

Experiences in slag viscosity measurement by rotation cylinder method

Lasse Forsbacka

Laboratory of Metallurgy, Helsinki University of Technology, Finland

There has been a project on slag viscosities involving a development of an apparatus for measuring viscosities at high temperatures in Laboratory of Metallurgy of Helsinki University of Technology. Lot's of experience has been gained during the project, which might interest those who are involved with similar projects. This article is a review of methods and techniques, which were developed for viscosity measurement.

Key words: slag, viscosity, measurement

1 Introduction

Usually scientific articles emphasise results of the research in question, but methods and techniques of achieving the results are only briefly explained. A lot of experience gained in practical measurements, often by trial and error, is only recorded in the mind of a researcher himself. No doubt, that a development of a functional viscosity measurement apparatus wouldn't have been such a task. The construction and methods have been improved after every breakdown until now, the apparatus is adequately durable even at the top operating temperature 1750°C.

In this article, every part of an experimental arrangement is demonstrated, and methods of a successful viscosity measurement are reviewed.

2 Experimental arrangement

The experimental arrangement for viscosity measurement is presented in Fig. 1. For clarity the picture does not show all the details including the cooling system. The furnace is air-cooled, and the top and bottom stoppers of the furnace tube are water-cooled.

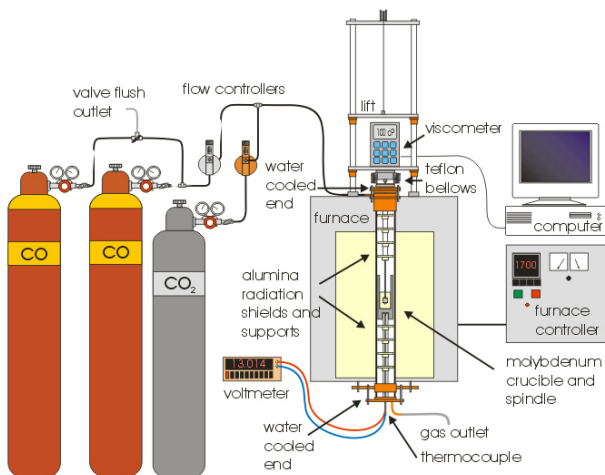


Fig. 1 Experimental arrangement

3 Furnace

The furnace is Entech ETF 50 –175V, which has maximum continuous temperature 1750°C. A controller unit contains Eurotherm 903P-unit, where the temperature control programs are made.

Care should be taken when the furnace tube is placed on position. The crucible stands actually in the direction of the furnace tube, but the spindle points always directly towards the ground. That is why the furnace tube has to be placed as vertically as possible. A plumb line can be let to hang through the furnace tube so that the verticality can be inspected. The furnace stands on legs with adjusting screws so that the whole furnace can be tilted in order to get the furnace tube vertical.

The furnace tube may bend and bulge during time, especially if the tube is forced to be vertical. Therefore, the furnace tube should only be fastened in one place at the bottom end, which also guarantees that in a case of breakdown the hot furnace tube won't drop on the floor.

The furnace has a narrow, uniform temperature zone, and the crucible has to be placed precisely in the middle of it. Before the first measurement the furnace temperature profile must be inspected with all radiation shields in place, which is done by lifting a thermocouple in a furnace. A result of such an experiment is represented in a Fig. 2.

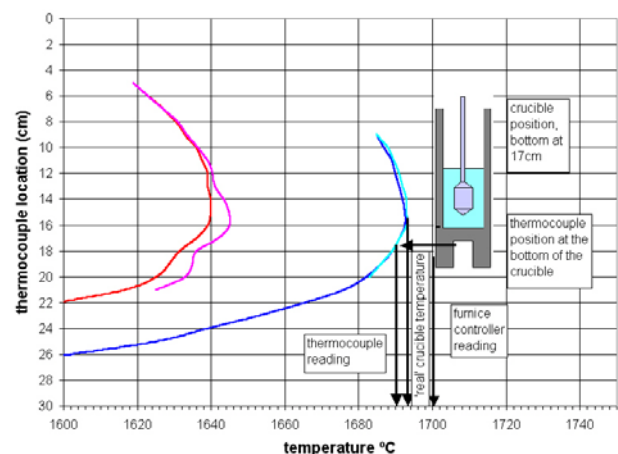


Fig. 2 Furnace temperature zones at 1650° and 1700°C

4 Viscometer

The programmable Brookfield LVDV-II+ viscometer is designed for measurement of viscosity at a given shear rates. The principle of operation is to drive a spindle, which is immersed in the test fluid, through a calibrated spring. The viscous drag of the fluid against the spindle is measured by the spring deflection, which is detected with a rotary transducer.

The measurement range is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in, and the full scale of rotating spring. The LV in the model type stands for low viscosity, which means that the viscometer has a calibrated spring that is more supple than in other DV-II models. The LV model also comes with the different set of standard spindles.

