# Investigation of the impact of oxygen potential on sulfur mass transfer at Slag/Iron interface

*Weimin Cao*[1)]*, Luckman Muhmood*[2)] *and Seshadri Seetharaman*[1)]

*1) Division of Materials Process Science, Department of Materials Science and Engineering, Royal Institute of Technology, SE-10044, Stockholm, Sweden*

*2) CSIRO, Process Science & Engineering, Melbourne, Australia*

**Abstract:** In this work, sulfur dynamic mass transfer at the slag/iron interface was investigated by using X-ray sessile drop method in dynamic mode. The experiments were carried out with pure iron and CaO-$SiO_2$-$Al_2O_3$-FeO slag (alumina saturated at the experimental temperature) contained in alumina crucibles at a temperature of 1873 K under non-equilibrium conditions. The gas atmosphere was a mixture of CO, $SO_2$ and Ar with well-controlled partial pressures of oxygen and sulfur. During the sulfur mass transfer, the impact of oxygen potential on iron droplet oscillation was monitored. The change in interfacial tension results in the change of iron droplet shape. The circularity of droplet, which describes the droplet shape, was calculated as a function of time to determine the droplet oscillations. The impact of oxygen potential was investigated by determining the amplitude of droplet oscillations and the interfacial velocity of the sulfur transfer. Experimental results indicate that the amplitude of oscillations and interfacial velocity increase as the oxygen potential increases. The order of magnitude for the interfacial velocity was found to be $10^{-3}$ m/s. The experimental results were also explained by previous *ab initio* calculations. The thermo-physical and thermo-chemical properties of slag were also found to influence interfacial velocity. As the slag basicity increases, the activity of FeO increases, the sulfur capacity increases, and the viscosity of the slag decreases. These changes make sulfur move faster along the interface, resulting in a higher interfacial velocity.

**Keywords:** Mass transfer, Slag/iron interface, oxygen potential, interfacial velocity

## 1. Introduction

In steel making processes, especially during steel refining, the dynamic interfacial phenomena play an important role [1, 2]. Significant number of research work [3-9] has been carried out over the years to study the dynamic interfacial phenomena between slag and metal. Kozakovitch [3] observed that the desulfurization of iron was accompanied by a rapid decrease in the slag/metal interfacial tension. Gaye et al [4] reported that the chemical reactions occurring along the slag-metal interface change the metal droplet shape instantaneously, due to the change of the interfacial tension which is induced by interfacial mass transfer. In order to have a better understanding of the mass transfer and chemical reactions along the interface, it is essential to follow the change of metal droplet shape. This is likely to be affected by the change of interfacial tension and the consequent mass transfer rate of the surface active species. Several dynamic measurements were carried out in the present research group earlier [6-11]. Jakobsson et al [8] investigated the sulfur transfer from gaseous phase to iron droplet through alumina-saturated CaO-$SiO_2$-$Al_2O_3$-FeO slag. The changes of the shape of the metal droplet during sulfur transfer were captured. A semi-empirical model was used to calculate the interfacial velocity, in which the order of magnitude of the interfacial velocity was estimated to be $10^{-6}$ m/s. Brooks et al

[9] studied the dynamic interfacial phenomena during high temperature reaction between an Fe-Al alloy droplet and a $CaO-SiO_2-Al_2O_3$ slag system. The local equilibrium model and utilizing kinetic data were used to determine local composition, temperature, and electrical potential. The electrocapillary effect was found to be dominant, and the thermocapillary effect was found to be negligible. Recently, Muhmood et al [10] proposed a concept of interfacial velocity for slag/metal interface. The interfacial velocity can be measured from X-ray images directly, based on the changes of metal droplet surface area at a given instance. In their work, contact angles were manually measured by X-ray images in 6 seconds with 150 X-ray images, and later used for explaining metal droplet oscillations. It was observed that several factors such as slag composition, gas composition and temperature may influence the interfacial velocity. The maximum interfacial velocity of sulfur on $CaO-SiO_2-Al_2O_3-FeO$ slag-iron interface was measured to be in the order of $10^{-4}$ m/s.

