Interfacial Properties of Dilute Fe–O–S Melts on Alumina Substrates

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Compilations and data pertaining to the wettability and interfacial properties of Fe-melts and dilute Fe–O–S alloys on alumina substrates have been collected and compared. The properties included the surface tension of liquid Fe; the surface tension of Al_2O_3 ; measurements of work of adhesion and contact angles; and the effects of sulfur and oxygen on the surface tension of liquid Fe and on the contact angle. Based on the comparisons, recommendations for estimating these interfacial properties as well as the tension of the Fe–O–S (liquid)/ Al_2O_3 interface are given.

KEY WORDS: interfacial tension; surface tension; work of adhesion; contact angle; iron melt; alumina; solute element; oxygen; sulfur.

1. Introduction

The role of heterogeneous reactions in steelmaking is extremely important. During melting, refining and solidification, there are processes that involve all combinations of pairs among gas, liquid and solid. Quantifying interfacial phenomena and interfacial properties of the phases involved in steelmaking is a critical part of our ability to synthesize models that can be used in computer simulations of the unit operations in steelmaking. Since many grades of steel are deoxidized with aluminum, alumina inclusions and alumina clusters are of interest to steelmakers. Also, the role of inclusions in nucleating pores during solidification and the behaviors of both pores (*i.e.*, bubbles) and inclusions in the interdendritic liquid of solidifying steels can be studied in more depth if quantitative models can be developed. For these reasons, we undertake this review and analysis to provide a unified source of the interfacial properties between dilute Fe–O–S melts and Al_2O_3 substrates. Since our interest extends from the melt to the solidification range, many of our derived results that follow are extrapolated to below the melting point of pure iron (*i.e.*, 1808 K).

2. Surface and Interfacial Properties of Pure Liquid Iron and Al_2O_3 System

2.1. Surface Tension of Pure Liquid Iron

Keene^{1–3)} made extensive compilations of the data on surface tension of pure liquid iron, γ_o , and temperature coefficient, $d\gamma_o/dT$. In his latest work,³⁾ 31 sets of data were selected (Table 25 in Ref. 3)) by carefully evaluating the measurement techniques and contamination of

samples in different research work, and the average of the eleven highest values among his selections was recommended as the value of γ_o which is given by

$$\gamma_o = 1.909 - 0.00052(T - 1803) \dots\dots\dots (1)$$

where γ_o is in Nm^{-1} and T is in K. However, the temperatures corresponding to the eleven highest values to obtain the average were within a large range from 1803 to 1873 K, but not at a fixed temperature. In other words, some of the data at temperatures over 1803 K in the set of eleven led to an underestimation of γ_o at 1803 K. From the same 31 data sets, we select fourteen sets, which were obtained only by sessile drop and levitating drop methods, then calculate the value of γ_o at a reference temperature of 1808 K, the melting point of pure iron, by using the given $d\gamma_o/dT$ listed in Table 25 of Ref. 3). All of these data and $d\gamma_o/dT$ are shown in Table 1 with asterisk mark along with six additional data sets which we selected from recent measurements with sessile drop and levitating drop methods. The additional values of γ_o at the same 1808 K were also calculated according to the corresponding $d\gamma_o/dT$ and listed in Table 1.

To show the difference between sessile drop and levitating drop methods, Fig. 1 is plotted by relating the γ_o to the measurement methods and reported years. Obviously, the values obtained by the levitating drop method are markedly higher than those by sessile drop method, since contamination of the iron drop in levitating drop measurement is much lower. For this reason, we suggest that the average value of seven solid points by levitating drop method in Fig. 1 is more reasonable, which gives 1.936 Nm^{-1} as the γ_o at 1808 K. The average value of temperature coefficient corresponding to the seven levitating drop measurements is calculated as

Table 1. Selected data of γ_o at 1808 K and $d\gamma_o/dT$.

Researcher, year	γ_o at 1808 K N m^{-1}	$d\gamma_o/dT$ $10^{-3} \text{ N m}^{-1} \text{ K}^{-1}$	Reference
Sessile drop method			
Van Tszin-ten*, 1960	1.873	-0.20	3 (18)**
Eremenko, 1963	1.838	-0.23	3 (182)
Tavadze, 1965	1.783	-0.50	3 (114)
Eremenko, 1965	1.856	-0.23	3 (186)
Ayushina, 1968	1.850	-0.23	3 (195)
Levin, 1971	1.657	-0.49	3 (104)
Krinochkin, 1971	1.815	-0.34	3 (188)
Nizhenko, 1975	1.856	-0.23	3 (148)
Kasama, 1983	1.852	-0.51	3 (189)
Nogi, 1986	1.720	-0.49	4
Kharlasin, 1991	1.852	-0.49	5
Jimbo, 1992	1.919	-0.43	6
Xue, 1996	1.849	-0.40	8
Levitating drop method			
Soda, 1978	1.907	-0.410	3 (190)
Keene, 1982	1.939	-0.565	3 (113)
Keene, 1982	1.933	-0.704	3 (113)
Keene, 1985	1.919	-0.570	3 (126)
Kasama, 1983	1.953	-0.430	3 (189)
Nogi, 1986	1.978	-0.490	4
Lee, 1993	1.925	-0.396	7
Average of γ_o by levitating drop method and corresponding average $d\gamma_o/dT$			
	1.936	-0.51	

* Only the first author is given in this column.

