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Possibilities of applying rheological measurements in metallurgy

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Analysis and modelling

ABSTRACT

Purpose: The purpose of this paper is to analyse from the literature point of view the issues concerning modern methods of measuring the viscosity of liquid steel and solid-liquid steel in the course of rheological research with the use of a high temperature rheometer. The paper reviews the subject of measuring and modelling the viscosity value of steel with the use of equations and data available in the literature. It also presents the difficulties connected to rheological measurements of liquid steel and metallurgical slag.
Design/methodology/approach: The main purpose of this paper is to present the issues relating to rheological measurements and the possibilities of their application in metallurgy.
Findings: The paper describes the issues pertaining to the viscosity measurements of liquid and metallurgical slag.
Research limitations/implications: In the future the authors are planning to develop an empirical model which would include rheological parameters and would be used to calculate the viscosity of liquid iron solutions on the basis of conducted rheological measurements of liquid steel.
Practical implications: The results of investigation might be used in the future in semi-solid metal (SSM) forming. A fundamental and detailed understanding of the steel rheology is crucial for industrialization.
Originality/value: The paper presents the issues connected to the subject of and difficulties encountered in the course of rheological measurements of liquid ferroalloys and metallurgical slag.
Keywords: Steel ;Viscosity; Rheology; Rheological models; Rheometer

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1. Introduction

Steel rheological research is extremely innovative but also difficult to conduct from the technical point of view. Main problems concerning the rheological measurements of liquid ferroalloys include: the high melting temperature of the analysed medium, high reactivity of steel - especially its oxidation, relatively high costs of experiments - connected to the use and short life span of tools used for the above mentioned experiments.

The innovative character of the rheological measurement of steel stems from the possibility of designing an experiment that would involve the use of a cutting edge measurement tool - the high temperature rheometer. This device is equipped with a furnace which allows to heat the analysed alloy up to the desired temperature (above 1500°C), to control the temperature of the alloy during the measurement and also to continuously modify the force values affecting the analysed medium. The high temperature rheometer, also known as the multipoint absolute viscometer [1], is an universal device used to analyse both Newtonian and non-Newtonian fluids. Until recently the research into liquid ferroalloys with high melting temperatures was practically impossible due to the unavailability of measurement instruments. Viscometers, which used to be the only instruments available to measure viscosity of fluids, allowed only a single point measurement of the relative viscosity value in low temperatures. In case of measurements conducted with conventional viscometers it was impossible to apply different forces to the analysed medium, which in practice prevented the researchers from conducting research into non-Newtonian fluids.

Currently the dominating opinion is that the liquid steel is a Newtonian fluid defined by the change in the viscosity value depending only on changes in temperature, pressure and the chemical composition. The purpose of authors' research [2,3,4] is to verify the current knowledge concerning liquid steel viscosity and to expand it by conducting rheological research into ferroalloys in a fully liquid or solid-liquid state.

The rheological measurements (including the viscosity measurements) of liquid steel are rarely conducted and rheological models allowing the viscosity value calculations are very often only theoretical (relying on thermodynamic values) or semi-empirical ones (developed for low melting point metal alloys [5]). That is why, there is a need to develop an empirical rheological model for liquid steel which would take into account the values of such rheological parameters as: shear rate, shear time in relation to the analysed medium. The equations allowing to calculate the viscosity of ferroalloys are implemented in commercial software used for thermodynamic calculations such as FactSage. They are also used in the applications designed to model the casting process, e.g. ProCAST. From this point of view the ferroalloy viscosity is one of the most important features influencing the chemical reactions at the boundaries of metal and slag phases in steelmaking processes and blast furnace processes.

The rheological measurements concerning solid-liquid ferroalloys can provide helpful information in order to develop and model the thixotropic forming process [6]. In case of the above mentioned processes the ferroalloy viscosity plays a key role in filling of the matrix properly and the pushing out the deformed material in the thixotropic forging process. It also affects directly the casting of the liquid metal during the casting operations in solid-liquid state. The formation of steel in solid-liquid state and of high melting point alloys (e.g. titanium, chromium, nickel) are in contrast to thixoforming of low melting point alloys (e.g. aluminium, magnesium), still being perfected and improved in laboratory conditions. They have not been applied in the industrial environment yet.

