A Sessile Droplet Study of Iron-Carbon-Sulfur Alloys on an Alumina Substrate

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Abstract: Reactions at interfaces such as inclusion separation and refractory attack are extremely important for steel refining. These phenomena involve study of interfacial tensions and contact angles at the heterogeneous interface. In the present work, the contact angle between molten iron and alumina substrate and the surface tension of iron alloys containing different amounts of sulfur and carbon were determined experimentally using the Sessile Drop Technique. A CCD video-camera was utilized to image the melt profile. The contact angle and surface tension were calculated from computer generated solutions of the Young-Laplace equation. In the present study, contact angles and surface tensions of molten iron alloys with different sulfur contents in the range of 0.0092-0.651 wt% and also iron-0.035 wt% sulfur containing 0.5-4.0 wt% carbon were measured at 1873K in an argon-5% hydrogen gas atmosphere. The addition of sulfur to liquid iron caused a decrease in both the contact angle between liquid iron and alumina substrate and the surface tension of molten iron. On the other hand, addition of carbon to liquid iron at constant sulfur content caused an increase in the contact angle between molten iron and alumina substrate and also the surface tension of iron-carbon-sulfur alloys. Considering the data for iron alloys with 0.035% sulfur and various carbon contents, it was concluded that carbon decreases the surface tension of the liquid iron by increasing the activity of sulphur in the bulk, however carbon itself increases the surface tension of molten iron and the over-all effect is that the surface tension increases with carbon content.

Keywords: Sessile drop, Surface tension, Contact angle, Iron, Alumina.

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1. Introduction:

In the steelmaking industry, a fundamental knowledge of refractory wear caused by liquid steel and slag is necessary. Investigations of surface reactions help in understanding the corrosion resistance of refractories which generally consist of oxides such as alumina, silica, magnesia and lime. Another important issue in the steel industry is inclusion separation. It is well known that for efficient inclusion removal and higher quality of clean steel, higher interfacial tension between liquid steel and solid particles is beneficial since the driving force for inclusions to ascend through the melt and separate from the molten steel is increased. To understand the mechanism of dynamic wetting between liquid iron and solid inclusions in iron, an accurate value of the surface tension of liquid iron is necessary.

Liquid steel contains a number of dissolved elements like carbon, oxygen and sulfur in very small quantities (ppm). Oxygen and sulfur are known to be surface active elements which prefer surface sites to those in the bulk. Presence of surface active elements even in small quantities decreases the surface tension of the melt dramatically. In the present work, the effects of sulfur and carbon on the surface tension of liquid iron in contact with alumina substrate are investigated.

For measuring the surface tension of molten metal in either chemically inert or reactive systems, the sessile drop method has generally been used. In this method, a liquid drop is placed on a flat, highly polished solid substrate and the contact angle is measured as it tends towards the equilibrium value.

1.1 Wetting properties of metal/oxide systems

Oxide dissolution at high temperature is inevitable in metal/oxide systems. Oxidation and reduction reactions between metal M and oxide A_nO_m result in M_pO_q oxide formation. Studies have been carried out by Kapilashrami *et al*. [1] on wetting characteristics of liquid iron on dense alumina by X-ray sessile drop method. Formation of a product layer has been reported at different oxygen partial pressures between the liquid drop and the substrate. Soon after the contact angle has decreased to the equilibrium value, the liquid drop begins moving away from its original position. SEM-EDS analysis has shown that a layer of $FeAl_2O_4$ has been formed on the substrate according to the reaction:

$Fe + \underline{O} + Al_2O_3 = FeAl_2O_4$

This is probably the reason that the drop changes its position in order to reach a new alumina surface as a suitable oxygen potential is imposed. From the thermodynamic point of view, this reaction occurs in the temperature range 1800-2000 K for different amounts of dissolved oxygen in liquid iron. The product layer formation is shown in Figure 1.