The measuring range of viscosity is 1.5 – 600.000cPas with the standard spindles, where the lowest viscosity is measured with the largest spindle and highest speed, and the highest viscosity with the smallest spindle and lowest speed. The user can select from 54 different speeds. The viscosity accuracy is $\pm 1.0\%$ of full-scale viscosity range. The full scale, or in other words, the maximum viscosity reading at the selected spindle and speed, can be discovered if the “auto-range” button is pressed any time during the measurement. These limits are for the calibrated spring only. More errors may rise from the spindle construction, temperature measurement, etc.

All units can be displayed in SI or CGS units. The basic DV-II unit contains a laboratory stand, set of spindles, temperature probe, guard leg, carrying case and connecting cables. It also contains software for making programs to control the viscometer.

The viscometer is installed in the lift, which enables immersion and removing of the spindle in and out from the liquid slag. The viscometer has a level on the top cover for adjusting the apparatus so that the spindle hangs vertically. However, when the standard spindle is replaced by a custom made spindle with very a long shaft, it is better to use plumb line which is more accurate and can also be used for centralizing the spindle in the furnace tube. The procedure is following: The plumb line is attached to viscometers spindle connection, and the lift is lowered to down position. Then the lift is moved horizontally so that the plumb line is in the centre of the upper end of the furnace tube. Then, the lower end of the furnace tube is inspected. If the plumb line does not lie in the centre, the furnace tube is not vertical. Furnace tube is adjusted by tilting the furnace by adjusting screws in the legs. After the furnace tube is verified to be vertical the viscometer is lifted to highest position. If the plumb line is moved from the centre of the furnace tube, it means that the viscometer is not vertical and neither would the spindle be when installed. Correction is done by adjusting screws under the lift, so that the plumb line will move back to the centre of the furnace tube.

5 Software

Wingather is an optional Brookfield’s software for MS-Windows, which purpose is to collect data from the viscometer and then save, view, print, plot and analyse this data. The saving format options are the default ASCII text format (*.dvd), which is compatible with Brookfield’s DVGather software, and Lotus-123 format (*.WKS), which allow it to be imported into most spreadsheet programs.

The imperative feature of this program for the present work is that it allows the use of the user-made special spindles. The system (or spindle) dependent constants “the spindle multiplier constant” (SMC) and “the shear rate constant” (SRC) can be programmed in the computer’s memory, after which the software can calculate a viscosity and a share rate from the torque reading. If Wingather program is not used, the viscosity may be calculated from torque reading, as long as the SMC is known.

During the experiments, it was found out that the program is not very stable, and the data editing is rather limited. In consequence, the data was collected manually from the screen and edited in the MS-Excel.

6 Spindle and crucible

The spindle and the crucible were lathed of molybdenum rod. A cross section of the crucible is presented in Fig. 3. The 20mm deep hole in the bottom is made for an alumina stand. The container is 90mm deep, which may seem to be exaggerated. However, when the crucible is filled with slag powder or pressed slag pellets, it is completely full. After melting, the volume of the slag is less than 50% of the powders volume. Because the molybdenum crucibles are expensive, it is tempting to try to clean the used crucibles for re-use. Unfortunately, the solid slag is very difficult to remove from the bottom of the crucibles. It is possible to drill the most of the slag away with percussion borer, and turn the rest in a lathe, but this requires a lot of effort, and often an extra pair of a cutter. Because of grain growth at high temperatures, crucibles become brittle, and by time they will crack because difference of thermal expansion between molybdenum and slag¹.

The size of the spindle has to be such that it is useable in the wanted viscosity range. Normally, a set of spindles can be used in viscosity measurement, so that when viscosity decreases too low for a particular spindle, a bigger spindle is replaced. However, the high temperature and the air-tightness of the furnace prevent the change of the spindle during the measurement.

¹ Some experiments suggest that hydrogen as a part of protective gas further embrittlement.

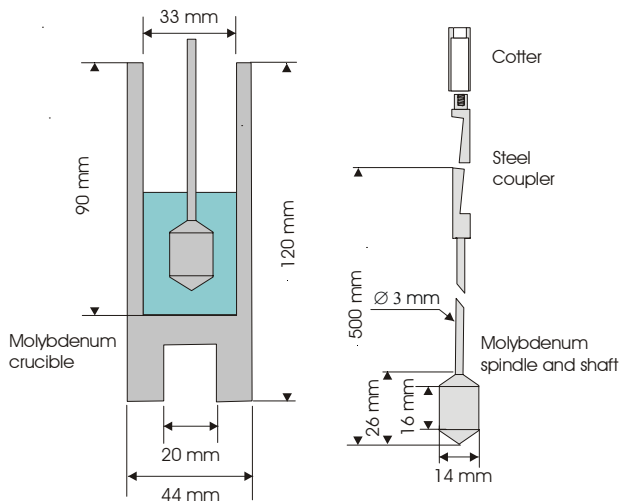


Fig. 3 Crucible, spindle and coupling to viscometer

Usually small spindles are not accurate at low viscosity, because the calibrated spring does not get enough resistance, and the viscosity reading varies as loose spring deflects back and forth. According to handbook, the viscosity can't be measured under 10 percentage of torque, and the viscosity accuracy is $\pm 1.0\%$ of full-scale viscosity range, when standard spindles are used. The lower is the torque-%, the bigger is the error margin.

