Liquidus temperatures and viscosities of Shougang iron blast furnace slags

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Abstract: The blast furnace process continues to be the principal technique used for ironmaking in the world, contributing to over 1 billion tonnes of steel production annually world wide. The impurities present in the original ore result in several hundred million tonnes of waste product in the form of complex oxides, known as slag. The major chemical components of the iron blast furnace slag are Al_2O_3, CaO, MgO and SiO_2 that account for over 95 weight percent. Phase equilibria and viscosity data in the system Al_2O_3-CaO-MgO-SiO_2 have been used for iron blast furnace slag for many years. In addition to major components, minor components such as sulphur, TiO_2 and FeO are also present in the iron blast furnace slags. Modern ironmaking industry requires more accurate data to optimise operation of the blast furnace.

In the present study granulated iron blast furnace slags have been collected from Shougang. Liquidus temperatures of these industrial slags have been determined by high temperature equilibration, quenching and Electron Probe X-ray Microanalysis (EPMA) technique. The viscosities of the industrial slags have been measured using the custom designed rotating bob apparatus which enables control of the gas atmosphere and rapid quenching of the samples on completion the experiment. The microstructures and phase compositions in the quenched slag samples after the viscosity measurements are determined by EPMA. Corresponding synthetic slags have been used to evaluate effects of minor components such as sulphur, TiO_2 and FeO on liquidus temperature and viscosity of the iron blast furnace slags.

It was found that the liquidus temperatures of the industrial BF slags are in the range of 1410 to 1440 ^oC. The liquidus temperatures of the synthetic slags are 40-50 degrees higher than the corresponding industrial slags. Presence of minor components such as sulphur, TiO_2 and FeO in the slag appear to decrease of the liquidus temperature. The viscosities of the industrial BF slags are in the range of 0.3 to 0.4 Pa.s at 1500 ^oC. The viscosities of the synthetic slags are 30% higher than that of corresponding industrial slags at 1500 ^oC. The differences of liquidus temperatures and viscosities between industrial slags and synthetic slags will provide useful indications that will assist the application of the results of the synthetic slags to improve the operation of the iron blast furnace.

Key words: ironmaking, blast furnace slag, liquidus temperature, viscosity

1. Introduction

The principal components of current iron blast furnace slags are described by the system Al_2O_3-CaO-MgO-SiO_2 [1,2]. Al_2O_3 and SiO_2 are usually introduced from iron ore and coke/coal ash and CaO and MgO are usually added as flux. The targets of optimum slag compositions are to minimise slag mass and operating temperature whilst satisfying requirements for sulphur and alkali removal, and slag tapping [3,4]. In modern ironmaking operations the hot metal and slag temperatures are controlled within a narrow range to obtain stable operation of the blast furnace. More accurate data on the physical and chemical properties of the slag, such as, liquidus temperature and viscosity are required to optimise the operation of the blast furnace.

In addition to Al_2O_3, CaO, MgO and SiO_2, up to 5 wt% of other components, such as S, TiO_2, MnO and FeO may also be present in the BF slags. [5]. According to Osborn et al, [5] these minor elements could decrease the liquidus temperatures of the actual BF slags by up to 100 degrees. However, Baldwin reported [6] that the liquidus temperatures of the actual BF slags are close to those calculated from Osborn's phase diagram [5]. It is important to ensure the slag to be fully liquid inside the blast furnace because: 1) presence of significant fractions of solids in the slag will sharply increase its viscosity, which results in difficulties of tapping and sulphur removal [7]; 2) presence of solid in the slag will affect its hydraulic properties, which is important for cement-making [6].

A large number of data on liquidus temperatures and viscosity of the Al_2O_3-CaO-MgO-SiO_2 slags have been reported. [1-2, 5] However, the differences between the actual slags and the Al_2O_3-CaO-MgO-SiO_2 slags have to be determined before the information of these synthetic slags can be used with confidence by industry. The aim of the present study is to experimentally determine the liquidus temperatures and viscosities of Shougang BF slags and corresponding synthetic slags to provide indications on how fundamental data of synthetic slags can be applied to industrial practice.