** The numbers in parentheses after 3 are the reference numbers listed in Keene.³⁾

Fig. 1. The calculated surface tension of pure liquid iron (γ_o) at 1808 K from selected data sets of γ_o and $d\gamma_o/dT$ measured with different methods in different years.

$-0.51 \text{ N m}^{-1} \text{ K}^{-1}$. Thus, the surface tension of pure liquid iron becomes

$$\gamma_o = 1.936 - 0.00051(T - 1808) \quad (2)$$

Another well cited compilation by Iida and Guthrie⁹⁾ gives

$$\gamma_o = 1.872 - 0.00049(T - 1808) \quad (3)$$

Fig. 2. Relation of the surface tension of pure liquid iron (γ_o) and values of $(1 + \cos \theta)$ for liquid iron on Al_2O_3 with temperature.

Equations (1), (2) and (3) are plotted in Fig. 2 for comparison. The temperature coefficients of the three equations are almost the same. The surface tensions at 1823 and 1873 K calculated from Eq. (2) are 1.928 and 1.902 N m^{-1} , respectively. These values agree closely with the relatively new data of 1.97 N m^{-1} at 1823 K and 1.90 N m^{-1} at 1873 K determined by Takiuchi *et al.*^{10,11)} in 1991 with sessile drop method, where no corresponding $d\gamma_o/dT$ were provided. These data are not included in the above compilations and higher than those calculated from Eqs. (1) and (3). Therefore, we recommend γ_o by Eq. (2) which is used in the following calculations.

We note that there remain some ambiguities in the selection and analysis of oscillation of levitating drop, and that chemical potential of oxygen is not always made equal in solid-liquid-gas phases, in particular in gas phase, in the two measurement methods. The latter reservation should be removed in the measurement of γ_o in the near future.

2.2. Work of Adhesion and Contact Angle of Liquid Iron on Al_2O_3 Substrate

Also shown in Fig. 2 are data on $(1 + \cos \theta)$ which is related to the work of adhesion, W_{ad} in N m^{-1} , by

$$W_{ad} = \gamma(1 + \cos \theta) \quad (4)$$

where θ is the contact angle of a drop of liquid iron on an Al_2O_3 -substrate in degree and γ is the surface tension of liquid-Fe which may not be pure. A summary of the measured values of θ is given in Table 2. The contact angles in Table 2 are used to calculate $(1 + \cos \theta)$ which are plotted in Fig. 2. Takiuchi *et al.*¹¹⁾ suggested that the contact angle should decrease generally with an increase of temperature; however, the contact angle of liquid-Fe on Al_2O_3 exhibits considerable scatter in Fig. 2, making it difficult to select a unique value at one temperature and impossible to determine the dependence on temperature. Eustathopoulos and Drevet²⁴⁾ classified the liquid Fe- Al_2O_3 system as being in the "reactive range" according to an equilibrium calculation of the

Table 2. Contact angles of liquid-Fe on Al_2O_3 .

Temperature, K	Contact angle, Degrees	Reference (Year)
1823	124	6 (1992)
1873	135	10 (1991)
1923	135	10 (1991)
1973	135	10 (1991)
2023	132	10 (1991)
1823	131	11 (1991)
1823	135	11 (1991)
1873	128	12 (1992)
1873	141	13 (1979)
1973	131	13 (1979)
1873	144	14 (1960)
1873	118	15 (1973)
1873	130	16 (1980)
1873	136	17 (1983)
1823	121	18 (1961)
1823	128	19 (1959)
1843	128	19 (1959)
1843	136	20 (1962)
1873	141	21 (1982)
1873	133	22 (1989)
1873	125	23 (1990)

mole fraction of dissolved oxygen (X_{O}) in the liquid. Hence, depending on the purities of the gas, substrate and iron in an experiment, the contact angle varies with time as the system approaches chemical equilibrium. The twenty-one data of $1 + \cos \theta$ have an average of 0.331 which gives $\theta = 132^\circ$. This value of θ is slightly less than that (135°) recommended in the review of Cramb and Jimbo.²⁵⁾ Examination of Fig. 2 indicates a slight decrease of $(1 + \cos \theta)$ with an increase in temperature. Since liquid Fe on Al_2O_3 is in the “reactive range”, however, we believe that there should be a slight decrease of θ [i.e., an increase of $(1 + \cos \theta)$] with temperature. Because of the uncertainty in the contact angle, we assume that it is independent of temperature in the range of steelmaking temperatures. Actually, in the experiments of Takiuchi *et al.*,¹⁰⁾ a dependency of contact angle on temperature was not observed.

Using $\theta = 132^\circ$ and the surface tensions of Eq. (2), the work of adhesion of pure liquid iron is calculated by Eq. (4), resulting in

$$W_{\text{ad}} = 0.945 - 1.687 \times 10^{-4} T \quad \text{..... (5)}$$

with W_{ad} in N m^{-1} and T in K.

