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MATHEMATICAL MODELS FOR CALCULATING THE VALUE OF DYNAMIC VISCOSITY OF A LIQUID

MATEMATYCZNE MODELE DO OBLICZANIA WARTOŚCI LEPKOŚCI DYNAMICZNEJ CIECZY

The objective of this article is to review models for calculating the value of liquid dynamic viscosity. Issues of viscosity and rheological properties of liquid ferrous solutions are important from the perspective of modelling, along with the control of actual production processes related to the manufacturing of metals, including iron and steel. Conducted analysis within literature indicates that there are many theoretical considerations concerning the effect of viscosity of liquid metals solutions. The vast majority of models constitute a group of theoretical or semi-empirical equations, where thermodynamic parameters of solutions, or some parameters determined by experimental methods, are used for calculations of the dynamic viscosity coefficient.

This article presents equations belonging to four groups of models for calculating the value of the dynamic viscosity coefficient: rheological models, non-rheological models, non-rheological and rheological models for calculating viscosity of metals. The last group of equations is developed by own experiments – high temperature rheological liquid steel measurements.

Keywords: viscosity models, rheology, viscosity, viscosity of metals

Celem prezentowanego artykułu jest dokonanie przeglądu modeli służących do obliczania wartości współczynnika lepkości dynamicznej cieczy. Zagadnienia lepkości oraz właściwości reologicznych ciekłych roztworów żelaza są ważne z punktu widzenia modelowania, a także sterowania rzeczywistymi procesami technologicznymi w odniesieniu do wytwarzania metali, w tym surówki i stali. Z przeprowadzonej analizy literaturowej wynika, że istnieje wiele teoretycznych rozważań nad zjawiskiem lepkości ciekłych roztworów metali. Zdecydowana większość modeli stanowi grupę równań teoretycznych, bądź półempirycznych, w których do obliczania wartości współczynnika lepkości dynamicznej wykorzystywane są wielkości termodynamiczne roztworów lub pewne wielkości wyznaczone metodami eksperymentalnymi.

W artykule zaprezentowano równania należące do czterech grup modeli służących do obliczania wartości współczynnika lepkości dynamicznej: modele reologiczne, modele niereologiczne oraz modele niereologiczne oraz reologiczne wykorzystywane do obliczania lepkości metali. Ostatnia grupa równań została opracowana w ramach badań własnych – wysokotemperaturowych pomiarów reologicznych ciekłej stali.

1. Introduction

Rheology is a branch of science that has developed as a branch of physics. Today, however, it is an independent area of knowledge that dates back over 70 years. The objective of rheology is to be able to anticipate either the behaviour of a body caused by the force system applied to it, or the force system that causes the specific behaviours of a body [1].

The rheological behaviour of a material is described by the relationships between stresses, strains, shear rates, and the time in which the material has been subjected to such strains. Such relationships are called rheological equations of the state of the material, or for short – rheological equations [2]. The main task of rheology is to formulate models for describing the behaviours of bodies that have been subjected to a force impact. Descriptions of behaviour of ideal solid and liquid bodies have been formulated in the form of mathematical models that have taken into account the relationships between the

stress, strain, strain rate and the stress growth rate (rheological function [3]).

The concept of the ideal body simplifies theoretical considerations and enables mathematical methods to be applied to the analysis of interesting phenomena. Ideal bodies are only extreme cases which real bodies resemble to a lesser or higher degree. In specific conditions rheological properties of real bodies are approximated by mathematical rheological models; these are combinations of three basic rheological models of ideal bodies, such as [1]:

- Hooke's ideally elastic body,
- St. Venant's ideally plastic body,
- Newton's ideally viscous fluid.

Viscosity is a measure of "friction existing in a fluid" or "resistance" that occurs in a liquid or gas during a flow.

The viscosity effect in metallurgical processes is amongst the most important factors affecting the behaviour of reacting phases (metallic, slag and gaseous), with regard to the kinetics

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of mass exchange or chemical reactions [4]. Viscosity plays a significant role in all metallurgical processes – ironmaking, steelmaking, ladle refining, steel casting, and processes related to solidification. It is very important from the standpoint of flow of liquid phases, which are continuously moving during those processes as well as due to the internal structure of the metallic or slag phase, and related abilities to absorb impurities, or their ability to deform in their semi-solid states.

2. Mathematical models

2.1. Rheological models

Rheological properties of many real systems may be described by a Newton’s concept of the ideally viscous fluid (Newtonian fluid). The rheological graph of a Newtonian fluid is made in the coordinate system: shear stress τ versus shear rate $\dot{\gamma}$. The graph of the dependence:

$$\tau = f(\dot{\gamma}) \tag{1}$$

is called the flow curve.