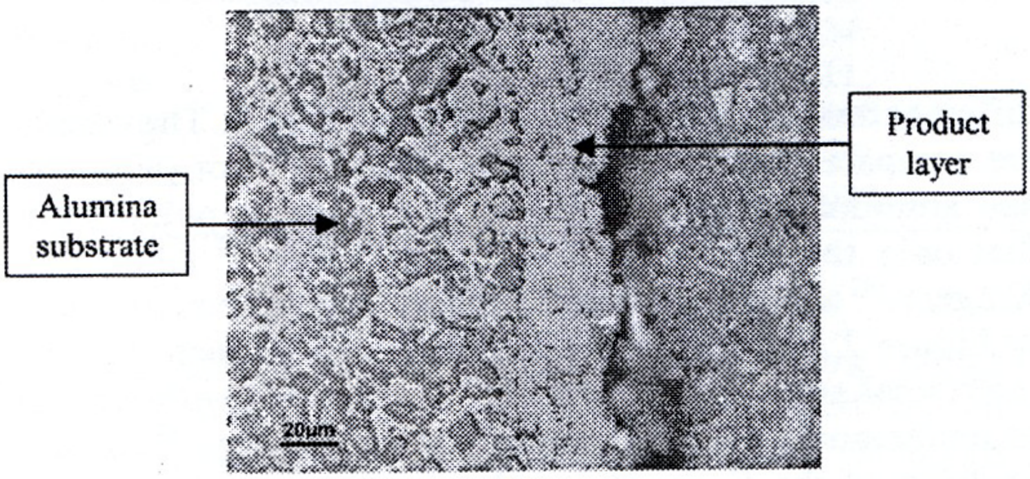


Figure 1, Formation of product layer on the alumina substrate at 1823 K and oxygen partial pressure of 9.9 $x10^{-4}$ Pa [1].

1.2 Surface active elements

The term "surface active" is applied to elements which decrease the interfacial tension significantly even at ppm levels. Group VI elements, namely oxygen, sulfur, selenium and tellurium are among the strongest surface active elements in metallic solutions. Metallic alloying elements in larger amounts can have similar effects on the surface tension of the metallic surfaces. Generally, elements with low surface tension decrease the surface tension of elements with high surface tension [2-5].

Different equations have been derived to measure the effect of surface active elements on the surface tension of solutions. [6-8], Equation 1-1 was suggested by Sahoo *et al.* [8] to measure the effect of surface active components on the surface tension by considering the changes of the adsorption coefficient K with respect to temperature. In this equation, segregation of the solute, activity of the component and the temperature are considered:

$$\gamma = \gamma^0 - A\,(T - T^0) - RT\,\Gamma_s\;\ln[1 + k_1\,a_i\,e^{-\Delta H^0/RT}] \qquad \text{Eq 1-1}$$

where γ^0 is the surface tension of the pure metal in N/m, A is a constant which expresses the surface tension variation of pure metal at temperatures above the melting point of the pure metal $(-\,d\gamma/dT)$ in N/ (m.K), T^0 is the temperature at which γ^0 is measured, R is the universal gas constant, Γ_s is surface excess in saturation in kg mol/m^2, k_1 is a constant which stands for the entropy of segregation, a_i is the activity of component i in the alloy and ΔH^0 is enthalpy of segregation in kJ/kg mol. In stainless steel, the activity coefficient of sulfur is modified by chromium through the interaction parameter e_S^{Cr} as shown by Equation 1-2.

$$log f_s = e_S^S\,[wt\ pct\ S] + e_S^{Cr}[wt\ pct\ Cr] \qquad \text{Eq.1-2}$$

McNallan and Debroy [4] have calculated surface tension for both stainless steel containing 18 pct chromium and the Fe-S binary system as a function of sulfur concentration and temperature. With surface tension measurements for Fe-S and Fe-O systems, it should be noted that it is the soluble O or S which decreases the surface tension and not the total concentration of these elements. Presence of other elements affects the concentration of soluble O and S. It has been reported that in most steels, 0.04 wt% aluminum is sufficient to reduce the soluble oxygen content to less than 5 ppm [9]. Surface tension of Fe-S system as a function of sulfur content has been reported in various works [7,10-12] Halden and Kingery [12] have suggested that surface activity decreases by decreasing the atomic size and ability of polarization (polarizability) in the order of: S > O > N > C. Their results show carbon effect is almost negligible. However, carbon decreases the interfacial energy by reacting with the alumina substrate. On the other hand, carbon slightly increases the interfacial energy by lowering the oxygen activity.

