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HIGH-TEMPERATURES RHEOMETRIC ANALYSIS OF SELECTED HETEROGENEOUS SLAG SYSTEMS

WYSOKOTEMPERATUROWE BADANIA REOMETRYCZNE WYBRANYCH HETEROGENICZNYCH UKŁADÓW ŻUŻLOWYCH

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 dipping zone. The presence of solid components (particles) in the melts determines the rheological character of the entire system. Identifying the rheological character of semi-solid slag systems provides opportunities for the development of mathematical modeling of liquid phase flows in a dripping zone of the blast furnace, allowing e.g to indentify the unstable parts of a metallurgical aggregate.

Author have performed study of synthetic aluminosilicates slag concentration of TiO_2 in the range up to 30%, systems were doped solids TiN also, it was made in order to assess the impact of the type forming areas/units of the SRO nature on the rheological identification mentioned systems. The high-temp rheometric measurements were performed at temperatures in the range between 1310-1490°C. The obtained results made it possible to carry out the rheological characteristics of analyzed liquid and semi-solid slag systems.

Keywords: slag viscosity, high temperature rheometry, blast furnace, semi-solid slag rheology

Powszechnie wiadomym jest, że współczynnik lepkości dynamicznej żużli wielkopiecowych wraz ze zmianami stężeń związków tytanu w warunkach redukcyjnych może ulegać gwałtownym zmianom. Związki tytanu wydzielając się z cieczy jonowej są odpowiedzialne za zagęszczanie układu powodując problemy z przepływem cieczy w dolnych partiach pieca. Zawartości stałych elementów w roztworze determinują jego charakter reologiczny. Jego identyfikacja daje możliwości rozwoju oraz nowego podejścia do modelowania numerycznego przepływu cieczy przez strefę ściekania. W pracy przedstawiono wyniki badań układów krzemianowych typu wielkopiecowego domieszkowanych TiO_2 do 30% oraz domieszkowanych TiN, w celu oceny wpływu tworzących się obszarów typu SRO na charakter reologiczny systemu. W pracy przedstawiono wyniki badań reometrycznych dla układów krzemianowych typu wielkopiecowego domieszkowanych TiO_2 w zakresie do 30% oraz do domieszkowanych TiN. Badania wykonano w zakresie temp. 1310-1490°C oraz w atmosferze redukcyjno-obojętnej. Wykonano identyfikację reologiczną badanych systemów żużlowych. Wykonano wysokotemperaturowe pomiary reometryczne oraz identyfikację reologiczną badanych systemów żużlowych.

1. Introduction

In many metallurgical processes, liquid slag and metal are subjected to a dynamic force impact, including an electric arc impact, the dripping of hot metal in the blast furnace in countercurrent flow with the reduction gas, and gas stream impact. Dynamic effects during flow, crystallization and precipitation of solid particles depend on many non-rheological factors. So far it has been very difficult to measure the parameters that may be considered rheological in this actual processes. The influence of impact dynamics of these variables on liquid and semi-solid slag systems, including changes in force impact over time, their value and direction, and thus the shear rate, is very often neglected.

Most numerical models that allow calculating dynamic viscosity coefficients of liquid ionic solutions are largely based on thermodynamic characteristics. Semi-empirical models based partially upon laboratory tests occur.

Recently researchers have been developing and describing many models used to determine the viscosity of aluminosilicate slags: Urbain, KTH, Iida, QCV [1-5].

The viscosity (η) of liquids e.g. slag is distinctly dependent on the temperature and structure of the fluid [6]. It is a measure of the ability of slag to flow when the shear stress is applied. Most slag and metallic fluids show the characteristics of Newtonian fluids, in case of which viscosity is independent of the shear rate [6]. As a result viscosity is defined by the Newton's equation (1):

$$\tau_{xy} = \eta \frac{dv_x}{dy} \qquad (1)$$

where:

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η − constant of proportionality, aka. dynamic viscosity coefficient, Pas,

τ_{xy} − shear stress, Pa,

$\dfrac{dv_x}{dy}$ − the gradient of normal velocity to the shear stress, so called shear rate, s^{-1}.

The literature referring to the topic contains numerous rheological models which make it possible to calculate the viscosity values for non-Newtonian fluids. The simplest models include [6-8]: Ostwald de Waele'a power law model, Herschel-Bulkley model, Bingham model.

The above mentioned models allow to calculate viscosity values of the plastic material which shows the characteristics of a solid body and sometime: slurry, suspensions or semi-solid liquids. It is elastic till the moment it exceeds the critical stress (known as yield point or yield stress) and then it deforms plastically (Bingham model). Herschel-Burkley model, on the other hand, is a non-linear version of Bingham model. It illustrates the behaviour of plastic material which is characterized by shear thinning the moment the critical stress is exceeded.

