

W. ŚLĘZAK*, M. KOROLCZUK-HEJNAK*, P. MIGAS*

HIGH TEMPERATURE RHEOMETRIC MEASUREMENTS OF MOULD POWDERS

WYSOKOTEMPERATUROWE POMIARY REOMETRYCZNE ZASYPEK KRYSZALIZATOROWYCH

Issues of viscosity and rheological properties of powder moulds are important from the perspective of modelling, along with the control of continuous casting process. Conducted analysis within subject literature indicates that there are many theoretical considerations concerning the effects of viscosity of powder moulds. The objective of this study was to perform rheological measurements of powder moulds, the study contains the results of rheological tests of seven chemical compositions with a carbon content from 5.0 to 10.7% and which were tested with applied shear rates from 10 to 40 s⁻¹, which are similar to those in a real process: the velocity of strand passes/drawing and mould movements.

Keywords: powder moulds, viscosity, rheology, rheometer

Zagadnienia lepkości oraz właściwości reologicznych zasypek krystalizatorowych są ważne z punktu widzenia modelowania, a także sterowania rzeczywistymi procesami technologicznymi w odniesieniu do procesu ciągłego odlewania stali. Z przeprowadzonej analizy literaturowej wynika, że istnieje wiele teoretycznych rozważań nad zjawiskiem lepkości ciekłych roztworów zasypek krystalizatorowych. Celem niniejszej pracy było wykonanie pomiarów reologicznych zasypek krystalizatorowych, w pracy zawarto wyniki badań siedmiu składów chemicznych o zawartości węgla od 5.0 do 10.7% przy zastosowanych prędkościach ścinania od 10 do 40 s⁻¹, odpowiadającym prędkościom rzeczywistym wynikającym z prędkości wyciągania pasma oraz ruchów krystalizatora.

1. Introduction

Nowadays, over 95% of global steel production is cast with the continuous method. As steel quality requirements are increasing, manufacturers should be striving to meet these requirements at every stage of production. This can be accomplished by continuous optimisation of the process, that is, by application of the equipment and materials that are properly selected to the steel that is manufactured. To no lesser extent, this also applies to the steel continuous casting process where the appropriate selection of both the process parameters and the mould powder type may considerably allow the elimination of cast strand defects.

The selection of the mould powder type depends on the mould geometry, oscillation conditions, casting speeds and the steel grade. The chemical constitution of the mould powder should be properly selected so that, depending on the steel grade cast, the appropriate softening, melting and fluidity temperatures, along with the adequate viscosity, are obtained. It is decisive when it comes to the effectiveness of the casting process.

Mould powders play an important role in the continuous casting as they perform the following functions:

- Protect the steel meniscus against oxidation
- Provide thermal insulation

- Absorb non-metallic inclusions
- Lubricate the strand and ensure uniform heat transfer [1, 2].

Lubricating and insulating mould powders, as opposed to other powders, have a higher basicity. This increases the ability to assimilate non-metallic inclusions by the slag. The mould powder lubricates the mould by flowing down between the mould wall and the formed shell, and as a consequence the solidifying strand does not make contact with the mould walls directly. However, filling the gap with the liquid mould powder also improves the conditions of heat abstraction by the mould wall, enabling higher strand withdrawal speeds to be applied. The mould powder viscosity is an essential parameter, as the lower the viscosity, the easier the mould powder gets into the gap [3].

