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Determination of the surface tension of liquid stainless steel

Z. LI*
Department of Materials Science and Engineering, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan; Department of Materials, Imperial College, Exhibition Road, London SW7 2AZ, UK
E-mail: z.li@imperial.ac.uk

K. MUKAI
Department of Materials Science and Engineering, Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan

M. ZEZE
Yawata R&D Lab, Technical Development Bureau, Nippon Steel Corporation, Kitakyushu 804-8501, Japan

K. C. MILLS
Department of Materials, Imperial College, Exhibition Road, London SW7 2AZ, UK

The surface tensions (σ) and temperature dependencies ($d\sigma/dT$) of several commercial 4-series ferritic stainless steels have been measured using the sessile drop technique on an Al_2O_3 plate over the temperature range 1789 to 1883 K in an atmosphere of high purity ($P_{O_2} < 10^{-19}$ MPa) argon gas. Precise densities of liquid stainless steels have also been obtained using the modified sessile drop method in order to calculate accurate values of the surface tension. The surface tensions of liquid stainless steels decreased markedly with increasing sulphur concentration in the steels. The variation of surface tensions of liquid stainless steels can be described by the following equation $\sigma = 1790 - 182\ln(1 + 260a_S)$ (mN/m) when only S is considered or $\sigma = 1820 - 304\ln(1 + 383a_O) - 182\ln(1 + 260a_S)$ (mN/m) when both S and O are considered. The equations apply to the following compositional ranges: mass%O = 0.0022–0.0064, mass%S = 0.0008–0.05. The temperature coefficient of the surface tension ($d\sigma/dT$) of liquid stainless steel was found to change from negative to positive at a sulphur concentration of about 30 mass ppm in the steel. Nitrogen was found to have little effect on the surface tension of liquid stainless steel.

1. Introduction

Surface (σ_m) and interfacial tensions (σ_{ms}) of steels are important in the continuous casting process and subsequently in the quality of cast product since:

(1) the slag/gas entrapment decreases as σ_{ms} increases (σ_{ms}: interfacial tension between molten steel and slag);
(2) the shape of the meniscus, which determines the amount of slag infiltration into the channel between the mould and newly-formed steel shell (lubrication), is determined by σ_{ms}: $\sigma_{ms} = \sigma_m + \sigma_s - \varphi(\sigma_m\sigma_s)^{0.5}$ (σ_m and σ_s: the surface tensions of liquid steel and slag). The largest term in the equation is σ_m (thereafter σ_m is expressed as σ);
(3) the behavior of foreign particles (solid particles and bubbles) in front of solidifying interface (i.e. pushing or engulfment by a solidifying interface), is related to interfacial tension gradients induced by both the concentration and temperature gradients formed in the front of the solid-liquid interface [1], and also related to the wettability of the inclusion with liquid steel [2]. Despite the industrial importance there are few reliable data for the surface tension of commercial stainless steels.

It is important to note that the surface tensions of metals are different from other physical properties since they are dependent upon the surface composition and not upon the bulk composition. Consequently, surface-active elements, such as oxygen or sulphur, can have a marked effect on the surface tension even though they are only present in ppm levels. The varying concentrations of surface-active impurities in the alloy samples often result in large discrepancies between the surface tensions reported in different investigations. The

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*Author to whom all correspondence should be addressed.

TABLE I Chemical compositions (mass%) of stainless steels and activities of O and S at 1823 K

Steel	C	Si	Mn	Al	Cr	Ti	O	S	N	a_O	a_S
A	0.0435	0.287	0.189	0.1288	16.198	0.0044	24	13	111	2.0	8.9
B	0.0847	0.298	0.596	0.0890	15.995	0.0056	49	14	284	4.3	9.4
C	0.0689	0.316	0.572	0.0042	16.232	0.0028	64	105	325	6.9	70.2
D	0.0084	0.464	0.350	0.0562	10.858	0.2211	22	19	91	2.5	13.9
E	0.0056	0.126	0.141	0.0504	16.199	0.2930	22	18	90	1.1	7.6
F	0.0053	0.092	0.112	0.0806	17.346	0.2741	25	12	123	1.1	6.9
G	0.0059	0.145	0.131	0.0520	18.670	0.1541	52	11	106	2.7	6.4
H	0.0153	0.555	0.149	0.0216	19.105	0.0082	34	8	186	2.1	5.1
I	0.0076	0.467	0.124	0.0293	21.511	0.0042	56	38	106	2.8	22.6

The unit of O, S and N is mass ppm. a_O, a_S: $\times 10^{-4}$.

oxygen or sulphur contamination of steels has been recognized as a major problem in steel processing.

