

## EFFECT OF CaO/SiO<sub>2</sub> RATIO ON VISCOSITY AND STRUCTURE OF SLAG

Received – Prispjelo: 2014-07-10  
Accepted – Prihvaćeno: 2014-12-24  
Original Scientific Paper – Izvorni znanstveni rad

The objective of this work is experimental determination of temperature dependences of viscosity of the molten CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> system and assessment of impact of CaO/SiO<sub>2</sub> ratio on viscosity and structure of this system. Experimental measurements of viscosity were performed with use of the high-temperature viscometer Anton Paar FRS 1 600. Viscosity was measured in a rotational mode during heating at the rate of 3,3 °C/min in the temperature interval from 1 673 to 1 873 K. Viscosity in the molten oxide system is determined by the internal structure. Exact clarification of the change of structure of the oxide system caused by the increased content of CaO was performed by Fourier transform infrared spectroscopy.

*Key words:* viscosity; basicity; CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> system; ratio of CaO/SiO<sub>2</sub>; structure of slag

### INTRODUCTION

Oxide systems, among others the ternary CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> slag system, are technologically very important in a wide range of applications that include iron-making, steelmaking and ceramics processing. The change in the compositions of these systems has a dramatic impact on the thermo-chemical and thermo-physical properties, including heat capacity, density and viscosity [1, 2].

Viscosity is an important factor affecting the service properties of slags, as it plays an important role in the area of mass transfer at chemical reactions in metallurgical processes.

Viscosity depends mainly on the temperature and on chemical composition. Viscosity in metallurgical slags is determined by the internal structure. Higher concentrations of acidic oxides consume free oxygen ions (O<sup>2-</sup>) to produce increased bridged oxygen (O<sup>0</sup>) and polymerize the slag producing complex silicate structures, which increase the slag viscosity. Higher concentrations of basic oxides (e.g. CaO, Na<sub>2</sub>O, MnO) provide (O<sup>2-</sup>), which reacts with the (O<sup>0</sup>) in the silicate melts to produce a non-bridged oxygen (O<sup>-</sup>) and depolymerize the network structure of the slag [3-5]. Amphoteric oxides, such as Al<sub>2</sub>O<sub>3</sub>, can behave as either network modifiers or network formers, depending on the presence of other strong basic or acidic oxides.

The aim of this work was to determine experimentally the dependence of viscosity on temperature and on concentration of CaO for the ternary system CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>. Although the viscosities of CaO - SiO<sub>2</sub> -

Al<sub>2</sub>O<sub>3</sub>( - MgO) slags were measured by several researchers [6, 7], the range of basicity in these studies was limited to approximately CaO/SiO<sub>2</sub> ≈ 0,6 – 1,3 in respect to the tapped slag composition. Therefore, in the present study, the viscosities of CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> slags were measured to understand the viscous behaviour of slag under conditions of CaO/SiO<sub>2</sub> = 0,78 – 1,44. A correlation between the viscosity and the oxide system structure was verified by the Fourier transform infrared spectroscopy (FTIR).

### Experiment

#### Preparation of the samples

The ternary oxide system CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> (TS) was selected for this experimental study. A concentration series with the addition of 3; 6; 9; 10; 11; 12 and 15 wt. % of CaO was prepared for an assessment of the influence of CaO concentration and of basicity, i.e. of

Table 1 **Chemical composition of the concentration series / wt. %**

samples	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	B
TS	47,20	36,90	15,90	0,78
TS + 3 wt. % CaO	44,96	39,90	15,14	0,89
TS + 6 wt. % CaO	42,71	42,90	14,39	1,00
TS + 9 wt. % CaO	40,47	45,90	13,63	1,13
TS + 10 wt. % CaO	39,72	46,90	13,38	1,18
TS + 11 wt. % CaO	38,97	47,90	13,12	1,23
TS + 12 wt. % CaO	38,22	48,90	12,88	1,28
TS + 15 wt. % CaO	35,98	51,90	12,12	1,44

Note: B (basicity) = CaO/SiO<sub>2</sub>

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the CaO/SiO<sub>2</sub> ratio on viscosity of this oxide system. The systems were prepared from pure components. Individual samples were synthesized using the following reagent-grade chemicals: CaO (99,5 pct), Al<sub>2</sub>O<sub>3</sub> (99 pct) and SiO<sub>2</sub> (99,5 pct). Chemical composition of the samples is shown in Table 1.