Oxygen and sulfur are both surface active elements on iron surface, which are commonly present at slag/metal interface. It would be very interesting to see the impact of oxygen potential on sulfur mass transfer and interfacial velocity at slag/metal interface. In order to have a better understanding of the mechanism of sulfur transfer from gas phase to the liquid metal through the intermediate slag phase, sulfurization experiments were carried out in the present work to investigate the dynamic interfacial phenomenon. The interfacial velocity due to the sulfur mass transfer was determined at different partial pressures of oxygen at 1873 K.

In order to investigate the impact of oxygen potential, the shape changes of the metal droplet at different oxygen pressures need to be taken into account very carefully. In this work [11], around 14,000 X-ray images were analyzed and a circularity shape descriptor was used to determine the metal droplet oscillations induced by sulfur mass transfer at the slag/metal interface.

## 2. Experimental

### 2.1 Sample preparation

The slag used in the present work consisted 25wt% CaO, 50wt% $Al_2O_3$, 15wt% $SiO_2$ and 10wt% FeO. The composition of the slag was designed in such a way that it was close to the alumina-saturation boundary at the experimental temperature range according to the phase diagram [12]. This was to ensure that the slag would not have any reaction with the alumina crucible (purity 99.7%). Iron with 99.995% purity was used as the metal phase. FeO was produced from iron powder and $Fe_2O_3$, mixed in a suitable ratio to reach the FeO/Fe phase boundary. The mixture was heated in a closed iron crucible in argon atmosphere at 1273 K for 24 hours. X-ray diffraction (XRD) results indicated no peaks corresponding to iron metal, magnetite or hematite. The lattice parameter of the synthesized FeO was computed to be 4.30 Å from XRD, which is in good agreement with the value 4.304 Å given by literature [13]. All the slag components except FeO were heated at 1273K for 24 hours to remove the residual moisture and stored in a desiccator before use.

The gas atmosphere used in the present work was a mixture of CO, $SO_2$ and Ar with well-defined sulfur and oxygen potentials at the experimental temperatures. The materials used along with their purity are listed in Table 1.

Table 1. Chemicals and gases used for the dynamic Fe-Slag interfacial measurements [11]

| Material | $Al_2O_3$ | CaO | $SiO_2$ | Ar | CO | $SO_2$ |
|---|---|---|---|---|---|---|
| Purity | 99.97 pct | 99.95 pct | 99.8 pct | Argon plus (>99.99 pct) | S grade | S grade |

### 2.2 Measurement

In view of the extremely low oxygen partial pressures involved in these experiments, it is necessary to purify the gases with great care before mixing and introducing them into the reaction tube. Fig. 1 shows the gas-cleaning train with the various cleaning steps. Traces of moisture in Ar gas were removed by passing the gas through silica gel and magnesium perchlorate. $CO_2$ was absorbed by ascarite. The traces of oxygen were removed by passing the gas though copper turnings at 823K and through magnesium chips at 772 K. The oxygen partial pressure in argon after these purification steps was of the order of $10^{-18}$ Pa as shown by a $ZrO_2$-CaO oxygen probe kept in the out-going gas stream. The oxygen in CO was removed by passing through copper turnings at 903K. Stainless steel tubing with high vacuum gaskets was used in exit gas train to keep the oxygen permeations from the atmosphere as low as possible. The flow rates of the various gases were accurately controlled by mass flow meters, and the gases were mixed in a gas-mixture chamber before being introduced into the reaction tube. The partial pressures of oxygen and sulfur in the gas mixture at the experimental temperature were calculated by both ThermoCalc and FactSage. The database of SSUB3 was used in ThermoCalc. The database FACT in FactSage was chosen for the calculation. The partial pressure of oxygen and sulfur ($P_{O2}$ and $P_{S2}$) obtained from ThermoCalc and FactSage, as shown in Table 2, were found to be in good agreement with each other.