There have been many mathematical models developed in order to describe the behaviour of real bodies. These models also include ones that allow to estimate the viscosity values of suspensions while taking into consideration the amount and shape of particles (and not only the shear rate and shear stress values which were taken into consideration by other rheological models) [1,2,6]. The above mentioned models include, among others, the Krieger–Dougherty equation or Einstein equation was modified by Roscoe and that is how Einstein-Roscoe equation came into being:

$$\eta = \eta_0(1 - k\Theta_{eff})^m \qquad (2)$$

where:

η − viscosity of the suspension, Pas,

η_0 − the viscosity of the liquid phase remaining in the system, Pas,

θ_{eff} − solid phase volume fraction,

k – constant, for spherical molecules equal to 2.5,

m – exponent, experimentally found to be equal to 1.35.

The models which allow to calculate the viscosity of suspensions in metallurgy can be used to estimate the viscosity values of solid-liquid slag systems, fluxes and salt in semi-solid state.

Due to the extent of experimental difficulties, few high-temperature viscosity measurements of a semi-solid ionic system doped with solids are performed [7]. Rheological parameters – shear rate, time – are seldom used for the description of the rheological nature of liquid or semi-solid blast furnace slag systems. Analyses of changes in dynamic viscosity in relation to the conditions of dynamic gas flow in counterflow to liquid in a lump bed in the blast furnace are equally rare [8]. It arises from the common assumption that liquid slags/ionic solutions show a similarity to Newtonian body, shearing time-independent liquids.

2. Experimental approaches

The tests were conducted with a FRS1600 high-temperature rheometer, described in the paper [10], within a temperature range of 1310-1490°C for various values of shear rate and various times of shear stress impact on a liquid or a semi-solid system. Rheological characteristics were performed, which allow finding that the slag systems analysed in particular conditions of composition and temperature are dependent on shear rate. Slags with an increased TiO_2 content (8 samples), a slag with a standard hearth slag chemical composition (base slag) and slags doped with solid TiN particles (samples from 10 to 15) were analysed for concentrations presented in Table 1. The main goal of the study was to analyze/identification of rheological properties of selected slags systems.

TABLE 1

Selected chemical compositions of slags tested

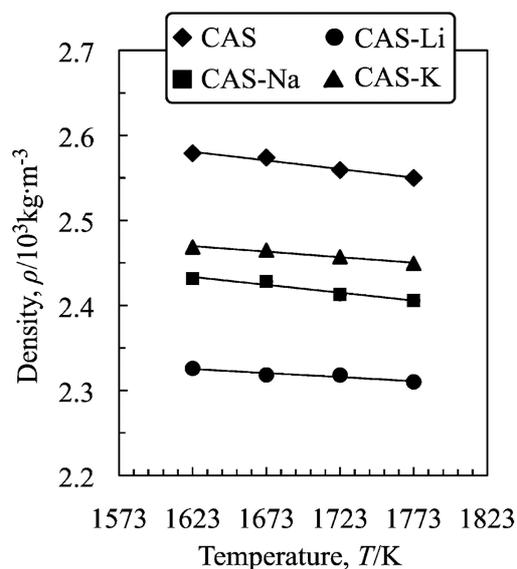| No. Sample	CaO	MgO	Al₂O₃	SiO₂	TiO₂	Na₂O	K₂O
	[%]						
1	43,99	7,70	7,96	38,87	0,00	0,23	0,21
2	42,78	7,64	7,91	37,91	0,45	0,22	0,20
3	42,59	7,67	7,98	37,60	1,48	0,22	0,20
4	41,75	7,60	7,90	36,89	2,87	0,22	0,20
5	42,54	7,22	10,86	32,98	5,81	0,13	0,22
6	36,30	7,64	11,02	29,88	14,73	0,15	0,14
7	32,69	8,48	11,46	25,19	20,73	0,13	0,24
8	31,35	8,22	9,80	25,46	24,85	0,13	0,22
9	28,95	7,62	9,10	24,31	29,73	0,13	0,22
					TiN		
10	41,28	6,89	7,52	36,99	3,44	0,22	0,20
11	40,99	6,85	7,46	36,70	4,14	0,22	0,20
12	34,65	6,53	7,55	30,45	17,67	0,18	0,17
13	32,64	6,49	7,47	28,87	21,58	0,17	0,16
14	42,96	6,83	7,89	38,25	0,78	0,23	0,21
15	42,65	6,96	7,80	38,24	1,90	0,22	0,21

Table 2 presents a cumulative list of measurement patterns for systems doped with "low" TiO_2 and TiN contents. The presented patterns within a temperature range of 1500-1310°C were executed at each of the individual temperatures (1490, 1460, 1400, 1370, 1340, 1310°C) separately. The chemical analysis was conducted with a Twin X, x-ray spectrometer.

