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The surface tension of steels

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Over many years NPL has carried out measurements of surface tension of steels using the levitated drop method. Much of this work has been to study variations in weld profile brought about by changes in Marangoni flow patterns in the liquid pool, and many of these data have remained unpublished. 49 ferritic and austenitic steels are compared, and relationships for surface tension, and the coefficient of surface tension against temperature, based on sulphur content of the steel, are presented. Data has been reassessed using the Cummings correction to allow for the effects of the levitation forces.

1. Introduction

Surface tension and Marangoni driven flow can be important in the processing of steel and steel products, but quantifying these effects in the form of process models can be difficult because of the lack of data available in order to validate the predictions. For instance, it is now largely accepted that variations in weld profile, which can occur during the automated TIG welding of steel, are due to differences in the fluid flow pattern in the weldpool [1], which arise from cast to cast variation in the content of surface active trace elements such as sulphur. But these conclusions could only be validated, and therefore accepted by industry, because of physical measurements on commercial steel alloys. Many of these data were supplied by NPL over a number of years, and have remained unpublished. Measurements were carried out using the levitated drop technique [2, 3], which has since been reviewed by Blackburn and Cummings [4], with the result that a correction is now applied to measurements to allow for the effects of the levitation forces. It would therefore seem appropriate to adjust the original data to allow for this correction. The results of measurements on 49 ferritic and austenitic steels are reviewed, and thus provide a basis for the validation of property and process models.

2. Heiple Roper theory

Heiple and Roper suggested that fluid flow in the weldpool was dominated by Marangoni convection at the surface [1]. For a given set of welding conditions, as would be fixed in an automated process, a steel with a negative surface tension-temperature coefficient ($d\gamma/dT$) will have a lower surface tension in the centre of the pool than at the margins. This will produce a radially outward flow, forming a shallow, broad weld profile. Conversely, a steel with a positive $d\gamma/dT$ will have a higher surface tension at the centre, radially inward flow, resulting in heat from the arc being carried to the bottom of the pool, and producing a deeper weld pool. In practice, this meant that if conditions for a full penetration weld were set on a steel with positive $d\gamma/dT$, and a different steel passed through, only partial penetration could be obtained, while if the conditions were set with a negative $d\gamma/dT$, and a different steel was welded, a hole could be formed. Mixing batches of steel could produce asymmetric profiles and weld wander, while slag spots caught in the flow could cause arc rooting and arc wander.

All of these phenomena could be explained in terms of the Marangoni flow on the surface of the weldpool [5].

3. The levitated drop method

Surface tension was measured using the levitated drop method [2, 3], in which a small droplet of metal is levitated in the magnetic field of an RF coil, and the frequency of oscillations of the droplet shape, resulting from its deformation in the field, are measured. The principal advantage of this technique is that the sample is not in contact with any other material, other than the gas atmosphere, so a significant risk of sample contamination is removed. If one considers the effect of oxygen on the surface tension of pure iron, 50 ppm O reducing the value by 30%, and that most substraits/containers used are oxides, then this can be seen as a significant advantage. In addition, very high temperatures can be readily obtained, and no other properties, other than melting point, and a rough value of density, of the material are needed, which is an advantage when studying commercial alloys, where little data of any kind may be available. Surface tension is obtained from the oscillations using the Rayleigh equation [6], which predicts a single oscillation frequency:

$$\gamma = \frac{3}{8}\pi \cdot m \cdot \omega^2 \qquad (1)$$

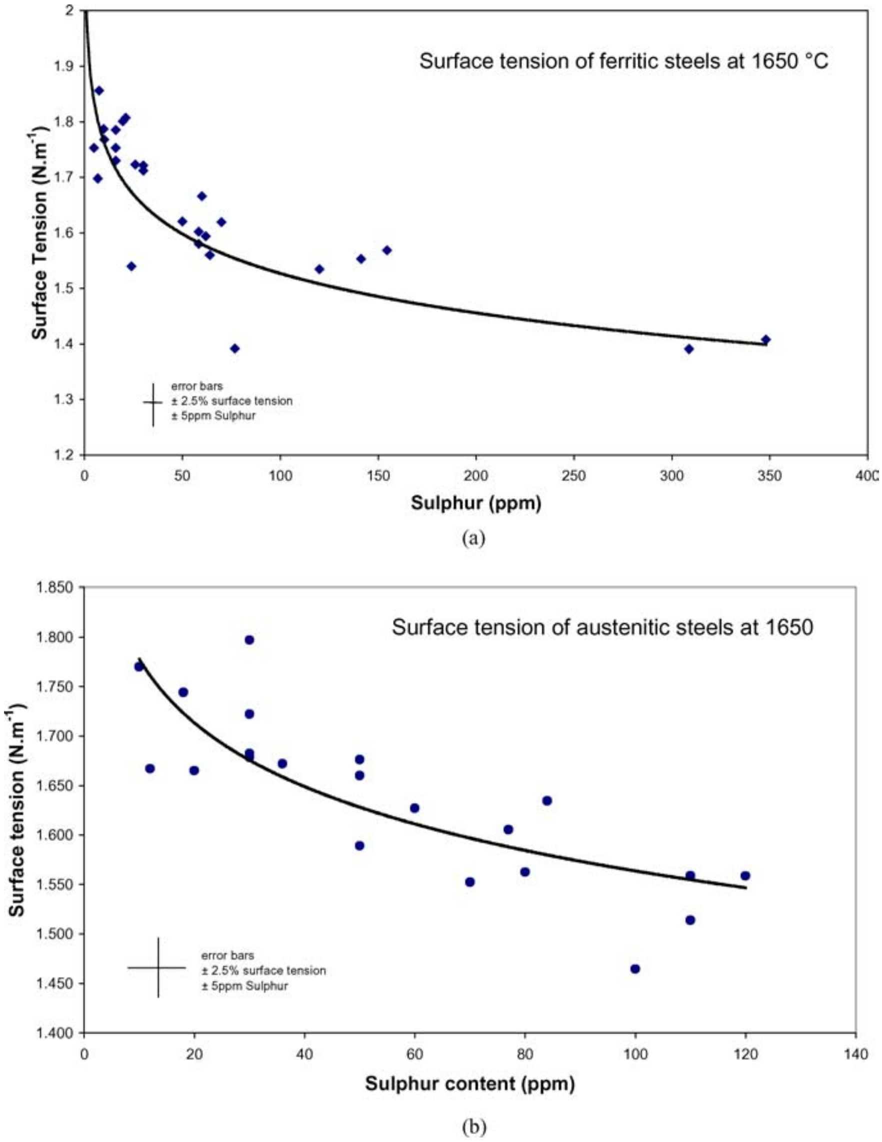

Figure 1 Surface tension of (a) ferritic steels, and (b) austenitic steels, with sulphur content.

where γ is the surface tension, m the mass of the sample, and ω the oscillation frequency. However, in practical measurements ca. 5 oscillation frequencies are found, due gravitational effects on the equilibrium shape of the drop. For much of the work reported in the literature a mean frequency was taken, but work by Cummings and Blackburn [4] has since shown that a correction must be made to the data to obtain the Rayleigh frequency (ω):

$$\omega_R^2 = \frac{1}{5}\sum_{n=1\,\mathrm{to}\,5}\omega_\mathrm{n}^2 - \omega_\mathrm{tr}^2\left(1.9 + 1.2\left[\frac{g}{2r(2\pi\omega_\mathrm{tr})^2}\right]^2\right) \tag{2}$$

where r is the radius of the drop, g acceleration due to gravity, ω_{1-5} the oscillation frequencies, and ω_tr the mean translation frequency. The amount of the correction depends, to a large extent, on the sample size and geometry of the levitation coil, which affects power and thus the translation frequencies. Therefore, if these do not change, then a generalised correction can be made to older results where some data were not recorded. In the work carried out at NPL the coil geometry has not been modified greatly, drop sizes vary between 0.45, and 0.65 g and an x-y translation frequency of ca. 4.5 ± 0.25 Hz is usually found. The apparatus is not sensitive to z (vertical) motion, but if we assume translation in all three planes is the same, the correction for an average sized drop would be in the region of $0.050\ \mathrm{N\cdot m^{-1}}$, and with a spread of frequencies (z being higher), a correction of $0.070\ \mathrm{N\cdot m^{-1}}$ is obtained. A correction of $0.060\ \mathrm{N\cdot m^{-1}}$ has therefore been applied to data for which no other information is available.

In a European Commission funded project [7] measurements on pure copper and pure nickel were carried out by three laboratories using this technique, and two others using sessile drop, and drop weight methods. Agreement between the laboratories was better than 4%, over a wide temperature range, which included the undercooled, and superheated regions. The error in individual measurement laboratories was ±2%. For commercial alloys we observe greater scatter, in part due to uncertainties and variations in composition of individual samples.