1.3 Wetting characteristics in the Fe-C-S system

It has been discussed in the studies on the Fe-C-S system, that carbon increases the sulfur activity. However, there has been significant discrepancy between the results reported in different investigations which have attempted to measure the surface tension of the iron-carbon system due to the difficulty of experimental determination [12-18]. Jimbo and Cramb [18] studied the effect of carbon content on the contact angle and the surface tension of liquid iron under 1atmosphere carbon monoxide gas at 1823K. They found that addition of 1% carbon caused 30mN/m increase in the surface tension value of molten iron. The measured data reported by Jimbo and Cramb[18], were in disagreement with other studies which showed no variations or a decrease with increase in the carbon content.. They have discussed that this disagreement is probably due to the contamination of iron with trace amounts of sulfur. Thus, carbon had increased the sulfur activity in the bulk and caused decrease in the surface tension. Jimbo and Cramb[18] found that contact angle decreased as carbon content increased at constant temperature and increased at constant carbon content as temperature decreased. It can be concluded that carbon by itself increases the surface tension, whereas in the presence of sulfur, it decreases the surface tension by increasing the sulfur activity.

2. Experimental aspects:

Wettability studies in the present work were carried out using iron samples with different sulfur and carbon contents. High purity iron was employed as the base metal for all the samples with different compositions. For preparation of samples with different carbon contents, a master alloy was prepared. Pure iron was placed inside a graphite crucible which was sealed with alumina paste to a graphite lid. The crucible was placed in a furnace and heated to 1873 K under a hydrogen atmosphere, held at this temperature for twelve hours and then cooled to room temperature. Specific quantities of master alloy were mixed with ferrous sulfide (FeS) and pure iron powders and four samples with different carbon contents were placed in an alumina crucible and heated to 1873K. The samples remained at that temperature for eight hours and then were cooled to room temperature. An identical procedure was used for samples with different sulfur amounts after ferrous sulfide was added to pure iron powder. Alloys were analyzed for carbon and sulfur before and after surface tension measurements. Due to reaction with hydrogen, the sulfur content decreased after each experiment. Tables 1 and 2 show analyses after experiments with Fe-S and Fe-C-S alloys respectively.

Table 1, Chemical analysis of Fe-S alloys

Sample No.	Sulfur content, (wt %)	Carbon content, (wt %)
S_1	0.0041	0.009
S_2	0.0092	0.0079
S_3	0.0137	0.0080
S_4	0.0564	0.007
S_5	0.488	0.0086
S_6	0.651	0.0078

Table 2, Chemical analysis of Fe-C-S alloys

Sample No.	Carbon content, (wt %)	Sulfur content, (wt %)
C_1	0.5	0.0342
C_2	1	0.0351
C_3	2	0.0374
C_4	4	0.0305