Figure 1 presents measured density values obtained by the authors [11]. The Archimedes's method for two various immersed bobs was used for the measurement. One can observe that for liquid slag systems of the CaO-SiO_2-Al_2O_3-R_2O (R_2O=Li,K,Na) type the densities are within a range of 2,3-2,6*10^3kg/m3 and slightly decrease with an increase in temperature within the range of 1573-1773K.

TABLE 2

Rheometric measurement patterns for selected samples 10-15

Temp. [C]	Shear rate [s⁻¹] and time for steps of measurements [min]																	Total measurement time (for one temp.) [min]	Frequency of data recording [s]			Duration to setpoint temperature in sample [min]
	2	5	30	50	100	150	250	2	250	2	250	2	250		Linear variable							
															2-200	200-2						
1490- 1310	2	2	2	2	2	2	2	2	2	2	2	2	2		12	12	50	20	10	15	30

Fig. 1. Temperature dependences of the density for CaO-SiO$_2$-Al$_2$O$_3$-R$_2$O melts [11]

To calculate the theoretical value of slag density, empirical equation 3 presented by Mills [12] was used:

$$V = \Sigma \ X_1 V_1 + X_2 V_2 + X_3 V_3 + ... + X_n V_n \tag{3}$$

at 1773K; V (10^{-6}m^{3}mol^{-1}) values for: CaO=20.7; FeO= 15.8; Fe$_2$O$_3$ = 38.4: MnO = 15.6; MgO= 16.1; Na$_2$O= 33; K$_2$O = 51.8; TiO$_2$ = 24; P$_2$O$_5$ = 65.7; SiO$_2$ = (19.55 + 7.97X$_{SiO2}$); Al$_2$O$_3$ = (28.3+ 32X$_{Al2O3}$ -31.45X$^2_{Al2O3}$); (dV/dT) =0.01%K^{-1} [12].

Table 3 presents the density values calculated for a slag sample after the experiment, on the basis of linear dimensions of the sample (its volume) and the slag mass in the solid state. They were compared with the theoretical values obtained by calculations from equation 3.

TABLE 3

Slags densities values

N^o. sample	ρ g/cm^3	
	after experim	theoretical
1	2.417	2.516
2	2.592	2.562
3	2.615	2.526
4	2.640	2.566
5	2.679	2.432
average	2.589	2.520

The presented values are comparable with values obtained by authors [10] and are within the range of 2.42-2.68*10^{3}kg/m3.
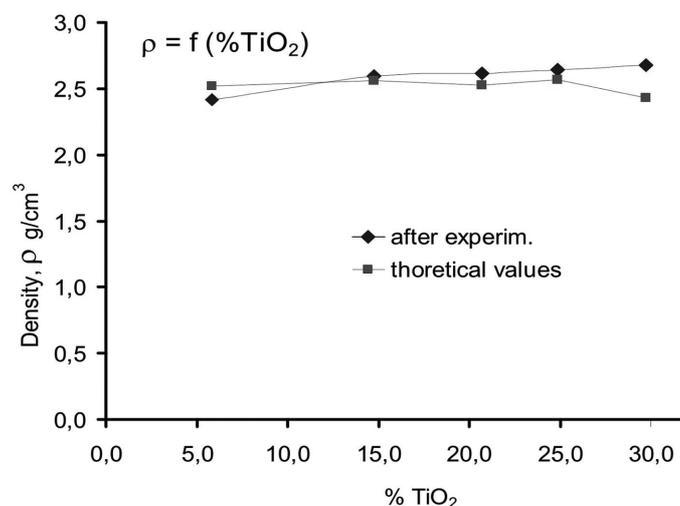
Fig. 2. Slags densities vs. TiO$_2$ %

The change in the density values of the slags analysed as a function of concentration is presented in graph 2. A difference in the trend line between the theoretical values and the experimental ones can be noticed. Therefore, the average value of density obtained after the experiment, which is presented in table 3, was used to calculate the Reynolds number. When comparing the values for the slags tested with literature values [11] at a temperature of 1773K, slight differences can be seen, they may result from the addition of titanium oxide to the systems examined.

For liquids flowing in an annular gap, in the measurement method with concentric cylinders (cup and bob) there is a critical, upper limit of the shear rate (or rpm) between a laminar flow and a turbulent flow. It is possible to determine analogical limit values shear rate by the Taylor number (Ta) which is expressed by the following formula 4 [13]:

$$Ta = \left[\omega_c \cdot \rho \cdot R_i^2 \cdot \sqrt{\delta_{cc}^3} \right] \tag{4}$$

where:

ω_{cc} – characteristic angular velocity (where Taylors vortices appear) [rad/s],

ρ – fluid density [kg/m3],

R$_i$ – bob radius [m],

δ_{cc} – cylinder radius ratio [-].