The other method of presenting this dependence is plotting the viscosity curve as a function of shear rate:

$$\eta = f(\dot{\gamma}) \tag{2}$$

In subject literature, many attempts have been made to describe the flow curve with an appropriate rheological mathematical model. The foregoing models are necessary for the analytical solving of problems related to the non-Newtonian fluid flow. Rheological models constitute a group of equations which, apart from the dynamic viscosity also, take other rheological parameters into account - shear rate, shear time. Often the relationship between the shear stress and the shear rate is plotted in the logarithmic coordinates.

The simplest mathematical rheological model that is described by a non-Newtonian fluid flow curve within the range of intermediate shear rates is the so called Ostwald – de Waele power law model in the form of [5, 1]:

$$\tau = k(\dot{\gamma})^n \tag{3}$$

where:

- k – empirically determined constant [N s/m²],
- n – empirically determined index exponent (-),
- τ – shear stress [Pa],
- $\dot{\gamma}$ – shear rate [s⁻¹].

The power law created by W. Ostwald and A. De Waele is the simplest mathematical rheological model of a generalized Newtonian fluid, containing only two constants that need to be determined.

Using the apparent viscosity definition ($\eta \neq 0$, when viscosity changes its value at a constant shear rate value), the so called generalized Newton law may be formulated:

$$\tau = \eta' \dot{\gamma} \tag{4}$$

where:

- τ – shear stress [Pa],

- η' – apparent viscosity [Pa·s],
- $\dot{\gamma}$ – shear rate [s⁻¹].

Equation (4) is only suitable for calculations when a quantitative determination of apparent viscosity has been performed [1]. Therefore, formulations of models that enable this viscosity to be calculated with a better or worse approximation have been attempted for many years.

Most viscosity models have been formulated for the non-Newtonian fluid group that can be described with the generalized Newton law. Many authors believe that the equation (4) enables – in conjunction with an appropriate viscosity model – viscoelastic fluids to be described [1]. This ability results from the fact that in models of viscoelastic fluids, at least one time constant occurs that characterises the elastic effect of a fluid. It follows from the characteristics of the curve determined by Ostwald (the Ostwald model – equation 3) that, within the shear rate range in which a laminar motion occurs, the generalized Newtonian fluid is characterised by two parameters – η_0, η_∞ – limiting viscosities at (respectively) a very low and a very high shear rate. They are used for determining the apparent viscosity value. Often in viscosity models also the τ_m parameter is used – the shear stress at which:

for $\eta_\infty \ll \eta_0$

$$\eta' = \frac{1}{2} (\eta_0 + \eta_\infty) \tag{5}$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],

Because for many generalized Newtonian fluids, viscosity η_∞ is much lower than η_0 . The equation (5) may be simplified as follows:

$$\eta' \approx \frac{1}{2} \eta_0 \tag{6}$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],

The shear stress corresponding to the apparent viscosity of $1/2 \eta_0$ is identified by the symbol $\tau_{1/2}$. The above four components ($\eta_0, \eta_\infty, \tau_m, \tau_{1/2}$) occur in many viscosity models [1].

Viscosity models proposed by various authors are either empirical, or theoretical, or empirical and theoretical. The simplest functions only describe the apparent viscosity within narrow ranges of shear rates. The viscosity models that enable the viscosity value to be calculated within a wide range of shear rates are usually characterized by a complicated formula and are seldom useful for the solving of technical problems. From the perspective of the range of application of viscosity models, these models may be divided into three groups [1]:

- models describing the apparent viscosity within the range of medium shear rates,
- models describing the apparent viscosity within the range of low and medium shear rates,
- models describing the apparent viscosity within the whole range of shear rates for the laminar flow.

A viscosity model that fairly accurately describes the apparent viscosity within the range of medium shear rates is the Ostwald – de Waele power law model (equation 4).

The range of low and medium shear rates may be described with a model formulated by S. B. Ellis, H. Eyring or J. L. Sutterby [1]. Out of these models the Ellis model is most often quoted in the subject literature:

$$\eta' = \frac{\eta_0}{1 + \left(\frac{\tau}{\tau_{1/2}}\right)^{\alpha-1}} \quad (7)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- τ – shear stress [Pa],
- $\tau_{1/2}$ – shear stress corresponding to the apparent viscosity of 1/2 η_0 [Pa],
- α – index exponent, for many alloys it assumes a value within the range 1-3 [-].

The exponent ($\alpha-1$) is the slope of the line obtained by plotting the dependence:

$$\log\left(\frac{\eta_0}{\eta'} - 1\right) = f\left[\log\left(\frac{\tau}{\tau_{1/2}}\right)\right] \quad (8)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- τ – shear stress [Pa],
- $\tau_{1/2}$ – the shear stress corresponding to the apparent viscosity of 1/2 η_0 [Pa],

The other model enabling the viscosity to be calculated at low and medium values of shear rate is a bi-parameter Eyring model:

$$\eta' = \eta_0 \frac{\arcsin h(\beta\dot{\gamma})}{\beta\dot{\gamma}} \quad (9)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- $\dot{\gamma}$ – shear rate [s^{-1}],
- β – characteristic time [s].

