Estimate of the surface tension and the viscosity of the slag in the magnesium injection process

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Abstract: Sulfur content of steel can be reduced to a lower level with a low content of hot metal, which can be implanted by employing the magnesium injection process in the blast furnace to have an efficient desulfurization of the liquid iron. However, the slag surface tension and viscosity will change with the increase of MgS content of desulfurization product, which may cause operation trouble. It is necessary to know the relationship between the surface tension and viscosity with the composition of MgS contained slag.

In this paper, the melting temperature and surface tension of FetO-SiO_2-CaO- MgO-Al_2O_3-TiO_2-MnO-MgS slag with different compositions including magnesium sulfide will be first evaluated with the sessile drop contact angle method. The viscosity is then predicted by using the optical basicity ratio model. Furthermore, by applying Pelofsky equation, the surface tension could be calculated with the viscosity values. Finally, the experimental surface tension is correlated with measured values.

Key words: Viscosity, Surface tension, Optical Basicity, Magnesium sulfide, Pelofsky eq

1. Introduction

The demand of low sulfur content of steel is increasing in the modern industry product; therefore an effective desulphurization of molten iron could be beneficial to the following successful sulfur elimination in steel-making. Although low oxygen content of iron is one of favorable condition for desulphurization, the low temperature of molten iron is not advantageous to the desulphurization. In order to make up for this shortcoming, magnesium injection has been used to enhance the desulphurization of hot metal. Although the sulfur could be eliminated efficiently with magnesium treatment, problems of resulfurization, increase of melting point, viscosity and difficulties of removing slag may occur at the end of processing [1]. There are rare reports about the above mentioned slag properties in the literature, therefore, a fast way is required to determine these properties of slag to find the relationship between the slag properties and change of MgS content. A technique of sessile drop contact angle method is used to measure the melting point and surface tension of blast furnace type slags, then viscosity could be estimated with the measured data.

There are several models to predict the viscosity of slags in the references[2~4] and the model of modified optical basicity with ratio of basicity of basic to acidic oxides from Seetharaman et.al [5] has been demonstrated that accurate value could be predicted in blast furnace. Due to the similarity of slag component , this model has been also used to calculate the viscosity of MgS contained iron slags.

2. Model of Estimating Surface Tension and viscosity

A.Shankar and G.Noruerop presented ratio model[5] which utilizes the ratio of optical basicity and the ratio of optical basicity to calculate the viscosity

$\ln \eta = \ln A + B/T$ (Arrhenius-behavior)

$\ln A = -0.3068B - 6.7374$ $B = -9.897\Lambda_{NEW} + 31.347$, where Λ_{NEW} was defined as follows

$$\Lambda_{NEW} = \frac{\frac{\Sigma((X_B n_B \Lambda_B + \cdots)}{\Sigma(X_B n_B + \cdots)}}{\frac{\Sigma(X_A n_A \Lambda_A + \cdots)}{\Sigma((X_A n_A + \cdots)}} \cdots \quad (1)$$

X_A、X_B are the mole fraction of acidic and basic oxides. n_B and n_A are the number of oxygen of basic and acidic oxides. Λ_A and Λ_B are the optical basicity of acidic and basic oxides(Assumption 1 sulfur equal to 0.71 oxygen.).

In general surface tension decreases with increase of temperature [6] and could be correlated to viscosity from equation proposed by Pelofsky[7], which is defined as follows

$$\ln\gamma = B/\eta + \ln A \quad (2)$$

where γ is surface tension, B is a function of (Mk/R), M is molecular weight, k is the thermal conductivity, R is gas constant, η is viscosity, A is regarded as surface tension of solid phase when viscosity achieve infinity.

As to the optical basicity of magnesium sulfide, it could be calculated with pauling electronegativity as shown in equation (3)[15].