The mould powder is dosed manually or automatically from the top of the mould. The powder placed onto the surface of the liquid steel should form a liquid layer on the liquid steel contact face as soon as possible, so therefore the liquidus temperature of the mould powder should be lower than the liquidus temperature of the liquid steel. The melting rate of the mould powder depends on the amount of components accelerating the melting process, such as sodium, potassium and fluorine carriers. When heated, the powder loses some carbon by the reactions with oxygen. This is followed by the

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND

formation of a sintered layer which begins melting, first forming a doughy, and later, a liquid layer. This layer forms a buffer that supplies liquid slag to the gap between the strand and the mould. The liquid slag gets into the gap between the mould and the strand in those periods of the oscillation cycle when the mould moves faster than the strand. A film of liquid and solid slag forms within the gap, and the liquid slag film, providing lubrication, moves together with the strand [1,3]

A diagram showing the effect of the mould powder within the mould is presented in Fig. 1. A thin strand shell layer starts forming at the meniscus arc, with the shell exposed to the impact of liquid steel pressure. The formation of the shell at the meniscus arc decreases as the thermal insulation of the liquid steel face in the mould increases. In addition, when this face is covered by the mould powder, the surface properties of the steel change and thus the conditions for the meniscus formation do likewise. When a proper mould powder is applied, a meniscus with a short height and a short radius is obtained, and subsequently the tendency to form surface defects such as fissures, oscillation marks and depressions decreases. Therefore it is vital to influence the meniscus parameters (height, radius) by selecting a mould powder with an appropriate chemical constitution and as low a viscosity as possible [3].

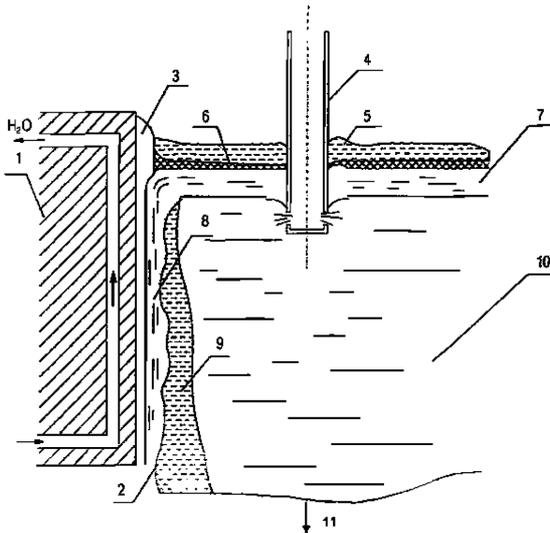


Fig. 1. Diagram of the effect of mould powder in the continuous casting machine mould; 1 – mould, 2 – oscillation marks on the strand surface, 3 – the rim of solid slag formed from the molten mould powder, 4 – submerged entry nozzle, 5 – solid mould powder, 6 – sintered mould powder layer, 7 – liquid mould slag, 8 – a layer of drawn liquid slag, 9 – solidifying shell, 10 – liquid steel, 11 – direction of strand withdrawal [3]

A number of mould powder viscosity tests were carried out [4-8]. Although the "cup and bob" method was mainly employed, the Inclined Plane Test was also used. Prior to the measurement, carbon had been removed from the mould powders by holding them at a temperature of 800°C. Carbon is added to control the mould powder melting rate, and the carbon particles separate the mineral particles and slow down the agglomeration of molten slag granules, resulting in the melting rate being slower [1]. Another problem was the possibility of fluoride evaporation. However, analyses conducted after the

holding and initial melting did not reveal any substantial losses of sample weights other than from decarbonization [4, 5]. The dynamic viscosity strongly depends on the chemical constitution of the mould powder and the temperature: this grows as the Al₂O₃/SiO₂ ratio grows, and decreases as the CaF₂ content increases. Generally, it can be observed that viscosity grows as the lattice forming components do likewise.

A few models describing the viscosity of the mould powders can be found in a number of examples of literature, e.g. the Riboud Model, Iida Model, KTH Model, Urbain Model, and the Mills Model. These are based primarily on the Arrhenius equation and on the slag structure. The Riboud Model is the simplest one to describe; it classifies the chemical constituents into five various categories and sums up their mole fractions X. Viscosity may be calculated from the Weymann equation using dependences 1 - 3 [1, 8].

