CALCULATION OF ACTIVATION ENERGY OF VISCOSITY FOR EVALUATION OF METALLURGICAL SLAG MELTS STRUCTURE

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Measurements of metallurgical slag viscosity were performed. The studied slags have been found to have close viscosity (η) values over a wide temperature range from 1453 to 1873 K. The results demonstrate that the viscosity decreases with the increase of CaO/SiO$_2$ ratio. Temperature inflection points (T') are found in the $\eta = f(T)$ dependence, and they are consistent with the chemical composition of slags below 1453 K. The value of T' increases with the increase of CaO/SiO$_2$ ratio. The activation energy of viscosity E_η was calculated by using the Frenkel equation. With the increase of temperature, E_η decreases and does not depend on the chemical composition of slags. In the temperature region from 1473 to 1573 K, the temperature dependence of $E_\eta = f(T)$ demonstrates energy deviations from the trend line indicating the relaxation of structurally sensitive bonds. The results obtained are of practical importance for the selection of rational slags for different metallurgical processes.

Keywords: slag, viscosity, activation energy, structure

1. Introduction

Nowadays, the most common theory of slag melts is the ion theory, which allows one to substantiate a number of phenomena (e.g. electrical conductivity) unexplained by the molecular theory [1]. For metallurgical melts, the ion theory was first proposed by Temkin [2]. In accordance with the ion theory of the slag structure, the particles forming the molten slag are not neutral molecules as in Ref. [3], but ions that interact electrochemically. In slag melts, the interaction between the constituent particles (covalent, ionic, metallic, etc.) can be different, and this determines their properties.

Today there are many models and concepts of slag melts structure which use the ion theory [4–8]. This confirms the scientific validity and practical importance of ion theory, but even this theory does not provide a full explanation of the slag melts structure (for example, the presence in the melt of the indivisible covalent bond O=Si=O, which forms polymer silicate phases/molecules).

At all stages of the steel smelting process, the slag is an integral product of smelting. The physical properties of the slag, in particular its viscosity, determine the quality of the metal and the intensity of the process, which affects the energy consumption. Viscosity is one of the main technologically important properties of metallurgical slags and slag-forming mixtures, the property which depends on their chemical composition and temperature. The change of slag viscosity influences the diffusion of sulphur, nitrogen and oxygen in the system 'metal-slag'. The viscosity also directly affects the stability of the lining of metallurgical equipment [9].

Metallurgical slags can be a raw material for the construction industry (for example, as an additive in the production of mineral wool), which is a part of the European Raw Materials Alliance (ERMA) cyclical plan [10]. Therefore, it is very important to study the slag properties. This knowledge improves metallurgical technology and extends the use of slag.

2. Theory

Viscosity (internal friction) is the property of a liquid, as well as gaseous and solid bodies, to resist

their flow, i.e. the movement of one layer with respect to the other, under the action of external forces. According to Newton for the liquid in the laminar flow mode, the following equation is applicable:

$$P = \eta \left(\frac{\mathrm{d}v}{\mathrm{d}y} \right) S. \tag{1}$$

Here P is the force required to move the fluid layer in the direction parallel to the flow, $\mathrm{d}v/\mathrm{d}y$ is the speed gradient in the direction y perpendicular to the motion, S is the area, and η is the dynamic viscosity coefficient. Based on Eq. (1), viscosity is defined as the force P applied to the unit of shear area S, with a speed gradient $\mathrm{d}v/\mathrm{d}y$.

The prediction of viscosity of oxide melts (metallurgical slags, glass, etc.) is considered in Refs. [1, 4, 7, 9, 11]. Their analysis demonstrates that there are different approaches to assess the temperature dependence of viscosity of different oxide systems.