Where Λ is optical basicity of slag, Xav is average electronegativity of chemical compound.

$$\Lambda = \frac{0.75}{X_{av} - 1.35} \quad (3)$$

Xav is average electronegativity of chemical compound, which is given in formula (4),

Where Xi is pauling electronegativity of element, ni is the number of element.

$$x_{av} = \frac{\sum_{i=1}^{N} X_i n_i}{\sum_{i=1}^{N} n_i} \quad (4)$$

$\gamma = 1.36(x - 0.26)$ γ is the correct constant[17], which was used to determine pauling electronegativity of sulfur and magnesium. In this way optical basicity of magnesium sulfide is estimated as 1.507(basic) , while optical basicity of calcium sulfide is 1.9((basic).

In measure of surface tension, the change of density with composition and temperature is also necessary considered. A linear relationship between density and optical basicity has been found in reference [13].

$$\rho = \rho_0 \exp(E/RT) \quad (5)$$ and

$$E = m + n \cdot \boldsymbol{\Lambda} \quad (6)$$

Λ is optical basicity, which is given in equation (7)

$\Lambda = \frac{\sum x_i n_i \Lambda}{\sum x_i n_i}$……………………………………………………………. (7)

3. Experiment

3.1 Sample preparation

Due to the difficulty in preparing the blast furnace slag with conventional heating furnace, an experimental ESR (electro slag remelting) unit is applied to melt the synthesis slags. In order to reduce oxidizing and vaporization of slag component, Argon gas is introduced into the cover of ESR. $MgSO_4$ and carbon are mixed to get magnesium sulfide with aid of high remelting temperature. The slag is first ground down to powder and then mixed with liquid of amylum. The mixer is subsequently extruded to a cylindricl disk of 3mm in diameter and height. It is then placed on the substrate contacted with thermal couple in the sessile drop contact angle measurement instrument SCA20, as shown in Figure1.

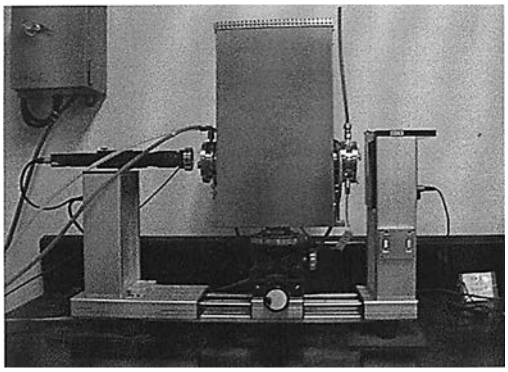


Figure1. Sessile drop contact angle measurement instrument

3.2 Measurement of slag liquidus temperature and surface tension

Sessile drop contact angle method of SCA20 (shown in Figure 1) is used in measurement of liquidus temperature and surface tension of slags and the profile of liquid drop is calculated with Young-Laplace Fitting method.

Slag sample is gradually softened during heating. It then starts to melt and finally becomes fluid when the temperature nearly reaches to the melting point. Measurement error of surface tension can be reduced with Molybdenum substrate [8]. The chemical composition of oxides is analyzed by XRF and the concentration of sulfur is analyzed by carbon and sulfur analyzer.

4. Results and Discussion

4.1 The melting point and equilibrium phase of solid and liquid in high temperature

One exemplar measurement of liquidus temperature of slag sample is given in Figure 2, which shows a cone shape formed when the slag starts to become liquid.

The measurement of sessile drop contact angle method is calibrated with CaO-Al2O3 slag system. Results indicate that measurement temperature has difference of 53℃(error of 3.6%) higher than the temperature read from phase diagram as shown in Figure18.

The error might come from the change of thermal conductivity with temperature [11] and material of substrate [12].

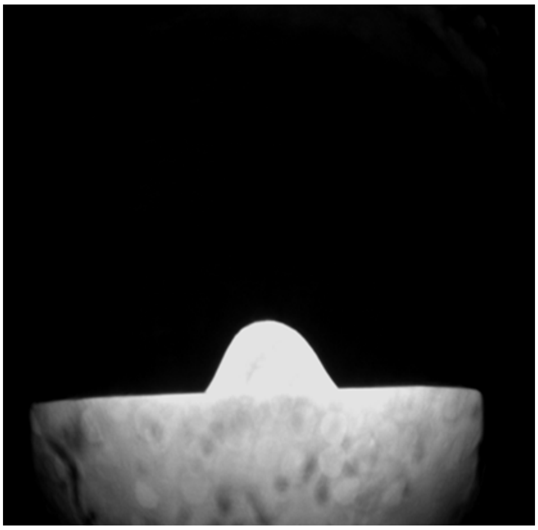


Figure2.The shape of slag which melt is observed by sessile drop contact angle method.