- Lattice/network forming: $X_{SiO_2}' = X_{SiO_2} + X_{P_2O_5} + X_{TiO_2} + X_{ZrO_2}$
- Lattice breaking: $X_{CaO}' = X_{CaO} + X_{MgO} + X_{FeO} + X_{B_2O_5} + X_{Fe_2O_3} + \{X_{MnO} + X_{NiO} + X_{CrO} + X_{ZnO} + X_{Cr_2O_3}\}$
- Al₂O₃: $X_{Al_2O_3} + \{X_{B_2O_5}\}$
- CaF₂: X_{CaF_2}
- Na₂O: $X_{Na_2O} + X_{K_2O} + \{X_{Li_2O}\}$

$$\ln \eta = \ln A_W T + B_W T \tag{1}$$

where:

η – viscosity coefficient, Pa·s

T – temperature, K

A_W, B_W – Weymann constants

$$A_W = \exp(-19,81 + 1,73X_{CaO}' + 5,82X_{CaF_2} + 7,02X_{Na_2O} - 35,76X_{Al_2O_3}) \tag{2}$$

$$B_W = 31140 - 23896X_{CaO}' - 46356X_{CaF_2} - 39159X_{Na_2O}' + 68833X_{Al_2O_3} \tag{3}$$

The viscosity effect in metallurgical processes is amongst the most important, influencing the behaviours of reacting phases (metallic, slag and gaseous) with regard to the kinetics of mass exchange or chemical reactions [9, 10, 20]. Viscosity also plays a significant role in all metallurgical processes – ironmaking, steelmaking, ladle refining, steel casting, and processes related to solidification. Viscosity is very important from the standpoint of the flow of liquid phases as they are continuously moving during the aforementioned processes [11]; it is also important due to the internal structure of the metallic or slag phase, along with related possibilities of contamination absorption, or the ability to deform in their semi-solid states [12,13, 14].

For the purposes of the simulation of metallurgical processes, it is necessary to have access to experimental data. This concerns a broad range of chemical compositions and temperature as regards metal, and also oxide phases such as metallurgical slags [10]. Data originating from measurements taken at high-temperature is necessary for the engineering of new processes, and for the optimization of those already in existence – that is, better control of the process, and/or improvement of product quality. Many mathematical models have been created in the past years that can assist in describing thermodynamics, kinetics, fluid flow and heat exchange: obtaining

of "good" (correct) data from measurements was the basis for the creation of accurate models. Because of the difficulties related to obtaining access to specialist instrumentation such as high-temperature rheometers – along with the degree of complexity that burdens rheological measurements – very little data [15-19] concerning liquid ferrous solutions can be obtained from subject literature.

2. Research methodology

The rheological tests were conducted with a FRS1600 high-temperature rheometer, presented schematically in Fig. 2.

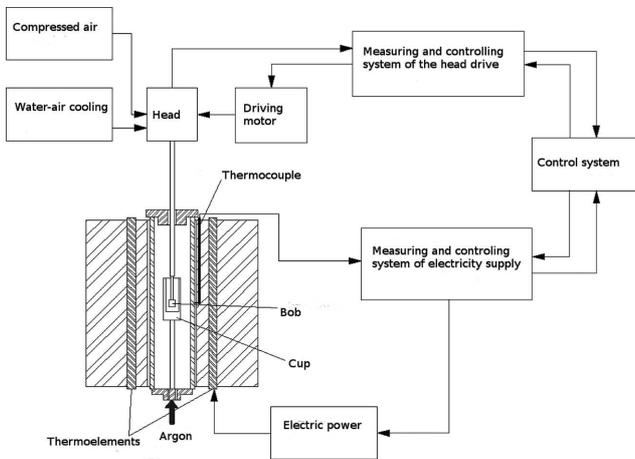


Fig. 2. High temperature rheometer FRS1600 [11-12, 17-19]

The measurement is performed in a fixed crucible into which a sample of the material tested is placed, then a rotating bob is immersed within the material being tested. The crucible is then placed inside a ceramic tube, being a component of a heating furnace. The furnace, which is built of four electrically heated SiC type heating elements, enables the maximum temperature of 1520°C to be obtained within the sample. The whole device is shielded from the outside with an insulating material. The temperature inside the furnace is controlled by a change in feeder power in the measurement and control system. The heating rate, along with maintaining the temperature at a constant level, are set in the control panel of the Rheoplus software of the rheometer. Rotational movements of the bob are controlled by a motorised measurement head – the bob being suspended on a ceramic tube placed with a bolt in an air bearing. In order to ensure low temperatures of the head, it is cooled with water and air.