On the other hand, too large spindles at high viscosities strain the spring out of the measurement range. At low viscosity, it would seem that the bigger the spindle the more exact would be the measurement, if only the spindle fit in to the crucible and measurement range is not exceeded. However, in practice this is not so. First, if the gap between the spindle and crucible is too narrow, the "boundary effects" become remarkable. This effect is taken account when the system dependent constant (SMC) for a particular set-up is measured, but for two separate experiments, the crucible is not exactly in the same position, and the boundary effect is thus different. Second, the more restrictive factor is that heavy spindle at the end of a long shaft sways easily at low viscosity and high rotational speed. This causes extra resistance for the spring, and viscosity seems to be higher than it really is. This aspect recommends that the spindle should be light (small) especially at low viscosity. Consequently, the best size of the spindle is an optimum, which takes account the accuracy of the spring deflection and the increased sway of the spindle.

The spindle size in the Figure 3 is applicable. But, at very low viscosities ($>5\text{cPas}$) a bigger spindle has been applied, because torque percentage went under 10-% with this spindle. However, this caused extra problems because the increased sway at different rotational speeds gave different viscosity readings. The error was minimised in determination of system dependent constant (SMC) by calculating an average SMC using different rotational speeds, and using the same averaging in actual measurements. The coned ends of the spindle

help the molten slag to drain off when the spindle is lift from the slag.

Comparison of a custom made and four standard spindles may clarify the problem (Fig. 4). The uppermost is custom made. It is made of solid molybdenum, weights 7.4g, and is 500mm long.. The second spindle from the top is a standard spindle, made of aluminium, weights 5.2g and is 115mm long. According to handbook this spindle can be used to measure accurately viscosity down to 1.5cPas (using 100RPM). It is clear that the custom made spindle becomes very inaccurate when viscosity approaches 1.5cPas, especially because 60rpm can't be exceeded (Chapter 10.2).



Fig. 4 Comparison of a custom made spindle and four standard spindles

The requirement of a long shaft plays maybe the most difficult part in the viscosity arrangement. Only a small bend in the shaft or a tilt in the coupling contributes to large displacement of the spindle. The left-handed, inch-measure, threading of the standard spindle connection was also problematic. The answer for the second problem was a Brookfield's fast coupling set, which was modified for a normal threading. The piece, which was attached to the molybdenum shaft was custom made by a precision instrument maker, while the rest of the coupling is from the commercial coupling set.

Neither the molybdenum shaft nor the threading is ever absolutely straight. The straightness of the shaft (connected to the custom part of the coupling) was inspected in the pillar-type-drilling machine. The spindle is slowly rotated above a target cross and deviation from the centre of the cross is seen. The shaft is slightly bent until the spindle stays in centre of the cross (Figure 4).



Fig. 5 Straightening a spindle shaft

7 Radiation shields

Heat radiation is the main mean to transfer energy at temperatures above 1000°C. In order to keep the furnace hot, save energy, and to protect surroundings and viscometer from heat radiation, it is necessary to use radiation shields.

The radiation shields were made of aluminium oxide tubes and aluminium oxide discs. The holes on discs were made with special made diamond grinder with pillar type drilling machine. A disc was fixed in a position in a hole made in plywood, which was placed in water containing box. Water served as cooling agent during grinding.

Two sizes of alumina tubes were used. The other was cut in pieces (approx. 15mm) to serve as seats for discs. These seats were joined to longer alumina stands by small alumina pivots, which were clued to place by water glass reagent.

In final assembly, the spindle shaft rotates inside the upper radiation shield's stand and the thermocouple is placed through the lower radiation shield. The lower radiation shield also serves as a stand for crucible.

8 Furnace atmosphere

The spindle and the crucible were made of molybdenum, which has a melting point of 2623°C. Unfortunately molybdenum oxidises readily. The oxide vaporizes rapidly at high temperatures, preventing formation of a protecting oxide layer, which would otherwise stop the reaction. Vaporized molybdenum oxide penetrates in the pores of aluminium oxide furnace tube and radiation shields, colours them red and softens aluminium so that the furnace tube may bend, bulge or a hole may form. At cooler zones of furnace, sublimation of molybdenum oxide forms whiskers. In order to prevent detrimental oxidation and breakdown of the spindle, crucible and furnace tube, the furnace has to be hermetically sealed and an inert or a reducing atmosphere has to be applied.

The temperature at which the oxidation becomes excessive in air can be estimated by realising that the furnace tube is sealed at the top and the only opening is the out-let pipe on the bottom of the furnace tube. Hot air won't go downwards and the furnace can be supposed to contain a small volume of air that is in equilibrium with the highest oxide of molybdenum (MoO_3). The equilibrium of solid MoO_3 and the gaseous molybdenum oxides in air can be calculated in thermodynamic calculation program HSC, and the results are presented in a Figure 5. If the furnace is thought to be open, so that no equilibrium is reached and vaporisation becomes continuous, the temperature at which the vaporisation of oxides slows down to insignificant level can also be estimated from the equilibrium diagram. The smaller the vapour pressure of oxide species, the slower is vaporisation of oxides in the air. From experience it is known that when vapour pressure is less than 10^{-10} bar, the vaporisation is already very slow. From the Figure 5,

it is seen that the corresponding temperature is 450°C. Above this temperature reducing atmosphere should be applied.

