

HIGH-TEMPERATURE RHEOMETRY OF SELECTED METALLURGICAL SLAGS AND PRECIPITATED FINE SOLIDS

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Introduction

The applying of burden materials containing titanium compounds in the blast furnace process and the processes of forming titanium carbides and nitrides has a direct impact on the physical and chemical properties of slag and pig iron, thereby affecting the course of the process, its efficiency and economy. It is known that the dynamic viscosity coefficient of slag – with an increased titanium compounds content in the reducing conditions of the blast furnace - may rapidly change. The products of the reduction reaction, precipitation and separation of titanium compounds are responsible for the thickening effect of the slag and the problems of permeability of blast furnace, causing anomalies in the functioning of the unit. The presence of solid components (fines) in the melts determines the rheological character of the entire system¹⁻⁶.

Measurement apparatus

The main parts of the FRS1600 high temperature rheometer are the measuring system consisting of a crucible with bob (Figure 1b) made from graphite inside of the heating furnace and top-head of unit (Figure 1a). For the rheometry tests of slags a perforated side surface of the bob (Figure 1b) was used in order to eliminate possible slippage between the bob and the tested medium^{6,7}.

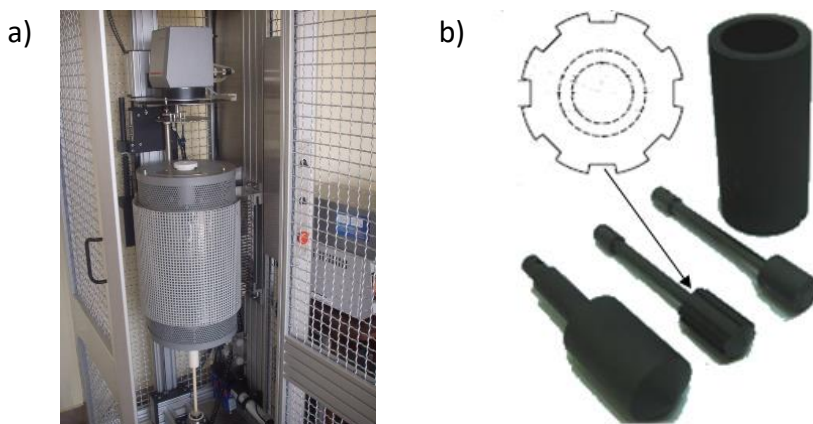


Figure 1: Measurements setup: a) Unit and b) Systems

An inert gas - argon mixture with purity of 5.0 - is injected into the furnace tube to enable a protective atmosphere to be maintained during rheological measurements that last hours⁵.

Experiments conditions

The rheological research focused on multi-component synthetic slags of the blast furnace type in the systems: $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ with increased concentration Al_2O_3 (7–26 wt%) or doped with TiO_2 (4-28 wt%) or with solid synthetic TiN (to be comparable with possible products of reductions of TiO_2 by C or N_2). The range of temperatures was 1310-1500°C. The heating regime and schema of shear rate were varied^{5,6}.

Additional experiments were performed to study the precipitation of Ti-containing phases, such as Ti(C,N) , TiC and TiN , in the freezing slag. The reduction of TiO_2 by carbon from the crucible was observed.

High-temperature rheometry results

The viscosity curves of tested samples at the selected temperatures were presented in Figure 2. Presented rheological characteristics reveal that at specific temperatures, and for specific concentrations of TiO_2 in the system all tested samples are similar to the Newtonian ideal body. However, at a temperature of 1490°C, the curve shows deviations from perfect viscous fluid.

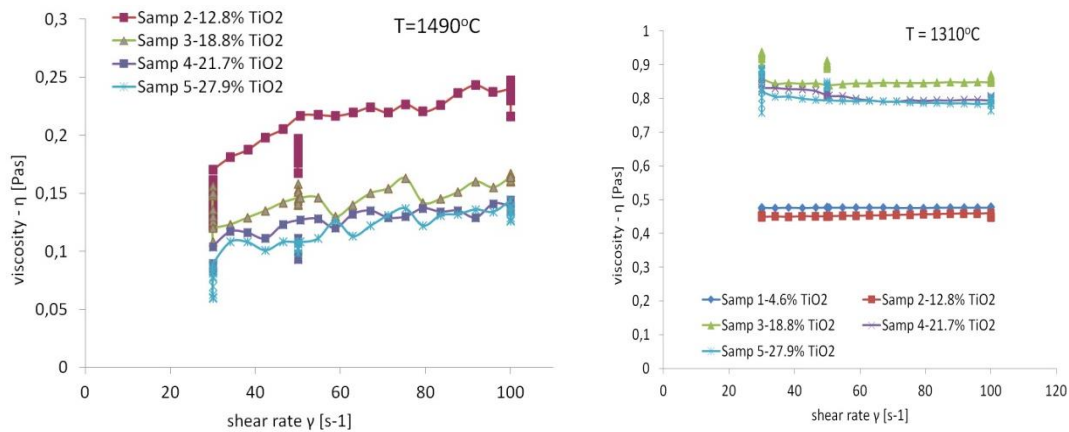


Figure 2: Flow curves for slags with an increased TiO_2 content

In an almost completely liquid system in which only modest amounts of solids Ti(C,N) exist, titanium plays the role of a network modifier by diametrically decreasing the dynamic viscosity, and as a result the slag system shows small deviations from the perfect Newtonian body. However, when the temperature decreases, a substantial quantity of solids precipitate in the possible form of perovskite or others fine solids, intensively raising the coefficient of dynamic viscosity of the system but without any significant influence on its rheological nature.