Sutterby has presented the generalized Eyring equation that aims at better describing experimental data:

$$\eta' = \left[\eta_0 \frac{\arcsin h(\beta\dot{\gamma})}{\beta\dot{\gamma}}\right]^{\alpha-1} \quad (10)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- $\dot{\gamma}$ – shear rate [s^{-1}],
- β – characteristic time [s],
- α – constant, $\alpha > 1$ [-].

In 1961, the Steiger-Ory model, named after its authors (K. Steiger-Trippi, A. Ory) was formulated:

$$\dot{\gamma} = c_1 \cdot \tau + c_1 \cdot \tau^3 \quad (11)$$

Generalization of formula (9) is also applied to calculate viscosity in the whole range of shear rates.

The Powell model is the first model of this type:

$$\eta' = \eta_\infty + (\eta_0 - \eta_\infty) \left[\eta_0 \frac{\arcsin h(\beta\dot{\gamma})}{\beta\dot{\gamma}}\right] \quad (12)$$

η' – apparent viscosity [Pa·s],

- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- $\dot{\gamma}$ – shear rate [s^{-1}],
- β – characteristic time [s].

The model proposed by Sutterby (10) was generalized into the whole range of shear rates by Eyring:

$$\eta' = \eta_\infty + (\eta_0 - \eta_\infty) \left[\eta_0 \frac{\arcsin h(\beta\dot{\gamma})}{\beta\dot{\gamma}}\right]^{\alpha-1} \quad (13)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- $\dot{\gamma}$ – shear rate [s^{-1}],
- β – characteristic time [s],
- α – constant, $\alpha > 1$ [-].

The whole range of shear rates is also described by the G.R. Seely model, which is a three-parameter model assuming that viscosity changes exponentially with stress:

$$\eta' = \eta_\infty + (\eta_0 - \eta_\infty) \exp -\sigma\tau \quad (14)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- σ – normal stress [Pa],
- τ – shear stress [Pa].

R.L. Peek, Jr. and D.A. McLean have proposed the following model:

$$\eta' = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \frac{\tau}{\tau_m}} \quad (15)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- τ – shear stress [Pa],
- τ_m – shear stress [Pa] when $\eta' = \frac{1}{2}(\eta_0 + \eta_\infty)$.

The Riener-Philippoff model is similar to the Peek and McLean model. In this case, however, the stress ratio is raised to the second power:

$$\eta' = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \left(\frac{\tau}{\tau_m}\right)^2} \quad (16)$$

The generalization of dependences (14) and (15) is in the D.M. Meter model [1]:

$$\eta' = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \left(\frac{\tau}{\tau_m}\right)^{\alpha-1}} \quad (17)$$

where;

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- τ – shear stress [Pa],
- τ_m – shear stress [Pa],
- α – exponent.

The following models constitute a group of equations that have been originally developed for polymers. Now, however, they are also applied to calculate the value of metals viscosity coefficient.

The first model of this type is the M. M. Cross [6, 7] equation:

$$\frac{\eta' - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (c \cdot \dot{\gamma})^p} \quad (18)$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- c – Cross constant [-],
- p – Cross exponent [-],

A small modification to the Cross model has been introduced by P. J. Carreau [6, 7]

$$\frac{\eta' - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + ((c_1 \cdot \dot{\gamma})^2)^p} \quad (19)$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- c – Carreau constant [-],
- p – Carreau exponent [-],

M. Gahleitner [6] has modified this equation (19):

$$\frac{\eta' - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + ((c_1 \cdot \dot{\gamma})^{p_1})^p} \quad (20)$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- c – Carreau constant [-],
- p_1 – Gahleitner exponent [-], when $p_1 = 2$ the model is identical to model (19),

p – Carreau exponent [-],

A further modification to model (19) has been introduced by K. Yasuda, thus creating an equation enabling the pseudo-plastic fluid viscosity value to be calculated. This equation is often quoted in the literature:

$$\frac{\eta' - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + ((\lambda \cdot \dot{\gamma})^{p_1})^{\frac{1-p}{p_1}}} \quad (21)$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- λ – relaxation time [s],
- p_1 – Yasuda exponent [-],

p – index: $p < 1$ – for shear thinning fluids, $p > 1$ – for shear thickening fluids, $p = 1$ – for ideally viscous fluids [-].