Graphite bobs (diameter 16 mm) and cups (with a smooth inner surface) were used for the tests. Figure 3 presents technical drawings and the picture of tools used for the measurements.

In this study, the measurement methodology in a system of coaxial Searle type cylinders was used for conducting high-temperature rheological measurements of powder moulds.

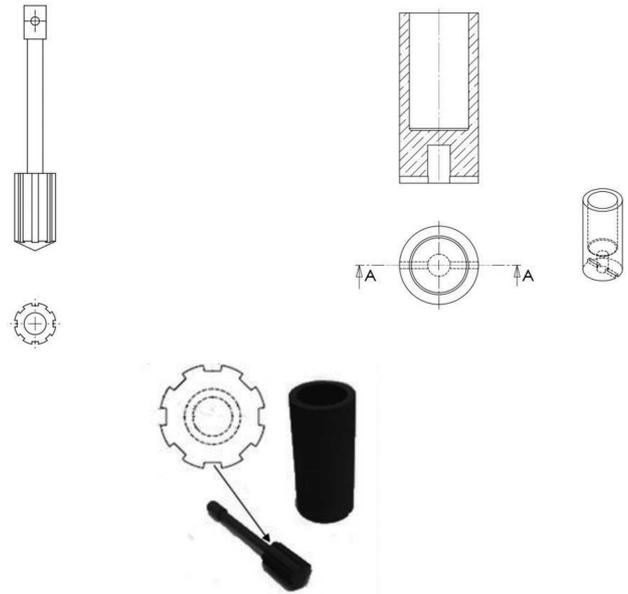


Fig. 3. The geometry of bob and cup used for measurements

Mould powders applied for slab casting were used for the tests, and the casting speeds for products of this type are between 0.6 and 2m/min. For the applied geometry of the measurement system, the corresponding rotational speeds were calculated based on formulas 4 and 5.

$$\omega = \frac{V}{r} \tag{4}$$

where:

ω – angular velocity, rad/min

V – linear velocity, m/min

r – radius, mm

$$f = \frac{\omega}{2\pi} \tag{5}$$

where:

f – rotational speed, rpm

For instance, for $V = 2\text{m/min}$ and $r = 8\text{ mm}$, the angular velocity was 250 rad/min, and the rotational speed was 39.8 rpm. For $V = 1\text{m/min}$, $f = 19.9\text{ rpm}$.

Table 1 presents the measurement diagram of the rheological measurements of mould powders. The measurements were performed using the same methodology at each of the temperatures. However, for a temperature change of 100°C, the speed = 20rpm = const. (3.49 s^{-1}) was used.

TABLE 1

Measurement scheme

Time [min]	Speed [rpm]	Shear rate [s^{-1}]
2.5	15	2.62
2.5	20	3.49
2.5	30	0.57
2.5	40	0.73
2.5	10-40	1.75-6.98
2.5	40-10	6.98-1.75

3. Analysis of Findings

In this study, the powder moulds were examined (Table 2).