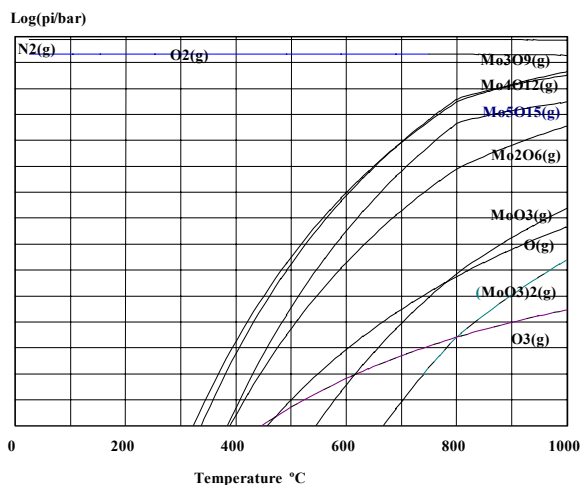


Fig. 6 Partial pressures of molybdenum oxides in air

The partial pressure of oxygen, at which the molybdenum oxide is in equilibrium with metallic molybdenum can be calculated by using a thermodynamic library in HSC and performing necessary calculations in a spreadsheet program (Fig. 7). Equilibrium calculation has been also performed for chromium, because the present study concentrates on chromium containing slags. Partial pressure of oxygen should be below the molybdenum equilibrium line ($\text{Mo} + \text{O}_2 = \text{MoO}_2$) in order to avoid oxidation, but above the chromium equilibrium line ($4/3\text{Cr} + \text{O}_2 = 2/3\text{Cr}_2\text{O}_3$) in order to avoid reduction of chromium oxide in the slag to metal.

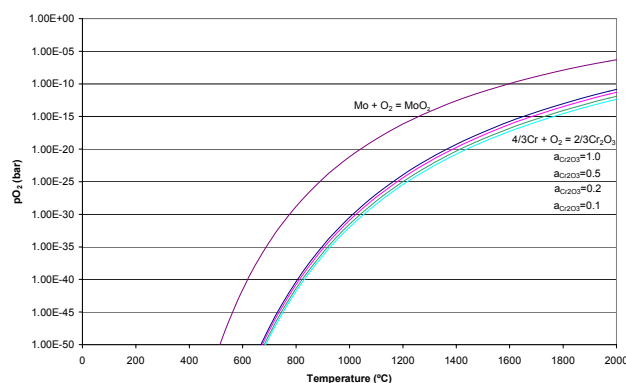


Fig. 7 Partial pressure of oxygen and temperature at which molybdenum and chromium are in equilibrium with their oxides

Unfortunately, the required partial oxygen pressures are so small that they are impossible to obtain in practise by using pure inert gas. Even the most pure commercial argon has much higher impurity levels of oxygen.

One way to solve this problem is to use mixture of carbon monoxide (CO) and carbon dioxide (CO_2). Oxygen partial pressure can be calculated from a reaction equation ($\text{CO} + 1/2\text{O}_2 = \text{CO}_2$) and equilibrium with molybdenum as well as carbon can be calculated. It

is seen in the Figure 7 that the mixture of 1-10% CO₂/CO is applicable for measurement of Cr₂O₃ containing slags in molybdenum crucible. Other advantages in using CO₂/CO mixture are that the gas flow rates do not need to be adjusted during warm up and cooling the furnace, and small air leaks are effectively neutralised by large amount of carbon monoxide. Disadvantage is that carbon monoxide is poisonous and need extra care to avoid any leak to laboratory environment. It would be advisable to build furnace to a closed room with good ventilation. Of course, the carbon monoxide is let out of the building directly from furnace.

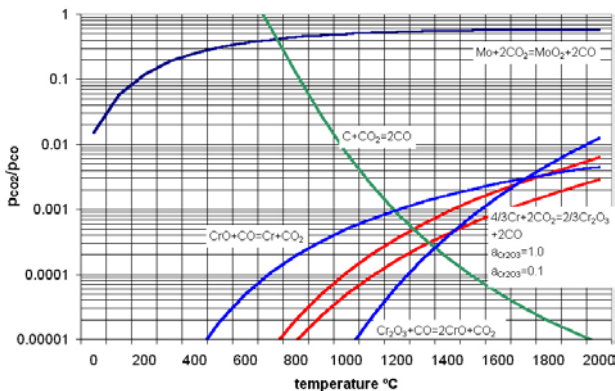


Fig. 8 Oxidation of Mo, Cr and C in CO₂/CO atmosphere at 1 bar pressure

9 Gas valves and flow controllers

Gas flow system is designed so that gas bottles can be changed during the measurement while the furnace is hot (Fig. 1). This enables to use a gas bottle until it is practically empty. It is also possible to use pure argon below slag melting point and then change to CO/CO₂ mixture at the measurement temperature.