The measurement of sessile drop contact angle method has been calibrated with CaO-Al2O3 slag system. Result indicated that value of measurement is higher than the temperature read from phase diagram. The difference is 53℃ with error of 3.6% as shown in Figure 3.

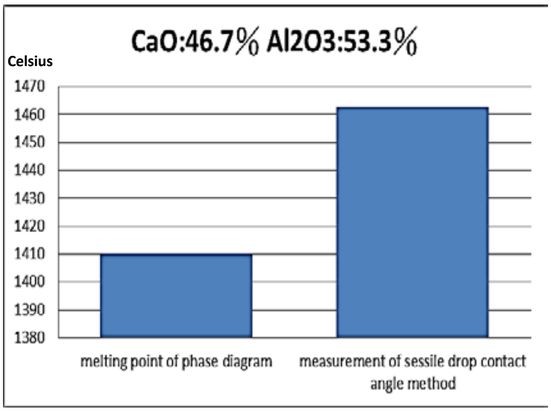


Figure 3 The difference between sessile drop contact angle method and melting point of phase diagram in CaO-Al_2O_3 slag.

The error might come from the change of thermal conductivity with increase of temperature [11], selection material of substrate [12] and size of sample in sessile drop contact angle method.

The compositions of slag produced by ESR are listed in Table 1. Content of magnesium and calcium sulfide are low due to the oxidization and evaporation loss of MgS during remelting operation .

Figure 4 to Figure 7 show the result of melting point of sample1A ~7A and the diagram indicate that melting point of CaS contained slag is higher than the melting point of slag with zero content of CaS.

Table 1.The chemical composition of slag was identified by XRF and analytic method of carbon and sulfur

wt%	CaO	MgO	Al_2O_3	SiO_2	MnO	TiO_2	TFe	CaS	Measured Temperature	Measured Surface Tension(mN/m)
Sample1A	40.29	6.08	14.78	32.42	1.13	0.6	2.1	0.63	1425	496
Sample2A	39.44	6.44	15.33	32.86	1.24	0.64	1.58	0.39	1450	482
Sample3A	40.28	7.58	15.69	32.96	1.28	0.6	1	0.15	1443	682
Sample4A	40.21	7.7	15.89	33.2	1.27	0.62	1.04	0.142	1429	520
Sample5A	40	7.52	15.67	33.36	1.42	0.58	1.28	0.128	1542	461
Sample6A	40.19	8.11	15.73	33.52	1.37	0.56	0.99	0.12	1442	634
Sample7A	39.63	8.02	15.82	33.11	1.22	0.52	1.46	0.142	1436	750
Sample1B’	50.71	7.22	13.02	25.56	0.39	0.6	0.63	0	1422	1012
Sample1A’	40.55	6.12	14.88	32.63	1.13	0.6	2.1	0	1386	678
1B(B=2,S=2%)	48.9	6.97	12.55	24.64	0.6	0.81	0.39	3.53	1433	476

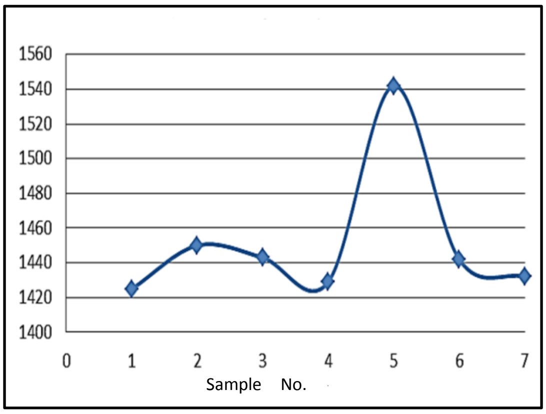


Figure 4. Variation of melting point of sample1A~7A which contain different concentration of calcium sulfide.