2. The concept of viscosity

Viscosity is a feature of solid, liquid or gaseous bodies which causes the deformation rate of the body to be proportional to the shear stress present in this body. Viscosity is a feature of fluids, gases and plastic solid bodies. It characterises their internal flow resistance. Viscosity is defined for the laminar type of flow which refers to the flow of layers not subject to mixing. This flow takes place at low rates. Viscosity refers to the ability of transferring the momentum between neighbouring layers of fluid moving at different rates. The phenomenon occurs as a result of shear stress present at the boundaries. The difference in the rate of layers is referred to as the shear rate. One can name two different types of viscosity:

Dynamic viscosity

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{1}$$

where:
τ- shear stress,
$\dot{\gamma}$ - shear rate.

Pascal second is the unit of dynamic viscosity in the system SI or centipoise in the system CGS (1 Pa s = 1000 cP).

Kinematic viscosity

$$\nu = \frac{\eta}{\rho} \tag{2}$$

where:
ρ - fluid density.

$\frac{m^2}{s}$ is the unit of kinematic viscosity in system SI or centistokes in the system CGS $\left(cSt = \frac{mm^2}{s}\right)$.

Newtonian fluids are ideally viscous. They are characterized by a linear relation of the shear stress to the shear rate (Equation 1). In case of laminar flow by using the Newton law one can calculate viscosity resistance accompanying the movement in the viscous medium of bodies of different shape and flow rate (fluids, gases, pastes, suspensions, emulsions).

In case of Newtonian fluids the dynamic viscosity value measured for a given chemical composition is constant in a given temperature and given pressure conditions. Non-Newtonian fluids are characterized by changes of dynamic viscosity with time. Industrial viscosity measurements of non-Newtonian fluids involve the same instruments which are used in case of viscosity measurements of Newtonian fluids. The measurement procedures, however, are modified and additional indexes are used to characterize the viscosity of the fluids.

In case of non-laminar flows (also known as turbulent flows) the theoretical model is more complex and requires the implementation of other measures, e.g. turbulent viscosity.

The concept of relative viscosity (also known as agreed viscosity) is used in order to compare the features of different fluids. Relative viscosity refers to a non-dimensional number calculated according to a defined relation, e.g. as a relation between the viscosity of the analysed fluid and the model fluid:

Relative viscosity

$$h_{wzg} = \frac{h_c}{h_w} \tag{3}$$

where:
h_c - dynamic viscosity of the analysed fluid in temperature T_c expressed in Pa s,
h_w - dynamic viscosity of the model fluid (usually water) in given T_w - expressed in Pa s.

3. Rheology, rheometry and viscometry

Rheology is a science which deals with deformation aspects (flow) of real bodies under the influence of stress applied to them. Rheological research is not focused on the movement of the body in its entirety but in the movements of some of its elements with relation to others. According to the definition presented by Reiner and Scott Blair [7] rheology is a study of matter deformation, and among other things of its flow.

Rheology describes the phenomena which occur in a wide area between the solid and liquid state. Rheology can be treated then as a science dealing with the behaviour of real substances which when subject to deformation show more than one basic rheological property: elasticity or viscosity.

Rheology is an interdisciplinary science, which results in the existence of a wide variety of approaches, experimental methods and results applications:

Four basic directions of rheological research can be named [1]:

1. Phenomenal rheology or macrorheology - a direction of rheological studies which focuses on the description of phenomena occurring in the course of real bodies deformation in a macro scale. In this type of approach the molecular structure of the matter is not taken into consideration, the continuous medium approach is used.
2. Structural rheology and microrheology - this type of research aims to discover the relations between the substance structure at the micro level and its rheological properties. Microrheological research have wide applications especially in the study of polymers.
3. Rheometry - deals with empirical assessment of rheological parameters characterising the properties of fluids.
4. Applied rheology or technical rheology - this direction of research concentrates on describing the flow of fluids with complex rheological properties in processes of the practical importance.