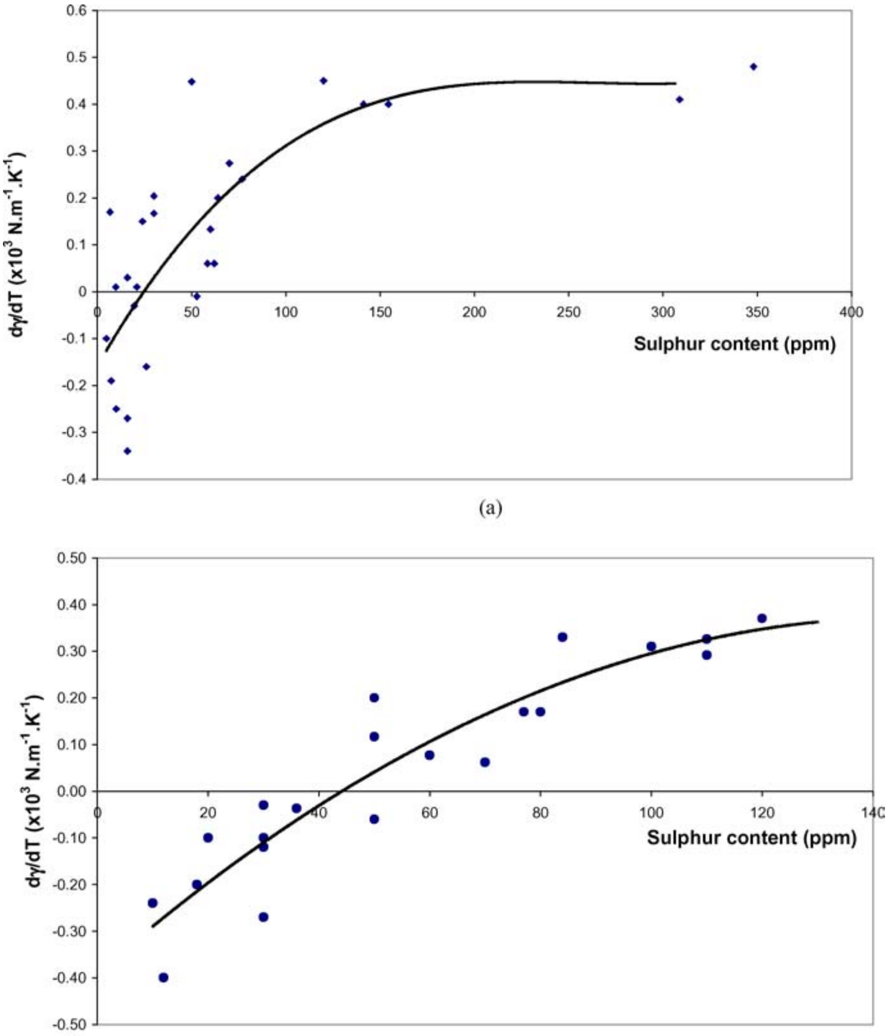

Figure 2 Surface tension coefficient ($d\gamma/dT$) of (a) ferritic steels, and (b) austenitic steels, with sulphur content

4. Results and discussion

The surface tension of pure iron is known to be markedly dependent upon the concentration of surface active elements such as oxygen and sulphur in the metal. In alloys, the surface tension will be dependent upon the concentration of soluble oxygen or sulphur, and not the total quantities, as inclusions have no influence on surface tension. Most steels contain elements such as Al, Si, Mn and Cr, which will reduce the soluble oxygen, so that it is unlikely to be above 10 ppm. Unless there are excessive quantities of oxygen it can therefore be assumed to have no effect on the surface tension. These elements, however, have little effect on the level of soluble sulphur, so in case of the austenitic steels, the total measured sulphur is approximately equal to the total soluble sulphur, and so can be related to the surface tension can therefore be related to total sulphur levels (Figs 1 and 2). The compositions, and fitted data for the ranges of steels covered in this work are given in Tables I and II. The surface tension for austenitic steels containing up to 130 ppm S, at 1650°C can be related to the total sulphur content (ppm), denoted S, thus:

$$\gamma_{1650}(\mathrm{N}\cdot\mathrm{m}^{-1} = -9.296E\text{-}02\ln(S) + 1.992 \qquad (3)$$

and the coefficient of surface tension to temperature ($d\gamma/dT$) can be derived from:

$$d\gamma/dT(\times 10^{-3}\ \mathrm{N}\cdot\mathrm{m}^{-1} = -3.545E - -05\ (S)^2 + 0.0104(S) - 0.3899 \qquad (4)$$

Ferritic steels are more likely to contain Ca, which acts as a getter for sulphur, thus reducing the soluble sulphur S. We have estimated $\underline{S}$ as the total S_{total} (ppm) minus 0.8 Ca (ppm). The surface tension for ferritic steels containing up to 300 ppm $\underline{S}$, at 1650°C, can be related to the soluble sulphur content (ppm):

$$\gamma_{1650}\ (\mathrm{N}\cdot\mathrm{m}^{-1}) = -1.025E - -01\ \ \ln(S) + 1/999 \qquad (5)$$