2.3. Surface Tension of Pure Alumina

In order to estimate the tension of the liquid-Fe/ Al_2O_3 interface as a function of temperature, we examined the data on the surface tension of both solid and liquid Al_2O_3 first. Measured and estimated surface tensions of both liquid- and solid- Al_2O_3 are summarized in Table 3 and plotted in Fig. 3. The data can be found in the references that are cited herein and citations to original works were checked to avoid duplication.

The work of Rhee³⁰⁾ is often cited, and his estimate of the surface tension of (0001) of Al_2O_3 is shown in Fig. 3. Rhee used contact angles as a function of temperature and applied Antonoff's rule to arrive at the surface tension shown as the broken line. When Rhee

Table 3. Surface tension of molten and solid Al_2O_3 .

Temperature, K	Surface tension, N m^{-1}	Reference
Liquid		
2325–2990	$1.381 - 3.078 \times 10^{-4} T \text{ (K)}$	28
2473	0.576	21
2323	0.690	29
2323	0.680	29
2353	0.700	29
2323	0.574	30
Solid		
1748	0.930	25
2293	0.700	26
2293	0.577	26
2293	0.551	26
1873	0.750	27
2323	0.690	29
2323	0.680	29
2323	0.650	29
2123	0.905	29
2143	0.925	29
1848	0.681	30*
1636	0.724	30*
1629	0.725	30*
1636	0.770	30
1636–2325	$0.925 - 1.2 \times 10^{-4} T \text{ (K)}$	30*

* Applied Antonoff's rule.

compared his estimate to independent measurements of the surface tension, there was good agreement. The only measurements consulted, however, were in the range of 0.55 to 0.77 N m^{-1} marked as Ref. 30) (S), Ref. 26) (S) and Ref. 27) (S) in Fig. 3.

The line in Fig. 3 for liquid- Al_2O_3 is the result of sixteen measurements [Ref. 28) (L)] of surface tension in the temperature range shown. With one exception [Ref. 30) (L)], they agree to within 0.05 N m^{-1} of the other data for liquid- Al_2O_3 . Notice, however, that extrapolation of the line of liquid- Al_2O_3 to lower temperatures gives the result that the surface tension of the liquid is greater than the surface tension of the solid of Rhee's line [Ref. 30) (S)], which is not likely. There are three data for solid- Al_2O_3 , however, that are above the extrapolation of the surface tension of liquid- Al_2O_3 . The upper line in Fig. 3 is a line that passes through the average of the two at 2123 and 2143 K with a slope of $-1 \times 10^{-4} \text{ N m}^{-1} \text{ K}^{-1}$, which was said to be “widely accepted for solid-alumina” by Rhee.³⁰⁾ This line is given as

$$\gamma_1 = 1.128 - 1 \times 10^{-4} T \quad \text{..... (6)}$$

with γ_1 , the surface tension of solid-alumina, in N m^{-1} and T in K. The value calculated from this equation agrees closely with the measured data of surface tension at 1748 K. Equation (6) is, therefore, used to estimate the tension of the liquid-Fe/ Al_2O_3 interface in a later section.

Also, for liquid- Al_2O_3 ($2293 < T < 3000 \text{ K}$), we rely on the linear equation of the solid line in Fig. 3 cited in the compilation of high temperature properties by Kawai and Shiraishi²⁸⁾; it is

Fig. 3. Surface tension of liquid (L)-Al₂O₃ and solid (S)-Al₂O₃.

$$\gamma_1 = 1.379 - 0.000308T \quad \text{.....(7)}$$

also with γ_1 in N m⁻¹ and T in K.

2.4. Interfacial Tension between Liquid Iron and Alumina

The interfacial tension is given by the Young's equation at the triple junction, *i.e.*,

$$\gamma_2 = \gamma_1 - \gamma \cos \theta \quad \text{.....(8)}$$

where γ_2 is the interfacial tension between liquid-Fe and Al₂O₃. For our assessment of the liquid-Fe/Al₂O₃ interfacial tension, the contact angle selected is $\theta = 132^\circ$ (Fig. 2), and the surface tension of liquid-Fe is taken to be given by Eq. (2). Since the surface tension of the Al₂O₃ is given by Eq. (6), then the tension of the liquid-Fe/Al₂O₃ interface could be calculated from Eq. (8). For liquid-Fe/Al₂O₃, the interfacial tension is linear:

$$\gamma_2 = 3.04 - 4.41 \times 10^{-4}T \quad \text{.....(9)}$$

with γ_2 in N m⁻¹ and T in K.

The surface and interfacial properties of the liquid-Fe and alumina system depending on temperature, in the range of steel refining and casting processes, are summarized in Fig. 4, in which the γ_0 is from Eq. (2), γ_1 from Eq. (6), γ_2 from Eq. (9), W_{ad} from Eq. (5) and θ is constant as 132° . All of these are used below.

3. Surface and Interfacial Properties of Dilute Fe-O-S Melt with Alumina

3.1. Effect of Oxygen and Sulfur on Work of Adhesion

The effect of the surface active elements, oxygen and sulfur, on the work of adhesion (W_{ad}) of liquid-Fe on Al₂O₃ has been measured. The data are presented in Table 4 as either the effect of the concentration of the element on W_{ad} or as the effect on θ . Unfortunately, there is not a direct calculation of $dW_{ad}/d([\%i])$ from $d\theta/d([\%i])$ because expansion of Eq. (4) gives

$$\frac{dW_{ad}}{d([\%i])} = -\gamma \sin \theta \frac{d\theta}{d([\%i])} + (1 + \cos \theta) \frac{d\gamma}{d([\%i])} \quad \text{.....(10)}$$

Hence, in order to calculate the change in the work of adhesion from the change in the contact angle requires that $d\gamma/d([\%i])$ is known. Here, $\%i$ is in mass%.