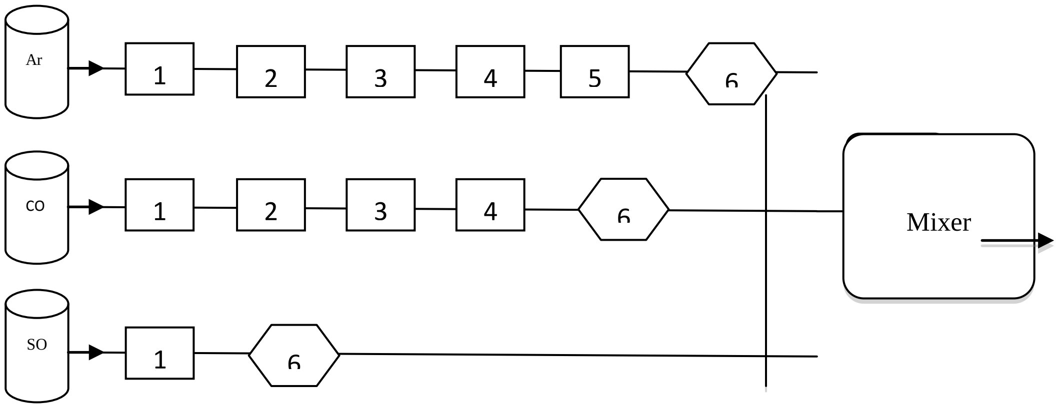


Figure 1. Schematic diagram of gas cleaning system 1- silica gel; 2-magnesium percholorate; 3- ascarite; 4-copper turnings; 5-magnesium chips; 6- flowmeter. [11]

Table 2. Experimental gas flow rates and the partial pressures of oxygen and sulfur in the present experiments at 1873K [11].

| | Inlet gas flow rate (ml/min) | | | $P_{O2}$ (Pa) | | $P_{S2}$ (Pa) | |
|---|---|---|---|---|---|---|---|
| | Ar | CO | $SO_2$ | TC | FS | TC | FS |
| Exp. I | 50 | 244.5 | 2.54 | $7.47\times10^{-6}$ | $7.20\times10^{-6}$ | $3.15\times10^{2}$ | $3.28\times10^{2}$ |
| Exp. II | 50 | 163.8 | 5.1 | $7.12\times10^{-5}$ | $6.85\times10^{-5}$ | $9.55\times10^{2}$ | $9.76\times10^{2}$ |

*TC and FS indicate the calculated values from ThermoCalc and FactSage, respectively.

The apparatus used for the X-ray sessile drop measurements consisted of an X-ray image analyzer and a graphite resistance furnace, as shown in Fig. 2. More details of apparatus can be found in work [11]. An IBM PC equipped with an image acquisition card enabled the recording of the X-ray images at a rate of 25 frames per second. The resolution of the image in the present work is 1024*760 pixels, and 1 pixel corresponds to 0.09mm.