A set of equations has been proposed to express mathematically the temperature dependence of dynamic viscosity. In particular, Bachinsky (see, e.g. [11]) proposed the following equation:

$$\eta = \frac{B}{V - b}. \tag{2}$$

Here B and b are constants, and V is the specific volume of a liquid as a function of temperature and pressure. For some binary and triple silicate melts, an empirical Le Chatelier equation (see, e.g. [9]) has been proposed:

$$\log\log\eta = A - BT. \tag{3}$$

Here A and B are constants, and T is temperature. Equation (3) in various modifications is used to calculate the viscosity of different glass materials. Studying the experimental dependence of viscosity on temperature it was found [11] that in practice it is useful to apply the empirical formula

$$\log\eta = A + \frac{B}{T^2}. \tag{4}$$

According to Frenkel [12], the viscosity has the form of an exponential equation, similar to the Arrhenius equation, characterizing the dependence of the reaction velocity constant on temperature,

$$\eta = A \cdot \mathrm{e}^{\frac{E_\eta}{RT}}, \tag{5}$$

where A is the constant for the liquid, R is the universal gas constant, and E_η is the viscosity activation energy. There are also other equations of the temperature dependence of viscosity, e.g. the Vogel, Tamman, Fulcher equation

$$\ln[\eta(T)] = A_{\mathrm{VTF}} + \frac{B_{\mathrm{VTF}}}{R(T - T_\mathrm{V})}, \tag{6}$$

where A_{VTF}, B_{VTF} and T_V (Vogel temperature) are the constants determined by adjustment to the experimental data, and the Adam-Gibbs equation

$$\ln[\eta(T)] = A_{\mathrm{AG}} + \frac{B_{\mathrm{AG}}}{TS_{\mathrm{conf}}(T)}, \tag{7}$$

where A_{AG} and B_{AG} are adjustable constants, and $S_{\mathrm{conf}}(T)$ is the configuration entropy. Also, the Douglas equation is proposed for silicate glass (see, e.g. [13]):

$$\eta(T) = AT \exp\left(\frac{B}{RT} \right)\left[1 + C \exp\left(\frac{D}{RT} \right) \right]. \tag{8}$$

Here A, B, C and D are constants.

The variety of mathematical equations for the temperature dependence of dynamic viscosity indicates the complexity of the nature of fluid viscosity. The difficulties encountered in using the mathematical equations for the calculation of viscosity are due to the lack of a mathematical apparatus for analyzing the inextricable chain 'structure–property' solutions and melts of multi-component systems depending on their composition and temperature. The influence of the structure can only be considered semi-empirically, for example, by determining the activation energy of the system.

3. Research materials and experimental methods

In Table 1, we present the chemical composition of metallurgical slags obtained in the experiments.

Measurements of the viscosity of the slags given in Table 1 were performed in an induction furnace blown by argon 5.0 (<2 ppm O_2) in molybdenum crucifixes using a rotary rheometer MCR 301 AntonPaar [14]. A molybdenum

Table 1. Chemical composition of metallurgical slags.

No. of slags	Chemical composition of slags, % mass							CaO/SiO$_2$
	SiO$_2$	Al$_2$O$_3$	CaO	MnO	MgO	Fe$_{total}$	S	
5482	40.7	8.5	45.2	0.29	4.6	0.27	0.89	1.111
5483	40.7	8	46	0.16	4.5	0.23	0.85	1.130
5494	41.2	7.8	45.7	0.1	4.3	0.23	0.69	1.109
25622	38.8	6.73	47.9	0.24	5.63	0.66	0.69	1.235
25643	39.7	6.81	46.9	0.41	4.43	0.45	0.63	1.181

crucible with the pre-melted slag was installed in a graphite heater located in the induction furnace and then heated to 1773 and 1873 K. The soak time at this temperature was about 30 min. The temperature was controlled by two type B thermocouples. The viscosity measurements were performed with a continuous cooling of the slag at a speed of 10 K/min and a constant torque rate of 30 rpm. The viscosity values were recorded automatically every 1 K. For each slag, three measurements were performed (two from 1773 K and one from 1873 K). The results of the experiments are presented in Figs. 1 and 2.