Fig. 4. Summary of the change of surface and interfacial properties of the liquid-Fe/solid Al₂O₃ system with temperature.

Keene²³ collected many data sets of the effect of oxygen and sulfur on the surface tension of liquid-Fe and gave the mean values of $d\gamma/d([\%O])$ and $d\gamma/d([\%S])$ as -25.54 and -10.98 N m⁻¹ mass%⁻¹, respectively, as $[\%O]$ and $[\%S] \rightarrow 0$. Since both γ and θ vary with $[\%i]$, then $dW_{ad}/d([\%i])$ varies with $\%i$. Hence, the calculated values entered in Table 4 are the average values in the limited range of concentration for each entry. In this calculation, θ is 132° based on the average of $1 + \cos \theta$ in Fig. 2, and γ is calculated from Eq. (2).

The variability in the work of adhesion in dilute Fe-O and Fe-S alloys shown in Table 4 indicates the difficulty in selecting data. In dilute concentrations, many of the data indicate that the work of adhesion decreases with an increase in the solute. This is true for an Fe-S melt because the replacement of Fe-O-Al bonds by Fe-S-Al bonds in the interface of Fe/Al₂O₃ will lead to a decrease of the adhesion force between Fe and Al₂O₃. For an Fe-O melt, however, the situation is much more complex. At low concentrations of oxygen, an alumina substrate may dissolve into the liquid-Fe. On the other hand, at relatively high concentrations of oxygen, a reaction layer of the system FeO-Al₂O₃ forms between the original Al₂O₃-substrate and the melt. It is known that factors which enhance reactivity between a melt and the sub-

Table 4. Effect of oxygen and sulfur on the work of adhesion of liquid-Fe on Al_2O_3 .

Element <i>i</i>	$d\theta/d([\%i]),$ deg. (mass%) ⁻¹	$dW_{ad}/d([\%i]),$ N m^{-1} (mass%) ⁻¹	Range, mass%	Reference
O	-186	258*	≤0.05	14
O	674	-974*	≤0.03	10
O	—	-8.72	≤0.01	16
O	—	-14.5	≤0.02	10
O	—	-92.0	≤0.006	12
O	—	8.0	$0.006 \leq [\%O] \leq 0.04$	12
S	-445	631*	≤0.025	14
S	337	-490*	≤0.05	10
S	—	-7.8	≤0.03	16

* Calculated as described in the text.

strate also lower the contact angle,²⁴⁾ and hence may change the W_{ad} greatly. In order to determine the effect of sulfur and oxygen on the work of adhesion of liquid-Fe with alumina substrate, the influence of sulfur and oxygen content in liquid-Fe on both the contact angle of liquid-Fe with Al_2O_3 and surface tension of liquid-Fe must be investigated.

3.2. Effect of Oxygen and Sulfur on Contact angle

Some of the data sets of contact angle against oxygen content in liquid iron at 1873 K are shown in Fig. 5. Obviously, it is difficult to select a good set or do averaging analysis on these data sets because of the great scatter. Here, the effect of oxygen on the contact angle is analyzed by referring to the data by Nakashima *et al.*¹²⁾ plotted as the crosses. They reported their results in 1992 and had the benefit of referring to previous experience of others,^{10,11,26)} and, importantly, the purity of alumina substrate used in their experiment was the highest so far. Also, they provided adequate information to do thermodynamic calculations pertaining to the reactivity of the system.

The equilibrium constant, K , of the reaction

is given by³¹⁾

$$\log K (= \log a_{\text{Al}}^2 a_{\text{O}}^3) = -64\,000/T + 20.57 \dots (11)$$

where the square brackets indicate the elements dissolved in liquid iron. The activities, a_{Al} and a_{O} , are calculated from the recommended interaction parameters³¹⁾ for estimating the activity coefficients, f_{O} and f_{Al} , as defined by $a_{\text{Al}} = f_{\text{Al}} [\% \text{Al}]$ and $a_{\text{O}} = f_{\text{O}} [\% \text{O}]$.

The contact angles reported by Nakashima *et al.*¹²⁾ are shown as the data labeled total oxygen in Fig. 5. They measured oxygen using a technique that reported total oxygen. In addition, they measured the aluminum content after 40 min duration and found it to be in the range of 150–200 ppm (not present in the starting material). With chemical analysis of both $[\text{Al}]$ and $[\text{O}]$ provided, we are able to deduce the chemical behavior of the system. First, by taking the position that all of the aluminum is dissolved, a calculation of the concentration of oxygen in equilibrium with Al_2O_3 gives only about 4 to 6 ppm of dissolved oxygen. Clearly the total oxygen contents reported in Fig. 5 must represent the sum of oxygen in solution and the oxygen combined in

Fig. 5. Contact angles given by Nakashima *et al.*¹²⁾ as a function of total oxygen. The other points are dissolved oxygen contents (calculated) for 150 and 200 ppm of aluminum. Other dotted lines are from Refs. 10), 11) and 26).