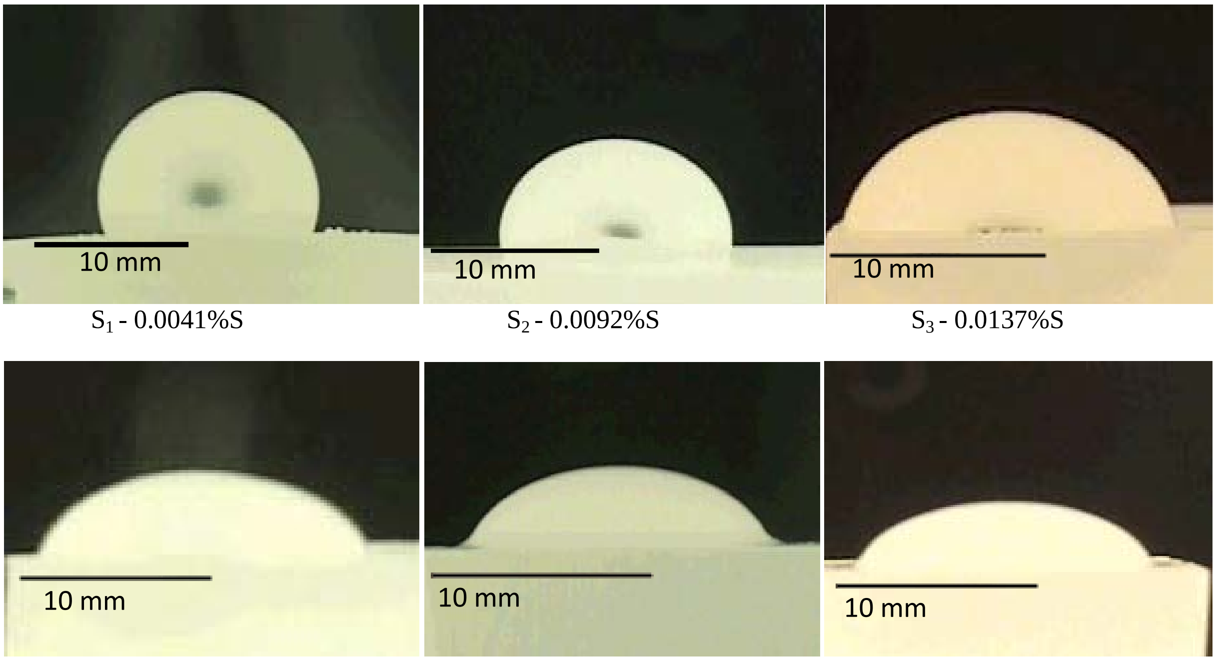
The samples were cut from the centre of the resulting ingot and were degreased in acetone and cleaned ultrasonically before each experiment. High purity alumina substrates (with purity of 99.6%) used in this work were in the form of thin squares (1 x 1 inch) and ultrasonically cleaned in acetone. The surface roughness was found to be Ra=3µm. Ar+5 % H_2 gas mixture, supplied by Linde was used in order to prevent oxidation. The moisture in the gas was removed by passing the mixed argon + hydrogen gas through calcium sulphate columns. The apparatus for sessile drop measurements consisted of three main parts: a high temperature resistance furnace, a gas cleaning system and an optical tube with CCD video camera and Vision Gauge software. The sample (~1.5-2.5 grams) was placed on the alumina substrate and the substrate positioned horizontally in the alumina tube on an alumina holder. The horizontal tilt of the substrate was adjusted by laser level. During heating, the shape of the droplet was constantly recorded using a CCD video camera and Vision Gauge software.

The contact angle between the iron droplet and alumina substrate and the surface tension of Fe-S and Fe-C-S alloys were evaluated from optical images taken during sessile drop experiments using the software mentioned previously. The image analysis part of this program, developed at the Division of Metallurgy, Royal Institute of Technology, defines the edge of the droplet by varying the number of points using a binary image. This input is then analyzed on the basis of the Laplace equation to generate the contact angle and surface tension. For the convergent calculation, the Gauss-Newton method is used. The curvature radius of the apex (determined from the number of pixel per centimeter of the liquid droplet), density difference, $\Delta\rho$, and the apparent weight of the droplet are considered as the initial conditions.

3. Results and discussion

3.1 Effect of sulfur on iron wettability

The wetting behavior of the samples was studied at 1873 K as a function of composition. Figure 2 shows images of the samples with different sulfur contents. All images were taken 20 minutes after the droplet was melted in order to ensure that equilibrium condition was reached. The effect of sulfur as a surface active element on the wetting behavior of iron is shown clearly in these pictures. The contact angle between the liquid drop and the substrate progressively decreases with relatively small increases in sulphur content from S1 to S4. At the highest sulfur contents, the contact angle does not change as much. Contact angles and surface tension for different sulfur contents are reported in Table 3.