The next systems $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ with increased concentration Al_2O_3 (from 7 to 26 wt%) were analysed and it can be concluded from the nature of the flow curves that the analysed system (with high concentrations of Al_2O_3) with fine solids is not a Newtonian body. It may be supposed that this is a system that has been diluted by shearing. This effect is characteristic to polymer solutions or suspensions of solid particles in liquids⁶.

Fines solids precipitation from solution

The amounts of solid particles in the basic slag were changed in the 0.1÷0.7 range of volume fraction of TiN. Those values were the results of the theoretical calculations, made by using thermodynamic data bases (Fact Sage) for the analysed TiO_2 concentration.

Figure 3 presents the shape and size of the synthetic TiN which are representative for the solid in the liquid slag solutions. The high temperature range was between 1310-1490°C. Totally liquid blast furnace's slags are systems which show similarity to ideal viscous Newtonian bodies. During temperature or system type changes (for heterogenic) – these systems change their rheological character.

A reduction and precipitation study was performed to verify the possibility of the formation and precipitation in certain conditions.

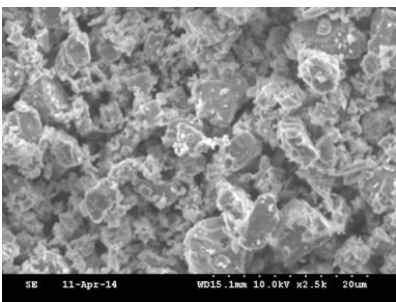


Figure 3: Shape and sizes of synthetic TiN in the doped slag system

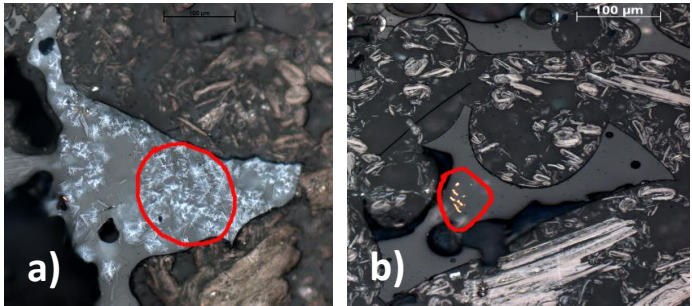


Figure 4: Precipitated titanium compounds from liquid slags

As shown in Figure 4a, the shape and size of the titanium compounds are bigger and having quite different shapes (for 1490°C and 28% TiO_2) than Figure 4b (1310°C and 4% TiO_2) (photos from optical microscope).

Figure 5a and 5b presents titanium concentration in compounds from EDS.

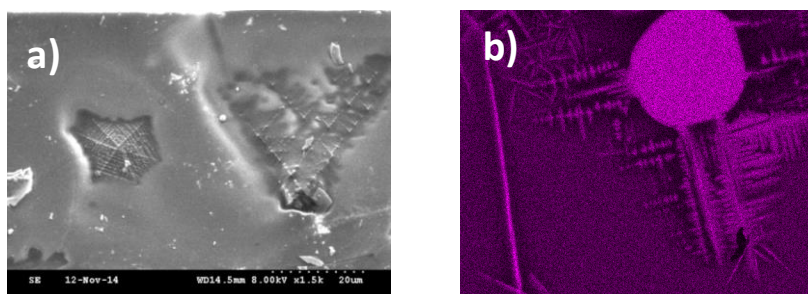


Figure 5: Shape and sizes of titanium compounds as results of precipitation

Conclusions

The addition of titanium oxide to the slag at high temperatures and a for shear rates up to 250 s^{-1} does not change its rheological nature and the slag is similar to a Newtonian perfect fluid. This changes for high TiO_2 concentrations and at lower temperatures (between $1370\text{--}1340^\circ\text{C}$) caused shear-thinning or shear-thickening body by turning into a semi-solid system. The addition of TiN solid particles changes the slag nature into time-dependent; at the same values of shear rate the structure recomposes and falls apart. The type of formed precipitates influences the rheological nature of the semi-solid slag system^{3,6}.

It seems necessary to conduct further rheometric research within this area, in parallel to identification of precipitating inclusions in terms of their structure and chemistry. Research in order to identify the size and shape of precipitated solids in particular conditions of temperature and chemical composition of the slag is necessary.

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