The stainless steel containing about 16 mass% Cr is one of important stainless steel grades. In order to reduce inclusion and bubble entrapment in this grade of stainless steel, it is necessary to study the effect of O and S on the surface/interfacial properties with a solid substrate. The surface tensions and wettabilities of liquid model alloys (Fe-16mass%Cr-O/S alloys) with alumina have been measured previously with the sessile drop method [3, 4]. In this work, the sessile drop method has been used to (i) measure the surface tensions of liquid commercial stainless steels and (ii) determine the effect of sulphur and nitrogen on the surface tensions of liquid commercial stainless steels.

2. Experimental

Nine commercial stainless steels were employed in this work. These were all 4-series alloys with a ferritic microstructure. Their chemical compositions and the activities of O and S at 1823 K are shown in Table I. The activities of O and S were calculated using the recommended interaction parameters of first and second orders [5]. Cylindrical pieces ($\phi 8 \times 8$ mm, 3 g) of stainless steel were used as samples, and high purity Al_2O_3 (99.8%) plate (25.7 × 25.7 × 2.5 mm) as a substrate. In the experiments carried out to determine the effect of S content on surface tension, the steel samples were doped with S by drilling a hole into a cylindrical sample (ϕ 8 × 6 mm) of steel F or G and covering this with a disc of the steel (ϕ 8 × 2 mm). The S was added as high purity FeS. The effect of N concentration on the surface tension of liquid stainless steel (steel H) was carried out by adjusting the nitrogen partial pressure in the atmosphere. The surface tensions of liquid stainless steels were determined at temperatures of 1789, 1836 and 1883 K.

The details of the apparatus and experimental procedure have been described elsewhere [3, 4]. The experimental apparatus consisted of a furnace with $LaCrO_3$ heating elements, a gas purification system, an oxygen sensor, a photographic system and a digital/calculation system (computer). The experimental procedure can be summarized as follows: (i) leveling the sample on the plate, (ii) replacing atmosphere in the reaction tube with high-purity Mg-deoxidised argon, (iii) heating the furnace and maintaining at the experimental temperature, (iv) taking photographs of the liquid droplet at the desired intervals, (v) digitizing the image contour of the droplet into computer, and (vi) obtaining the surface tension using Rotenberg's method [6]. The oxygen partial pressure in the gas outlet was measured to be less than 10^{-19} MPa with an oxygen sensor fabricated with ZrO_2-CaO solid electrolytes. Chemical analysis was carried out on the post-measurement samples. N and O were determined using the infrared adsorption and thermal conductimetric methods after fusion in a He gas flow. S was determined by the infrared adsorption method after combustion in an induction furnace.

In order to obtain the accurate values of the surface tensions of stainless steels, the densities of liquid stainless steels at 1768–1874 K were measured using the modified sessile drop method [7] in this study. The maximum measurement error was estimated to be ±2% for the surface tension.

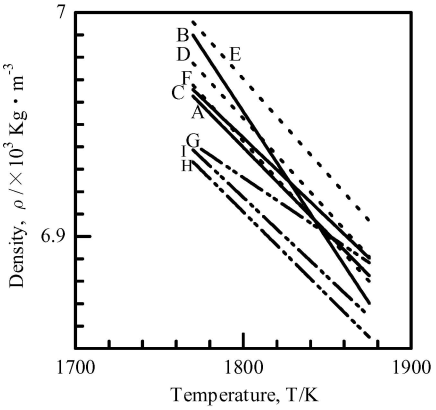
3. Results and discussion

3.1. Density of liquid stainless steel

Precise density data for liquid stainless steels are necessary to obtain accurate surface tension values using the sessile drop method. However, there have been very few measurements reported for the densities of liquid stainless steels. In this study, the densities (ρ) of liquid stainless steels A-I measured by the modified sessile drop method are shown in (Fig. 1). The total maximum relative error of this method is estimated to be ±0.75% [7].

3.2. Surface tension of liquid stainless steel

The measured surface tensions of liquid stainless steels A-I are shown in Figs 2a–c. The surface tensions of liquid stainless steels A, B and C at any specific temperature decreased in the order of $A > B > C$ with the increasing concentrations/ activities of O and S from A to C. The same changes can be found for H, G and I, and also for F and D. The oxygen activities in the samples H, G, D and I are similar, but the sulphur activities increased in the order of $H < G < D < I$, which results in decreases of the surface tensions in the order of $H > G > D > I$. Thus it can be concluded that the surface tensions of the liquid stainless steels are dependent on the concentrations of O and S in the steels,