TABLE 2
Chemical compositions of analyzed powder moulds [%]

Chemical composition/Name of powder mould	MP1	MP2	MP3	MP4	MP5	MP6	MP7
SiO ₂	31.5	31.5	34.4	31.2	34.2	33.0	33.0
CaO	37.0	37.0	27.0	37.1	29.1	27.0	27.5
MgO	1.8	1.5	3.9	1.1	2.6	1.5	1.3
Al ₂ O ₃	5.5	5.5	4.7	5.8	5.7	5.2	5.0
Na ₂ O/K ₂ O	6.5	6.9	11.8	7.2	8.8	7.5	12.5
Fe ₂ O ₃	1.8	1.5	1.6	1.0	1.5	1.2	2.0
MnO ₂	0.4	0.3					
F	10.0	9.0	8.8	10.0	6.9	8.0	8.7
Cfree	4.5	4.0	3.6	4.1	4.3	8.2	4.0
C total	5.8	5.0	5.7	5.3		10.7	6.5
Basicity	1,17	1,17	0,78	1,19	0,85	0,82	0,83
Softening point, °C	1070	1070	880	1085	1085	1000	1000
Melting point, °C	1150	1150	1050	1150	1105	1020	1090
Fluidity point, °C	1160	1170	1070	1160	1115	1070	1120

Figures 4-7 present the results of the conducted rheological tests of mould powders. The tests were conducted in accordance with the schedules presented in Table 1.

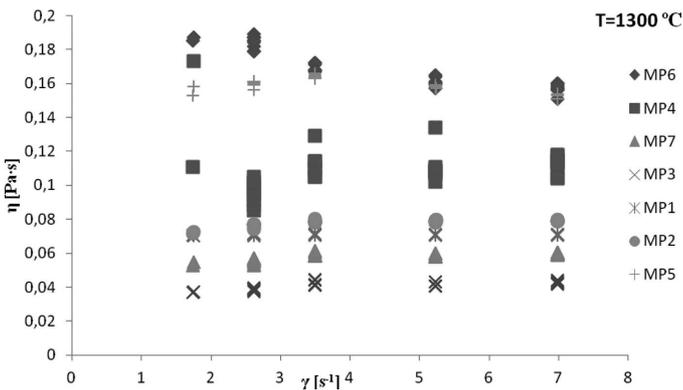


Fig. 4. The viscosity curves of investigated powder moulds in 1300°C

Figure 4 presents the viscosity curves of the mould powders tested within a selected shear rate range at a temperature of 1300°C, where the viscosity reached values from 0.04 to 0.06 Pa s for the MP3 and MP7 powders characterised by the highest concentration of K₂O and Na₂O. This was up to 0.18-0.2 Pa-s for the MP5 and MP6 powders. Prior to burning out, the MP6 powder was characterised by having the highest carbon content in its chemical composition. The course of the viscosity curves is similar to that of the ideally viscous body.

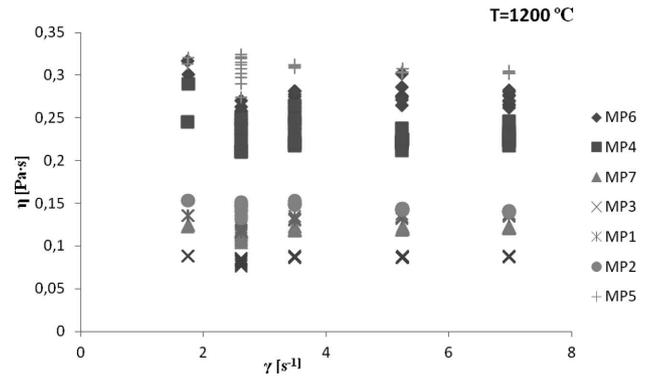


Fig. 5. The viscosity curves of investigated powder moulds in 1200°C

Figure 5 presents the viscosity curves of the mould powders tested within a selected shear rate range, and at a temperature of 1200°C. Viscosity reached values from about 0.1 Pa s for the MP3 and MP7 mould powders, and up to 0.3-0.35 Pa·s for the MP5 and MP6 powders. The MP1 and MP2 powders are characterized by stable and comparable values of viscosity: they both contain MnO, and the F content is at its upper limits. The further course of the viscosity curves is similar to the graphs of the ideal Newtonian body.