Furnace atmosphere is controlled by adjusting gas flow rates with gas flow controllers. The used flow controllers are PC Brooks 8842 and PC 8845 with needle valve sizes 1 and 4 correspondingly. These flow controllers are designed to maintain a constant differential pressure across an integral manual flow regulating valve. PC 8840 series valves are designed to control flows when downstream pressure is constant (in this case normal air pressure) and upstream pressure is variable (PC 8940 series valves other way around).

Different gases have different flow rates through controllers and must be, therefore, determined for each used gas. The calibration can be done with a soap bubble flow meter (Fig. 9). In our study, two different sizes of flow meters were used, because the flow rate of CO was much larger than the flow rate of CO₂. The result is represented in Fig. 10.

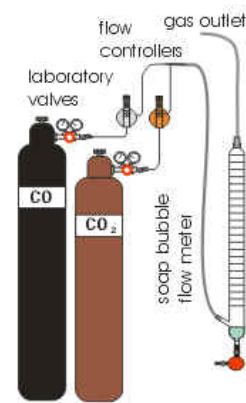


Fig. 9 Flow rate determination with a soap bubble flow meter

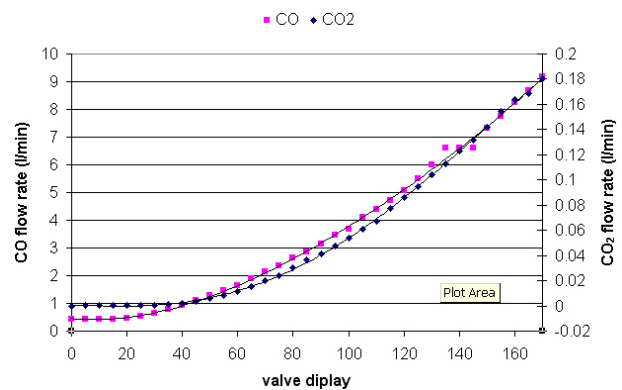


Fig. 10 Flow rates of CO and CO₂

10 Determination of system dependent constant

10.1 Calculation of system dependent constant

Viscometer is calibrated when delivered. It is certified to have error limits within $\pm 1\%$ of the maximum viscosity range when the standard spindles are used. However, if the user wants to use custom-made spindles, the system-dependent constant has to be determined. For example, the system-dependent constant (a) may relate the applied force (F) to the viscosity (η). Instead of the force, electric voltage (U), torque (τ) or any other measure of applied force can be used depending on the display of the apparatus.

Equation 1

$$\eta = aF$$

$$\eta = aU$$

$$\eta = a\tau$$

The easiest method to determinate the system constant is to use three standard viscosity fluids, and measure the applied forces. When viscosity is plotted against force, straight line should be observed, where the slope is the system-dependent constant.

In the Brookfield's viscometer the constant is called the Spindle Multiplier Constant (SMC), and it is calculated by a different procedure. At first, the custom-made spindle is immersed into a standard fluid, and the torque at certain rotational speed is measured. Second, the new full-scale viscosity range is calculated using Equation 2.

Equation 2

$$R1 = \frac{100\eta}{Y}$$

Where R1 is a new full-scale viscosity range, η is viscosity of a standard fluid and Y is the torque-% reading at the selected rotations per minute. (The accuracy of calibrated spring is $\pm 1\%$ of the R1).

The SMC is then

Equation 3

$$SMC = \frac{R1 \cdot rpm}{TK \cdot 10000}$$

Where the rpm is rotations per minute and TK is a torque constant, which is obtainable from the Brookfield's viscometer manual, and is 0.09379 for LVDV-II+ viscometer.

10.2 Determination of system constant at room temperature

In principle only one measurement with one standard fluid and one rotational speed would be sufficient for determine an apparatus constant. However, it is better to use more standard fluids covering wider viscosity range, and several rotational speeds. This way the validity of the apparatus constant at different viscosities and rotational speeds can be checked. For example, the long shaft of the spindle may cause oscillations at high rotational speeds, and thus more resistance for spindle rotations. Therefore, the corresponding SMC value might be different for low and high speeds. If the difference is great, the spindle construction has to be improved or the shaft has to be straightened.

The SMC constant can be selected so that it best represent true viscosity of the slag, e.g. a different SMC may be used in different viscosity ranges, an average SMC may be used, or if SMC shows linear variation, an regression formula might be considered. In any case, the standard fluids should be selected so that they have approximately same viscosities that the slag to be measured.

In the present study three silicon oils with nominal viscosities of 10, 50, and 500cPas (100, 500, 5000cP) at 25°C served as standard fluids. In order to keep the temperature at exact 25°C during measurement, the crucible, half filled with silicon oil, was placed in a water bath (Haake DC30) and the temperature was let to settle before measurement.

The spindle construction represented in Figure 3, gave little variation in SMC determination with these standard oils. At lower viscosities ($>5\text{cPas}$) this spindle construction gives too little resistance to be exact in measurements.