2. Experimental

2.1 Liquidus temperature

The experimental method used in the present study to determine the slag liquidus temperatures involves high temperature equilibration, quenching and electron probe X-ray microanalysis (EPMA). The experimental procedure is similar to that described in previous publications by the authors [8-9].

In brief, approximately 0.2 g granulated industrial slag was placed in a graphite crucible (10mm diameter and 10mm high). The crucible was placed in a basket made from pure Mo wire. Equilibration experiments were carried out in an atmosphere of ultra high purity Ar gas in a vertical recrystallised alumina reaction tube heated by lanthanum chromite elements (PYROX, France). The crucible containing the sample was suspended by Mo wire. The samples were equilibrated at predetermined temperatures for times from 1 to 6 hours depending on the slag composition and temperature, and then quenched into ice-cooled water. The influence of reaction time has been tested at the beginning of the project to ensure that phase equilibrium has been achieved. The corresponding synthetic slags were prepared from high purity (99+%) MgO, SiO_2, Al_2O_3 and $CaCO_3$ powders. When necessary FeO, FeS or TiO_2 was added to introduce FeO, sulphur or TiO_2 respectively. The mixtures of the powders were mixed and pelletised for the equilibration experiments.

The quenched slag samples were mounted in epoxy resin and polished for metallographic examination. The polished samples were coated with carbon using a JEOL (Japan Electron Optics Ltd) Carbon Coater for electron microscopic examination. A JXA 8200 Electron Probe Microanalyser with Wavelength Dispersive Detectors was used for further analysis. The analysis was conducted at an accelerating voltage of 15 kV and a probe current of 15 nA. The ZAF correction procedure supplied with the electron probe was applied. The standards used for EPMA include alumina (Al_2O_3) for Al, magnesia (MgO) for Mg, rutile (TiO_2) for Ti, hematite (Fe_2O_3) for Fe, chalcopyrite ($CuFeS_2$) for S and wollastonite ($CaSiO_3$) for Ca and Si. These standards were provided by Charles M Taylor Co., Stanford, California, USA. The average accuracy of the EPMA measurements is within 1 wt %.

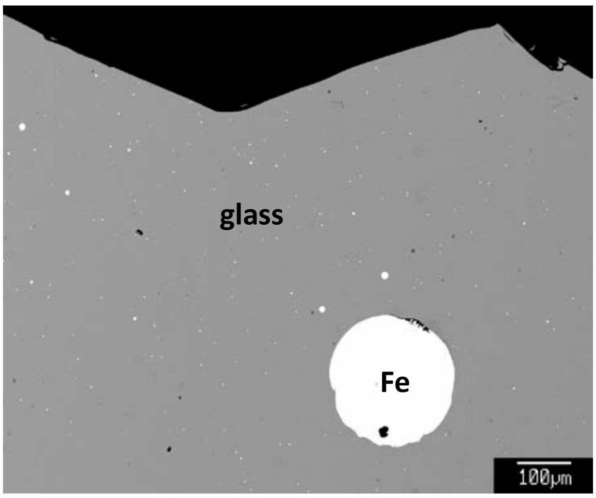
2.2 Viscosity

The viscosities of the actual and synthetic slags have been measured using an experimental apparatus recently developed in the Pyrometallurgy Research Centre [10-11]. This apparatus allows the slag viscosity measurements to be carried out in controlled or gas-tight atmospheres, and with a possibility of quenching the sample after the measurements have been completed. A Brookfield DVIII+ rheometer was used for the viscosity measurements. The rotating spindle and crucible were made from pure Mo. The rheometer was confined in a gas-tight chamber, the upper end of the reaction tube was connected with the chamber and the lower end of the reaction tube is closed by glass window. The detailed procedure of the viscosity measurements is similar to that reported previously [10-11]. Each set of bob and crucible used has been individually calibrated together with the rheometer, using standard calibration liquids (0.0092, 0.0484, 0.0968, 0.51 and 0.96 Pa.s) at 298.0 K, to minimise the uncertainties of the measured viscosities.