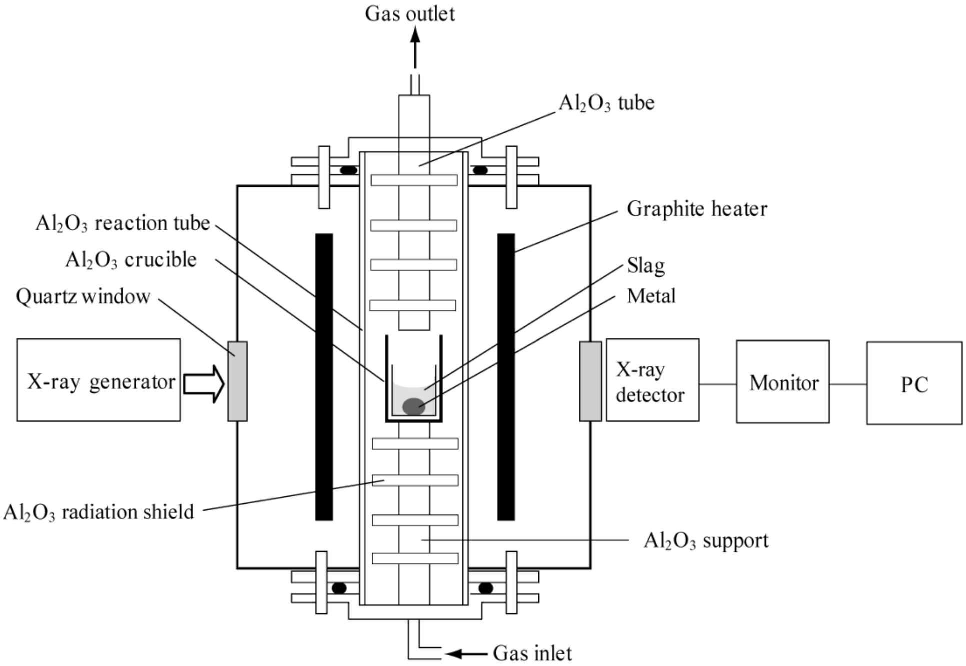


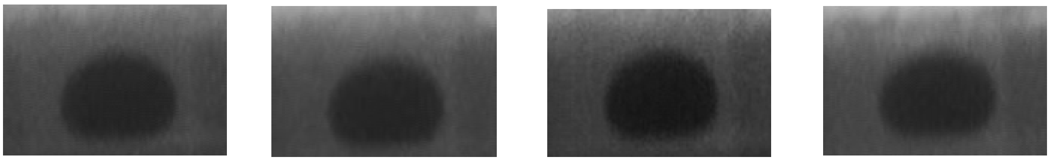
Figure 2. Schematic diagram of the X-ray sessile drop unit [11].

In the present measurement, a piece of pure iron was placed in an alumina crucible. The slag components in suitable proportions were well-mixed and added to the top of the iron metal. Extreme care was taken to ensure that the crucible bottom was planar and even. Purified argon gas was passed through the reaction tube and the gas was allowed to flow for approximately 12 hours in order to flush the system completely. The furnace was heated to 1873 K at a heating rate of 5 K/min. After reaching this temperature, the furnace was allowed to stabilize for at least 1 hour. The gas mixture consisting of CO, $SO_2$ and Ar (purified as described earlier) was introduced into the reaction tube. The shape of the drop was monitored every 5 min in the computer due to the 30 min recording capability of the image system. The shape changes of the droplet were analyzed using an image analysis software [14]. The graphic part of the image analysis program, used together with this software, was developed at the Division of Materials Process Science, Royal Institute of Technology (KTH).

Calibrations of the sessile drop measurements were earlier carried out in the Division of Materials Process Science, KTH [8, 10]. The measurements of the standards were carried out with pure copper, nickel and silver metals on alumina substrate in pure argon atmosphere. According to these studies, the surface tension of these metals as a function of temperature could be described equations in agreement with literature.

## 3. Results

In the sessile drop experiments undertaken in the present study, the changes of the shape of the iron drop immersed in molten slag were followed by X-ray imaging at 1873 K. The partial pressures of oxygen in the gas mixture, $P_{O2}$ were $7.2\times10^{-6}$ Pa and $6.8\times10^{-5}$ Pa. The corresponding partial pressures of sulfur, $P_{S2}$, were $9.8\times10^{2}$ Pa and $3.3\times10^{2}$ Pa. The change in the sulfur partial pressure was much less compared to that of oxygen pressure. The small changes in the sulfur partial pressure were unavoidable due to the restriction in the choice of the gas mixture composition. Fig. 3 shows the X-ray images taken at 0 min, 46min, 47min and 360min after $SO_2$ injection from one of the experiments. In both experiments, it was observed that, after $SO_2$ injection, there was a depression formed at the top portion of the metal droplet. The drop reverted to the rounded form shortly afterwards, only to get back to the depression again. This cyclic phenomenon was observed repeatedly. The same was also observed in previous experiments [8, 10].