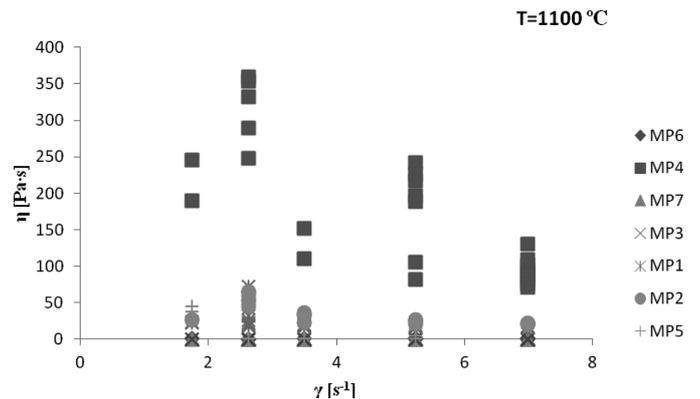


Fig. 6. The viscosity curves of investigated powder moulds in 1100°C

At a temperature of 1100°C the course of the viscosity curves deviates from what would be an ideally viscous state (at Figure 6). The viscosity considerably increases for all the chemical compositions tested. However, the highest values of the dynamic viscosity coefficient are characteristic to the MP4 powder, which at temperatures of 1300 and 1200°C featured the highest fluctuations of the dynamic viscosity coefficient depending on the changes in the shear rate.

Figure 7 presents a change in the dynamic viscosity coefficient depending on the changes in the temperature from 1200 to 1300°C, and at a rotational speed of 20 rpm. In accordance with the process theory, as the temperature increased (at a constant value of shear rate/rotational speed), the values of the dynamic viscosity coefficient decreased from about 0.07 to 0.05 Pa·s, for the MP5 sample (with the lowest values of the dynamic viscosity coefficient), and from 0.25 to 0.2 Pa·s, for the MP3, MP6 samples (with the top values of the dynamic viscosity coefficient).

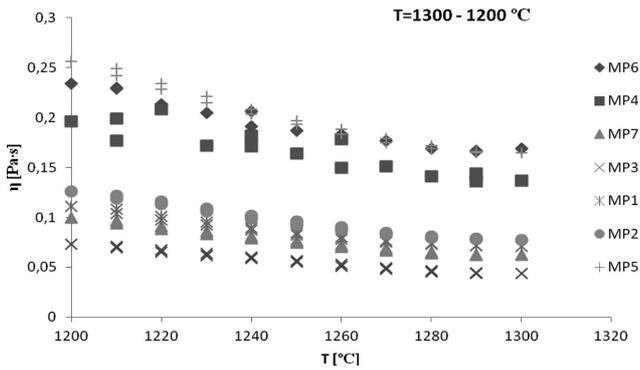


Fig. 7. The viscosity changes of investigated powder moulds in 1300-1200°C

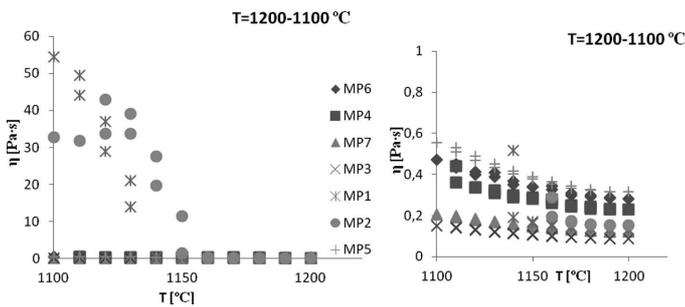


Fig. 8. The viscosity changes of investigated powder moulds in 1200-1100°C

Figure 8 presents the changes in the dynamic viscosity coefficient of mould powders for temperature changes from 1200 to 1100°C. In this case, the values of dynamic viscosity coefficient of the MP3, MP4, MP5, MP6 powders are within the range of the tenth parts of a pascal second, whereas those values for MP1 and MP2 reach the value of 30-50 Pa·s at temperatures of 1100-1150°C.