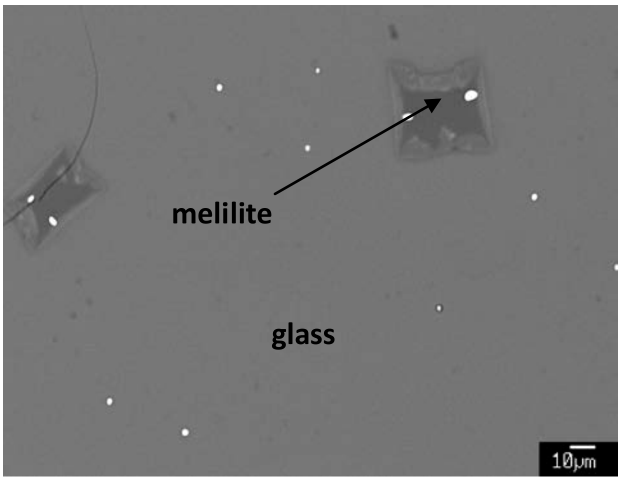
3. Results and discussions

3.1 Liquidus temperature

Typical microstructures of granulated BF slags from Shougang are presented in Figures 1 and 2. Figure 1a shows a typical microstructure of granulated BF slags from Jingtang No 1 blast furnace. It can be seen that the slag was fully liquid containing iron droplets at temperature. Figure 1b shows a typical microstructure of Jingtang BF slag reheated and quenched from 1420 ^{o}C. It can be seen that a small fraction of melilite phase was present at 1420 ^{o}C indicating that liquidus temperature of this slag is slightly higher than 1420 ^{o}C.



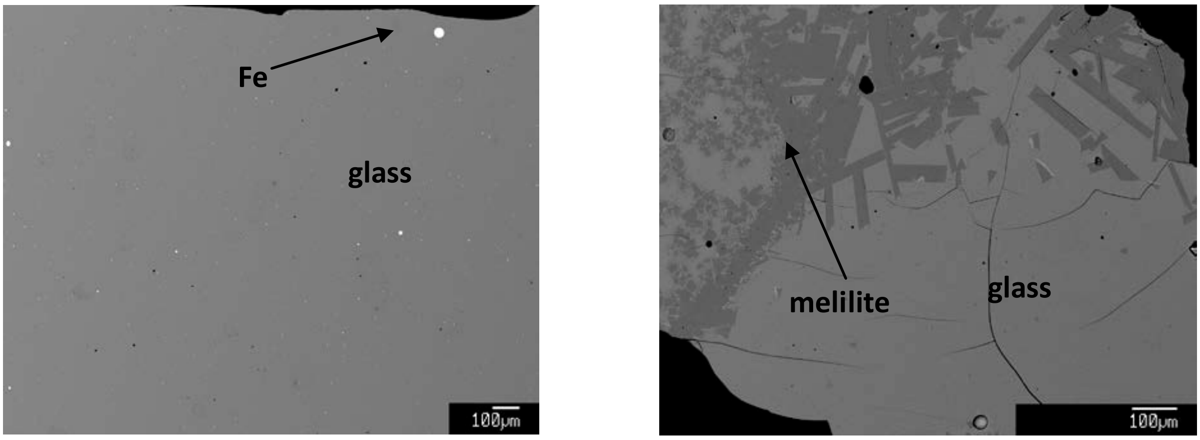
a. as-received slag



b. slag quenched from 1420 ^{o}C

Fig. 1 Typical microstructures of Jingtang blast furnace slag

Figure 2a shows a typical microstructure of granulated BF slags from Qiangang No 1 blast furnace. There was only liquid and small iron droplets present at temperature. Figure 1b shows a typical microstructure of Qiangang BF slag reheated and quenched from 1400 ^oC. The presence of melilite phase indicates that liquidus temperature of this slag is higher than 1400 ^oC. A separate quenching experiment shows that only liquid was present at 1420 ^oC, which locates the liquidus temperature of this Qiangang slag between 1400 and 1420 ^oC.