Viscometry is a section of rheology which focuses on determining the relations between the shear stress and the shear rate. Such measurements are very common and have been conducted for a long time in order to determine the rheological properties of Newtonian fluids, i.e. the viscosity value. Most of viscometers are designed to study Newtonian fluids and are not used in case of the non-Newtonian ones. Such viscometers make it possible to measure simultaneously the shear stress value and the shear rate in many points of the system. The structure of efflux viscometers of the Engler type or the falling ball viscometers of the Hoeppler type is based on the hydrodynamic effects present in the device. The viscosity values obtained as a result of such measurements have only a comparative character. It is necessary to use an absolute multipoint viscometer in order to determine simultaneously the shear stress and the shear rate values in many points of the system in such a way that would allow the flow description using the flow curve ($\tau = \eta \cdot \dot{\gamma}$). This absolute multipoint viscometer is referred to as a rheometer. A single point on the flow curve fully characterises the Newtonian fluid. Yet it is not sufficient to describe the rheological properties of a non-Newtonian fluid. Two fluids with different rheological properties can have the same intersection point on the flow curve - they can be characterised by the same viscosity value for a given shear rate. That is why, it is important to characterise the flow of the non-Newtonian fluid in the widest possible range of shear rate values.

4. Fluid classification

Research development concerning the fluid flow can be divided into three stages resulting from the fluid classification adopted in each case.

The first stage included analysing the fluid flow on the basis of the flow of ideal fluids, i.e. non-viscous and incompressible ones. In case of such a flow the shear stress is not present as it is a non-viscous flow. The concept of the ideal fluid fails in the majority of real fluid flows.

The second stage of fluid mechanics development was brought about by Prandtl who developed and described the theory of boundary layer in 1904 [6]. This theory made it possible to develop the concept of the simplest real fluid - the Newtonian fluid.

The increasing importance of practical processes involving the use of fluids with complex rheological properties led to the beginning of the third stage of rheology and fluid mechanics development. As a result of these studies it was concluded that there are many fluids which do not comply with the Newton law and thus belong to the group of non-Newtonian fluids. Figure 1 presents a fluid classification scheme

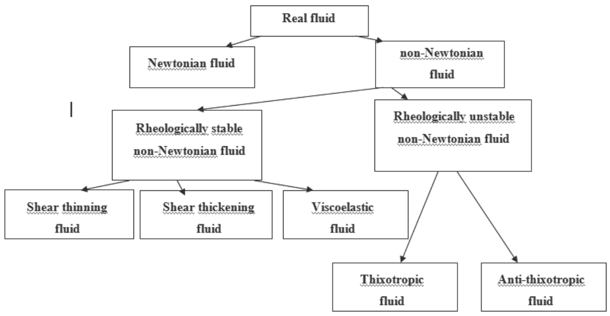

Fig. 1. Fluid classification [1]

Fluids whose viscosity is not a constant value in given temperature and pressure are referred to as non-Newtonian fluids. In general it can be said that the viscosity of such fluids depends on the time and the shear rate.

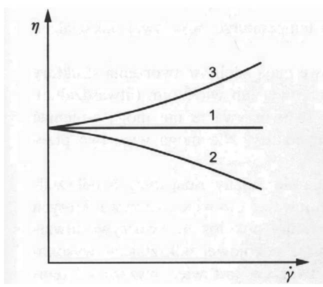

Fig. 2. Viscosity curves for fluids without the flow boundary: 1) Newtonian fluid, η = const; 2) shear thinning fluid, $\eta \neq const$; 3) shear thickening fluid, $\eta \neq const$

The viscosity curve No. 1 in Figure 2 refers to the Newtonian fluid whose viscosity does not change with time and irrespectively of changes in shear rate it is constant. Curves No. 2 and 3 constitute examples of non-Newtonian fluids. Viscosity curve No. 2 represents the shear thinning fluid - in this case the viscosity value decreases with an increase in the shear rate. Curve no. 3 presents the viscosity of shear thickening fluid whose viscosity values increase with an increase in the shear rate. In practice the most commonly encountered fluids are those characterised by thinning of the structure under the influence of the applied forces.

5. Rheological measurement methods in metallurgy

Rheometry is a section of rheology which with the use of proper tools deals with the measurement of rheological properties. The term "rheological properties" is understood as a set of parameters describing the fluid flow [1]. Viscometry, on the other hand, is a branch of rheometry which focuses on determining the relations between the shear stress and the shear rate.

The rheometer is a measurement device allowing an absolute measurement of the viscosity value (on the basis of the known forces in the system and the geometry of the measurement system) within the widest range of shear rate possible. In the course of laboratory research the values of shear rate were selected in such a way that they would reflect the real process. The measurement methods include the following:

- capillary methods,
- falling ball methods
- rotation methods,
    - coaxial cylinders
    - cone - plate,
    - plate-plate,
    - with a movable cylinder,
- oscillation methods.