A: ρ=6.9572-7.6314×10^{-4}(T-1778) 1778-1874K
B: ρ=6.9830-1.1395×10^{-3}(T-1776) 1776-1871K
C: ρ=6.9598-7.1542×10^{-4}(T-1778) 1778-1873K
D: ρ=6.9675-8.2345×10^{-4}(T-1782) 1782-1871K
E: ρ=6.9881-8.4476×10^{-4} (T-1779) 1779-1873K
F: ρ=6.9625-8.3422×10^{-4} (T-1776) 1776-1874K
G: ρ=6.9389-5.0651×10^{-4} (T-1775) 1775-1872K
H: ρ=6.9348-7.4547×10^{-4} (T-1768) 1768-1873K
I: ρ=6.9359-7.0782×10^{-4}(T-1779) 1779-1874K

Figure 1 The densities of liquid stainless steels A-I with temperature.

or more accurately, on the activities of O and S in the steels.

The temperature dependence of the surface tensions of the liquid stainless steels, dσ/dT is also dependent on the concentrations/activities of O and or S in the liquid steel. It can be seen from Fig. 2a and b that steels A, B, D, E and F show negative temperature coefficients of the surface tension due to their lower O and S concentrations. In contrast, the surface tension of steel C (with higher O and S contents) increases as the temperature increases (positive temperature coefficient).

The effects of Al, Ti, Si, C, etc. on the surface tensions of liquid stainless steels can not be directly discussed from the present experimental results since (1) their concentrations are relatively low and (2) they mainly influence the oxygen activity, and may affect the sulphur activity slightly.

3.3. Effect of S on surface tension

The effect of sulphur content on both the surface tension (σ) and its temperature dependency (dσ/dT) was determined using stainless steels F and G. The results are shown in Figs 3 and 4. The surface tensions of liquid stainless steels decreased markedly with increasing sulphur contents. The temperature dependencies of the surface tension (dσ/dT) of liquid stainless steel F change from negative to positive as the sulphur content of steel F increased from 12 mass ppm to 84 mass ppm. For sample G, the temperature coefficient of surface tension containing 11 mass ppm S is also positive, this may be caused by the relatively high O content (52 ppm) in the sample. From Fig. 4, the "crossover point" (where dσ/d$T = 0$) occurred at sulphur concentration of about 30 mass ppm. This agrees with the results for stainless steels (Type 304 and 316) reported by Mills and Brooks [8] and the calculated values due to McNallan *et al.* [9] for Fe-18Cr-8Ni alloys.