a. as-received slag b. slag quenched from 1400 ^oC

Fig. 2 Typical microstructures of Qiangang blast furnace slag

The bulk composition of as-received Jingtang BF slag was measured by XRF and shown in Table 1. It can be seen that in addition to Al_2O_3, CaO, MgO and SiO_2, sulphur, TiO_2, MnO and FeO were also present in the slags in small amounts. EPMA measurement of the glass phase indicates that there was only 0.1 wt% FeO present in the liquid phase at temperature and the rest iron was present in the slag as iron metal which is constant with the microstructure shown in Figure 1a. At 1420 ^oC it has shown that there was a small fraction of the melilite phase present in the slag. EPMA measurement of the glass phase shows that the composition of the glass phase quenched from 1420 ^oC is close to that in as-received slag, again confirming that proportion of solid phase was low. EPMA measurements show that the composition of the melilite is the solid solution of akermanite ($2CaO.MgO.2SiO_2$) and gehlenite ($2CaO.Al_2O_3.SiO_2$). No sulphur, TiO_2, MnO and FeO were detected in the melilite phase.

The synthetic slag corresponding to the Jingtang BF slag was prepared from pure powders of Al_2O_3, CaO, MgO and SiO_2 by recalculating the four major components to 100 wt%. It can be seen from Table 1 that this synthetic slag is completely liquid at 1480 ^oC but has melilite present at 1460 ^oC giving the liquidus temperature of the slag approximately 1470 ^oC. This result shows that the liquidus temperature of the synthetic slag is 50 degrees higher than that corresponding industrial slag (1420 ^oC). Further experiments shown in Table 1 confirm that additions of sulphur, TiO_2 and FeO in the synthetic slag can significantly decrease its liquidus temperature. The quenching experiments of Shouqin and Qiangang BF slag show similar results, i.e., the liquidus temperatures of the synthetic slag are 40-50 degrees higher than that corresponding industrial slag. This conclusion provides confidence for the metallurgist to use fundamental phase diagrams in the system Al_2O_3-CaO-MgO-SiO_2 in air as the predictions of the liquidus temperatures from four major components are always higher than the actual slags. On the other hand, however, it indicates that the current operating temperatures (hearth temperatures) based on the predictions of the synthetic slags can be possibly decreased provided that the viscosity and sulphur removal properties are satisfied.

Table 1. Bulk composition of as-received Jingtang BF slag measured by XRF and compositions of glass measured by EPMA, L = liquid; M = melilite

Sample	By	Temperature	Phase	Composition of glass (wt%)								
		^{o}C	present	CaO	MgO	Al_2O_3	SiO_2	FeO	TiO_2	MnO	S	CaO/SiO_2
industrial	XRF	as-received	L only	39.5	8.0	16.1	34.0	0.3	0.7	0.2	1.3	1.16
	EPMA	as-received	L only	39.3	8.3	16.2	33.9	0.1	0.7	0.3	1.2	1.16
		1420	L + M	39.3	8.3	16.2	33.9	0.1	0.7	0.3	1.2	1.16
synthetic	EPMA	1480	L only	40.4	8.4	16.4	34.6	0.0	0.0	0.0	0.0	1.17
	EPMA	1460	L + M	40.4	8.4	16.4	34.6	0.0	0.0	0.0	0.0	1.17
	EPMA	1450	L + M	40.1	8.3	16.2	34.3	0.0	1.0	0.0	0.0	1.17
	EPMA	1440	L + M	40.3	8.7	15.4	34.8	0.0	0.0	0.0	0.9	1.16
	EPMA	1440	L + M	39.8	8.9	14.7	35.2	1.2	0.0	0.0	0.1	1.13
	EPMA	1410	L + M	38.7	8.3	16.3	34.7	0.2	0.0	0.0	1.8	1.11

The effects of minor elements, such as, sulphur (in form of CaS), FeO, MnO, TiO_2, CaF_2 and B_2O_3 on liquidus temperatures of the BF slag are predicted by FactSage 6.2 [12] as shown in Figure 3. It can be seen that all minor elements continuously decrease the liquidus temperatures of the BF slags in melilite primary phase field. In case of TiO_2 addition the liquidus temperatures start to increase when the TiO_2 concentration in the slag is greater than 7.5 wt% where $CaTiO_3$ becomes the primary phase. This behavior of TiO_2 has been confirmed by recent experimental studies. [8-9]. Quantitative effects of these minor elements on liquidus temperatures of the BF slags need to be verified by further experimental work.