The method of analysing viscosity with the use of the capillary viscometer involves a capillary with a known geometry. A decrease in pressure is measured along the capillary with a determined flow coefficient. The structure of such a viscometer is very complex. The geometry of a capillary is usually very small in relation to the entire installation connected to the measurement. That is why, in order to obtain a constant flow coefficient it is necessary to use displacement pumps. It is important to maintain stable temperature and monitor carefully the changes in the flow and pressure while the viscometer is working. Coaxial cylinders rheometer are the most popular of the already mentioned types of rotation rheometers.

In case of the falling ball method the viscosity measurement consists in measuring the rate at which the ball submerges and emerges from the analysed fluid. The measurement is conducted in a cylindrical tube. Due to the high temperatures of the analysed fluids the method requires taking special safety precautions in the course of measurement.

As for the rotation measurement methods, the viscous resistance is measured on a rotating disc or cylinder. In case of the rotation measurement method it is possible to read torque from the device, which is transferred by the layer of fluid placed between two elements. In the course of the measurement the analysed sample shears with a specific volume change as a result of the rotation of the measurement element.

The oscillation method is the last way of measuring viscosity. In this case the system, similarly to the rotation method with coaxial cylinders, consists of an outer cylinder and an inner cylinder submerged in the fluid (the so called crucible). The crucible oscillates around the axes of cylinder in the course of measurements. This methods is applied in case of high viscosity fluid measurements (including steel and solid-liquid slag).

Figure 3 presents a scheme of viscosity measurement methods used in metallurgy.

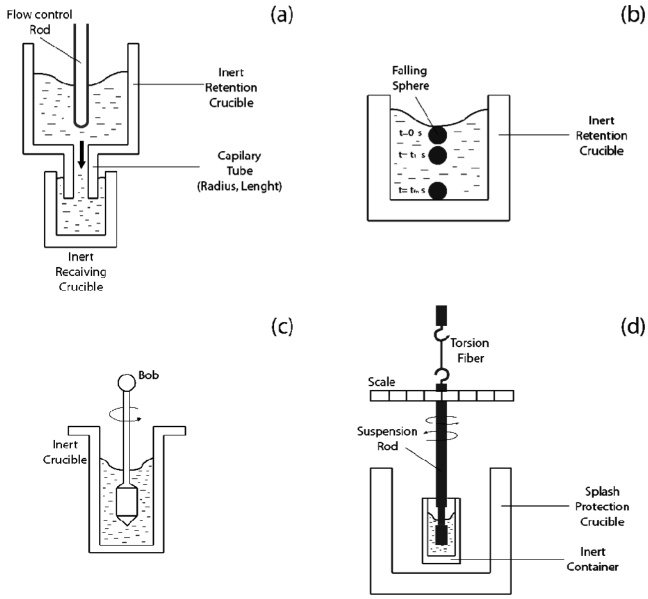

Fig. 3. Viscosity measurement methods used in metallurgy a) capillary method, b) falling ball method, c) rotating cylinders method, d) oscillation method [8]

6. The application of rheological research in metallurgy

The purpose of conducting rheological research is to determine the values of rheological parameters characterizing the fluid flow. Viscosity is the most important rheological value, which is vital for proper understanding of hydrodynamic and kinetic phenomena taking place during metal casting.

- The rate at which gas bubbles and non-metallic inclusions appear in the metal is closely connected to viscosity.
- The rate at which the reaction takes place at the metal-slag boundary can be determined by continuous viscosity measurement of this media.
- Viscosity allows to determine the values of other parameters: diffusivity, thermal conductivity of the liquid metal.

The rheological parameters values obtained in the course of rheological research can be used to simulate the solidification phenomena, liquid metal movements, the influence on the chemical reaction kinetics in the metal-slag-gas system as well as other phenomena occurring in liquid metals. All mathematical and physical models of the above mentioned phenomena present viscosity (rheological properties) as one of the fundamental parameters.