### Measurements of dynamic viscosity

The viscosity measurements were carried out with use of the rotating viscometer Anton Paar FRS 1 600. This instrument measures the torque of graphite spindle rotating in graphite crucible filled with oxide melt. The speed range of the spindle is 0 - 200 rpm. A high temperature furnace system with a maximum temperature limit of 1 873 K monitored by a Pt - 13 % Rh/Pt thermocouple was used in the instrument. The graphite crucible containing 55 g of the oxide system was placed into the furnace. In order to avoid oxidation of the graphite crucible and spindle, the nitrogen gas (purity > 99,9999 %) was used at a flow rate of 250 l/h. The furnace was heated to 1 673 K at the heating rate of 15,3 °C/min. and held for 30 min. in order to stabilize the temperature and homogenize the oxide melt. The graphite spindle was then immersed into the oxide melt. On the basis of measurements of viscosity dependence on the shear rate an optimum shear rate of 85 s<sup>-1</sup> was chosen for the viscosity measurement. The viscosity was measured during heating up to 1 873 K at the heating rate of 3,3 °C/min.

### Determination of structure

The structural characteristics of the selected samples were determined by Fourier transform infrared spectroscopy (FTIR). The samples TS + 9 wt. % CaO, TS + 10 wt. % CaO, TS + 11 wt. % CaO and TS + 12 wt. % CaO were prepared by quench cooling. This method allows very rapid cooling of the investigated system at certain stage of melting.

The basic structural unit of the equipment consists of the Tamman resistance furnace, the working workspace of which contains a rotary system with graphite crucibles with the investigated melt. It is essentially a turret system, the turning of which causes a fall of crucible with the melt into liquid nitrogen placed under the working space of the furnace, followed by immediate freezing of the melt and thus to fixation of the phases corresponding to the temperature of the sample before its fall. The temperature during the experiment was determined by thermocouple of the type B (Pt - Rh), furnace working space was filled with argon. The heating rate was 5 °C/min. In this manner, samples were prepared at the temperature of 1 723 K. The samples were then mechanically disintegrated, homogenized and subjected to FTIR analysis already at normal temperature.

The infrared spectroscopic analysis of the powder samples was performed on the instrument Thermo

Nicolet 6 700 working in the middle region of infrared light (4 000 - 400 cm<sup>-1</sup>). IR spectra of the analysed sample were obtained using a single reflection ATR technique on a diamond crystal using 32 scans with a resolution of 4 cm<sup>-1</sup>. The obtained spectra were processed with Omnic software.

## RESULTS AND DISCUSSION

### Dynamic viscosity temperature dependence

Dynamic viscosity temperature dependences of all the measured systems are shown in Figures 1 and 2. Figure 1 shows the temperature dependences of the systems with additions of 0; 3; 6 and 9 wt. % of CaO (TS, TS + 3 wt. % CaO, TS + 6 wt. % CaO and TS + 9 wt. % CaO) measured during heating (1 700 K - 1 850 K). Figure 2 shows these dependences for the systems enriched with 10; 11; 12 and 15 wt. % of CaO (TS + 10 wt. % CaO, TS + 11 wt. % CaO, TS + 12 wt. % CaO and TS + 15 wt. % CaO) measured during heating, too. It is evident from these figures that viscosity of the systems decreases exponentially with the increasing temperature. In the systems with additions of 3, 6, and 9 wt. % of CaO viscosity decreases with the increasing CaO content. It is evident from Figure 2 that with further addition of CaO (TS + 10 wt. % CaO) the viscosity increases. While the system TS + 9 wt. % the viscosity measured at 1 773 K was 0,279 Pa·s, then in the system TS + 10 wt. % the viscosity measured at the same temperature was 0,302 Pa·s. It is therefore valid for the systems with addition of 10; 11; 12 and 15 wt. % of CaO, that viscosity with the increasing CaO content increases, although in the systems with addition of 11; 12 and 15 wt. %, this trend is less evident.