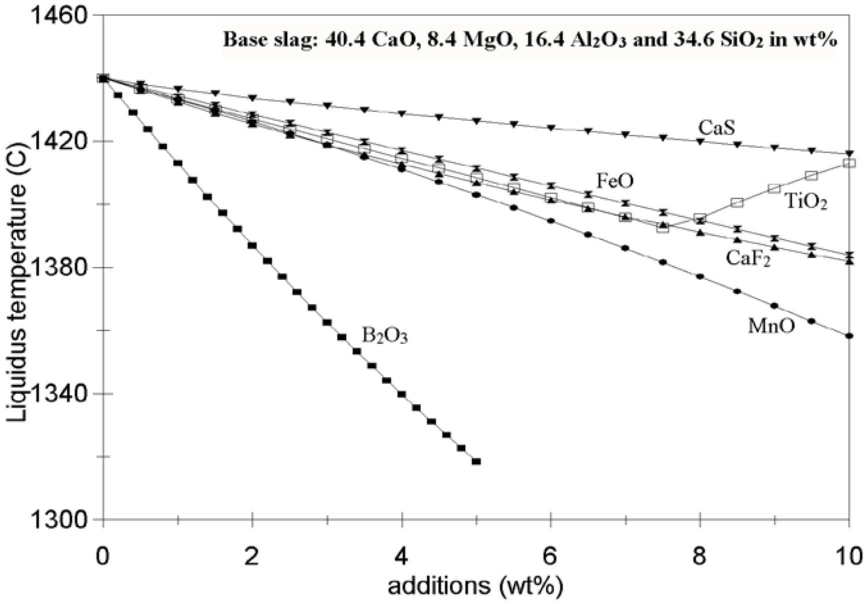
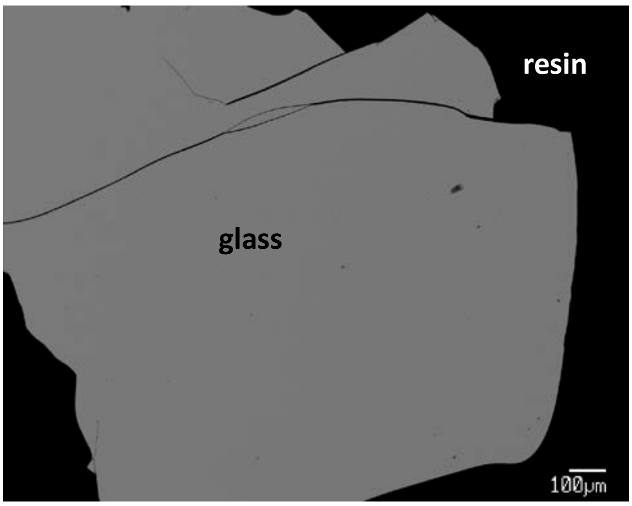


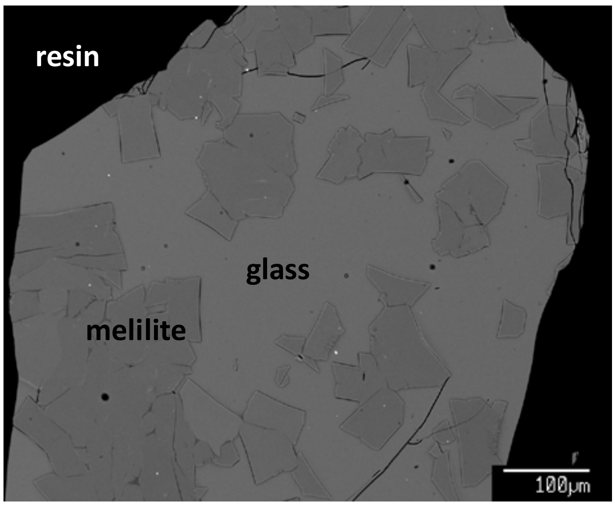
Fig. 3 Predicted Effects of minor elements on liquidus temperature of BF slag calculated by FactSage 6.2