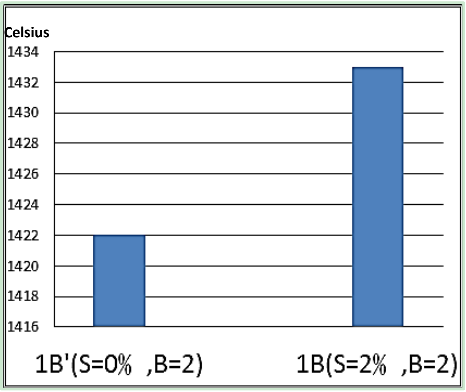


Figure 5. Melting point of 1B(S=2%,B=2)

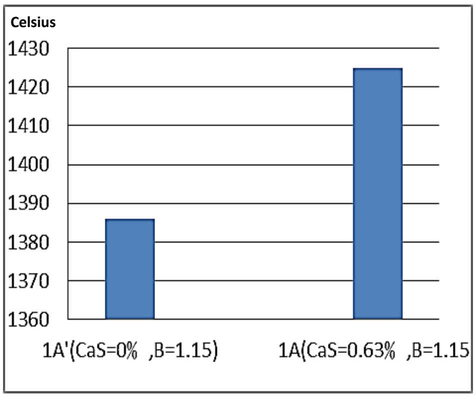


Figure 6.Melting point of 1A (CaS=0.63％,B=1.15)

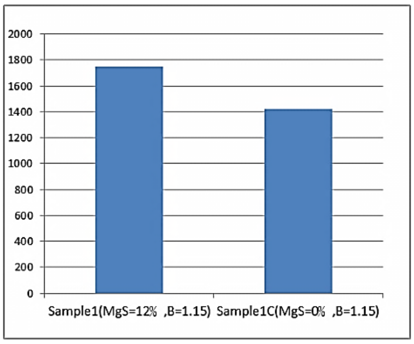


Figure7 Melting point of sample1(MgS=12％,B=1.15)

In order to find the trend of change of melting temperature with the change of MgS content, melting point and equilibrated solid phase has been calculated in several composition of blast furnace slag containing MgS with software Factsage and database of SlagA . The results are listed in Table2 and Figure 8~16.

From the simulated results, it seems also that the slag melting temperature increases with content of CaS or MgS. The effect of raise of melting temperature is more prominently for MgO solid phase.

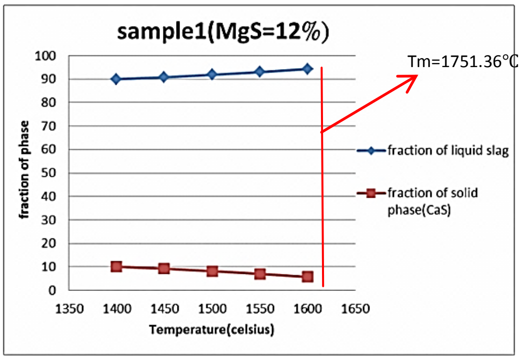


Figure 8. Melting point and ratio of solid phase

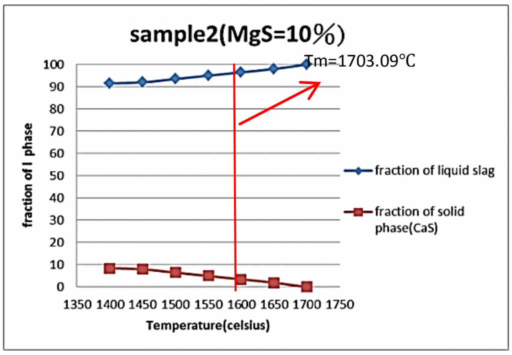
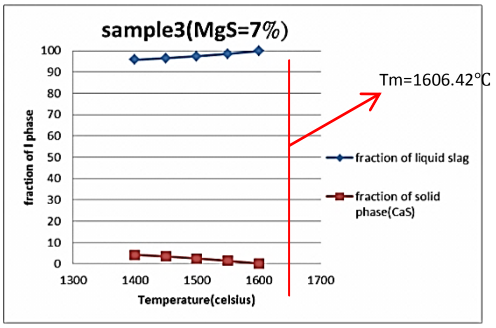