A turbulent flow occurs when the Reynolds number reaches its critical value, assumed by the author [13] at 1000. The

Re number characterises the ratio of forces caused by mass inertia to fluid flow resistances. The flow instability compatible with the Reynolds theory manifests in both types of moving cylinders (methods: Couette's and Searle's) [13]. The Reynolds number is expressed by formula 5:

$$Re = \frac{\omega\left((R_e + R_i)\,(R_e\text{-}R_i)\,\rho\right)}{2\eta} \tag{5}$$

where:

$\omega-$ bob angular velocity [rad],

R_e, R_i – outer and inner cylinder radiuses respectively [m],

$\rho-$ fluid density [kg/m^3],

$\eta-$ dynamic viscosity index of fluid [Pa·s].

Table 4 presents the physical parameters of the liquids analysed and the linear dimensions of the space where the flow of the liquid is forced with a particular shear rate. Based on these parameters the Reynolds numbers for the specific measurement system and liquid were calculated.

Table 5 presents calculated Reynolds number simulations for an ionic solution and a ferrous solution (hot metal). For a graphite bob with a diameter of 16 mm and an alundum bob with a diameter of 27 mm. Four fundamental directions of rheological research can be distinguished [20]:

1. Phenomenological rheology or macro-rheology – describes phenomena occurring during deformations of actual bodies in a macro scale, while neglecting the molecular structure.
2. Structural rheology or micro-rheology – looks for a relationship between the substance structure at a micro level and its rheological properties.

TABLE 4

Conditions assumed to determine the flow type of the selected liquids

Average	Density	Viscosity index of liquids		
	kg/m^3	Pas		
Slag	2589	0,1	0,25	0,5
Pig iron	7000	0,001	0,004	0,008
Bob diameter, mm	Dimensions/gaps of measuring systems, m			
16	R_e	0,015	r - gap	**0,007**
	R_i	0,008	R_{rep}	0,0035
27	R_e	0,015	r - gap	**0,0015**
	R_i	0,0135	R_{rep}	0,00075

3. Rheometry – empirically determines the rheological parameters characterising Newtonian and non-Newtonian fluid properties.
4. Technical or applied rheology – a description of fluid flow in processes with a practical significance, e.g.: stirring, extrusion, sedimentation, fluid forcing through, etc. [20].

For theoretical identification of the flow nature during a measurement for a specific bob/cup measurement system for comparable conditions of shear force impact, it was necessary to calculate the Reynolds number. In this connection, the densities of the slags examined, for samples 1-5, were determined.

TABLE 5

The Reynolds number values for a liquid slag and iron flow in particular linear conditions

Bob diameter mm	Speed - N rpmn	Shear rate - γ s^{-1}	Linear rate - V m/s	Reynolds number Re (slag)			Reynolds number Re (pig iron)		
				0,1	0,25	0,5	0,001	0,004	0,008
				Pas					
16	10	2	0,008	2,2	0,9	0,4	590,0	147,5	73,7
	27	5	0,023	5,9	2,4	1,2	1593,0	398,3	199,1
	50	8,72	0,042	10,9	4,4	2,2	2950,5	737,6	368,8
	287	50	0,24	62,6	25,1	12,5	16935,8	4233,9	2117,0
	860	150	0,72	187,7	75,1	37,5	50748,2	12687,1	6343,5
	1146	200	0,963	250,1	100,0	50,0	67625,0	16906,2	8453,1
	3000		1,257	654,8	261.9	130.9	177028,6	44257,2	22128,6
27	10	2	0,014	0,6	0,2	0,1	156,7	39,2	19,6
	27	5	0,038	1,6	0,6	0,3	423,0	105,7	52,9
	50	8,72	0,071	2,9	1,2	0,6	783,4	195,9	97,9
	287	50	0,406	16,6	6,7	3,3	4496,9	1124,2	562,1
	860	150	1,216	49,8	19,9	10,0	13475,1	3368,8	1684,4
	1146	200	1,620	66,7	26,6	13,3	17956,3	4489,1	2244,5
	3000		2.121	174.6	69.8	34.9	47012.2	11753.0	5876.5