3.2 Viscosity

Viscosities of the actual and synthetic slags have been measured in Ar gas using Mo bob and crucible. This experimental apparatus developed at Pyrometallurgy Research Centre enables the sample to be quenched after the viscosity measurements have been completed. Figure 4a shows a typical microstructure of the actual Jingtang slag quenched from 1450 ^oC after the viscosity measurements. It can be seen that only liquid was present at 1450 ^oC in the actual slag. Figure 4b shows a typical microstructure of the synthetic Jingtang slag quenched from 1450 ^oC after the viscosity measurements. It can be seen that melilite phase was also present during the viscosity measurement at 1450 ^oC. EPMA measurements of these quenched samples confirm that the compositions of the actual and synthetic slags are the same as those given in Table 1 and less than 0.2 wt% MoO_3 was present in the slags.



a. industrial slag



b. synthetic slag

Fig. 4 Typical microstructures of industrial (Jingtang) and synthetic slags quenched from 1450 ^oC after viscosity measurements

The viscosities of the actual and synthetic Jingtang slags are shown in Figure 5. It can be seen that the viscosities of the Jingtang slag are 0.16 Pa.s at 1600 ^oC and 0.53 Pa.s at 1420 ^oC. It can be seen from Figure 5 that the viscosities of the corresponding synthetic slag are significantly higher than those of the actual slag in the temperature range investigated. At temperatures above 1470 ^oC the viscosities of the synthetic slag are 0.06-0.09 Pa.s higher than those of the actual slag. 1470 ^oC is the liquidus temperature of the synthetic Jingtang slag determined by the equilibration experiments (see previous section) and is confirmed again by the viscosity data. However, at 1450 ^oC in which melilite phase is present (Figure 4b) the viscosity of the synthetic slag is 0.24 Pa.s higher than that of the actual slag, which represents 57% increase.

The present study shows that the minor elements present in the BF slag can significantly decrease the viscosity. The individual effect of each minor element needs to be identified in further studies. It also shows that the accurate and reliable liquidus temperatures are very important guide in selection of BF slags. The BF slag is "long slag" in the operating temperature range above the liquidus. However, formation of the solid phase can sharply increase the viscosity of the slag resulting in operating difficulties. Experimentally determined viscosities of the Baosteel BF slag [13] with the close composition to the Jingtang slag are shown in Figure 5 for comparison. It can be seen that the viscosities of the actual Jingtang BF slag are very close to those of actual Baosteel BF slag.