Figure 9. Melting point and ratio of solid phase



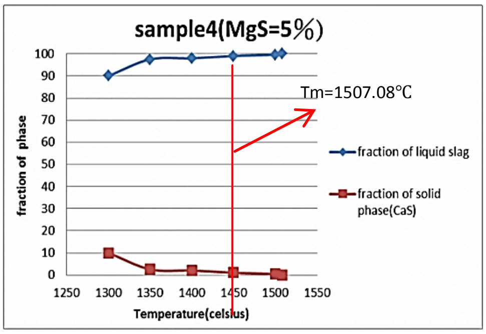
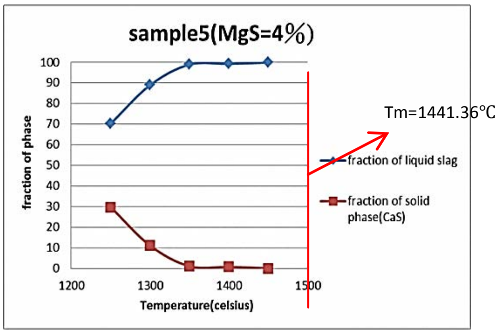


Figure 10.Melting point and ratio of solid phase and

Figure 11. Melting point and ratio of solid phase



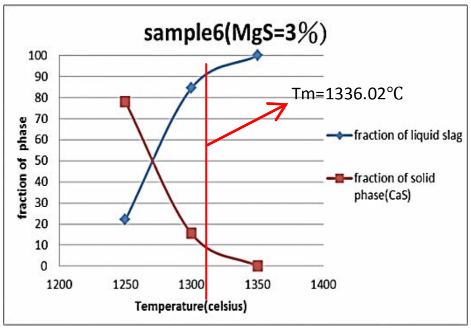
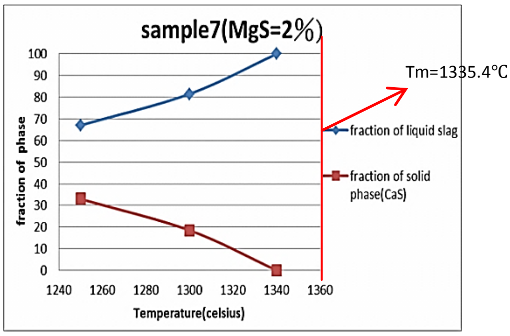