Al_2O_3 in the iron drop. The second calculation fixes both the total aluminum and the total oxygen and then partitions them between their dissolved amounts and the combined amounts in Al_2O_3 while assuming equilibrium with Al_2O_3 . The calculations give similar results for 150 and 200 ppm of total $[\text{Al}]$; the thick solid curve in Fig. 5 is presented to show the effect of dissolved oxygen on the contact angle of liquid-Fe on Al_2O_3 .

The second calculation also reveals that below a critical concentration of oxygen, there must be dissolution of Al_2O_3 . At 150 ppm of total $[\text{Al}]$ the critical concentration of oxygen is 60 ppm, and at 200 ppm of total $[\text{Al}]$ it is 80 ppm. Since the initial sample contained *ca.* 400 ppm oxygen, the dissolution of Al_2O_3 seemed unlikely at least at early stage of experiments; rather, the melt was probably in contact with a reaction layer that formed early and persisted and caused the contact angle to decrease at the very low concentrations of oxygen. Reaction layers have been reported at both low and high concentrations of oxygen in nickel on a substrate of Al_2O_3 ,¹³⁾ also with an abrupt drop in the contact angle at very small oxygen contents. In an early study,²⁶⁾ researchers detected no reaction layer at 26 ppm of oxygen in iron on Al_2O_3 and no indication of a precipitous drop of contact angle at small concentrations of oxygen, although this region was not studied by them

Fig. 6. Contact angle as a function of sulfur content. The thin solid curve is redrawn from the review by Nakashima and Mori³³⁾; the circles are data from Nogi and Ogino²⁷⁾ and solid points from Ogino *et al.*³²⁾ The broken curve is parallel to the thick solid curve, which is a regression of the selected points with cross marks, to a contact angle of 132° at no sulfur.

in the detail of Ref. 12). It is also important to note that the oxygen potential in the early work²⁶⁾ was varied and controlled through the gas phase.

Based on the aforementioned facts, the effect of oxygen on the contact angle is best represented by the thick curve in Fig. 5 that is defined by the concentrations of dissolved oxygen. Without a reaction layer at the very low concentrations of oxygen, the dissolution of Al_2O_3 provides no reason for an abrupt decrease in θ as $[\%O] \rightarrow 0$. Hence, an extrapolation of the curve to our recommended contact angle of 132° is reasonable. The thick curve in Fig. 5 is well represented by

$$\theta = 132 - 6.3 \ln(1 + 400[\%O]) \quad \text{..... (12)}$$

The effect of $[S]$ on the contact angle is shown in Fig. 6 and from two different papers of the same authors (Ogino and Nogi^{27,32)}). The thin solid curve drawn in Fig. 6 is from the review paper of Nakashima and Mori³³⁾ who cited the measured data of Ogino *et al.*³²⁾ but seemed to have rearranged the data by considering that the contact angle was 138° at zero sulfur rather than the measured 125°. Thus, it appears that the data set for sulfur is actually rather restricted. Considering that the angle should be high at zero sulfur content and not high at higher $[\%S]$ in liquid iron, we regressed the data with cross marks in Fig. 6 by using the same form of Eq. (12) for oxygen and obtained the thick solid curve drawn in Fig. 6, the one on which we mostly rely.

The thick solid curve implies that sulfur has just a little effect on the contact angle. According to our experience, an enrichment of sulfur at the interface between an Fe-S melt and Al_2O_3 is theoretically and practically true. On the other hand, the Fe-S melt is slightly reactive with Al_2O_3 , although not to the degree of an Fe-O melt. Hence, it is reasonable that this enrichment of sulfur and reaction at the Fe-S/ Al_2O_3 interface induces a reduction of the contact angle between an Fe-S melt and Al_2O_3 , at least in dilute Fe-S melts. Also, this reduction of contact angle should not be as much as that in an Fe-O

Fig. 7. Measured surface tension of Fe-O melts at 0.02 and 0.04 mass [%O] by various researchers in different years.

melt. Accepting the fact that contact angle decreases as sulfur increases and assuming $\theta = 132^\circ$ at zero sulfur content, we prefer to adopt the dotted line in Fig. 6, which shows that the contact angle decreases by the angles relative to the thick solid curve in Fig. 6. The dotted line is given by

$$\theta = 132 - 0.63 \ln(1 + 640[\%S]) \quad \text{..... (13)}$$

By ignoring the interaction of oxygen and sulfur on the contact angle and assuming that the $d\theta/d([\%i])$ is independent of temperature, we can approximate the results, in the range $[\%O] \leq 0.05$ and $[\%S] \leq 0.06$, as

$$\theta = 132 - 6.3 \ln(1 + 400[\%O]) - 0.63 \ln(1 + 640[\%S]) \quad \text{..... (14)}$$

where the concentrations are in mass% and θ is in degrees.