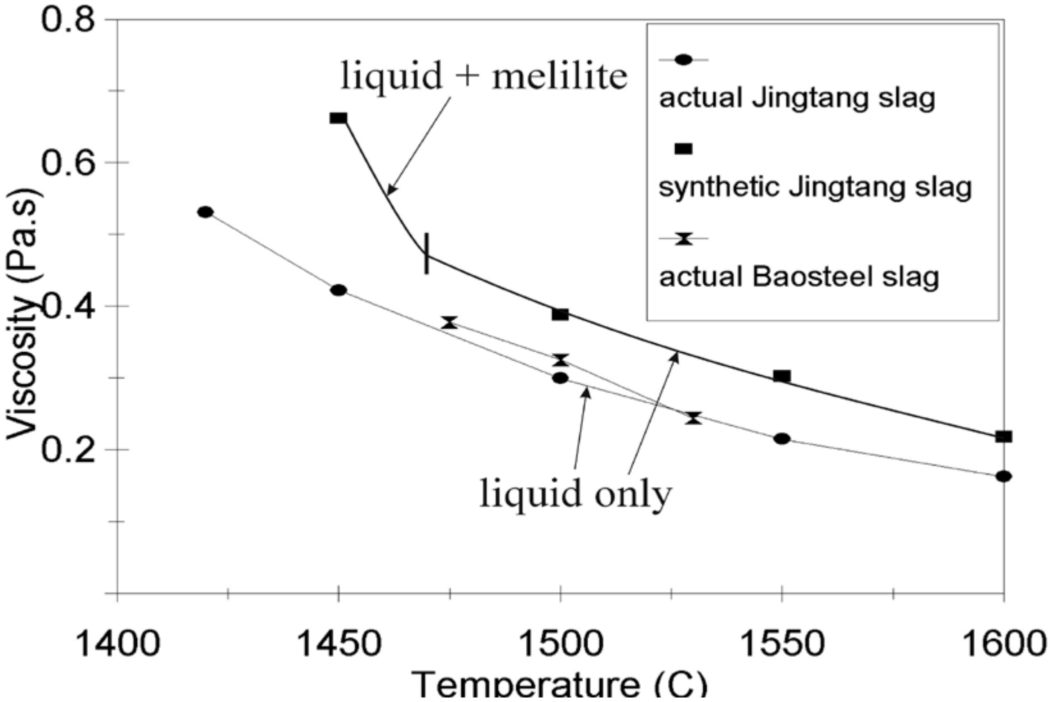


Fig. 5 Experimentally determined viscosities for Jingtang BF slag and corresponding synthetic slag,
The compositions of the actual Jingtang and synthetic slag are given in Table 1,
Baosteel slag: CaO 40.9, MgO 8.0, Al_2O_3 15.5 and SiO_2 35.6 wt% [13]

The effect of temperature on viscosity can be expressed as the Arrhenius-type relationship shown below [14]:

$$\eta = Ae^{\frac{Ea}{RT}} \quad (1)$$

Where η is viscosity (Pa.s); A is the constant (Pa.s); Ea is the activation energy (J/mol); R is the gas constant (J/mol/K) and T is the absolute temperature (K). It can be rewritten as

$$\ln(\eta) = \frac{Ea}{RT} + B \quad (2)$$

The ln(η) should be a linear relationship with $\frac{1}{T}$. Figure 6 shows plots of ln(η) versus $\frac{1}{T}$ for Jingtang BF slag and corresponding synthetic slag. It can be seen that in the temperature range investigated (1420 to 1600 ^{o}C) a good linear relationship has been shown for the actual Jingtang slag (R-squared, 0.9995). The activation energy derived from the plot is 174 kJ/mol for the Jingtang BF slag. In case of the synthetic slag, a good linear relationship has also been shown at temperatures above the liquidus 1470 ^{o}C (R-squared, 0.992). The activation energy of the synthetic slag is calculated to be 158 kJ/mol.