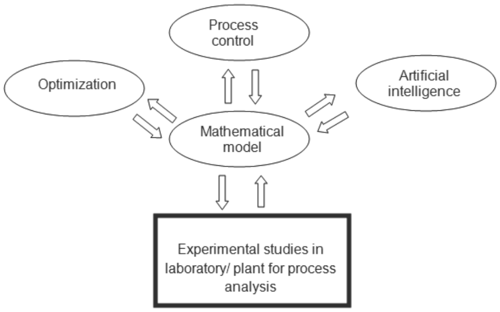

Fig. 4. Scheme illustrating the application of mathematical modelling in steelmaking processes [9]

Figure 4 presents a scheme illustrating the stages of mathematical modelling of the phenomena occurring in steelmaking processes. This modelling has 4 levels:

- Conducting the experimental analysis - within the interests of the authors of this paper - in the context of rheological research into liquid ferroalloys [2,3,4],
- The application of neural networks, expert systems, etc. for modelling artificial intelligence tools,
- Process optimisation
- Process control

The authors [9] developed a list of driving forces present in steelmaking processes causing the flow (movement) of liquid products of metallurgical processes. The knowledge concerning the type and size of the forces present in the actual processes is important in order to replicate them in laboratory conditions. Furthermore, these values are used for numerical modelling of metallurgical processes. That is why, it is important to characterise the driving forces from the quantitative and qualitative point of view. In case of rheological research it is important for shear rate to be analysed in the widest range possible keeping in mind the values present in real conditions. The selected types of steelmaking processes together with accompanying types of driving forces were presented in Table 1.

It is assumed that fluids in steelmaking conditions behave in general like Newtonian fluids - they show constant shear stress irrespective of the shear rate, or as incompressible fluids - they show changes in density with time [9].

Most of the existing rheological models allowing to calculate the viscosity values are purely theoretical ones. They use themophysical values (enthalpy, Gibbs free energy, mole fractions, etc.). Part of the above mentioned models is based on experimental data and constitutes a group of semi-empirical equations. However, the research that helped to develop these models most commonly referred to low melting metals (aluminium, copper, antimony).

Table 1.
Driving forces and intensity of agitation in steelmaking processes [9]

Processing and transfer operations	Driving forces	Intensity of agitation
Oxygen steelmaking	• jet momentum (from top injection) • buoyancy (from bottom injection)	approximately tens of m/s to hundred of m/s
EAF steelmaking	• arc (plasma) momentum • buoyancy (from bottom injection)	tens of cm/s to a couple of m/s
Tapping	• gravitation forces	few m/s to tens of m/s
Continuous casting	• gravitational for ces • electromotive for ces in the mould region	tens of cm/s to a couple of m/s mm/s in the submould region

The simplest and the oldest relations include the Moelwyn - Hughes model, which was developed for two component solutions [5]:

$$\eta = (\eta_1 X_1 + \eta_2 X_2)\left(1 - 2\frac{\Delta H_m}{RT}\right) \tag{4}$$

in which:
η, η_1, η_2 - viscosity of alloys and metals [Pa·s],
X_1, X_2 - mole fraction [ppm],
R - gas constant [J/(mol·K)],
T -temperature [K],
H_m - molar enthalpy of mixing liquid alloys [kJ/mol].

The extension of the above mentioned model came in 1987 when a formula for multi-component metal solutions was developed by Du Sichen, Boygen and Seetharaman [5]:

$$\eta = A\exp\left(\frac{G^*}{RT}\right) \tag{5}$$

$$A = \frac{hN\rho}{M} \tag{6}$$

$$G^* = \sum_{i=1}^{n} X_i G_i^* + RT\sum_{i=1}^{n-1}\sum_{k=i+1}^{n} X_i X_k + \Delta G' \tag{7}$$

where:
G* - Gibbs activation energy [kJ/mol],
ΔG’ - Gibbs free energy change [kJ/mol],
T - temperature [K],
G^*_i -components activation energy [kJ/mol],
R -gas constant [J/(mol·K)],
ρ - alloys density [kg/m^3],
N - Avogadro’s number [mol^{-1}],
h - Planck constant [J·s],
M - atomic mass of alloy components [u].

In Poland M. Kucharski was involved in the development of equations used to calculate the viscosity of liquid metal solutions. He suggested the use of component activity coefficient and the partial molar volume in order to calculate the viscosity of liquid low melting metals [10].

7. The difficulties encountered in the course of rheological research into metallurgical fluids

The difficulties encountered are connected to the development of experimental methodology as well as the poor availability of rheological measurement instruments used in high temperature conditions (approx. 1500°C) and equipped with a head allowing the measurement of a very low value of torque. These difficulties result in the fact that the literature lacks experimental data based on rheological measurements of liquid iron solutions and viscosity is most commonly calculated using theoretical mathematical models.