By the Author [13] the Reynolds number at 1000 means that a given system is transforming into a turbulent flow state. Rheometric measurements for these type of flows (turbulent) cannot be identified. As a rule, measurements in such a high range of shear rates for which liquids turn into a turbulent flow state are limited. In Table 5 one can see that blast furnace slags within the range of shear rate up to $200s^{-1}$ (N=1146 1/min), and for viscosity coefficient from 0.1 to 0.5 Pas, at their density of 2589kg/m^3 (Table 4), should not turn into a turbulent flow state. However, for theoretical considerations of the liquid ferrous solution flow, it can be seen that the shear rate value at which the liquid turns into a turbulent flow state completely depends on the liquid density, dynamic viscosity and linear dimensions of the shear gap. For instance, for a gap of 7 mm, the turbulent flow occurs already within the shear rate range of 2-$5s^{-1}$ for a linear velocity of the bob at the level of hundredths of a meter per second (0.008-0.027m/s). However, for the same physical conditions, and for a gap of 1.5 mm, a turbulent flow occurs within a shear rate range of $8.72 - 50s^{-1}$ for a linear velocity of the bob (0.071-0.406m/s). The Authors [16] dealing with the modelling of the dripping zone in the blast furnace and its irrigation and retention identify the linear velocity of gas flow through the bed as 0,04 – 25m/s, or even up to 70m/s [17-18]. Therefore, the dynamic impact of gas on liquids dripping between coke lumps considerably exceeds the measurement range of modern rheometers [10]. For free dripping through the bed, without the physical impact of counter-flowing gas on liquids, it seems possible to determine a change in the viscosity coefficient in such shear conditions for the liquid examined. On the basis of the obtained values of the Reynolds number, one can find that the liquids (slag, hot metal) analysed will behave quite differently (dripping through the coke bed). It seems that deviations of liquid aluminosilicate systems from the Newtonian nature would rather arise from changes in their internal structure. However liquid ferrous solutions in the conditions described would turn into a turbulent flow state, which excludes possibilities of using rheometric tests for such high values of shear rates as those in the dripping zone conditions.

Authors reported [9] that were measured the slag viscosity under reducing conditions, using CaO-SiO_2-Al_2O_3-TiO_2 slags contained in a graphite crucible under a carbon monoxide atmosphere, they found that the slag viscosity increases rapidly as the initial TiO_2 content increases. These changes in the slag properties are not favorable for a blast furnace operation, since gas and liquid permeabilities inside the blast furnace are important aspects in the furnace operation, and since any difficulties in tapping the molten metal and slag out of the furnace could cause serious operational problems. Thus, the addition of titania bearing materials should be optimized to form a protection layer on the refractories without causing possible operational problems [9].

On the basis of tests and an analysis of findings, the authors [9 found that it was possible to form and precipitate solid titanium carbonitrides from slag in blast furnace conditions, depending on N_2, CO pressure, slag chemical composition and TiO_2 concentration in the slag.

It should be said that liquid slags doped with an increased content of titanium compounds are heterogeneous systems with a very complex internal structure [17-19]. The internal structure of liquid/slag significantly effects its rheological behaviour, also during dripping into the hearth, and during blast furnace tapping.

In this study, titanium compound reduction was analysed theoretically on the basis of thermodynamic calculations in the equilibrium state performed with the FactSage program.

A change in the thermodynamic potential of the reaction (ΔG_T^o) was assumed a criterion for the possibility of a reduction reaction occurrence. The calculations were performed for a temperature range 1200-2200°C corresponding to the temp prevailing in the blast furnace zones analysed (under-cohesive/dripping and tuyere zone). The first stage involved calculations for many (22) possible reactions of titanium reduction. The ΔG_T^o values for the selected reactions and temperatures characterising the under-cohesive and dripping zone in blast furnace hearth; reactions that are adequate for rheometric tests were selected and presented at Table 6.

TABLE 6

Possible titanium compound reduction reactions within the temperature range for the conducted rheometric measurements

L.P	Reakcje	ΔG_T^o = f(T)	ΔG_T^o Temp [°C]				$\Delta G_T^o = 0$
			1200	1550	2000	2200	Temp of inversion [°C]
1	3TiO2+C =Ti3O5+CO	y = -193,15*T + 204995	-26785	-94388	-181305	-219935	*1061*
2	Ti3O5+0,5C = 1,5Ti2O3+0,5CO	y = -74,933*T + 111352	21432	-4794	-38514	-53501	*1486*
3	TiO+2C = TiC+CO	y = -154,73*T + 195834	10158	-43998	-113626	-144572	*1266*
4	Ti2O3+5C = 2TiC+3CO	y = -467,17*T + 663122	102518	-60992	-271218	-364652	*1419*
5	Ti3O5+8C = 3TiC+5CO	y = -795,30*T + 1106616	152256	-126099	-483984	-643044	*1391*
6	TiO2+3C = TiC+2CO	y = -320,16*T + 440488	56296	-55760	-199832	-263864	*1376*

Regression equations of the change ΔG^o_T in the reaction temperature range analysed were presented, also inversion temperatures characterising the beginning of the reaction occurrence "towards" the titanium compound reduction were calculated.

