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# COMPREHENSIVE STUDY OF RHEOLOGICAL AND SURFACE PROPERTIES OF THE SELECTED SLAG SYSTEM IN THE CONTEXT OF ITS INTERNAL STRUCTURE

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Preliminary Note – Prethodno priopćenje

Rheological (dynamic viscosity, flow curves) and surface properties (surface tension) of real slag system were experimentally investigated. Measurements of dynamic viscosity were performed with use of the high-temperature viscometer Anton Paar FRS 1 600. The method of sessile drop was used for measurement of surface tension. Surface tension and dynamic viscosity were measured in the temperature interval from 1 200 to 1 600 °C. The structural characteristics of the selected samples were determined by X-ray diffraction (XRD). The samples for given analysis were prepared by quench cooling. Experimentally determined values of dynamic viscosity and surface tension were compared with the results of X-ray diffraction phase analysis.

*Key words:* slag system, internal structure of slag, phase transformation, viscosity, surface tension

## INTRODUCTION

The rheological and surface properties of inorganic oxide melts represent in the metallurgical industry one of the criteria of efficiency of the production process, not only in terms of product quality, but also from an economic point of view. The molten inorganic oxide systems represent from the physicochemical point of view complicated poly-component systems. Formation of slag melt is a result of a complex process consisting mainly of melting and dissolution of the initial constituents of the heterogeneous mixture, accompanied by a number of chemical reactions. It can be assumed that in addition to temperature changes in structure of the homogeneous phase, the properties of this heterogeneous system are considerably influenced also by variable amount of the segregated solid phase. For such highly heterogeneous systems it is impossible to derive even in the molten state some physicochemical properties, depending inter alia on the temperature (viscosity, surface tension) only on the basis of kinetic energy of particles, as it can be done in the case of simple liquids, but it is necessary to take into account also the precipitation and disappearance of individual phases on the basis of precisely specified conditions.

A number of theoretical models exists for calculation of viscosity [1-3] or of surface tension [4, 5] of slag systems. Their basic disadvantage consists, however, in their low compatibility with the associated character of the melt and disrespect to phase precipitations.

The present work is for the above mentioned reason focused on experimental studies of rheological and surface properties of selected real slag system. Temperature dependences of dynamic viscosity and surface tension are confronted with the changes in the phase composition of the given system. Surface tension and viscosity were selected as the criterion of macroscopic physicochemical properties of the slag melt in connection with its micro-heterogeneity due to its relatively high impact on the efficiency of steelmaking processes.

## EXPERIMENT

### Preparation of the samples

A real slag system was chosen for the experimental research, the chemical composition of which is shown in Table 1. This system was annealed at the temperature of 800 °C for 12 hours in order to eliminate graphite and decompose the carbonates and hydroxides.

Table 1 **Chemical composition of the slag system / wt. %**

| component | concentration / wt. % | component | concentration / wt. % |
|---|---|---|---|
| $Na_2O$ | 11,37 | $K_2O$ | 1,855 |
| MgO | 1,84 | CaO | 5,48 |
| $Al_2O_3$ | 18,93 | $TiO_2$ | 0,846 |
| $SiO_2$ | 48,22 | $Fe_2O_3$ | 7,67 |
| $P_2O_5$ | 0,418 | MnO | 0,0785 |
| $SO_3$ | 3,29 | | |

### Measurements of rheological properties

The rheological properties measurements were carried out with use of the rotating viscometer Anton Paar

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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 from 0 to 200 rpm. A high temperature furnace system with a maximum temperature limit of 1 565 °C monitored by a Pt – 13 % Rh/Pt thermocouple was used in the instrument. The graphite crucible containing 50 g of the slag 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 1 200 °C at the heating rate of 6,5 °C / min. and held for 30 min. in order to stabilize the temperature and homogenize the oxide melt. During heating normal force was measured while acting on the surface of the investigated system. At the temperature of 1 050 °C the normal force decreased to zero, it means that the system was in the liquid phase. The slag was then reheated to the temperature of 1 565 °C and flow curves were constructed at that temperature. The viscosity was measured during cooling within the temperature range from 1 600 °C to 1 200 °C at the cooling rate of 4 °C / min.