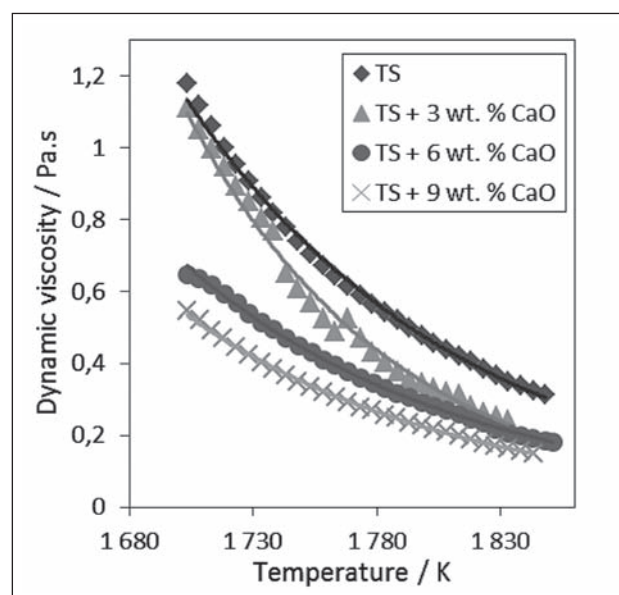
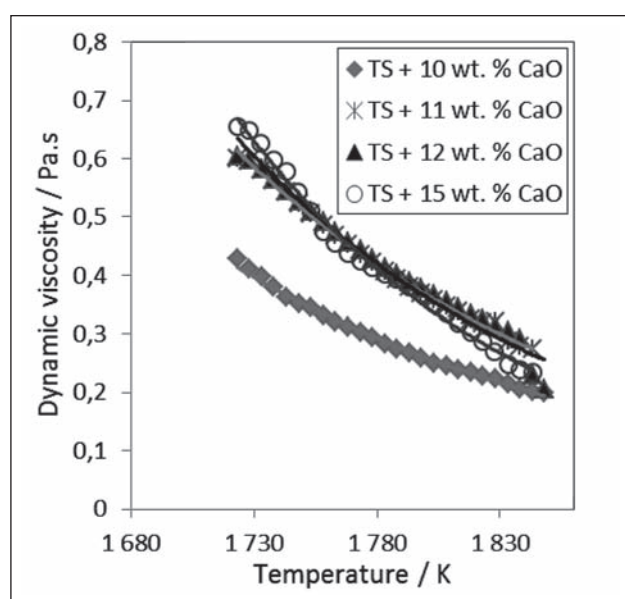


Figure 1 Temperature dependence of viscosity of the CaO concentration series during heating.

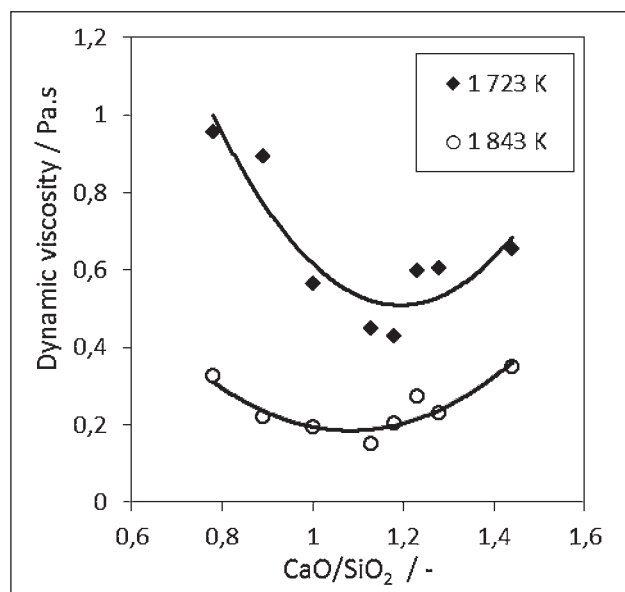
## Influence of basicity (CaO/SiO<sub>2</sub> ratio) on dynamic viscosity and structure

Influence of basicity, i.e. of the viscosity ratio CaO/SiO<sub>2</sub> of the investigated systems at the temperatures of 1 723 K and 1 843 K is shown in Figure 3. It is evident from this figure that viscosity first decreases with the increasing basicity, while it achieves its minimum value at the CaO/SiO<sub>2</sub> ratio = 1,19 (1 723 K); 1,14 (1 843 K). At the higher values of the CaO/SiO<sub>2</sub> ratio the values of viscosity again increase. The basicity influence on the slag viscosity value is much more pronounced at lower temperatures.