Figure 13. Melting point and ratio of solid phase and

Figure 14. Melting point and ratio of solid phase



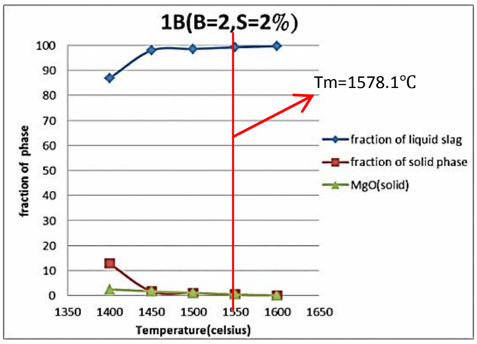


Figure 15 Melting point and ratio of solid phase

Figure 16. Melting point and ratio of solid phase

Table 2. Composition of sample calculated with Factsage

wt%	CaO	MgO	Al_2O_3	SiO_2	MnO	TiO_2	FeO	MgS	T_m Cal.	Fraction of solid
Sample1	36	6	13	31.5	0.5	0.5	0.5	12	1751.36	10%(1400℃)
Sample2	36.5	6.5	13.5	32	0.5	0.5	0.5	10	1703.09	7.76%(1400℃)
Sample3	38	6.5	14	33	0.5	0.5	0.5	7	1606.42	4.3%(1400℃)
Sample4	38.5	7	14.5	33.5	0.5	0.5	0.5	5	1507.08	1.88%(1400℃)
Sample5	39	7	14.5	34	0.5	0.5	0.5	4	1441.36	0.65%(1400℃)
Sample6	39	7.5	14.7	34	0.6	0.6	0.6	3	1336.02	15.5%(1300℃)
Sample7	39.3	7.5	15	34.4	0.6	0.6	0.6	2	1335.4	18.5%(1300℃)
1B(B=2,S=2%)	48.9	6.97	12.55	24.64	0.6	0.81	0.39	3.53	1578.1	12.76%(1400℃)
Sample1C	41	6.83	14.8	35.87	0.5	0.5	0.5	0	1425	20.5%(1300℃)

4.2 Surface tension and viscosity of slags

The density of different MgS contained slags at $1773^{0}K$ is presented in Figure 17, it can be seen that the density looks increase with content of MgS. The viscosity calculated with different models as mentioned before is presented in Figure 18. The results suggest that viscosity calculated with Factsage is sensitive to temperature, while the basicity ratio model is fit for wide range of liquid slags.

Figure 19 and Figure 20 correlate the data of surface tension and viscosity according the Pelofsky concept. It looks that surface tension decrease with decrease of viscosity.

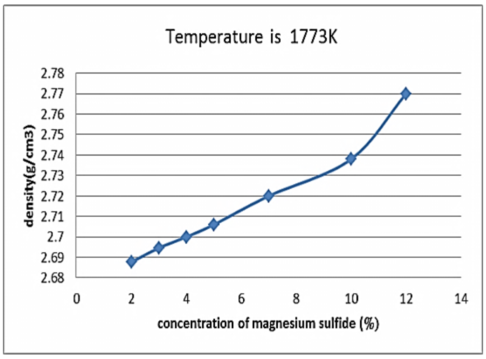


Figure 17 .Change of density of slag with MgS

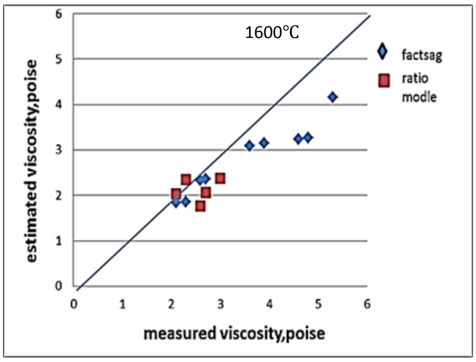


Fig18.Comparison between estimated viscosity and measured viscosity from literature with different models

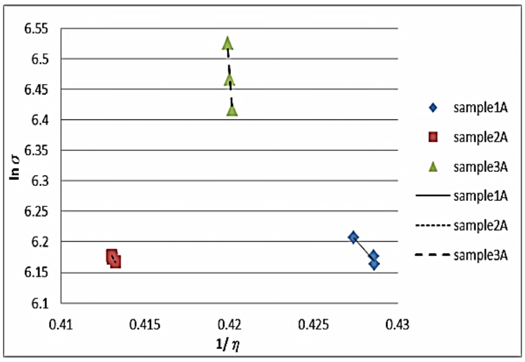


Fig19.lnσ and η^{-1} have linear relationship in slags.

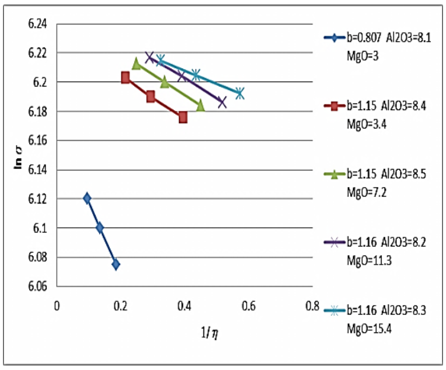


Figure 20 lnσ and η^{-1} have linear relationship in slags data from literature.

5. Conclusions

By applying the method of sessile drop contact angle method and optical basicity, the melting temperature, viscosity and surface tension of magnesium injection slag could be estimated with different magnitude error. The melting temperature looks increase with contents of MgS.

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