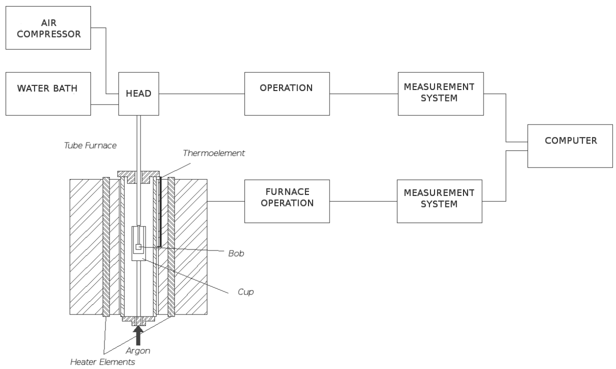

Fig. 5. Scheme of a high temperature rheometer FRS1600

Figure 5 presents a scheme of a high temperature rheometer FRS1600 equipped with a pipe furnace allowing to reach the temperature of approx. 1520°C. The above mentioned rheometer works in a system of concentric cylinders, with a rotating inner cylinder. The device is also equipped with an air bearing which allows to conduct very detailed measurements. Unfortunately, the presence of the air bearing makes it impossible (considering its present structure) to install the device inside the vacuum chamber as this bearing requires the air access. Due to this fact rheological research is conducted in the protective atmosphere, which ensures the protection of the analysed material against oxidation. It is not, however, fully controlled in the course of the measurement.

The materials used to make measurement tools must be selected in such a way that they would not react with the analysed sample and ensure the presence of shear stress in the system. In case of reducing slag platinum is the material to be used for measurement tools. Yet due to its price it is not used for research purposes. Molybdenum could also be used. It is, however, subject to oxidation during the experiments in an atmosphere that is not fully controlled. What is more, due to high temperatures and different thermal expansion of steel and ceramics the measurement tools (with Al_2O_3) are vulnerable to high thermal stress. This leads to their frequent replacement and as a consequence it increases the research costs.

The precision of temperature measurements is another major problem that is encountered by researchers in the course of rheological measurements of steel and metallurgical slag. Considering the current structure of the device no direct method of temperature measurement of the sample has been developed. The sample temperature is determined on the basis of temperature measurement conducted in the furnace and estimated using the previously developed mathematical equations. Despite the progress made when it comes to rheological research into liquid ferroalloys and slag, there is still much to be done about the constancy and stability of temperature in the entire sample volume as well as the constancy of linear dimensions of the measurement tools used. It is directly dependent on high material costs and development costs concerning such measurement systems.

To sum up, it needs to be emphasized that the rheological measurements of liquid steel are one of the most difficult measurements of such type. They require highly specialized equipment as well as significant experience in interpreting the obtained results.

Acknowledgements

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References

[1] Z. Kembłowski, Rheometry of non-Newtonian fluids, WNT, Warsaw, 1973 (in Polish).
[2] P. Migas, M. Korolczuk-Hejnak, M. Karbowniczek, Rheological measurements of selected grades of liquid steels, Rheology - Theory and Application 2 (2011) 191-202.
[3] M. Korolczuk-Hejnak, P. Migas, Selected grades of steel as rheologically defined liquid bodies, Archives of Metallurgy and Materials 57/2 (2012) 583-591.
[4] M. Korolczuk-Hejnak, P. Migas, Analysis of selected liquid steel viscosity, Archives of Metallurgy and Materials 57/4 (2012).
[5] W. Gąsior, Z. Moser, Modeling of metals viscosity - comparative analysis, Publishing House „AKAPIT", Cracow, 2010, 47-55 (in Polish).
[6] G. Hirt, R. Kopp (Eds.), Thixoforming, Semi-solid metal processing, WILEY-VCH Verlag GmbH & Co. KGaA, Wienheim, 2009.
[7] M. Reiner, Theoretical rheology, PWN, Warsaw, 1958 (in Polish).
[8] I. Sohn, D.J. Min, A reviewer of the relationship between viscosity and the structure of calcium-silicate-based slags in ironmaking, Steel Research International 83/7 (2012) 611-630.
[9] D. Mazumdar, J.W. Evans, Modeling of steelmaking processes, CRC Press Taylor and Francis Group, USA, 2010.
[10] M. Kucharski, Viscosity of metals solutions, melted salts with a common anion and slags, AGH Scientific Books, Cracow, 1989 (in Polish).