Usually, the most accurate viscosity reading is obtained when the torque-% reading (and the speed of the spindle) is highest possible. In practice this not always true, because the highest possible torque-% reading may require excessive high speeds of the spindle, which causes increased resistance due oscillation, as explained before. Therefore, during determination of SMC, and also during actual experiments the highest applied speed was 60rpm, and when 60rpm was too much, the speed was decreased, so that the highest possible speed was used.

10.3 Determination of system constant at high temperature with SRM

At high temperature the system dependent constant is obviously slightly different than in room temperature, because the crucible and the spindle expands. It has been recommended to determinate the system dependent constant also at high temperature.

A high temperature standard reference material (SRM) has been developed in BCR program of the EU². The composition of this material is 19.46% Li₂O, 14.06 Al₂O₃ and 63.8% SiO₂. It was recommended that viscosity measurements should be repeated on the SRM according to a strict protocol in an attempt to reduce the scatter shown by the results:

- The sample should be dried overnight at 110°C before measurements
- -Molybdenum or platinum components were preferable to graphite
- -A neutral (N₂, Ar) or reducing (Ar+10%H₂) atmosphere should be provided
- -Samples (SRM) should not be heated above 1400°C
- -All thermocouples should be checked against calibrated thermocouples
- -The difference between T_{melt} and T_{measured} should be determined
- -Nature of the isothermal hot zone should be well known
- -Before measurements on the SRM slag the viscometer should be calibrated with at least two oils in the 0.1-1.0 Pas (100cP-1000cP) range as well as NBS710 glass at high temperature

The following temperature-viscosity relationships are recommended for SRM:

² Broadbent CP, Franken M, Gould MD, Mills KC. 4th International Conference on Molten Slags, Fluxes and Salts, Japan, 1992.

Equation 4

$$\log 10\mu = -4.504(\pm 0.019) + 7461T^{-1}$$

,or

Equation 5

$$\log 10\mu = -8.125(\pm 0.019) + \log T + 8127T^{-1}$$

However, experience shows that this SRM is far from perfect choice to be used as a reference material, because:

- Li_2O volatilise easily and causes changes in composition
- Li_2O is a strong fluxing agent and it may react with the aluminium oxide furnace tube and destroy it.
- Our experiment showed traces of strong volatilisation and consolidation on a furnace tube as a blue cover.
- Li_2O is expensive material and difficult to handle. It should be treated under nitrogen atmosphere in order to avoid hydration and carbonation in air. It also irritates hands and lungs.
- Li_2O could be replaced by lithium carbonate but it is even more expensive.
- Li_2O is difficult to analyse, and can not be analysed in every laboratory

Better SRM would be cheap, easy to handle and prepare, it should not volatilise or change composition. The SRM should be easy and cheap to analyse before and after the measurements, and it should not be able to react with ceramic furnace materials. Such material could be, for example, a 50/50 weight-% mixture of SiO_2 and CaO .

11 Preparing samples for measurement

The most important aim in preparing samples is ensuring that the slag will melt and form homogenous liquid when viscosity measurement will be taken. It is impossible to see into the furnace when the furnace is hot, and if the slag has not melt when the measurement starts, it is very easy to break the spindle. Anyway, if the sample does not melt, viscosity can't be measured.

The second important aim is to treat the oxide powders such a way that required amount fits in to the crucible. There must be enough molten slag so that the spindle can be immersed in required depth. Different oxides have different densities, and finer oxide grains require more volume than coarse grains.

The third important aim is to prepare oxides so that they form a slag, which is as close to the aimed target composition as possible. This is achieved by using oxides, which have little impurities, heat oxides before weighting at 400°C in order to remove moisture and water of crystallization and heat carbide forming substances at 800°C in order to remove carbon. Finally

the oxides must be weighted carefully. The reason for this aim is not so important is that the slag is analysed after measurement. Nowadays, the results are used for construction of mathematical viscosity models, and the viscosity of a wanted composition can be then calculated.

Two most important aims may be achieved by same methods. In practise, it is best to use method of minimal effort. These methods may be listed from the least effort to the most laborious one:

1. If the slag has low melting point and high density, the crucible can be filled with well-mixed oxide powder with slight treading. Good mixing breaks up agglomerates and helps melt down. 100grams is usually enough for crucible in Fig. 3.
2. If oxide mixture has lower density and 100g will not fit in to the crucible, it can be pressed in to pellets in hydraulic press. This also brings the oxide grains closer each other, which also helps meltdown.
3. If the slag has such a high melting point that the above mentioned methods are not enough, the slag can be pre-melted. Measurement crucible with oxide pellets can be heated in vacuum induction furnace (often in argon atmosphere), which can be warmed up much higher temperatures than the resistance furnace. After the slag has been melted once, the second meltdown is easier.
4. It is also possible to pre-melt oxide mixture in separate graphite crucible in vacuum induction furnace. After melting the slag must be crushed and mixed. Usually, when oxide species have reacted the volume has shrunk and it will easily fit in the measurement crucible. It is better to fill the vacuum furnace with argon, so that volatile oxides are not so easily vaporized. Too high temperatures should be avoided for the same reason. Some oxides react with graphite crucible and this method can't be used with them (Fe_2O_3 , Cr_2O_3). Even SiO_2 (SiO) will vaporize at high temperatures especially if carbon is present.