3.3. Surface Tension of Dilute Fe-O-S Melts

For the effect of oxygen, Keene²⁾ collected most of the data sets reported before 1988 and Tanaka and Hara³⁴⁾ added recent data sets. However, there is still lack of commonly acceptable equation to describe the relationship between $[\%O]$ and γ . On the basis of Refs. 2) and 34), Fig. 7 is plotted to show the measured data at 0.02 and 0.04 $[\%O]$ by different researchers in different years. An obvious tendency is that the scatter of data decreases quickly in recent years, falling into a small range after 1990, because of the progress of experimental techniques. Thus, the average of the most recent five data sets, which were obtained by Nakashima *et al.*¹²⁾ (1 873 K), Takiuchi *et al.*¹⁰⁾ (1 873 K), Takiuchi *et al.*¹¹⁾ (1 823 K), Jimbo and Cramb³⁵⁾ (1 823 K) and Taimatsu *et al.*³⁶⁾ (1 873 K), are more representative. These five works are summarized in Fig. 8, which also shows the averaged effect of oxygen content on the surface tension of Fe-O melts. Here, the mean value of γ at $[\%O] \rightarrow 0$ is taken as the average based on Eq. (2) at 1823 and 1 873 K. The average curve is given by

$$\gamma = 1.915 - 0.28 \ln(1 + 170[\%O]) \quad \text{..... (15)}$$

Fig. 8. Measured surface tension of Fe-O melts at 1823 or 1873 K from five works published after 1990 and the average of them. The averaged value of γ at $[\%O] \rightarrow 0$ is taken as the average of γ_o at 1823 and 1873 K, estimated from Eq. (2).

with γ in N m^{-1} and $[\%O]$ in mass%. It should be mentioned that, although Takiuchi *et al.*^{10,11)} found a difference between the effects of oxygen on the surface tension at 1823 and 1873 K, it is difficult to say that the difference is noticeable in this small temperature range in comparison with data by others.^{12,35,36)} Therefore, we recommend that Eq. (15) can be used in a larger temperature range from the melting point of dilute Fe-O melts to 1900 K, and that the effect of oxygen on surface tension of dilute Fe-O melt is rewritten as

$$\gamma = \gamma_o - 0.28 \ln(1 + 170[\%O]) \quad \text{..... (16)}$$

with γ in N m^{-1} and γ_o calculated from Eq. (2) at different temperatures. For higher temperatures, data by Mukai and Shinozaki³⁷⁾ can be consulted, but it appears that more work is needed to establish the effect of oxygen on the surface tension of iron for the high temperatures encountered in welding steel.

For the effect of sulfur, three works have often been cited which are listed as follows:

- (1) $\gamma = 1.913 - 0.195 \ln(1 + 365[\%S])$, by Cramb *et al.*³⁸⁾ at 1823 K
- (2) $\gamma = 1.788 - 0.195 \ln(1 + 185[\%S])$, by Belton³⁹⁾ at 1823 K
- (3) $\gamma = 1.910 - 0.235 \ln(1 + 185[\%S])$, by Ogino *et al.*⁴⁰⁾ at 1873 K

with γ in N m^{-1} and $[\%S]$ in mass%. These are shown in Fig. 9 where agreement among the three is good at $[\%S] \geq 0.05$ and reasonable at $[\%S] < 0.05$. Following the same averaging as done for oxygen, the effect of sulfur on surface tension of Fe-S melts is given by:

$$\gamma = \gamma_o - 0.2 \ln(1 + 330[\%S]) \quad \text{..... (17)}$$

with γ in N m^{-1} and γ_o calculated from Eq. (2) at different temperatures. Equation (17) is recommended for the temperature range of 1800–1900 K. Ignoring the effect of interaction between $[O]$ and $[S]$, the surface tension of dilute Fe-O-S melts can be represented by

$$\gamma = \gamma_o - 0.28 \ln(1 + 170[\%O]) - 0.2 \ln(1 + 330[\%S]) \quad \text{..... (18)}$$

in the range of 1800–1900 K.

Fig. 9. Three well cited works on the surface tension of Fe-S melt at 1823 or 1873 K and the average of them. The averaged value of γ at $[\%S] \rightarrow 0$ is taken as the mean of the γ_o at 1823 and 1873 K, estimated from Eq. (2).

We should point out that Keene *et al.*⁴¹⁾ reported a positive temperature coefficient of $\gamma(d\gamma/dT)$ for Fe-O-S alloys, but measurements were made at 1844 and 1923 K only. They combined the concentrations of oxygen and sulfur into one parameter as $X_O/(X_O + X_S)$, where X_O and X_S are the atom fractions of oxygen and sulfur, as a way of representing the effect of the two surface active elements. In Fig. 10, we have replotted their data at 1844 and 1923 K with a different parameter that combines the content of oxygen and sulfur because their parameter was undefined as X_O and X_S both approach zero. Although the two lines in Fig. 10 indicate that alloys with $(X_O + X_S)/X_{Fe}$ greater than 0.0015 have $d\gamma/dT > 0$, it is rather speculative in view of the scatter of data, which is typical of high temperature measurements of surface tension in a rather limited temperature range. Takiuchi *et al.*¹⁰⁾ determined γ over a greater temperature range ($1823 \leq T \leq 2023$ K) in dilute Fe-O alloys and found that $d\gamma/dT > 0$ when the oxygen content was more than 0.02%, approximately.