A model taking into account the viscosity curve, assuming that $\tau = \tau_c$ when viscosity is equal to $\eta = \frac{\eta_0}{2}$, assuming that the viscosity value η_∞ is lower than viscosity η_0 , has been formulated by I.M. Krieger and T. J. Dougherty [6, 7]:

$$\frac{\eta' - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{\tau_c}{\tau_c + \tau} \quad (22)$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- τ_c – critical stress [Pa],
- τ – shear stress [Pa].

The next equation taking account of the values related to the flow, i.e. the fluid viscosity at a shear rate approaching 0 and ∞ , has been formulated by G.V. Vinogradov and E.S. Malkin [6]:

$$\frac{\eta' - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + c_1 \cdot \dot{\gamma}^p + c_2 \cdot \dot{\gamma}^{2p}} \quad (23)$$

where:

- η' – apparent viscosity [Pa·s],
- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- c_1, c_2, p – constants [-].

In the years 1927 and 1958, S. B. Ellis and A. W. Sisko [6, 7] formulated a model for calculating viscosities for low and high shear rates. Both models contain the c constant of the equation and the p parameter:

$$\tau = \eta_0 \cdot \dot{\gamma} + c \cdot \dot{\gamma}^p \quad (24)$$

$$\tau = c \cdot \dot{\gamma}^p + \eta_\infty \cdot \dot{\gamma} \quad (25)$$

where:

- η_0 – limiting viscosity at a very low shear rate [Pa·s],
- η_∞ – limiting viscosity at a very high shear rate [Pa·s],
- $\dot{\gamma}$ – shear rate [s^{-1}],
- c, p – constants [-].

W. M. Philips and S. Deutsch [6] have formulated a model containing viscosity coefficients. Depending on the value of shear rate the viscosities η_0 and η_∞ are represented by different coefficients. In this equation it has been assumed that, at very low shear rates, coefficient c represents viscosity η_0 , whereas the expression $(c_1 \cdot c_2/c_3)$ represents viscosity η_∞ :

$$\tau = c_1 \cdot \frac{1 + c_2 \cdot \dot{\gamma}^2}{1 + c_3 \cdot \dot{\gamma}^2} \cdot \dot{\gamma} \quad (26)$$

where:

- c_1 – viscosity coefficient [Pa·s],
- c_2 – limiting viscosity at a very low shear rate [Pa·s],
- c_3 – limiting viscosity at a very high shear rate [Pa·s],
- τ – shear stress [Pa],
- $\dot{\gamma}$ – shear rate [s^{-1}].

The Bingham model does not contain parameters that are difficult to be interpreted directly in physical units (e.g. n in the W.H. Herschel and R. Bulkley model), therefore its results are usually presented in the system of two variables from this model.

The description of non-Newtonian fluids in the form of equations (7-26) has the advantage of determining their apparent viscosity, which significantly simplifies algorithmic procedures in numerical programming. This mathematical notation has also disadvantages such as the necessity to determine limiting apparent viscosities, which is not always technically and technologically feasible [8].

2.2. Non-rheological models

References contain numerous models that enable dynamic viscosity of fluids to be calculated using physical parameters, thermodynamic parameters, etc. In models of this kind the influence of rheological parameters on the dynamic viscosity is omitted. In this approach the dynamic viscosity value is presented as a constant value – that is, calculated from an equation. Out of this group of models we can distinguish a small group, where equations take into account the size and shape of particles of media investigated. Due to the need to determine the particle sizes these models are used for calculating the viscosity of slurries and polymers.

The A. Einstein model [9] is one of the best known models of this type:

$$\eta_R = \frac{\eta_S}{\eta_L} = 1 + 2.5\Theta_S \quad (27)$$

where:

- η_R – viscosity [Pa·s],
- η_S – viscosity of slurry [Pa·s],
- η_L – viscosity of the other liquid [Pa·s],
- Θ_S – volumetric fraction of solids [-].

The Einstein equation is only true for small values of the volumetric fraction of solids $\Theta_S \leq 0.050$.

R. Roscoe has formulated another equation [9]:

$$\eta_R = (1 - R\Theta_S)^{-n} \quad (28)$$

where:

- η_R – viscosity [Pa·s],
- Θ_S – volumetric fraction of solids [-],
- R – empirical parameter (for comparable particles it assumes the value of 1.35; for particles with various shapes this value is 2.5),
- n – empirical parameter (for comparable particles it assumes the value of 1.0; for particles with various shapes this value is 2.5),

The Roscoe equation shows a very good predictability for viscosity of heterogeneous siliceous alloys (slags). The behaviour of heterogeneous siliceous melts only resembles the behaviour of a Newtonian fluid at a small share of solids.