S_1 - 0.0041%S

S_2 - 0.0092%S

S_3 - 0.0137%S

S_4 - 0.0564%S

S_5 - 0.488%S

S_6 - 0.651%S

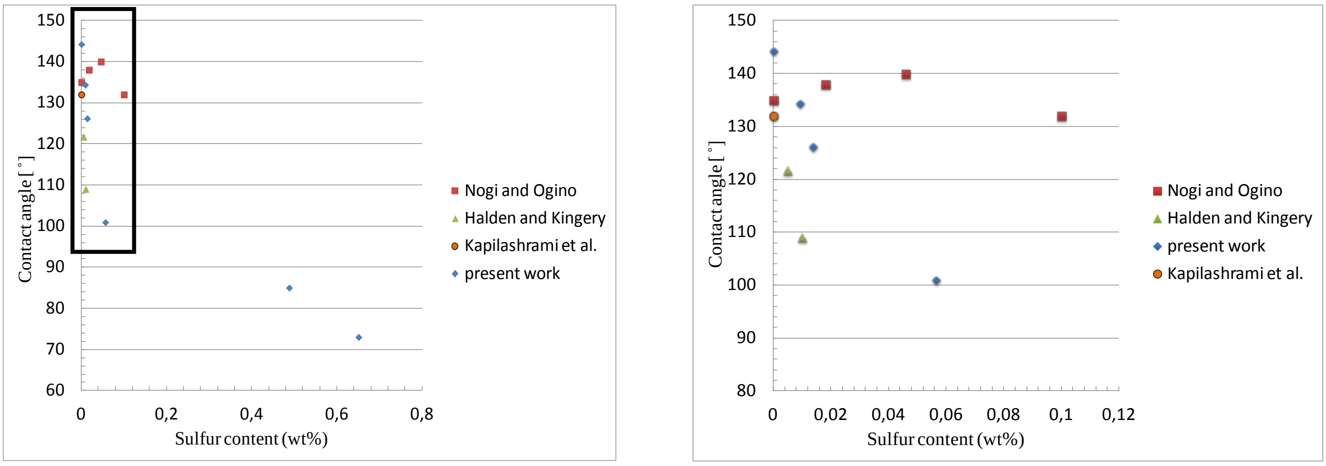
Figure 2, Optical images of the sessile drop samples with different sulfur contents at 1873 K

Table 3, Contact angle and surface tension values of Fe-S alloys containing about 0.008%C

Sample Number	Sulfur content (wt %)	Contact angle [˚]	Surface tension [mN/m]
S_1	0.0041	144	1877
S_2	0.0092	134	1582
S_3	0.0137	126	1377
S_4	0.0564	101	1206
S_5	0.488	91	1040
S_6	0.651	74	1144

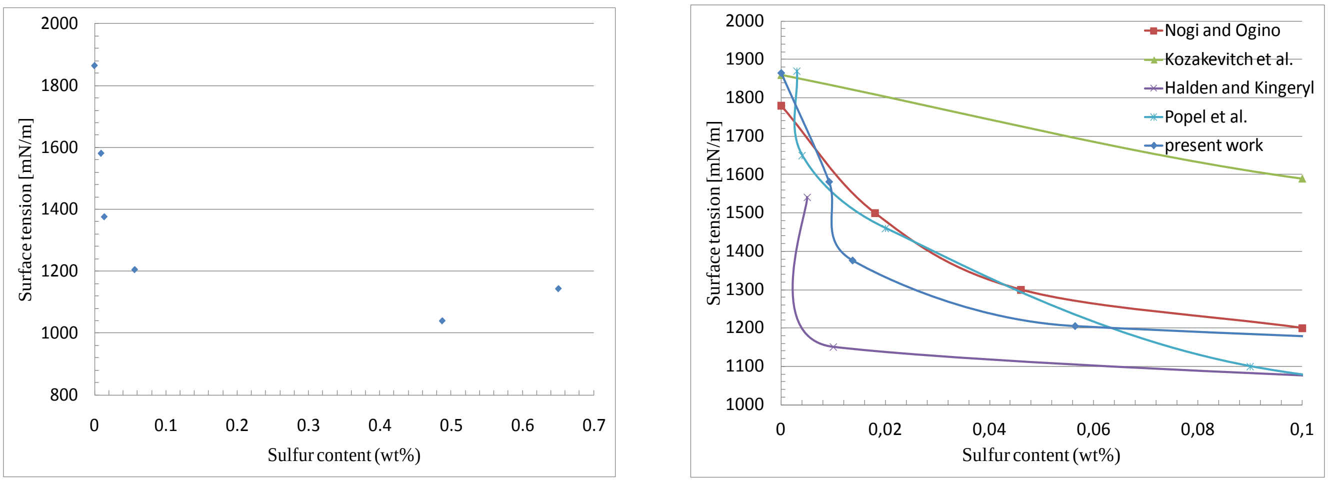
The results for contact angle are plotted in Figure 3(a) and are compared with those of Kapilashrami *et al.* [1], Halden and Kingery[12] and Nogi and Ogino[19], in Figure 3(b). Our results show that the contact angle decreased from 144 degree to 74 as sulfur content in the iron samples is increased from 0.0041 wt% to 0.651 wt%, however the rate of decrease is much greater at lower concentrations, when the sulfur content is less than 0.0564 wt%. For better comparison of the results, this part of the diagram with low sulfur content is magnified in Figure 3(b). The results from Nogi and Ogino[19] show that sulfur scarcely had any effect on the contact angle of molten iron while the results from the present study show that the contact angle is decreased with increasing sulfur. However, according to the data from the present work, the contact angles values are higher than those reported by Halden and Kingery[12]. The contact angle measured by Kapilashrami *et al.* [1] for pure iron at 1873 K is plotted on the same graph. The contact angle measured in this study is also higher than that of Kapilashrami *et al.* [1].