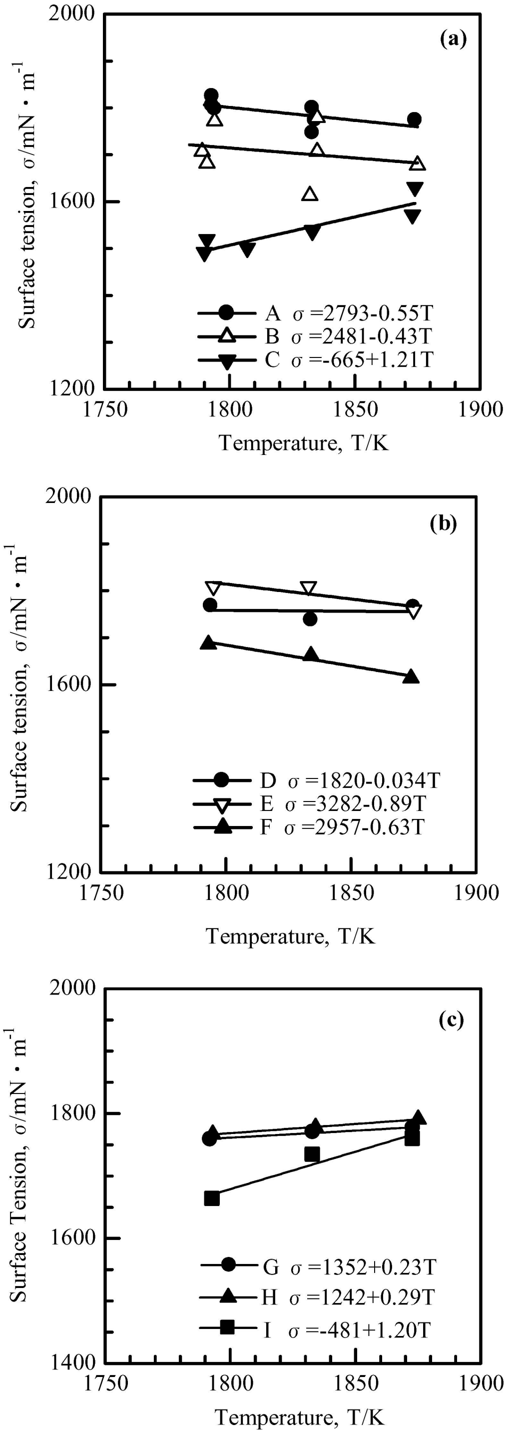


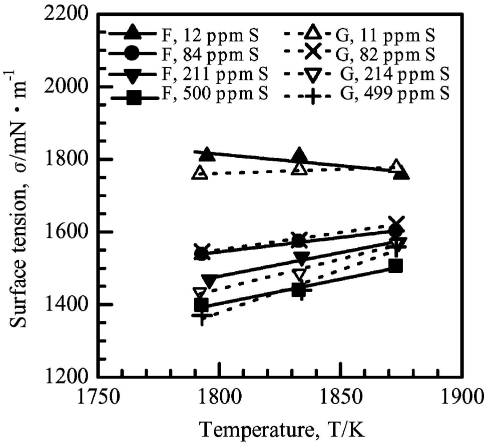
Figure 2 The Surface tensions of liquid stainless steels A-I as a function of temperature.

3.4. Szyszkiowski-type equation

Since Szyszkiowski-type equation [10] has been shown to be a suitable way of representing the reduction of surface tension by surface active components, the behaviour of sulphur adsorption can be described as follows:

$$\sigma = \sigma' - RT\Gamma_S^0 \ln(1 + K_S a_S) \quad (1)$$

where σ and σ' are the surface tensions (mN/m) of liquid stainless steel containing sulphur and zero sulphur, respectively, Γ_S^0 is the saturated surface excess concentration of sulphur for the (Fe-Cr)-S pseudo-binary melt



F, 12 ppm S: σ=2957-0.63T
F, 84 ppm S: σ=105+0.80T
F, 211ppm S: σ=-871+1.31T
F, 500ppm S: σ=-1028+1.35T
G, 11 ppm S: σ=1353+0.23T
G, 82 ppm S: σ=-159+0.95T
G, 214ppm S: σ=-1532+1.65T
G, 499ppm S: σ=-2865+2.36T

Figure 3 The surface tension of liquid stainless steels F and G with sulphur concentrations in the melt.

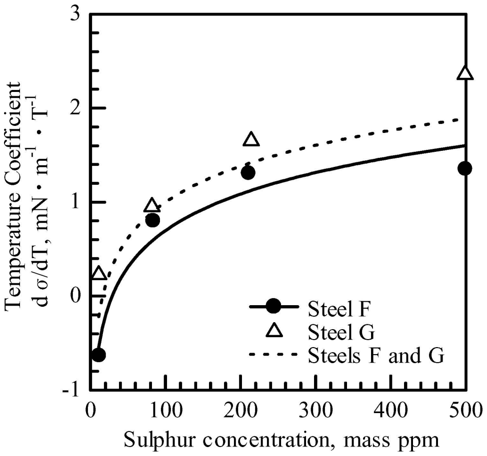


Figure 4 The temperature coefficients of the surface tensions of liquid stainless steels F and G as a function of sulphur concentration.

relative to the Fe-Cr solvent (major component) at the Gibbs dividing surface of $\Gamma_{\text{Fe-Cr}} = 0$, K_S is the adsorption coefficient of sulphur at the surface of liquid stainless steel and a_S is the sulphur activity in the liquid stainless steel, R is gas constant and T is Kelvin temperature (K).

The surface excess concentration of sulphur, Γ_S (mol/m^2), can be determined by calculating the slope of the surface tension to the logarithm of the sulphur activity curve according to the Gibbs adsorption equation.

$$\Gamma_S = -(1/RT) \cdot (\mathrm{d}\sigma/\mathrm{d}\ln a_S)_T \qquad (2)$$

In this work the value of $RT\Gamma_S^0 = 182\,\text{mN}\cdot\text{m}^{-1}$ obtained for liquid Fe-16mass%Cr-S melts [4] was adopted. The surface tension value of liquid stainless steels (sulphur free), σ', 1790 mN·m^{-1} at 1832 K was obtained by extrapolating the experimental data to zero sulphur concentration. These values were inserted into Equation 1. A value of $K_S = 260$ was found by fitting Equation 1 to the experimental data using the least squares method. The variation of surface tension of liquid stainless steel with sulphur activity ($a_S \leqq 0.03$) can thus be expressed by (mN/m):

$$\sigma = 1790 - 182\ln(1 + 260a_S) \quad (\text{mN/m})$$
$$(\text{mass\%O} = 0.0022\text{–}0.0064, \quad \text{mass\%S} \leqq 0.05) \qquad (3)$$