0 min 46 min 47 min 360 min

Figure 3. X-ray images of the iron drop in slag at 0 min, 46 min, 47 min, and 360 min from the $SO_2$ injection [11].

### 3.1 Interfacial oscillations

In the experiments [11], as also in the earlier studies, in the present laboratory [8, 10], no oscillations could be observed before the introduction of the gas mixture with defined sulfur and oxygen partial pressures into the system. Thus, the oscillations of the metal drop may only be attributed to the interfacial phenomena occurring at the slag/metal interface due to the transfer of the surface active elements, *viz.* sulfur and oxygen. This confirms the earlier observations [8, 10]. Since partial pressure of sulfur is much higher than that of oxygen in the system, it is reasonable to assume that the observed oscillations are primarily induced by sulfur transfer. Fig. 4 shows the schematic drawing of the mechanism of sulfur transfer from the gas phase to metal phase. The slag above the metal can be divided into two regions, I and II, respectively. The thermal convection in the metal and slag phases is assumed negligible in view of the uniformity of the temperature over the entire slag-metal system within ± 2 K. The sulfur in the slag phase will first reach the top of metal droplet in region I, reaching the point at the shortest distance to the slag-gas interface (the top of the metal drop), as can be seen in Fig. 4. The time difference between sulfur reaching the top point of the metal drop and a point 0.01 mm away from the drop was estimated to be about 0.1 s [10]. The difference in the dynamic interfacial tension results in a gradient in the interfacial tension along the metal droplet surface. Marangoni force due to the gradient of interfacial tension becomes the main driving force of the surface movement of sulfur. The concentration difference would lead to a mass flow on the liquid metal surface. This surface mass flow along with diffusion of sulfur into the bulk of the metal phase results in the removal of sulfur from the top of the droplet. This would lead to a temporary regaining of the droplet shape.

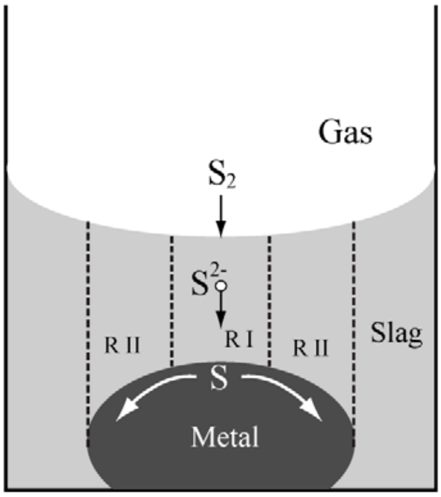


Figure 4. Schematic diagram of the slag/metal system. [11]

In order to investigate the impact of the oxygen potential on interfacial velocity, the oscillations of the droplet were taken into account very carefully. The frames extracted from the recorded video were analyzed using an image analysis software [14], where the droplet image was thresholded for edge detection, as shown in Fig. 5. This facility can analyze the changes of metal droplet shape. A uniform threshold value was used for converting all the X-ray images. This would help in identifying individual oscillations and also could record the time for depression and expansion. During the interfacial oscillations, it was observed that the contact angles and interfacial tension of the metal droplet changed instantaneously, which would result in the shape change of the metal droplet. In order to analyze the interfacial oscillations, a circularity shape descriptor was used to analyze the droplet shape changes in all X-ray images. The equation used can be represented as

$$C = \frac{4\pi * s}{l^2} \tag{1}$$

In Eq. (1), $s$ and $l$ are the area and perimeter of the metal droplet, respectively. A value of 1.0 for $C$ indicates a perfect circle. As the value approaches 0.0, it indicates an increasingly elongated shape. The changes in circularity value represent the droplet oscillations. In experiment 1, the largest droplets area change is 132 pixel$^2$, the largest droplets perimeter change is 43 pixels. The droplet is around 40 pixels high and 70 pixels wide. It can be seen that the area and perimeter in terms of droplet have significant changes. Based on calculated circularity values, droplet oscillations can be systematically investigated.