The results for surface tension are plotted as a function of sulfur content in Figure 4(a) and are compared to other reported values in Figure 4(b). Although the data of Nogi and Ogino[19] suggest that sulphur had little effect on the contact angle measurement, their results for surface tension show a marked decrease with increasing sulphur content which is in accord with the present findings. As mentioned above, the data from Halden and Kingery [12] show lower values than the present work. This is probably because the samples used by Halden *et al.*[12] contained oxygen from 0.0006 to 0.398 wt%, whereas oxygen contamination was avoided in the current study by using an Ar-5%H_2 gas mixture. In accord with previous work, the effect of sulfur on the surface tension of liquid iron becomes less pronounced when the sulfur content increases above about 0.05 wt%.



(a) (b)

Figure 3, Comparison of different data for the effect of sulfur content on the contact angle

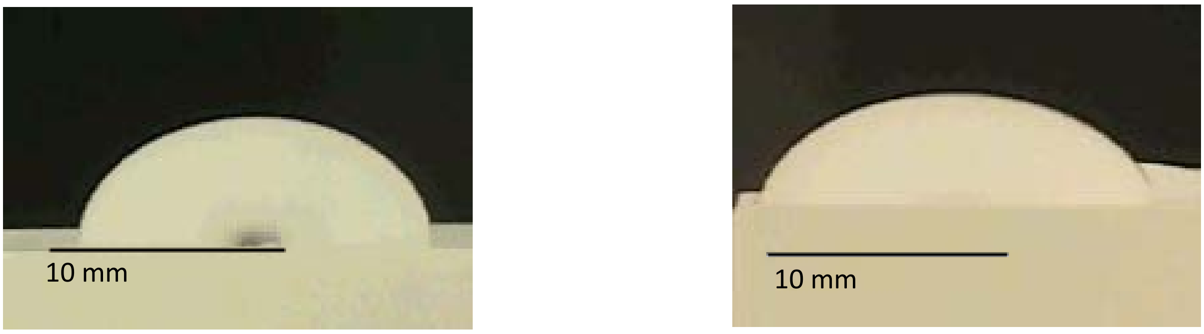


(a) (b)

Figure 4, Comparison of surface tension values measured in this work for Fe-S alloys with data from other studies

.2 Effect of carbon on iron wettability

In order to estimate the effect of carbon on the surface tension of liquid iron and also on the sulfur activity, experiments were conducted with Fe-C-0.035% S alloy samples with different carbon contents. Figure 5 shows the sessile drop images of these samples. From the pictures, it is evident that the contact angle has increased by increasing the carbon content and the semi-oval shape of the liquid drop with 0.5 % carbon has changed to a semicircle shape in the sample with 4% carbon. Contact angle and surface tension of these samples were measured using the same approach as described before. The experimental results are listed in Table 4 and are shown graphically in Figure 6.