12 Viscosity measurement procedure

The crucible is filled with 100g of a slag, and placed into the furnace. The spindle is placed on position and viscometer is let to auto-zero, the furnace is closed, and free rotation of the spindle, flow of cooling water and protective gas are verified. It is possible to save gas by waiting until the furnace reaches 400°C and then open the gas valve.

The furnace was programmed to heat up to the maximum temperature 1750°C at the speed of four degrees per minute. The time needed is thus about 7 hours.

When the maximum temperature was reached, the furnace was let to stay in the maximum temperature for one to three hours in order to stabilise the temperature variations, and ensure that high melting point slags form homogenous liquid. During that time the spindle was immersed into the molten slag, and let to heat up with the slag. Care must be taken when the spindle is immersed, because if the slag has not melt, the spindle shaft and possibly viscometer bearings might break. The spindle is let to rotate while slowly lowering the spindle, and the torque reading is followed constantly. First, the torque reading (as well as viscosity) should be zero. When the spindle touches slag, the torque reading starts to rise. If the slag has melt, the torque reading starts to rise slowly as spindle sink into slag. However, if the torque reading rises very fast and goes out of zone, it means that slag has not melt. After temperature stabilisation time, the first viscosity measurement is taken using several rotational speeds, but not speeds that exceeds 60RPM and not speeds, which torque-% is less than 10%.

The furnace was programmed to cool down in steps (50°C with lower and 20°C with higher melting point slags). The temperature was let to stabilize 30 minutes after every 50°C temperature drop and 20 minutes after every 20°C.

After measurements, the furnace was heated up again in order to help the slag drain off from the spindle, when the spindle was removed from the slag.

The furnace was then let to cool down to room temperature, which takes even more time than the heating up. At high temperatures, the furnace cools very quickly, and the power is needed to slow down the cooling rate. When the temperature is near 1000°C the cooling rate decreases so that power is no longer needed.

The protective gas flow was stopped when the temperature reached 400°C.

Sometimes it is appealing to use the same crucible and slag for several viscosity measurement trials. For example SiO₂-CaO-CrO_x system in equilibrium with metallic chromium was measured by this method (Fig. 11). Only two crucibles were needed for 14 trials. The first measurements (slag 1 and 8) were taken with binary SiO₂-CaO mixture. Then a 5-10g sample was taken for compositional analysis. After that a calculated addition of Cr₂O₃-Cr-SiO₂ or Cr₂O₃-Cr is added in pellet form, so that slag composition 1 becomes 2, and slag composition 8 becomes slag 9. This method is continued until all slag compositions are measured. This procedure saves both materials and effort. The equilibrium with metallic chromium was achieved by putting 10g of chromium flakes on the bottom of the crucible.

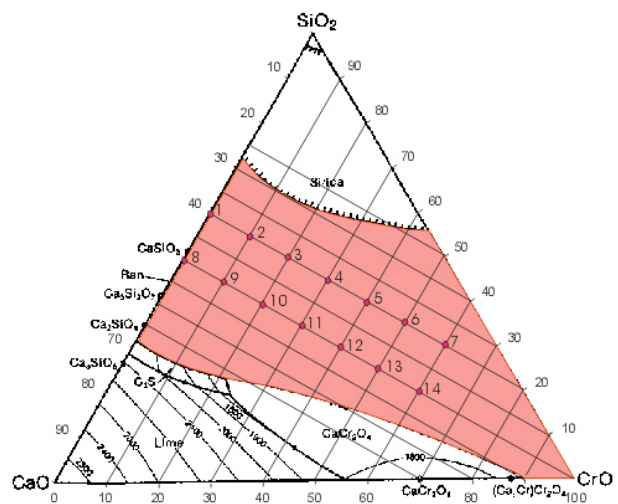


Fig. 11 Quasi-ternary phase diagram of SiO₂-CaO-CrO_x system in contact with metallic chromium³. Pink area corresponds to 1700°C liquidus, and red dots are measured slag compositions. Slags 1-8 were measured with one crucible and slags 8-14 with another.

13 Viscosity during cooling and heating cycles

In the first experiments, the viscosity was measured both during the cooling and heating cycles. It was believed that the viscosity would show hysteresis because of the differences of temperatures during the cycles. However, the hysteresis-behaviour seemed to be far too strong for the small temperature variations only. It was concluded that irrevocable compositional segregation takes place during the cooling cycle, where the solid phase collects on the sides of the crucible, and does not dissolve to the liquid during heating in convenient time. An example of such an experiment is represented in Fig. 12.