The Einstein-Roscoe model has been proposed as a modification of these two equations, to calculate the viscosity of a liquid with a share of solids [10]:

$$\eta = \eta_0 (1 - \alpha f)^{-n} \quad (29)$$

where:

- η – viscosity of the liquid with solid particles (slurry) [Pa·s],
- η_0 – viscosity of the liquid [Pa·s],
- f – share of the solid phase in the liquid [%],
- α – inverse of the maximum solid phase share coefficient [-],
- n – constant depending on the particle geometry (for spherical particles = 2.5) [-].

Parameters occurring in viscosity models may be determined from experimental data (η_0 , η_∞) or e.g. with a method proposed by R. H. Stewart. This method consists in finding an

empirical curve, plotted in an appropriate system of coordinates, with a similar course on a previously prepared working graph [1].

Viscosity is an essential kinetic parameter related to the transfer of momentum in gases or liquids. The mechanism of momentum transfer in liquids is different than in gases. In gases momentum is transferred as a result of collisions of molecules, in liquids as a result of impact of intermolecular forces that impede the movement of molecules. Differences in the mechanics cause a different nature of the temperature relationship; for gases the viscosity increases with the temperature increase, for liquids the viscosity decreases with the temperature increase. Methods for calculating viscosity are based mainly on certain empirical dependences indicating relationships between the viscosity of liquids and their structures.

The first dependence, which is approximately met by non-associated liquids, is as follows [11]:

$$\eta V = K \quad (30)$$

where:

- η – viscosity [P],
- V – molar volume of liquid [m³/mol]
- K – a constant equal to about $(5,6 \pm 1,3) \cdot 10^{-5}$ [kg·m²/10·s·mol].

The temperature dependence of liquid viscosity has been presented by J. Guzman, so it is often called the Guzman – Arrhenius equation (S. Arrhenius) [11]:

$$\eta = A \cdot e^{\frac{\Delta E_\eta}{RT}} \quad (31)$$

where:

- η – viscosity [P],
- A – reaction constant [-],
- R – gas constant [-],
- T – temperature [K],
- ΔE_η – viscosity activation energy [kcal/mol].

Determination of constants from the Guzman – Arrhenius equation was the subject of theoretical studies. One of the best known of them was prepared by E. N. C. Andrade and H. Eyring. Andrade assumed the existence of a system of oscillators. The essence of this theory is the occurrence of vibrations (perpendicular to the flow direction), which cause the transfer of angular momentum to the surfaces of neighbouring planes [11]:

$$\eta = C \frac{\sqrt{T_m \cdot M}}{\sqrt[3]{V^2}} \quad (32)$$

where:

- η – viscosity [P],
- C – the constant of equation equal to $6,12 \cdot 10^{-4}$,
- V – the constant that characterises the atomic volume of the element,
- T_m – melting temperature [K],
- M – relative atomic mass [u].

The foregoing equation gives satisfactory compliance of experimental data with calculated data near the melting temperature. However, at higher temperatures it is not possible to predict the value of viscosity – with the E. N. C. Andrade equation.

H. Eyring assumed that a liquid may be treated as a pseudocrystalline phase, in which molecule movements are

restricted to oscillations within a space limited by the neighbouring molecules. According to this theory a jump of a molecule to the adjacent free space in the pseudocrystalline lattice requires an energy barrier to be overcome. The Eyring theory leads to the following expression of the value of the constant in the Guzman-Arrhenius equation [11]:

$$A \approx \frac{N_0 h}{V} \quad (33)$$

where:

- N_0 – the Avogadro number [mol⁻¹],
- h – the Planck constant [J s],
- V – molar volume [m³/mol]

For molecular liquids, in which chemical bonds are executed with van der Waals forces, the activation energy of viscosity can be determined with expression [11]:

$$\Delta E_\eta \approx 0.41 \Delta E_{vap} \quad (34)$$

where:

- ΔE_η – viscosity activation energy [kJ/mol].
- ΔE_{vap} – molar internal energy of evaporation [kJ/mol].

The above equation is a consequence of an empirically proven fact that the value of energy potential of a jump may be related to the value of molar internal energy of liquid evaporation. If, in addition, we assume that the vapour behaves like the perfect gas and neglect the liquid volume as compared to the gas volume, we obtain the following equation [11]:

$$\eta = \frac{N_0 h}{V} e^{3.8 \frac{T_s}{T}} \quad (35)$$

where:

- η – viscosity [P],
- N_0 – the Avogadro number [mol⁻¹],
- h – the Planck constant [J s],
- V – atomic volume [m³/mol]
- T_s – absolute boiling temperature of the liquid under the normal pressure [K],
- T – temperature [K].

The accuracy of this equation is low – in particular for non-molecular liquids, therefore it is only used for estimate calculations.

E. T. Turkdogan has presented a simple correlation between the value of viscosity activation energy and the melting temperature of metals, and has obtained the following dependence [11, 12]:

$$\log \Delta E_\eta = 1,36 \log T_m - 3,418 \quad (36)$$

where:

- ΔE_η – activation energy [kJ/mol],
- T_m – absolute melting temperature [K].