From the analysis of the data obtained, the studied slags have close viscosity values in a wide temperature range from 1453 to 1873 K. It should be noted that with the increase of CaO/SiO$_2$ ratio in the slag, the viscosity decreases (see Fig. 2).

At the slag temperature below 1453 K, there are inflections on the viscosity–temperature (Fig. 1) charts. Thus, for the slags #25622 and #25645

the inflection temperature (T') is almost the same (1448 K), and for the slags #5483, #5482 and #5494 the values of T' are, respectively, at 1435, 1373 and 1368 K. The inflection temperature depends on the chemical composition of the slag. As the CaO/SiO$_2$ ratio increases, the inflection temperature T' also increases.

The dependence of viscosity on the chemical composition and temperature may be a consequence of changes in the structure which, at a constant chemical composition, depend on the temperature. The values of viscosity of all slags are similar in a temperature range of 1453–1773 K. This may be due to the structure and strength of the O=Si=O bonds. During the melt cooling process, new structural phases (usually crystalline) occur and grow, significantly affecting viscosity. The inflection temperature (T') (Fig. 1) indicates the formation of a critical mass of the crystalline phase in the slag melt, which causes a sharp increase of viscosity in a temperature range of 1367–1453 K.
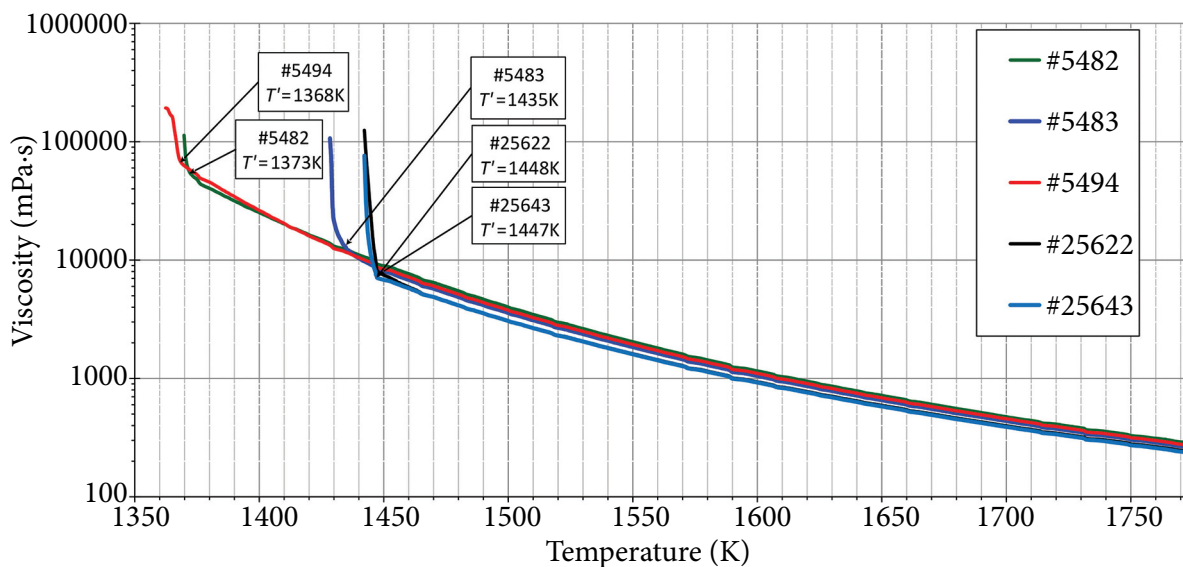

