius dependency, which may reflect
a continuous change in their internal structure as the temperature changes. The precipitation of finely dispersed solid particles in the slag volume is another possibility, which changes the nature of the flow and the nature of the liquid. For up to 10% TiO₂ in slag, its viscosity declines whereas fusibility drastically increases (there is a rise in the melting temperature), thus causing an increase in fluidity/castability [17].

By comparing both Figures 4 and 5, it can be observed that the nature of changes in the activation energy values is different, while these values are comparable. The authors [17] have obtained activation energy values between 26 and 37 kcal/mol for TiO₂ concentrations from 0% to 20% whereas, in this study, activation energy varies from 29 to 31 kcal/mol for TiO₂ concentrations from 0% to 3%. The values of activation energy for comparable slag systems (presented in Table 2) are almost twice the amount as those obtained in this study, and may be a result of a slightly different slag system that was analyzed. The kind of material used for the measurement tools could modify the energy value to a small extent. In the following study, the measurement systems/tools were made of graphite; therefore, the authors have obtained an inert-reducing atmosphere that is comparable to the atmosphere of a blast furnace in terms of quality. The biggest influence of shear rate on the activation energy value is observed at a temperature of 1500°C (where the reaction of TiO₂ reduction is most likely to be the most intensive), thus changing the internal structure of a wholly liquid system. The lowest energy value occurs exactly for this case (1500°C), and this can be identified as the depolymerizing impact of TiO₂ on the lattice structure of liquid silicates. For lower temperatures (1430°C, 1400°C), higher energy values were obtained: these were not as diverse in terms of the change nature and can be substantiated by the precipitation of solids in the system, along with changes in the lattice structure that were not so significant. Similar deviations are illustrated in Figure 5.

Figures 6a,b present changes in the viscosity coefficient values as a function of TiO₂ concentration (for samples 2, 3, and 4) and TiN concentration (for samples 5, 6, 10, and 11) at temperatures of 1500°C and 1460°C. For the presence of TiO₂ in the system, a slight influence of shear rate on the viscosity value can be seen. The values of viscosity coefficients change depending on the TiO₂ share and the shear rate within these ranges.

It can also be observed that an increasing number of solids in the liquid slag causes an increase in the viscosity coefficient of the whole system. In addition, a significant impact of the shear rate appears.

Viscosity coefficients for the selected samples 4 (TiO₂) and 11 (TiN) are compared in Figure 7. It can be observed that the viscosities for a system with the theoretical TiN content corresponding to the TiO₂ amount that reacted with nitrogen are not comparable. The viscosities for the system with TiN, for the temperatures of 1490°C and 1340°C, are much higher, and the system rheological character is changed.

The theoretically calculated amounts of TiN that may precipitate from the system at a given TiO₂ content – according to the obtained rheometric results (the values of viscosity coefficients) – are too excessive for the specific thermodynamic conditions. For the
system analyzed, the viscosity values should be comparable at a given constant temperature of 1490°C (for samples 4 and 11) and 1340°C (for samples 4 and 11).

Fig. 6. Change in the viscosity coefficient versus: a) TiO₂; b) TiN

Fig. 7. Differences in the component (sample 4 – TiO₂ and sample 11 – TiN) influence on viscosity

Fig. 7. Differences in the component (sample 4 – TiO₂ and sample 11 – TiN) influence on viscosity
4. Conclusions

Based on the performed rheometric tests, one can find that the analyzed four-component blast furnace slag CaO-SiO₂-MgO-Al₂O₃ shows similarities to Newtonian viscous liquid within a temperature range of 1400–1500°C, and a shear rate of 2–200 s⁻¹.

1) The addition of 0,48–2,87% TiO₂ to the blast furnace slag causes a decline in the dynamic viscosity coefficient value for low shear rates 2 s⁻¹.
2) For higher shear rates (20, 100 s⁻¹), the viscosity drop is insignificant. However, when TiN is added to the system, the opposite occurs in the behavior of the system, the viscosity growing with an increase in shear rate.
3) The conducted research has confirmed the effect of TiO₂, which, due to its nature, may be considered a network modifier, reducing the viscosity of the whole system.
4) The greater share of solids (TiN) in the system, the higher value of the viscosity coefficient. For low TiO₂ concentrations and adequate (comparable) TiN contents, the rheological nature of the liquid changes from a Newtonian system to a slightly shear-thinning system.

It seems necessary to conduct further work on the behavior of the solid-liquid rheological slag systems. The flow nature of the analyzed heterogenic systems is very important from the point of view of liquid behavior phenomena: stick and flowing through the coke bed in a blast furnace.

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