### Measurements of surface properties

Experimental measurement of surface properties (wetting angles, surface tension) was performed in a resistance observation furnace Classic by the sessile drop method. This equipment enables measurements up to the temperature of 1 600 °C. The temperature is measured by the thermocouple Pt - 13%Rh/Pt. Wetting angles were observed (photographed) using the camera Canon EOS 550D. The results were obtained at the heating mode (2,5 °C / min) under an inert atmosphere of argon with a purity (> 99,9999 %).

### Determination of structure

The structural characteristics of the selected samples were determined by X-ray diffraction (XRD). The given samples of the slag system were prepared by quench cooling at the temperatures of 1 050 °C, 1 100 °C, 1 150 °C, 1 200 °C, 1 250 °C, 1 300 °C, 1 350 °C and 1 420 °C.

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 a 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 the Pt – 13% Rh/Pt thermocouple, furnace working space was filled with argon. The heating rate was 5 °C/min. The samples were then mechanically disintegrated, homogenized and subjected to X-ray diffraction (XRD) analysis already at normal temperature. X-ray diffraction phase analysis of all the above mentioned samples was performed already at ambient temperature on refurbished, fully automated diffractometer URD - 6 (Rich. Seifert - FPM, Germany) under the following conditions:

- Radiation CoKα/Ni filter, voltage 40 kV, current 35 mA, step mode with a step of 0,05 ° 2Θ with time of the step of 3 s and with digital processing of the resulting data. A proprietary program RayfleX (RayfleX ScanX and RayfleX Analyze, version 2,289) was used both for measurement and for evaluation.
- For qualitative assessment the database of diffraction data PDF - 2, version 2 001 (International Centre for Diffraction Data, Pennsylvania, USA) was furthermore used.
- For semi-quantitative analysis the program RayfleX Autoquan version 2,6 was used.

## RESULTS AND DISCUSSION

### Evaluation of rheological properties

The curve of dependence of the normal force on the temperature for the slag system is shown in Figure 1. It is evident from this Figure that within the temperature range from 150 to 780 °C the normal force increases due to the volume expansion of the sample. At the temperature of 1 050 °C the normal force decreases to zero, it means that the system is in the liquid phase.

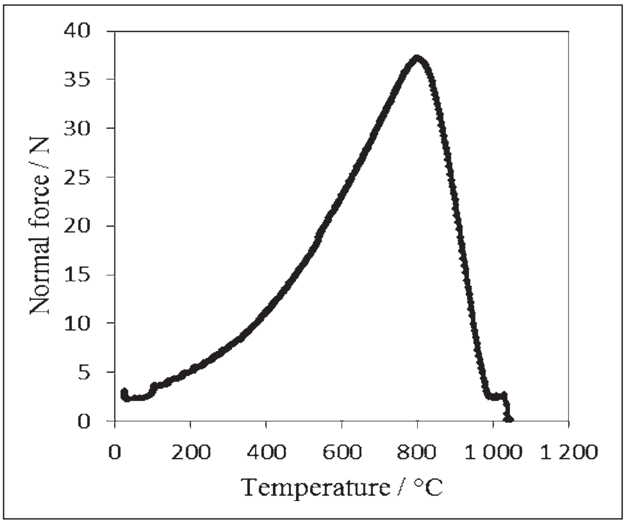


**Figure 1** Temperature dependence of normal force of the slag system.

Mathematical expression of the flow properties of liquids consists of rheological equations of the state, which usually express the relationship between the deformation shear stress and deformation of fluid. Flow curves are their graphical representations. From the shape of the flow curve it is possible to assess Newtonian of non-Newtonian behaviour of fluids. The following Figure 2 shows the flow curves of the slag system at the temperature of 1 565 °C. It is evident from the course of flow curves that the studied system exhibits non-Newtonian behaviour. Viscosity, or apparent viscosity of such a system is then not a constant at the given temperature and the given pressure, but it depends on other factors, such as the shear rate of the liquid or previous deformation of the liquid. This is demonstrated also by the differences between the first (A) and second (B) flow curve (see Figure 2).