On the basis of $\Delta G^o_T < 0$ values, possible titanium oxide reduction reactions (in the set conditions) were selected. It can be seen that the mentioned reduction reactions may occur primarily in the dripping zone or just under the cohesion zone, or potentially in the high temperature zone (tuyere zone).

As can be seen for a carbide forming reaction 3, this reaction may occur already at a temperature of 1266°C, the products of these reactions include titanium carbides, which as solids will thicken the slag system and influence the dynamic viscosity coefficient. The solid phase share in the system and its interaction with the liquid phase remaining in the system will affect its rheological nature.

The amount and the type of the precipitated solid phase, and most of all the chemical composition and internal structure of the liquid phase remaining in the volume, will influence the value of the dynamic viscosity coefficient of the whole system.

2.1. Rheological character – flow curves

Figure 3 presents viscosity curves for all temperatures in the range of 1310-1490°C, at which the tests were performed. Deviations from the Newtonian body nature of the systems investigated can be observed, the biggest deviations for all samples are for the highest temperatures of 1490°C, and
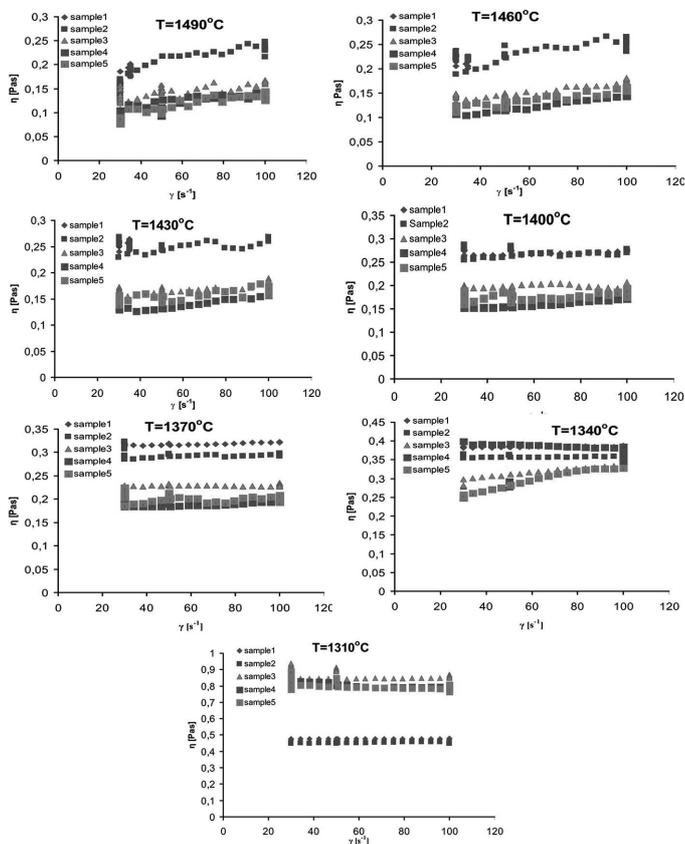
1460°C. Titanium cations, as network modifiers of aluminosilicate systems, effect the internal structure of a cross-linked solution probably causing its depolimerisation.

When the temperature decreases the nature of the liquid examined becomes more similar to the Newtonian body. Also the dynamic viscosity coefficient changes; at a temperature of 1310°C it increases by almost two to three times. For high temperatures the addition of titanium compounds to the system causes a decrease in the dynamic viscosity of a wholly liquid system. However, for low temperatures of 1310°C a reverse tendency can be observed, the addition of titanium to the slag increases the value of the dynamic viscosity coefficient. Such behaviour of a semi-solid system is in line with the findings presented by the authors [19-21]. Titanium compounds precipitating from the liquid are likely to cause its thickening. A change in the chemical composition of the liquid (saturated from titanium and calcium ions) remaining in the system causes a change in its internal structure, resulting in a viscosity increase. The forming structures of complex anion compounds will interact with each other as each of them has a different viscosity. This effect is enhanced by precipitation and the impact of solids such as: TiC, TiN, Ti(C,N), $CaTiO_3$ or others.

2.2. Heating regime

Figure 4a-d presents changes in the values of the dynamic viscosity coefficient of the selected slags with two changing heating regimes. The first heating regime was from the top temperature 1490°C – the sample was cooled at a rate of 1°C/min., next it was reheated to a temperature of 1460°C at a rate of 1-2°C/min. During these heating/cooling patterns the dynamic viscosity coefficient was measured at a constant shear rate of $40s^{-1}$. The temperature change directions are shown in Figure 4a as arrows, the patterns in the subsequent systems changed in the same directions. Dynamic viscosity changes of a very similar nature can be observed for the base slag and slags doped with titanium compounds. Only a high concentration of 20,73%TiO₂ in the slag causes a change in the curve nature. The analysed slag system achieves the same dynamic viscosity coefficients at higher temperatures.