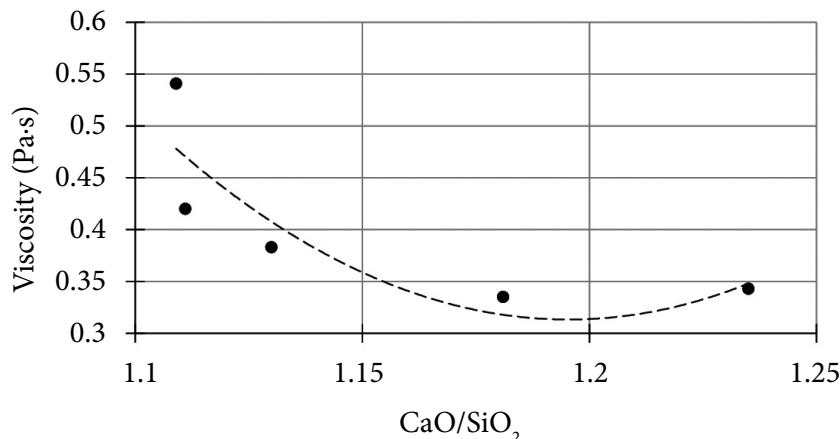Fig. 1. Viscosity of the investigated slags as a function of temperature.

Fig. 2. Connection between the viscosity and chemical composition of metallurgical slags at 1723 K.

4. Evaluation of the activation energy of viscosity

At temperatures close to the melting point, the thermal movement of the structural particles in liquids should be the same as in solid bodies [12]. Based on that, the nature of elasticity and fluidity of liquid is explained as thermal oscillation of structural particles about 'temporary' equilibrium positions. The equilibrium positions of the structural particles remain unchanged only for a limited time, so that each particle moves in the volume of the whole matter. This explains the long-term absence of a liquid state, which is characteristic of solids.

The transition of the structural particle from one equilibrium position to another is related to an increase in the free energy of the bond of a structural particle to the surrounding particles by the quantity E (activation energy). When the structural particle moves to a new position, excess energy is transferred, preventing the particle from returning to its original position.

Further, we demonstrate that with the increase of temperature the activation energy decreases, due to changes in the bonds of the structural particles of melt, accompanied by the increase in its volume and the degree of the bond structure disorder. The estimation of the activation energy of viscous current can be used to characterize the melt structural changes caused by the breakdown of structural particle bonds.

We used Eq. (5) to calculate the activation energy of viscosity E_η [15]. It is calculated in a narrow temperature range using the dependence ln (η) = $f(T)$. For the temperature sections with increments of 283 K, the dependence of ln (η) = $f(T)$ is linear, which can be interpreted as melt structure constancy, i.e. the activation energy does not change. The calculations of E_η for the studied slags demonstrate that with the increase of temperature the E_η decreases (Fig. 3) – it is the trend which is in agreement with the Frenkel's molecular kinetic theory of liquids.

As seen in Fig. 3, there is a small increase in the activation energy close to 1748 K. The energy spike is also observed close to 1573 K (slags #5482, #25643 and #25622). Slag #5494 has energy E_η lapses within a temperature range of 1473–1533 K. Unlike other slags, that of #5483 has a subtle deviation (reduction) of activation energy at about 1473 K. In the temperature range 1473–1573 K, the energy E_η deviation in the $E_\eta = f(T)$ dependence indicates the relaxation of structurally sensitive bonds. This conclusion is consistent with our studies of melting temperatures for slags #25622 and #5494 performed using a high-temperature microscope *Carl Zeiss* MNO-2. The temperature in the heating zone was controlled by a type S thermocouple. Prior to the experimental measurements, the materials were crushed, then compressed into a cylinder with a radius of 3 mm and a height of 4 mm. Corundum was used as the substrate on which the test material was placed. As a result of the melting, the full flow point was set to 1538 K for the slag #25622 and 1473 K for the slag #5494.