The temperature dependence of dynamic viscosity of the slag system was determined at cooling within the temperature range (1 565 ° C – 1 200 °C) (see Figure 3). It is evident from this Figure that viscosity increases exponentially with the decreasing temperature. At the temperature of approx. 1 250 °C a rapid increase of viscosity of the investigated system takes place.

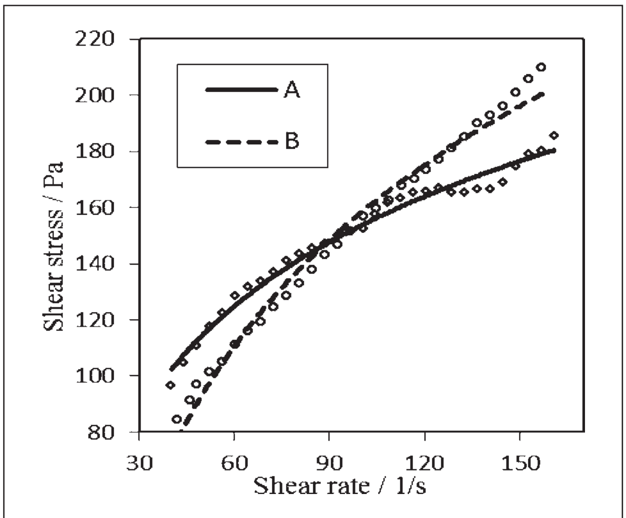


**Figure 2** Flow curves (A – the first flow curve, B – the second flow curve).

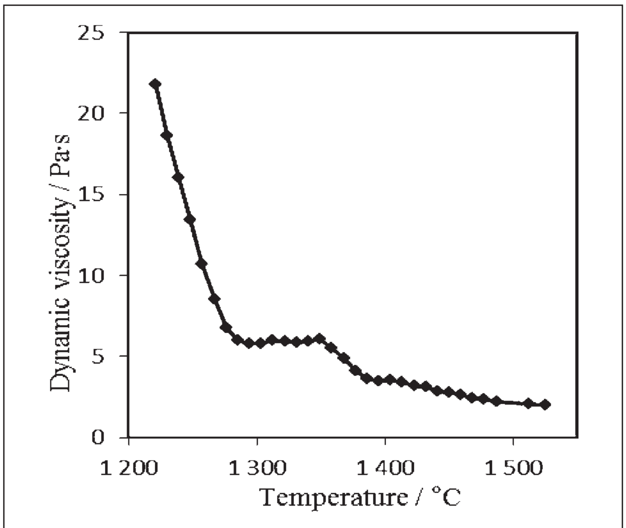


**Figure 3** Temperature dependence of the slag system dynamic viscosity during cooling.

## Evaluation of surface properties

The method of sessile drop is based on automatic recognition of geometric shape of a drop, which is sessile on a non-wettable plate [6]. Graphite plate was used as a non-wettable plate. Recognition of the drop shape is divided into two steps. Firstly, the approximate height of the drop in the image is estimated and secondly, the contour segments of the drop are found. The Laplace – Young equation is used for evaluation of the image.

It is evident from Figure 4 that the surface tension first increases rapidly with the temperature, which corresponds to the area of softening, melting of the sample (1 050 - 1 200 °C). At the temperature of 1 200 °C, the sample is already formed into a regular geometric shape. In the interval (1 250 °C – 1 450 °C), a slight decrease in surface tension with temperature takes place. Starting from the temperature of 1 450 ° C, the value of the surface tension again increases.