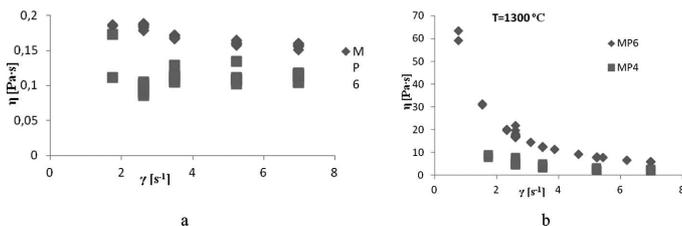


Fig. 9. The viscosity changes of investigated powder moulds in 1300°C: a) sample without carbon; b) sample with carbon

Figures 9a and 9b present the changes in the dynamic viscosity coefficient as a function of shear rate, for mould powders with carbon (base), and after baking them at a temperature of 800°C to eliminate solid particles of carbon from the system analysed.

Figure 9 illustrates the differences between the values of dynamic viscosity coefficient of the MP4 and MP6 mould powders at a temperature of 1300°C. The differences in the values of dynamic viscosity coefficient of mould powders arise from the fact that the viscosity curves in Figure 9a were obtained for samples after burning the carbon out. The viscosity curves in Figure 9b were obtained for mould powders not subjected to thermal treatment. The values of dynamic viscosity coefficient show substantial differences for a system

with (Fig. 9b) and without carbon (Fig. 9a), and the dynamic viscosity for the system with solid components is significantly higher than for a fully liquid system. Also, the changes in the rheological nature of the system tested with and without solid components can be observed: for the liquid system in Fig. 9a, one can find that it is a Newtonian system, while the solid components – carbon – cause deviations from the Newtonian nature – Fig. 9b.

4. Conclusion

Based on the conducted rheometric tests and analyses as regards the obtained findings, it can be observed that:

- All mould powders at a temperature of 1300°C, at shear rates from 1 to 8 s⁻¹ show the nature of flow similar to a Newtonian liquid; the MP6 and MP4 show slight deviations from a straight line. The MP4, MP5 and MP6 mould powders at this temperature also show the highest values of the dynamic viscosity coefficient. A change in viscosity coefficient – as a function of temperature within a range of 1300-1200°C – revealed a similar nature of changes, and the MP4, MP5 and MP6 powders reached the highest values of viscosity.
- Based on the comparison of the MP4 and MP6 powders at a temperature of 1300°C, one may find that the content of solid carbon particles influences the change of the rheological nature of the system analysed. The carbon-free system shows similarities to a Newtonian liquid, whereas the system with carbon is similar to a shear-thinning liquid.
- During temperature changes from 1200 to 1100°C, the MP1 and MP2 mould powders show a significant change in the viscosity coefficient; these powders have the highest basicity B1, and this increase may stem from the intensive precipitation of solid particles which causes the system thickening. For the MP3 and MP7 powders, the lowest values of dynamic viscosity coefficient are observed at a temperature of 1300°C, and these powders have the highest K₂O and Na₂O concentration in the system. These findings confirm the knowledge from the literature.

Based on the results obtained, it should be stated that further rheometric tests are necessary, as well as the conducting of tests as regards rheological analysis of mould powder systems – in particular, with solid carbon particles added.

Acknowledgements

Financial support of National Science Centre for research project “Developing an empirical model of the rheological properties of liquid metals on the example of iron solutions” no. 2011/01/N/ST8/07368 is gratefully acknowledged.

The research was conducted with the financial support from the statutory project no. 11.11.110.225.

REFERENCES

- [1] The Making, Shaping and Treating of Steel – Casting Volume CD, The AISE Steel Foundation, 2003.