Fig. 3. Viscosity curves for samples with TiO_2 in the temperature range of 1310-1490°C
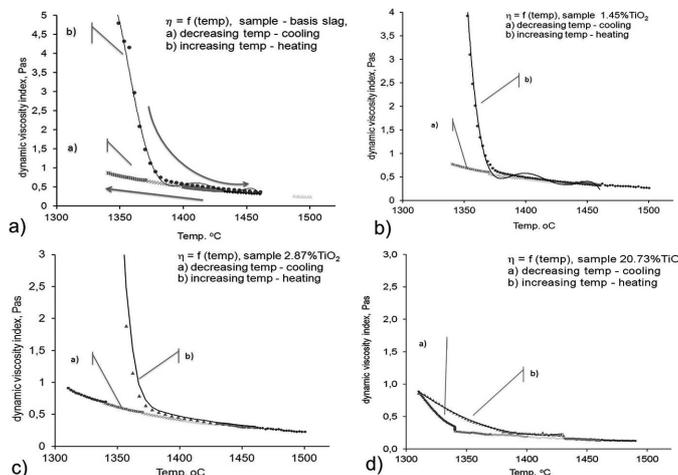

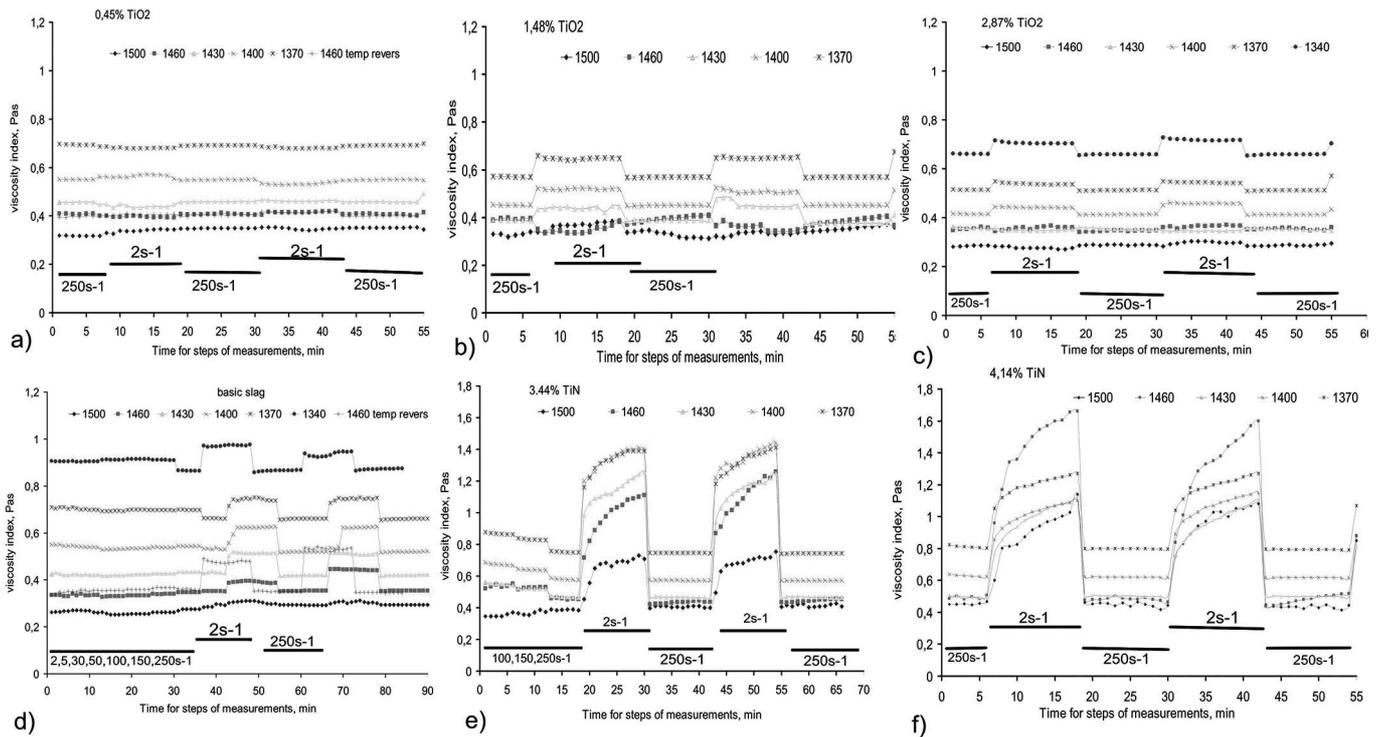Fig. 4. Changes in the viscosity coefficient of the selected slags versus variable temperature