Perhaps spurred by the findings of Keene *et al.*,⁴¹⁾ other researchers^{42,43)} considered that, at least at the

Fig. 10. Reproduction of the work of Keene *et al.*⁴¹⁾ on the surface tensions of dilute Fe-O-S melt at two temperatures.

very high temperatures encountered in the welding of steel, the $d\gamma/dT$ was positive when the steel contained surface active elements. Using thermodynamic data on the activities of oxygen and sulfur in steel and estimates of the surface excess and fractional coverage on the surface, Sahoo *et al.*⁴²⁾ derived

$$\gamma = \gamma_0 - RT\Gamma_s \ln(1 + k_i a_i e^{-(\Delta H^0/RT)}) \quad \dots\dots\dots(19)$$

where γ_0 is the surface tension of pure Fe, Γ_s is the surface excess, R is the gas constant, k_i and ΔH^0 are thermodynamic constants that relate to the adsorption of the element at the surface, and a_i is the activity of element i . The parameters k_i and ΔH^0 were calculated from data on the variation of the surface tension with temperature (again with limited data).

The surface tensions according to Eq. (19) and the parameters of Sahoo *et al.*⁴²⁾ and the surface tension according to Eq. (18) are compared in Fig. 11. At 1800 K (Fig. 11(a)), the two calculations compare favorably, and Eq. (18) gives surface tensions greater than those of Eq. (19). At 2000 K (Fig. 11(b)), the comparison shows less agreement, and Eq. (19) gives greater surface tensions. We believe that Fig. 11 and calculations for higher temperatures indicate a need for additional measurements of the surface tension of dilute Fe-S-O alloys because of the importance of Marangoni convection in welding processes. In the solidification and refining range of steels, the calculated surface tensions agree, at least within the errors of experimental measurements.

3.4. Interfacial Tension of Dilute Fe-O-S Melt with Alumina

The effects of [S] and [O] on the interfacial tension, γ_2 , are estimated after Eq. (8) and shown in Fig. 12. The effect of temperature on $d\gamma_2/d([\%i])$ is neglected in the temperature range of calculation. At the same time, it is assumed that the surface tension of solid-Al₂O₃ is not affected by [S] and [O].

The effects of oxygen and sulfur on the tension of the liquid-Fe/Al₂O₃ interface at 1800–1900 K can be approximated after Eqs. (6), (14) and (18) as

Fig. 11. Effect of surface active elements on the surface tension of Fe at (a) 1800 K and (b) 2000 K as the concentration of oxygen is fixed at 0.02 mass%. Curves with 1 based on Eq. (18) and assuming $d\gamma/dT$ is unaffected by temperature; curves with 2 are calculated from Sahoo *et al.*⁴²⁾ Eq. (19).

$$\begin{aligned} \gamma_2 = & 1.128 - 1 \times 10^{-4}T - [2.858 - 5.1 \times 10^{-4}T \\ & - 0.28 \ln(1 + 170[\%O]) - 0.2 \ln(1 + 330[\%S])] \\ & \times \cos[132 - 6.3 \ln(1 + 400[\%O]) \\ & - 0.63 \ln(1 + 640[\%S])] \quad \dots\dots\dots(20) \end{aligned}$$

where γ_2 is in N m⁻¹, T is in K and the concentrations are in mass%. In view of increasing interest in producing steel extra low in [O] and [S], Fig. 13 is plotted after the above equation to show the change of γ_2 with [O] and [S] as well as temperature in the range of $0 \leq [\%O] \leq 0.01$ and $0 \leq [\%S] \leq 0.03$.

3.5. Effects of [O] and [S] on the Work of Adhesion of the Liquid-Fe/Al₂O₃ System

The work of adhesion can be calculated by using Eqs. (4), (14) and (18). At 1873 K, the surface tension of pure liquid iron, γ_0 , is 1.902 N m⁻¹ after Eq. (2). Calculated value of W_{ad} by Eq. (4) are plotted in Fig. 14 against the [%O] or [%S] in liquid iron. The decrease of W_{ad} with increasing [%S] in Fe-melt was reported by Ogino *et al.*¹⁷⁾ which agrees qualitatively with the present calculation. A possible explanation is that the interfacial bonds Fe-O-Al are replaced by Fe-S-Al as sulfur increases.

However, the influence of [O] in liquid-Fe on W_{ad} is greatly different from the data by other researchers,^{11,12,17)} but in good agreement with those of

Fig. 12. Effects of oxygen and sulfur on the interfacial tension of dilute Fe-O-S melts on Al_2O_3 (calculated at 1873 K).

Fig. 13. Effects of oxygen, sulfur and temperature on the interfacial tension of dilute Fe-O-S melts on Al_2O_3 at very low concentrations of oxygen calculated by Eq. (20).

Takiuchi *et al.*¹¹⁾; specifically, the W_{ad} increases to about $0.8 N m^{-1}$ as $[O]$ increases to about 0.03 and then remains constant when $[O]$ further increases.