Fig. 6 (a) and (b) show part of calculated circularity as a function of time for 50 seconds video, corresponding to around 1250 X-ray frames. It can be seen from Fig. 6 (a) that calculated circularity first increases from 2770 seconds to around 2785, reaches the maximum value, then keeps decreasing to 2800 seconds. The same phenomena repeat afterwards. A similar trend is observed in Fig. 6 (b) as well.

Figure 5. Converted image from X-ray image by image analysis software [11].

As mentioned earlier, the sulfur transfer on slag/metal interface would change the shape of the droplet. Thus, the instantaneous changes of the calculated metal droplet circularity indicate the sulfur transfer on metal droplet surface. It also can be observed that the maximum oscillation times are roughly 30 and 20 seconds for Fig. 6 (a) and (b), respectively. The change in the oxygen pressures was quite significant in comparison to that for sulfur. In this case it is reasonable to attribute the faster interfacial oscillation to the increase in the oxygen partial pressure. The faster oscillation is indicative of the faster interfacial velocity. A detailed discussion of the impact of oxygen partial pressure on interfacial velocity will be presented in the next section. The amplitudes of the circularity were also calculated to analyze the droplet oscillation. The calculated standard deviations of circularity amplitude are 0.0429 and 0.0461 for Fig. 6 (a) and 6(b), respectively. This indicates the amplitude of the interfacial oscillation increases as the oxygen partial pressure increases. Experiments conducted independently [8, 10] are in conformity with the present observations.

### 3.2 Interfacial velocity

The metal droplet surface area representing the interfacial area would change during the interfacial oscillation [11]. Hence, it is possible to calculate the interfacial velocity due to the concentration difference of sulfur at the interface by change in droplet surface area. As it was reported in work [10], the interfacial velocity of sulfur is given by the following equation:

$$v_{\text{instantaneous}} = \frac{R_{t+\Delta t} - R_t}{\Delta t} \tag{2}$$

where $R_{t+\Delta t}$ and $R_t$ are the radius for the converted circle, $\Delta t$ is the time difference between these two radii.

Four frames were randomly chosen to calculate interfacial velocity for both experiments. These frames were analyzed using a Didge image digitizing software [15]. Surface area of metal droplet was then calculated by the input coordinates of the contour of the droplet. From the calculated average interfacial velocity, it can be seen that the velocity increases from $9.9 \times 10^{-4}$ m/s to $4.4 \times 10^{-3}$ m/s which is mainly attributed to the $P_{O2}$ increase.