It is important to note that the calculated values of activation energies of viscosity are completely independent of the chemical composition of the slags,
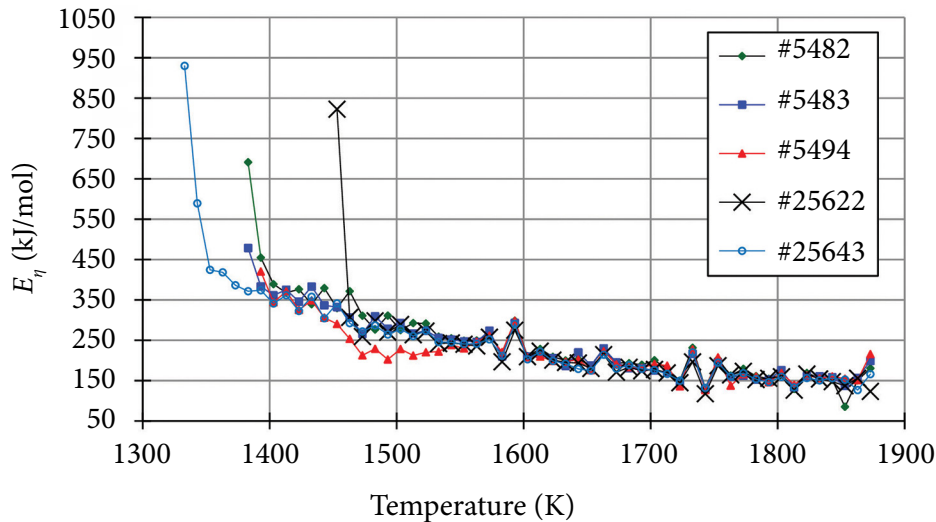
Fig. 3. Activation energy (E_η) of the viscosity of investigated slabs as a function of temperature.

which may indicate similar structural particle bonds in a temperature range of 1373–1873 K.

5. Discussion

The results obtained can give an idea of the structure of the studied slag melts if the necessary attention is paid to the ability of slag melts to conduct electric current. The electrical conductivity falls sharply during solidification further confirming the ionic nature of liquid slags. This behaviour of slag melts is explained by the fact that their viscosity is determined by larger ions (mainly $Si_xO_y^{z-}$ anions), while the electrical conductivity by more mobile ions (Ca^{2+}, Mg^{2+}, F^{2-}, etc). The electrical conductivity of slag melts (silicates), like molten salts, increases with the increase of temperature – this fact makes it possible to classify them as semiconductors.

Thus, the results obtained studying the dependences $\eta = f(T)$ and $E_\eta = f(T)$ may indicate that the structure of the slag melt in the temperature range 1373–1873 K is mainly represented by polymer (amorphous) structures which consist of $Si_xO_y^{z-}$ anions. The similarity of the structures and connections of the $Si_xO_y^{z-}$ anions demonstrates that E_η does not depend on the chemical composition. The presence of conductive ions (Ca^{2+}, Mg^{2+}, F^{2+}, etc.) in the melt at a lower temperature helps to strengthen the cation–anion bonds, and, as a consequence, the crystalline (solid) phase begins

to form. The formation of this phase in the melt at critical temperatures (Fig. 3) results in a sharp increase in their viscosity, and this is consistent with their chemical composition.

The analysis of our results is consistent with Ref. [16], where the phase composition of metallurgical slags and the heterogeneity of their melts were studied. In this paper, it was demonstrated that slag melts can contain quasi-crystalline phases in the temperature range 1723–1873 K, i.e. the slag melt can consist of two liquid phases, which differ in structural particles and the force of their interaction. Such phases might be the dielectric (amorphous) phase, consisting primarily of $Si_xO_y^{z-}$, and the electrically permeable quasi-crystalline phase with current conducting ions.

The study of the structure of slag melts requires, in addition to viscosity, to consider some other properties, in particular, electrical conductivity. The conductive ions interact with the polymer anions which determine the viscosity of the melt.

In conclusion, the viscosity of slag melts is an important physical property which allows one to improve the existing metallurgical technologies of slag melts and the scope of their application. Since today there is no common understanding of the melt structure, the estimation of the degree of structure influence can only be considered semi-empirically, for example, by studying the activation energy of viscosity. Despite some simplifications, the results obtained in this article

are consistent with generally accepted ideas about the structure of slag melts.

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KLAMPUMO AKTYVACIJOS ENERGIJOS SKAIČIAVIMAS METALURGINIO ŠLAKO LYDALŲ STRUKTŪRAI ĮVERTINTI

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