A viscous flow may be described by the process rate, like in the case of a chemical reaction or diffusion. The dependence of viscosity on temperature may be determined with the equation by H. Weymann and J. Frenkel [10]:

$$\eta = A^W \cdot T \cdot \exp\left(\frac{E_\eta^W}{RT}\right) \quad (37)$$

where:

- η – viscosity [Pa·s],
- A – the constant [-],
- W – the constant [-],
- T – temperature [K],
- E_η – activation energy [kJ/mol],
- R – the gas constant [J/(mol K)].

By analysing the temperature dependence of metals viscosity on the basis of the J. G. Kirkwood's structural liquid model, Chapman has indicated the following relationship [11]:

$$\eta^* (V^*)^2 = f(T^*) \quad (38)$$

where:

$$\eta^* = \frac{\eta \cdot \delta^2 N_0}{\sqrt{MRT}} \quad (39)$$

$$T^* = \frac{kT}{\varepsilon} \quad (40)$$

$$V^* = \frac{1}{\eta \cdot \delta^2} \quad (41)$$

where:

- η – viscosity [Pa·s],
- δ – the distance between atoms in the crystal [Å],
- N_0 – the Avogadro number [mol⁻¹],
- M – molar mass [u],
- R – the gas constant [J/(mol K)],
- ε/k – Lenard-Jones constants [K],
- T – temperature [K],
- n – the number of atoms in the unit [-].

The values of parameters k/ε as a function of absolute melting temperature of metals yield a simple relationship:

$$\frac{k}{\varepsilon} = \frac{1}{5,20T_m} \quad (42)$$

The above dependence may be used for estimating metals viscosity (except for low melting metals) if other data is unavailable.

T. Iida and R. I. L. Guthrie have proposed the expression for calculation of the parameter A (37), also based on theoretical equations [11]:

$$A = \frac{5,7 \cdot 10^{-5} M \sqrt{T_m}}{\sqrt{V_m^3 \exp\left(\frac{\Delta E_\eta}{RT_m}\right)}} \quad (43)$$

where:

- M – molar mass [u],
- T_m – absolute melting temperature [K],
- V_m – atomic volume in the absolute melting temperature [m³/mol],
- ΔE_η – activation energy [kJ/mol].

For high melting metals the activation energy of viscosity may be estimated from the dependence:

$$\Delta E_\eta = 5,06 \sqrt{T_m} \quad (44)$$

where:

- T_m – absolute melting temperature [K].

For low melting metals (Hg, Ga, K, In, Sn, Bi, Pb) the above equation assumes the form:

$$\Delta E_\eta = 3,14 \sqrt{T_m} \quad (45)$$

where:

T_m – absolute melting temperature [K].

There are many empirical relationships describing a change in viscosity of liquid binary solutions. Arrhenius has given the following equation [11]:

$$\log \eta_{1-2} = X_1 \log \eta_1 + X_2 \log \eta_2 \quad (46)$$

where:

X – mole fraction of the component [mol/m³].

J. Kendall and K. P. Monroe has presented the dependence in the following form [11]:

$$\log \eta_{1-2} = X_1 \log \sqrt[n]{\eta_1} + X_2 \log \sqrt[n]{\eta_2} \quad (47)$$

where:

X – mole fraction of the component [mol/m³].

2.3. Non-rheological models for calculating metals viscosity

In the subgroup of non-rheological models, equations enabling the value of dynamic viscosity coefficient of metals and their solutions to be calculated are distinguished. The equation formulated by E.A. Moelwen-Hughes [13, 14, 15] is amongst the simplest and the earliest dependences of this type:

$$\eta = (\eta_1 X_1 + \eta_2 X_2) \left(1 - 2 \frac{\Delta H_m}{RT} \right) \quad (48)$$

where:

η – viscosity of the solution [Pa·s],

η_1, η_2 – viscosity of the metals [Pa·s],

X – mole fraction of the component [mol/m³],

ΔH_m – molar enthalpy of the mixing [kJ/mol],

R – the gas constant [J/(mol K)],

T – temperature [K].

In 1987 D. Sichen, J. Boygen, S. Seetharaman proposed the following equations [13] for calculating the viscosity of multicomponent solutions:

$$\eta = A \exp \left(\frac{G^*}{RT} \right) \quad (49)$$

$$A = \frac{hN\rho}{M} \quad (50)$$

$$G^* = \sum_{i=1}^n X_i G_i^* + RT \sum_{i=1}^{n-1} \sum_{k=i+1}^n X_i X_k + \Delta G' \quad (51)$$

where:

G^* – the Gibbs energy of activation [kJ/mol],

$\Delta G'$ – change in the Gibbs free energy [kJ/mol],

G_1^*, G_2^* – activation energy of components [kJ/mol],

R – the gas constant [J/(mol K)],

ρ – alloy density [g/m³],

N – the Avogadro number [mol⁻¹],

h – the Planck constant [J s],

M – relative atomic mass of the alloy components [u].