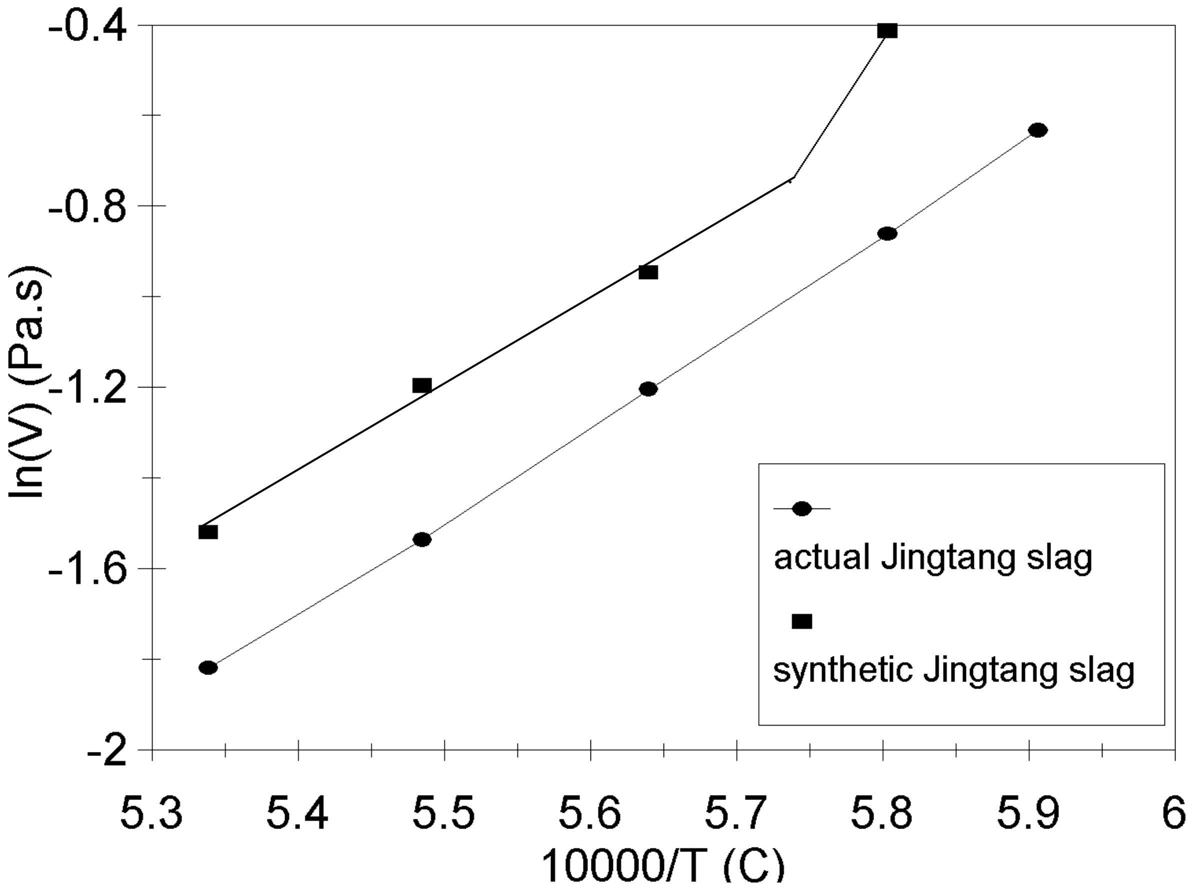


Fig. 6 Plots of ln(η) versus $\frac{1}{T}$ for Jingtang BF slag and corresponding synthetic slag,

The compositions of the actual Jingtang and synthetic slag are given in Table 1,

4. Conclusions

Granulated iron blast furnace slags have been collected from Shougang. Liquidus temperatures of these industrial slags have been determined by high temperature equilibration, quenching and Electron Probe X-ray Microanalysis (EPMA) technique. The viscosities of the industrial slags have been measured using the custom designed rotating bob apparatus, which enables control of the gas atmosphere and rapid quenching of the samples on completion the experiment. The microstructures and phase compositions in the quenched slag samples after the viscosity measurements are determined by EPMA. Corresponding synthetic slags have been used to evaluate effects of minor components such as sulphur, TiO_2 and FeO on liquidus temperature and viscosity of the iron blast furnace slags.

It was found that the liquidus temperatures of the industrial BF slags are in the range of 1410 to 1440 ^{o}C. The liquidus temperatures of the synthetic slags are 40-50 degrees Celcius higher than the corresponding industrial slags. The presence of minor components such as S, TiO_2 and FeO in the slag appears to decrease of the liquidus temperature. The viscosities of the industrial BF slags are in the range of 0.3 to 0.4 Pa.s at 1500 ^{o}C. The viscosities of the synthetic slags are 30% higher than that of corresponding industrial slags at 1500 ^{o}C. The activation energy is calculated to be 174 kJ/mol for the Jingtang BF slag and 158 kJ/mol for the synthetic slag. The differences of liquidus temperature and viscosity between industrial slags and synthetic slags provide useful indications about the application of laboratory-based results of the synthetic slags to improvement to the operation of the iron blast furnace.

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