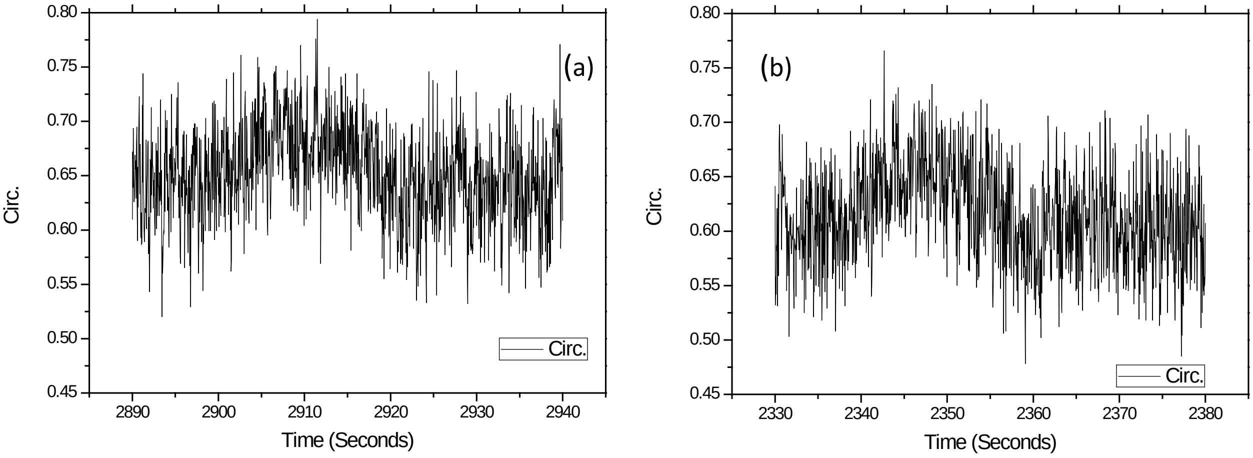


Figure 6. Calculated circularity as a function of time for two experiments. $P_{O2}$ and $P_{S2}$ are $7.2\times10^{-6}$ Pa and $3.3\times10^{2}$ Pa for (a) , and $6.8\times10^{-5}$ Pa and $9.8\times10^{2}$ Pa for (b). [11]

In our earlier studies [16-19], the interaction between oxygen and sulfur and solid iron surface as well as the average surface velocity were studied by Density functional theory and thermodynamics & statistical physics theories. After relaxation of the adatom on the iron surface, the height of O atom above the iron surface is 0.41 Å, whereas it is 1.025 Å for S. This means oxygen has a stronger bonding interaction with iron surface. The charge accumulation between O and iron surface is thus denser, which would weaken the bonding interaction between S and iron surface. When both oxygen and sulfur are present on the iron surface, the oxygen would displace sulfur from iron surfaces [20]. Thus, more sulfur atoms are released from the iron surface and contribute to the movement on the interface as $P_{O2}$ increases. This indicates that interfacial velocity of sulfur will increase correspondingly, in accordance with the trend observed in the present experiments.

Thermo-physical and thermo-chemical properties of slag were retrieved from ThermoSlag software [21]. These results as well as the interfacial velocities calculated are compared with the results of Muhmood et al [10], and presented in Table 3. As the slag basicity increases, it can be seen that the activity of FeO increases, the sulfur capacity increases, and the viscosity of the slag decreases. These changes make sulfur move faster along the interface, resulting in a higher interfacial velocity.

Table 3. Interfacial velocity and the themo-physical and themo-chemical properties of the slag at 1873 K. [11]

| | Basicity (%CaO/%$SiO_2$) | $a_{FeO}$ | logCs | Viscosity (poise) | Interfacial velocity (m/s) |
|---|---|---|---|---|---|
| Present work | 1.67 | 0.123 | -3.43 | 2.32 | ~$10^{-3}$ |
| Ref. [10] | 1.27 | 0.055 | -3.82 | 4.29 | ~$10^{-4}$ |

## 4. Conclusions

In the present work, the non-equilibrium dynamic interfacial studies of the interface between CaO-$SiO_2$-$Al_2O_3$-FeO slag and molten iron were carried out by monitoring the change of the apparent droplet shape by X-ray sessile drop technique. The partial pressure of oxygen and sulfur were well-controlled by a suitable mixture of CO, $SO_2$ and Ar gases. The circularity of the droplet was calculated as a function of time to determine the droplet oscillations, which were induced by the change in interfacial tension. The impact of oxygen potential was investigated on the amplitude of droplet oscillations as well as interfacial velocity of sulfur transfer. It can be seen that the amplitude of oscillations and interfacial velocity increase as the oxygen potential increases. This result was also explained by *ab initio* calculations. The order magnitude of the interfacial velocity was determined as $10^{-3}$ m/s. The thermo-physical and thermo-chemical properties of the slag were also found to influence interfacial velocity.

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