On the other hand, all the samples contain oxygen (0.0022–0.0064 mass%), and then the systems can be considered as (Fe-Cr)-S (0.0008–0.05 mass%)-O (0.0022–0.0064 mass%) alloys. Ogino *et al.* [11] expressed the surface tension of Fe-S-O systems by assuming that the additive property for the effects of O and S on the surface tension is applicable. Therefore, the effect of oxygen in the liquid stainless steels can be corrected as follows:

$$\sigma = \sigma^0 - RT\Gamma_O^0 \ln(1 + K_O a_O) - RT\Gamma_S^0 \ln(1 + K_S a_S) \qquad (4)$$

where σ^0 is the surface tension of liquid stainless steels without oxygen and sulphur (mN/m), Γ_O^0 is the saturated excess surface concentration of oxygen at the Gibbs dividing surface of $\Gamma_{\text{Fe-Cr}} = 0$ (mol/m^2), K_O is the adsorption coefficient of oxygen at the surface of liquid stainless steels.

The surface tensions of liquid stainless steels in O range (0.0022–0.0064 mass%) and S range (0.0008–0.05 mass%) can be derived by Equation 5 by combining the results of Fe-16mass%Cr-O alloys [3] with the present results. The calculated results obtained using Equations 3 and 5 are in good agreement with the experimental surface tension values (Fig. 5).

$$\sigma = 1820 - 304\ln(1 + 383a_O) - 182\ln(1 + 260a_S) \quad (\text{mN/m}) \qquad (5)$$

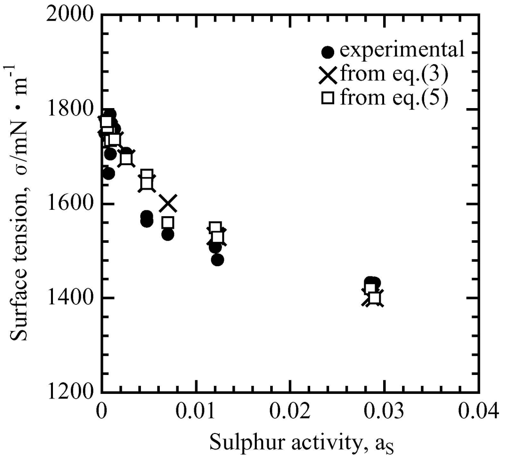


Figure 5 The surface tension of liquid stainless steel as a function of sulphur activity.

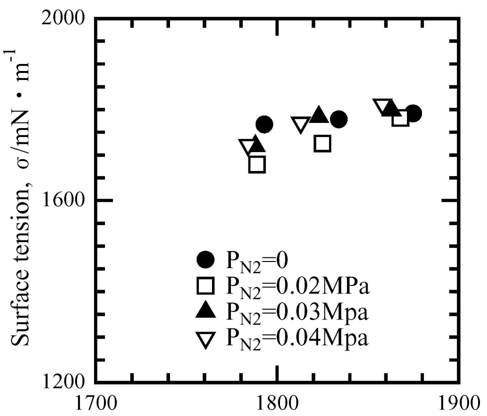


Figure 6 The surface tension of liquid stainless steel H as a function of temperature using different N_2 partial pressure in the atmosphere.

3.5. Effect of nitrogen on surface tension

The effect of N concentration on the surface tension of liquid stainless steel H was carried out by adjusting the nitrogen partial pressure in the atmosphere. The experimental results are shown in Fig. 6. Many investigators have found that nitrogen is mildly surface active in liquid iron [12, 13] and liquid Fe-Cr alloys [14]. In this study the effect of N on the surface tension of liquid stainless steel H was found to be slight. Values of $(\mathrm{d}\sigma/\mathrm{d}T)$ for liquid stainless steel H were found to increase with increasing nitrogen partial pressure.

4. Conclusions

(1) The surface tensions of liquid stainless steels were found to decrease markedly with increasing sulphur concentration in the steels.

(2) The variation of surface tension of liquid stainless steel with (i) sulphur activity and (ii) S and O activities can be described by the following equations: $\sigma = 1790 - 182\ln(1 + 260a_S)$ and $\sigma = 1820 - 304\ln(1 + 383a_O) - 182\ln(1 + 260a_S)$, respectively (mass%O = 0.0022–0.0064, mass%S = 0.0008–0.05)(mN/m).

(3) The temperature coefficient of the surface tension $(\mathrm{d}\sigma/\mathrm{d}T)$ of liquid stainless steel was found to change from negative to positive at a sulphur concentration of about 30 mass ppm in the steel.

(4) Nitrogen was found to have very little effect on the surface tension of liquid stainless steel.

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