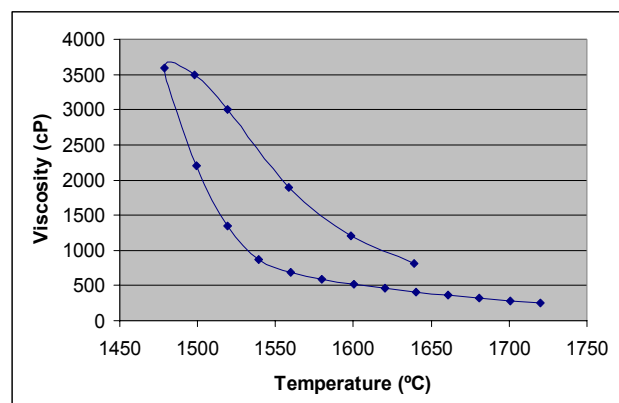


Fig. 12 Basic behaviour of viscosity during cooling and heating cycles

During stabilisation time at high temperature the slag forms homogeneous liquid. When the first measurements

³ de Villers JPR and Muan A, Liquidus-solidus phase relations in the system CaO-CrO-Cr₂O₃-SiO₂, J.Am.Ceram.Soc., 75 (1992)6, p.1333-1341.

are taken, the slag is a homogeneous liquid phase, and the viscosity follows Arrhenius equation. When the temperature decreases to the melting (liquidus) point, solid phase starts to segregate from the melt on top of slag, and on the walls and the bottom of the crucible according to temperature gradient.

This solid phase has different composition than the remaining liquid phase, as can be seen from a suitable phase diagram. When the amount of the solid phase increases so much that it touches the spindle, the viscosity seems to increase very rapidly, as schematically represented in Fig. 13.

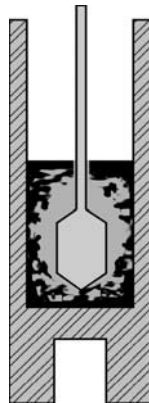


Fig. 13 Schematic illustration of solid growing in a crucible

In consequence, the viscosity may seem to increase smoothly well below the liquidus temperature, until the solid phase finally hinders the movement of the spindle. When the temperature is increased again, the viscosity is much higher than during the preceding cooling cycle. The reason for this is that the solid phase, which might have a very high melting point, does not melt again in reasonable time. Melting would need compositional homogenisation, which occur by diffusion and requires time.

Nevertheless, the measured viscosity below the melting point (liquidus) is not the viscosity of a same slag than above the liquidus, because the remaining liquid slag has diluted of some components, and the composition has altered. Therefore, the only “right” viscosity values can only be obtained at temperatures above the melting point, during the first cooling cycle, when no compositional segregation has occurred.

The existence of remaining solid phase at temperatures above the liquidus has also been proofed by adjusting the spindle height in the slag. At the normal position the viscosity was very high, but at a position few millimetres above the normal level, the viscosity decreased to very low values. At still higher position the viscosity seemed to rise again, which was taken as a proof of a solid slag cover.

In one trial, the spindle was raised several times up and down through the solid cover. This was thought to break the solid lid, which, as a heavier phase, was thought to sink on the bottom of the crucible. The spindle was then

removed from the slag and the furnace was let to cool down. The crucible was split in two halves, and an optical examination on the longitudinal section showed darker phase at the bottom of the crucible (Fig. 14). During splitting the crucible by sawing, and emptying the used crucibles by drilling, it was observed that the slag on the bottom on the crucible was harder than the slag on the top.

Compositional analysis was made by SEM-EDS, which also supported compositional segregation. The last solidified liquid has been collected in the centre of the crucible, i.e., in the middle of the longitudinal section (Fig. 14). The bottom phase differs from the top, maybe, because it has been solidified earlier (as the first solidified top was broken by the spindle and sank on the bottom).

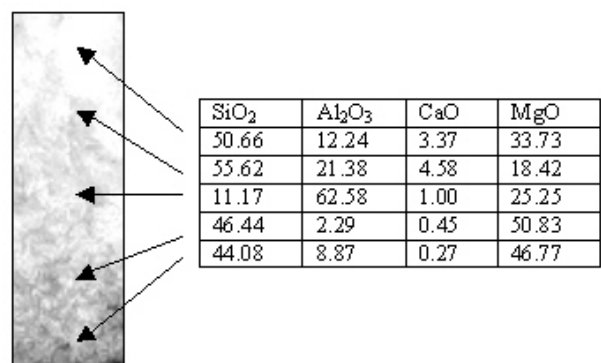


Fig. 14 Scanned image of a longitudinal section of the slag, and compositions from top to bottom. Contrast has been improved.

14 Sample analysis

The sample should be taken so that it best represents the total composition of the slag. As explained in the previous chapter, compositional segregation happens during solidifying. The best sample would be obtained by emptying the whole crucible and grind and mix the slag powder.

Sometimes the slag is very hard and all the slag all slag can't be removed by drilling and the crucible has to be broken if all slag is to be used in compositional analysis.

If the same slag is used for several viscosity measurement trials as explained in chapter 12, the error can be reduced by using 8-10 mm drill, and drilling deep hole in the midway of the centre and of the walls of the crucible.

The samples were crushed, mixed and analysed in a X-ray diffractometer. The amount of CrO was analysed with wet-chemical analysis.