The foregoing dependence has been modified by S. Seetharaman and D. Sichen to the form [13]:

$$G^* = \sum_{i=1}^n X_i G_i^* + 3RT \sum_{i=1}^{n-1} \sum_{k=i+1}^n X_i X_k + \Delta G' \quad (52)$$

The model by L. Ya. Kozlow, L. M. Romanov, N. N. Petrov, like the Moelwyn-Hughes model, uses also thermodynamic functions to forecast the viscosity value [13]:

$$\ln(\eta) = \sum_{i=1}^n X_i \ln(\eta_i) - \frac{\Delta H_m}{3RT} \quad (53)$$

therefore

$$\eta = \exp \left[\sum_{i=1}^n X_i \ln(\eta_i) - \frac{\Delta H_m}{3RT} \right] \quad (54)$$

where:

η – viscosity of the solution [Pa·s],

η_i – viscosity of the components [Pa·s],

X_i – mole fraction of the component [mol/m³],

ΔH_m – molar enthalpy of the mixing [kJ/mol],

R – the gas constant [J/(mol K)],

T – temperature [K].

The model by T. Iida, M. Ueda and Z. Morita, apart from the above mentioned physical parameters, takes also into account the values of Pauling ionic radii, and molar excessive Gibbs free energy [13]:

$$\eta = (\eta_1 X_1 + \eta_2 X_2) \left\{ 2 \left[1 + \frac{X_1 X_2 (\sqrt{m_1} - \sqrt{m_2})^2}{(X_1 \sqrt{m_1} + X_2 \sqrt{m_2})^2} \right]^{\frac{1}{2}} - 1 - \frac{5X_1 X_2 (d_1 - d_2)^2}{X_1 d_1^2 + X_2 d_2^2} - \Delta \right\} \quad (55)$$

$$\Delta = 0, 12 \frac{\Delta H_m}{RT} \quad (56)$$

$$\Delta = 0, 12 \frac{\Delta G^E}{RT} \quad (57)$$

where:

η – viscosity of the solution [Pa·s],

η_1, η_2 – viscosity of the alloy [Pa·s],

X_1, X_2 – concentration of the components in mole fractions [mol·m⁻³],

d_1, d_2 – the Pauling ionic radii [Å],

m_1, m_2 – relative atomic masses [u],

R – the gas constant [J/(mol K)],

T – temperature [K],

ΔH_m – enthalpy of the formation [kJ/mol],

ΔG^E – excessive molar volume of the n-component alloy [-].

In 2004 G. Kaptay published an equation, which was a modification of the Seetharaman and Du Sichen equation (of 1987). In the Kaptay model, in the equation for the Gibbs activation energy, the excessive Gibbs free energy was replaced by the enthalpy of mixing multiplied by coefficient α [13]:

$$\eta = \frac{hN}{\sum_{i=1}^n X_i V_i + \Delta V^E} \cdot \exp \left(\frac{\sum_{i=1}^n X_i \Delta G_i - \alpha \Delta H_m}{RT} \right) \quad (58)$$

where:

h – the Planck constant [J s],

N – the Avogadro number [mol⁻¹],

X_i – mole fraction of the component [ppm],

V_i – molar volume of the alloy components [m^3/mol],
 ΔV^E – the excessive molar volume of the n-component alloy [-].

ΔG_i – the change in the Gibbs free energy of the alloy components [kJ/mol],

α – coefficient of 0.155 – 0.015 [-],

ΔH_m – enthalpy of the formation [kJ/mol],

R – the gas constant [$\text{J}/(\text{mol K})$],

T – temperature [K].

M. Kucharski has proposed to use – for calculating viscosities of liquid solutions – the activity coefficients of components, partial molar volumes and viscosities [13, 26]:

$$\eta = X_1 \frac{V_1}{V} \left(\frac{\beta}{\beta_1} \right)^2 \gamma_1^\alpha \eta_1 + X_2 \frac{V_2}{V} \left(\frac{\beta}{\beta_2} \right)^2 \gamma_2^\alpha \eta_2 \quad (59)$$

$$\beta = \sqrt[3]{X_1} V_1 + \sqrt[3]{X_2} V_2 \quad (60)$$

$$\beta_1 = \sqrt[3]{X_1} V_1 + \frac{\sqrt[3]{(X_2 V_2)^4}}{V_1} \quad (61)$$

$$\beta_2 = \sqrt[3]{X_2} V_2 + \frac{\sqrt[3]{(X_1 V_1)^4}}{V_2} \quad (62)$$

where:

η – viscosity of the solution [Pa·s],

η_1, η_2 – viscosity of the metals [Pa·s],

X_i – mole fraction of the component [ppm],

V – molar volume of the alloy [m^3/mol],

V_i – partial molar volumes of the alloy components [m^3/mol],

γ_i – the activity coefficient of the components [-],

α – an empirical parameter [-].