Combining Eqs. (4) and (8), one has

$$W_{ad} = \gamma_1 + \gamma - \gamma_2 \quad \dots\dots\dots(21)$$

Assuming that the $[O]$ has no influence on the surface tension of alumina, γ_1 , the effect of $[O]$ on W_{ad} can be given by

$$\frac{dW_{ad}}{d([O])} = \frac{d\gamma}{d([O])} - \frac{d\gamma_2}{d([O])} \quad \dots\dots\dots(22)$$

By using our recommendations, the effect of $[O]$ on the interfacial tension between liquid-Fe and alumina, γ_2 , is calculated to be greater than that on the surface tension of liquid-Fe, γ , at low $[O]$. At high oxygen end, γ and γ_2 change with oxygen in the same way.

For pure liquid metals including iron, W_{ad} has been simply related to their surface tensions, γ_m , as

$$W_{ad} = k\gamma_m \quad \dots\dots\dots(23)$$

with $k \approx 0.4$.²⁴⁾ By using the data recommended in the

Fig. 14. Effect of oxygen and sulfur on the work of adhesion, W_{ad} , and constant, k , of dilute Fe-O-S melts on Al_2O_3 .

present work, the value of k becomes 0.33, which is close to 0.4. The effect of $[O]$ on k is also shown in Fig. 14. Eustathopoulos and Drevet²⁴⁾ mentioned that the W_{ad} of a reactive liquid metal/oxide couple is about twice of a non-reactive couple. In the present work, however, one can read from Fig. 14 that the constant k monotonically increases with $[O]$; *i.e.*, the reactivity of liquid-Fe with Al_2O_3 is enhanced when $[O]$ is increased, leading to the increase of k . At 500 ppm of $[O]$, the value of k is almost doubled. Because of the low reactivity between an Fe-S melt and alumina, the k - $[S]$ curve increases very slowly. Hence, we believe that the data and equations recommended in the present study are reasonable.

4. Summary and Recommendations

Data and compilations on the surface tensions, contact angle, and work of adhesion pertaining to the wettability of liquid-Fe on Al_2O_3 are collected and analyzed. In addition, the effects of oxygen and sulfur dissolved in the liquid-Fe on the wettability are also reviewed. From the above we have deduced simple working equations that are summarized here.

4.1. Surface Tension of Liquid-Fe

The surface tension of pure liquid-Fe recommended here is from Eq. (2) as

$$\gamma_o = 2.858 - 0.00051T$$

with γ_o in $N m^{-1}$ and T in K.

4.2. Contact Angle of Liquid-Fe on Al_2O_3

The contact angle of pure liquid iron on alumina substrates is assumed to be a constant in the range $1823 \leq T \leq 2023$ K. Based on an average of measurements found in the literature, we recommend $\theta = 132^\circ$.

4.3. Work of Adhesion of Liquid-Fe on Al_2O_3

The work of adhesion of pure liquid iron on alumina substrate is recommended as

$$W_{ad} = 0.945 - 1.687 \times 10^{-4}T$$

with W_{ad} in $N m^{-1}$ and T in K.

4.4. Surface Tension of Al_2O_3

For liquid- Al_2O_3 ($2293 < T < 3000$ K), we rely on the linear equation of the line cited in the compilation of high temperature properties by Kawai and Shiraishi²⁸⁾; it is

$$\gamma_1 = 1.379 - 0.000308T$$

For solid- Al_2O_3 ($T < 2293$ K), we recommend:

$$\gamma_1 = 1.128 - 0.0001T$$

In both equations, γ_1 is in N m^{-1} , and T is K.

4.5. Tension of the Liquid-Fe/ Al_2O_3 Interface

For the liquid-Fe/ Al_2O_3 interface, we found that

$$\gamma_2 = 3.04 - 0.000441T$$

This equation is applicable to solid- Al_2O_3 , but the procedure described in the text could be used to estimate γ_2 for liquid-Fe/liquid- Al_2O_3 .

4.6. Surface Tension of Fe-O-S Liquid

Our recommendation from melting point of dilute Fe-O-S melt to 1900 K is:

$$\gamma = \gamma_0 - 0.28 \ln(1 + 170[\%O]) - 0.2 \ln(1 + 330[\%S])$$

where γ and γ_0 are in N m^{-1} . Lacking data (except over a small temperature range), we assume that the effects of [O] and [S] are independent of temperature.

4.7. Effects of Oxygen and Sulfur on the Contact Angle

We can approximate the results, in the range $[\%O] \leq 0.05$ and $[\%S] \leq 0.06$, as

$$\theta = 132 - 6.3 \ln(1 + 400[\%O]) - 0.63 \ln(1 + 640[\%S])$$

where the concentrations are in mass% and θ in degree. It is assumed that the contact angle and $d\theta/d([\%i])$ are independent of temperature.

4.8. Effects of Oxygen and Sulfur on the Tension of the Liquid-Fe/ Al_2O_3 Interface

The effects of oxygen and sulfur on the tension of the liquid-Fe/ Al_2O_3 interface in the temperature range of 1800–1900 K can be approximated as

$$\begin{aligned} \gamma_2 = & 1.128 - 1 \times 10^{-4}T - [2.858 - 5.1 \times 10^{-4}T \\ & - 0.28 \ln(1 + 170[\%O]) - 0.2 \ln(1 + 330[\%S])] \\ & \times \cos[132 - 6.3 \ln(1 + 400[\%O]) \\ & - 0.63 \ln(1 + 640[\%S])] \end{aligned}$$

where γ_2 is in N m^{-1} , T is in K and the concentrations are in mass%.

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