- [2] K.C. Mills, A.B. Fox, The Role of Mould Fluxes in Continuous Casting – So Simple Yet So Complex, *ISIJ International* **43**, 10, 1479-1486 (2003).
- [3] J. Falkus [ed.], *Modelowanie procesu ciągłego odlewania stali*, Kraków, 2012.
- [4] M. Persson, M. Görnerup, S. Seetharaman, Viscosity Measurement of Some Mould Flux Slags, *ISIJ International* **47**, 10, 1533-1540 (2007).
- [5] Z. Zhang, G. Wen, P. Tang, S. Sridhar, The Influence of Al₂O₃/SiO₂ Ratio on the Viscosity of Mold Fluxes, *ISIJ International* **48**, 6, 739-746 (2008).
- [6] A. Dev, S. Riaz, Viscosity measurement of mould fluxes using inclined plane test and development of mathematical model, *Iron and Steelmaking* **39**, 6, 391-397.
- [7] H. Kim, I. Sohn, Effect of CaF₂ and Li₂O Additives on the Viscosity of CaO-SiO₂-Na₂O Slags, *ISIJ International* **51**, 1, 1-8 (2011).
- [8] Z. Elahipanah, Thermo-Physical Properties of Mould Flux Slags for Continuous Casting of Steel, M. Sc. Thesis, Royal Institute of Technology, Stockholm, 2012.
- [9] M. Karbowniczek, *Pienienie żużla w procesach stalowniczych*, Uczelniane Wydawnictwo Naukowo-Dydaktyczne, Kraków, 1998.
- [10] P. Migas, M. Karbowniczek, Interactions Between Liquid Slag And Graphite During The Reduction Of Metallic Oxides, *Archives Of Metallurgy And Materials* **55**, 4, 1147-1157.
- [11] K. Sołek, M. Korolczuk-Hejnak, W. Ślęzak, Viscosity Measurements For Modeling Of Continuous Steel Casting, *Archives Of Metallurgy And Materials* **57**, 1, 325-333.
- [12] K. Sołek, M. Korolczuk-Hejnak, M. Karbowniczek, An Analysis Of Steel Viscosity In The Solidification Temperature Range, *Archives Of Metallurgy And Materials* **56**, 3, 593-598.
- [13] Ł. Rogal, J. Dutkiewicz, Effect Of Annealing On Microstructure, Phase Composition And Mechanical Properties Of Thixo-Cast 100cr6 Steel, *Materials Characterization* **68**, 123-130.
- [14] Ł. Rogal and others, Characteristics Of 100cr6 Bearing Steel After Thixoforming Process Performed With Prototype, *China Transactions of Nonferrous Metals Society of China* **20**, 1033-1037 (2010).
- [15] G. Hirt, R. Kopp, Redaktorzy: Thixoforming. Semi-Solid Metal Processing. WILEY-VCH GMBH AND CO. KGAA, Weinheim, 2009.
- [16] M. Modigell, L. Pape, H.R. Maier, Rheology Of Semi-Solid Steel Alloys At Temperatures Up To 1500°C, *Solid State Phenomena* **116-117**, 606-609 (2006).
- [17] M. Korolczuk-Hejnak, P. Migas, Analysis Of Selected Liquid Steel, *Archives Of Metallurgy And Materials* **57**, 4, 963-969.
- [18] M. Korolczuk-Hejnak, P. Migas, Selected Grades Of Steel As Rheologically Defined Liquid Bodies, *Archives Of Metallurgy and Materials* **57**, 2, 583-591.
- [19] K. Miłkowska-Piszczek, M. Korolczuk-Hejnak, An Analysis Of The Influence Of Viscosity On The Numerical Simulation Of Temperature Distribution, As Demonstrated By The CC Process, *Archives Of Metallurgy And Materials* **59**, 4.
- [20] R. Przyłucki, S. Golak, B. Oleksiak, L. Blacha, Influence of an induction furnace's electric parameters on mass transfer velocity in the liquid phase, *Metalurgija* **51**, 1, 67-70 (2012).