2.4. Rheological models for calculating metals viscosity

The background of high temperature rheological measurements of stealmaking solutions are presented in [17-26]. The results of rheological measurements of liquid ferrous solutions which were used for developing statistical mathematical models describing the dependency of the liquid steel dynamic viscosity coefficient value on chemical composition and rheological parameters are presented in [21-24]. The details about models development are described in [23,24].

The Model MKH1 is a non-linear model:

$$\eta = -0.008626 \cdot Mn^3 + 0.1036 \cdot \sqrt[3]{S} - 0.00933 \cdot Mo + 0.007434 \cdot C + 0.3179 \cdot \lg T + 0.0187 \cdot \tau - 1.029 \quad (63)$$

where:

η – viscosity of liquid steel [Pa·s],

Mn – manganese content [%],

S – sulphur content [%],

Mo – molybdenum content [%],

C – carbon content [%],

T – temperature [$^{\circ}\text{C}$]

τ – shear stress [Pa].

The model MKH2 is also a non-linear model:

$$\eta = -0.008183 \cdot Mn^3 + 0.08477 \cdot \sqrt[3]{Ni} + 0.8355 \cdot \sqrt[3]{S} + 0.04064 \cdot \sqrt[3]{Cu} - 0.1273 \cdot \sqrt[3]{Cr} + 0.1644 \cdot Mo + 0.1738 \cdot C - 0.01759 \cdot Si + 0.0975 \cdot \lg T + 0.01767 \cdot \tau \quad (64)$$

where:

η – viscosity of liquid steel [Pa·s],

Mn – manganese content [%],

Ni – nickel content [%],

S – sulphur content [%],

Cu – copper content [%],

Cr – chromium content [%],

Mo – molybdenum content [%],

C – carbon content [%],

Si – silicon content [%],

T – temperature [$^{\circ}\text{C}$]

τ – shear stress [Pa].

The model MKH3 is a linear model:

$$\eta = -0.024 \cdot Mn + 0.0556 \cdot Si - 0.02697 \cdot Cr - 0.00183 \cdot Ni + 0.1062 \cdot Mo + 6.792 \cdot P - 0.2907 \cdot Cu + 0.7835 \cdot V + 0.01767 \cdot \tau - 0.04884 \quad (65)$$

where:

η – viscosity of liquid steel [Pa·s],

Mn – manganese content [%],

Si – silicon content [%],

Cr – chromium content [%],

Ni – nickel content [%],

Mo – molybdenum content [%],

P – phosphorus content [%],

Cu – copper content [%],

V – vanadium content [%],

τ – shear stress [Pa].

The above formulas (63-65) enabling to calculate the value of the liquid steel dynamic viscosity coefficient by using content of chemical elements, value of temperature and value of shear stress. However, these equations cannot be treated as universal algorithms for calculating the values of the liquid steel dynamic viscosity coefficient in a whole range of chemical compositions. On the other hand those equations are the first which combine chemical, temperature and rheological parameters to calculate the value of the dynamic viscosity coefficient. What is more this type of the equations enabling to calculate the value of the liquid steel dynamic viscosity depend on the changeable condition (force – shear stress), the other presented formulas treated liquid steel dynamic viscosity coefficient as a constant.

3. Summary

The following may be observed from the presented review of models for description of viscosity:

- the models known to date do not combine thermodynamic and rheological parameters in one equation, but they constitute groups of either thermodynamic, or rheological equations;
- most of the models that are dedicated to calculating metal solution viscosity are groups of either theoretical, or semi-empirical equations; due to measurement difficulties there is little experimental data from rheological measurements of liquid metal solutions;

- the existing rheological models used in special software for simulating also steel casting processes use equations, where one of the parameters is η_{∞} (the viscosity coefficient value at shear rates approaching infinity), thermodynamic databases do not contain values of this parameter, and it is virtually impossible to conduct measurements on liquids (metal solutions) with very low viscosity values (in the order of millesimal pascal-seconds);
- the presented rheological models for calculating metals viscosity (developed by own high temperature rheological liquid steel measurements) are the first which combine chemical, temperature and rheological parameters to calculate the value of the dynamic viscosity coefficient of liquid metal; those equations enabling to calculate the value of the liquid steel dynamic viscosity depend on the changeable condition (force – shear stress), the other presented formulas treated liquid steel dynamic viscosity coefficient as a constant.

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