It is evident from Figure 3 that the trend of viscosity values changes in dependence on the change of chemical composition between the samples with basicity of



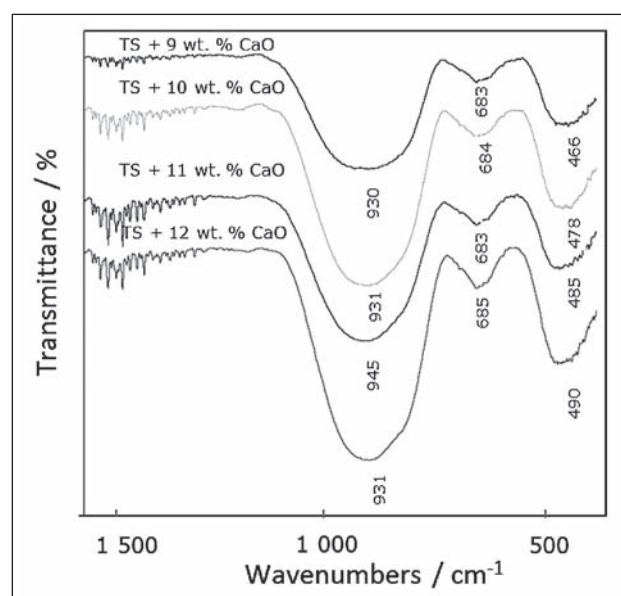
**Figure 2** Temperature dependence of viscosity of the CaO concentration series during heating.



**Figure 3** Viscosities of CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> system as a function of basicity at 1 723 K and 1 843 K.

1,13 and 1,28. Thus the samples with basicity of 1,13; 1,18; 1,23 and 1,28 were subjected to infrared spectroscopic analysis, in order to verify the relationship between the viscosity and the slag structure. FTIR spectroscopy allows differentiation of the various types of bonds in the material to be analysed at the molecular level. The resulting spectra are shown in Figure 4.

Characteristic bands for silicate systems can be observed in the FTIR spectra in the wavenumber region between 1 200 and 400 cm<sup>-1</sup> [8]. The course of all the infrared spectra achieved is based on presence of broad and non-sharp bands, which confirms amorphous character of all the studied samples. The spectra contain three main relatively broad bands belonging to various vibrations of Si - O and Al - O bonds. The most intense band around 930 cm<sup>-1</sup> may be attributed to the asymmetrical stretching vibrations of O - Si - O bonds in SiO<sub>4</sub> tetrahedrons.



**Figure 4** Mid - infrared spectra of samples (1 723 K).

The vibrations of Si - O - Si bands usually appear above 1000 cm<sup>-1</sup> and therefore higher incidence of O - Si - O bonds can be assumed [9]. Position of the most intense band around 930 cm<sup>-1</sup> may be related to the presence of SiO<sub>4</sub> tetrahedrons with two non-bridging oxygen atoms [10]. The sharper band at 680 cm<sup>-1</sup> is related to the asymmetric stretching vibrations of [AlO<sub>4</sub><sup>5-</sup>] structural units, and bands near 500 cm<sup>-1</sup> are typical for the Si - O - Si rocking vibrations, which indicate structured complex silicate structures [8].

## CONCLUSIONS

The results obtained by the experimental research can be summarized as follows:

- Viscosity of all the investigated oxide systems decreases exponentially with the increasing temperature.

- Dynamic viscosity is highly dependent on the chemical composition of the oxide system. Mutual ratio CaO/SiO<sub>2</sub>, i.e. basicity affects significantly the viscosity. Viscosity first decreases with the increasing basicity, while it achieves its minimum value at the CaO/SiO<sub>2</sub> ratio = 1,19 (1 723 K); 1,14 (1 843 K). At the higher values of the CaO/SiO<sub>2</sub> ratio the values of viscosity again increase. Effect of basicity on the viscosity value of slags is much more pronounced at lower temperatures.
- Viscosity in the slag systems is determined by the internal structure. At low CaO content, modification effects appear with its gradual increase. Silicate bonds (shift to lower wavenumbers) are often extended or destroyed and viscosity decreases. Defragmentation at certain critical concentration of CaO already reached such an extent that further increase of CaO is not decisive in this respect and partial viscosity of CaO is starting to show, which leads to the increase of viscosity in the system.

## Acknowledgements

This paper was created in the Project No. LO1203 “Regional Materials Science and Technology Centre - Feasibility Program” funded by the Ministry of Education, Youth and Sports of the Czech Republic.

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**Note:** The translator responsible for English language is Boris Škandera, Ostrava, Czech Republic