Fig. 5. Changes in the dynamic viscosity coefficient of a CaO-SiO$_2$-MgO-Al$_2$O$_3$ system slag doped with TiO$_2$ and TiN over time

In Figure 4a-b, curves showing viscosity changes as a result of heating and cooling only overlap in the higher temperature range from about 1370°C up. With an increase in the TiO$_2$ concentration, this temperature shifts towards higher values – Figure 4d. This may indicate the effect of time shift (heating) of dissolution/reaction of solids precipitated at low temperatures subsequently from the silicates solution. For low temperatures of 1350-1310°C, significant differences in dynamic viscosity values may be observed; this may result from differences in precipitation of solid particles and the thickening of the system over time.

Subsequently, possible amounts of solid precipitates and/or titanium nitride in slags were determined with the FactSage thermodynamic database, for the assumed particular thermodynamic conditions – temperature, pressure, and the chemical composition of the slag. Samples of slags doped with synthetic TiN (from Aldrich-Chemistry, fi<3μm) with the calculated TiN contents were made, next rheometric tests were performed.

2.3. Time dependency

In the presented Figures 5a-f and Figures 6a-b, the effect of the addition of TiO$_2$ and solid TiN components on a change in the dynamic viscosity coefficient over time are compared. The results and flow curves and viscosity curves of the blast furnace slags tested are included in the papers [7, 20].

Figure 5a-f presents changes in the dynamic viscosity coefficient of the slag systems tested without additions of TiO$_2$, and doped with TiO$_2$ and with solid particles TiN. Figures 5a-d and 6a show that within 0.45 – 5.81% TiO$_2$ and shear rates up to 250s^{-1}, at high and low temperatures the slag systems tested show a nature of time-independent fluids. However, Figures 5e, 5f and 6b clearly show considerable deviations

from this type of fluid. A considerable change in the nature of the whole system tested can be observed, resulting from a change in the dynamic viscosity coefficient over time – systems become time-dependent. At a constant slag system shear rate of 2s^{-1} the dynamic viscosity increases over time. For small, constant shear rates (2s^{-1}), Figure 5e, f, the systems thicken, which can be seen already at temperatures between 1460 and 1370°C. With an increase in the TiN concentration, the system appears less rheologically stable, which is caused rather by effects inside the internal structure than by a change in the flow nature, to a turbulent flow (Table 4).
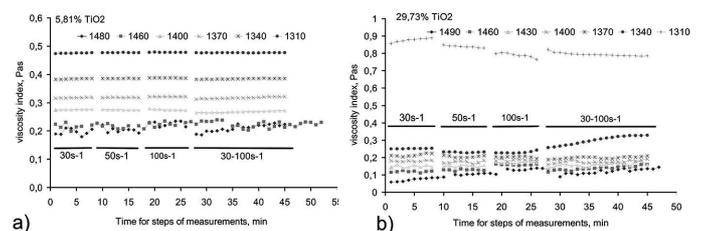

Fig. 6. Changes of the dynamic viscosity of the CaO-SiO$_2$-MgO-Al$_2$O$_3$ system slags doped with TiO$_2$ over time

Figure 6b illustrates changes in the dynamic viscosity coefficient during gradual adjustment of the shear rate from 30 to 100s^{-1}. It can be seen that for a sample doped with a high TiO$_2$ concentration – 29.73% at temperatures from 1490-1370°C, the system analysed is time-independent and the viscosity coefficient does not change with the shear rate changing over time. Its similarity to a Newtonian fluid can be found. However, in the temperature range of 1370-1340°C, the system shows deviations from such behaviour of perfect fluids, turning at a temperature of 1370°C into a shear-thickening system, and at a temperature of 1340°C into a shear-thinning

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system. The recomposition of the structure and its destruction caused by shear stress applied can be observed.

3. Conclusions

As a result of the conducted research and analyses one can find, as follows:

Liquid silicate solutions and ferrous solutions (hot metals) during dripping in the blast furnace through the coke bed, at the same temperature and pressure conditions and at the same reduction gas flow rate will show different flow natures. Slags and hot metal dripping freely between coke lumps will have a laminar nature. However hot metal sheared by gas will turn into a turbulent flow state at much lower shear rates than liquid slag. It results from the densities and dynamic viscosities of the systems tested.

The addition of titanium oxide to the slag at high temperatures and a shear rate up to $250s^{-1}$ 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 1370-1340°C by turning the semi-solid system into shear-thinning or shear-thickening.

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.

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 the chemical composition of the slag is necessary.

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