C_1 - 0.5%C C_2 - 1%C

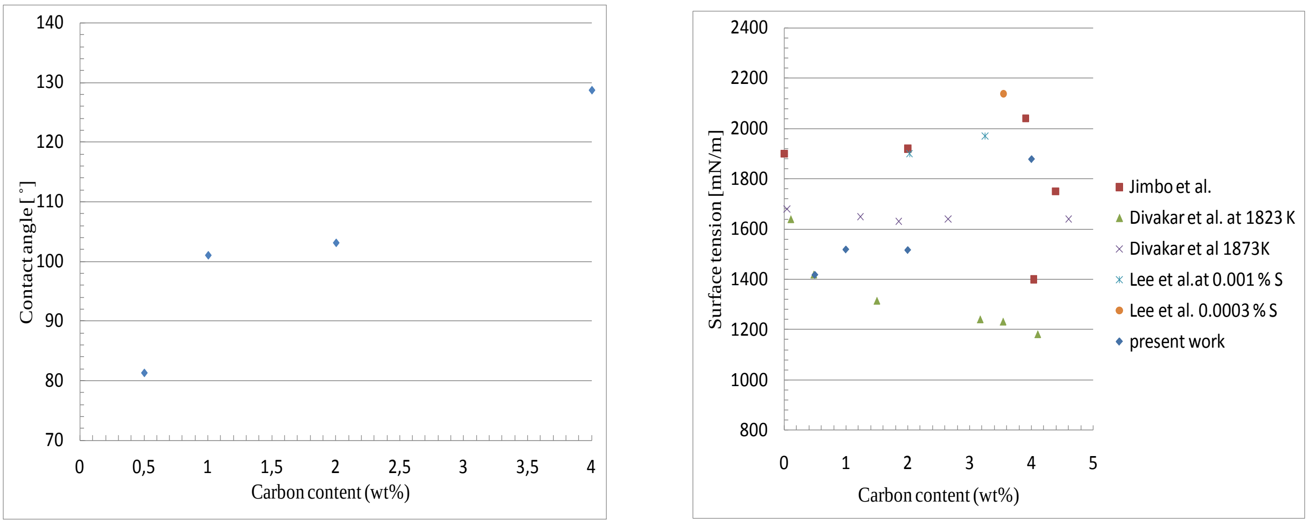
C_3 - 2%C C_4 - 4%C

Figure 5, Optical images of the sessile drop samples with different carbon contents at 1873 K

For comparison, data compiled by Jimbo *et al.* [14] and Divakar *et al.*[16] at two different temperatures, 1823 K and 1873 K, and Lee *et al.* [21] at two different sulfur contents, 0.001 and 0.0003 mass %, are also plotted. Clearly, the surface tension of the alloy samples containing extremely low sulfur contents of 0.001 and 0.0003 % show much higher values for surface tension, (1971 mN/m and 2138 mN/m respectively), while the surface tension values measured in the present work are lower due to the higher sulfur content, (0.035%). However, the values reported by Divakar *et al.* [16] at 1873K show no effect of carbon on surface tension, while the data at 1823 K show surface tension decreasing with increasing carbon content. Jimbo *et al.* [14] have discussed that decreases in temperature and increases in sulfur content in Fe-C-S system cause the surface tension to decrease. They have reported surface tension of Fe-4%C-0.02% S alloys decrease as carbon content increases above 4%. They suggested that scattering of the reported values was due to variations in sulfur activities. It can be concluded that at low carbon contents, carbon decreases surface tension by increasing the bulk sulfur activity, whereas at the same time carbon itself increases the surface tension. This can be seen at higher carbon contents.

Table 4, Contact angle and surface tension values of Fe-C-S alloys

Sample number	Carbon content, (wt %)	Contact angle [˚]	Surface tension [mN/m]
C_1	0.5	81	1417
C_2	1	101	1518
C_3	2	103	1516
C_4	4	129	1877



(a) (b)

Figure 6, Effect of carbon content on contact angle and surface tension of molten iron on alumina substrate at 1873K

4. Conclusions

The addition of sulfur, a surface active element, decreases the contact angle between liquid iron and alumina substrate and at the same time decreases the surface tension of molten iron. At sulfur contents higher than 0.05 percent, the iron droplet spreads on the alumina substrate, and further effect of sulfur on the surface tension of liquid iron becomes progressively less significant.

Addition of carbon to liquid iron at constant sulfur content caused an increase in the contact angle between molten iron and the alumina substrate with a corresponding increase in the surface tension of the alloy. It was concluded that while carbon decreases surface tension of liquid iron by increasing the activity of sulfur, the over-all effect is that carbon increases the surface tension of the alloy and this is particularly evident in alloys with higher carbon contents.

5. References

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