## Phase composition of the slag system

Figure 5 shows the phase changes of the investigated system in dependence on the temperature. On the basis of comparison of Figures 3 and 5 it is possible to assume a mutual connection between the dynamic viscosity and phase transformations of the slag system. At the temperature of 1 250 °C during cooling a precipitation of phases takes place (Albite, Magnetite), leading to a sharp increase in viscosity at this temperature. Conversely, with the increasing temperature the share of the crystalline phase in the melt decreases (the melt is completely amorphous above the temperature of 1 450 °C), which corresponds very well to the decrease of viscosity.

When comparing the results of the changes in surface tension and of phase transformations with the temperature (see Figures 4, 5) it is again possible to find mutual connections. The initial increase in surface tension with the temperature and reaching of the local maximum (at the temperature of approx. 1 250 °C) is associated with disappearance of individual phases. Drop of surface tension in the interval (1 250 - 1 450°C) is probably associated with the decrease of the share of the crystalline phase in the melt. Ambivalence of sur-

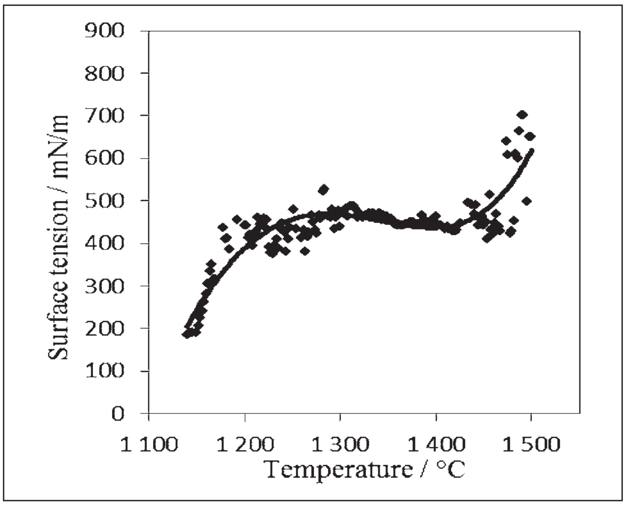


**Figure 4** Temperature dependence of the slag system surface tension.

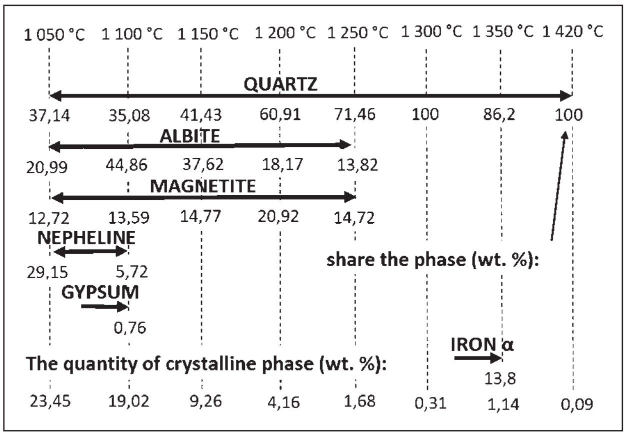


**Figure 5** Phase composition of the slag system with temperature.

face tension values above the temperature of 1 450 °C may be attributed to the beginning of the reduction processes in the melt and to sublimation of some components.

## CONCLUSIONS

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

- Viscosity of the investigated slag system increases exponentially with the decreasing temperature. Increase in viscosity is influenced also by precipitations of individual phases in the melt and by increasing the share of the crystalline phase.
- Increase of the slag system surface tension is associated with disappearance of individual phases in the melt. The declining trend of the surface tension with the increasing temperature is achieved in the case of the existence of a low share of the crystalline phase in the melt. The surface tension in amorphous systems decreases with the increasing temperature due to increasing kinetic energy of the particles.

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