The coefficient of surface tension to temperature ($d\gamma/dT$) is more difficult to fit due to the large scatter in the data at low sulphur levels (Fig. 2a), but a relation has been derived of:

$$d\gamma/dT(\times 10^{-3}\ \mathrm{N}\cdot\mathrm{m}^{-1} = 3.45E - 08(S)^3 - 2.728E - 05(S)2 + 7.085E - -03(S) - 0.1592 \qquad (6)$$

TABLE I Ferritic steels: composition and results of measurements

Ferritic	composition (wt%)											Composition (ppm)						T range°C		Measured values linear fit		$\gamma_{(calc)}$ N · m^{-1}
Steel	C	Si	Mn	Cr	Mo	Ni	V	Al	Ti	Nb	P	S	$S_{effective}$	Ca	$O_{(total)}$	N	min	max	Intercept N · m^{-1}	Slope ($\times 10^3$ N · m^{-1} · K^{-1})	@1650 °C
GEL	0.08	0.32	0.67		0.47			0.08	0.05		0.011	30	6.8	29	21	127	1700	1915	1.41_6	0.17	1.69_7
GEB			0.71									80	58.4	27			1545	1806	1.47_4	0.06	1.57_3
GEK	0.11	0.25	0.67					0.06	0.05		0.015	150	67.6	3	33	109	1535	1980	1.230	0.2	1.560
GET			0.92									80	24	70	63		1535	1840	1.35_2	0.15	1.600
P6		1.16	1.16		0.03			0.029			0.012	200	197.2	3.5	45	95	1600	1800	0.890	0.4	1.550
19	0.08	0.27	1.44	0.04	0.01	0.03	0.06	0.023	0.01	0.036	0.018	25	7.4	22		90	1595	1752	2.150	−0.19	1.83_7
28	0.09	0.26	1.51	0.05	0.04	0.05	0.06	0.019	0.01	0.039	0.018	30	19.6	13	80		1563	1704	1.83_9	−0.03	1.790
60	0.13	0.34	1.31	0.02		0.13		0.041	0.02	0.021	0.026	25	9.8	19		28	1539	1888	1.76_1	0.01	1.77_8
61	0.13	0.33	1.33	0.045	0	0.13		0.045	0.02	0.018	0.017	25	21	5		39	1592	1759	1.78_1	0.01	1.79_8
98J EN19	0.4	0.32	1.61	0.2	0.27	0.17		0.03			0.016	320	308.8	14	17		1559	1814	0.72_5	0.41	1.40_2
99J EN18	0.38	0.26	0.49	1	0.24	1.35		0.038			0.01	360	348	15	25		1568	1821	0.630	0.48	1.42_2
100J CMn	0.11	0.27	1.37	0.08	0.015	0.04		0.041			0.02	20	4.8	19	19		1570	1833	1.90_3	−0.1	1.73_8
DWI	0.041	<0.01	0.23	0.034	<.005	0.022	<0.05	0.053	0.004		0.006	120	120				1591	1736	0.80_5	0.45	1.54_8
K4512	0.016	0.43	0.43	11.5	0.01	0.14	0.09	0.003	0.3		0.019	20	16	5		140	1544	1772	2.31_9	−0.34	1.75_8
K4003	0.017	0.4	1.23	11.2	0.01	0.47	0.07	0.008	<0.01		0.02	20	16	5		130	1523	1757	1.67_2	0.03	1.72_2
K4016	0.067	0.37	0.89	16.1	0.07	0.29	0.07	0.003	<0.01		0.029	30	26	5		480	1544	1777	1.96_9	−0.16	1.70_5
K4000	0.036	0.34	0.36	13	0.08	0.46	0.06	0.004	<0.01		0.032	20	16	5		190	1601	1831	2.17_5	−0.27	1.730
IC 55												10	10				1582	1807	2.15_8	−0.25	1.74_6
WI IC79	0.11	0.25	0.49	2.16	1	0.14	0.01	0.002	0.006	0.005	0.012	50	50		33	139	1580	1869	0.89_4	0.448	1.63_3
WI IC80	0.11	0.18	0.5	2.15	1	0.14	0.01	0.009	0.006	0.005	0.012	30	30		19	152	1561	1928	1.38_5	0.204	1.72_2
WI IC83	0.09	0.21	0.48	2.21	1	0.05	0.01	0.019	0.006	0.004	0.004	30	30		30	147	1549	1855	1.43_5	0.167	1.71_1
WI IC215	0.14	0.25	0.48	2.19	1.02	0.15	0.01	0.003	0.006	0.005	0.012	70	70		85	130	1530	1901	1.17_1	0.274	1.62_3
WI IC255	0.13	0.23	0.52	2.24	0.97	0.06	0.01	0.005	0.006	0.004	0.01	60	60				1500	1909	1.44_3	0.133	1.66_2
GC			0.96									160	154.4	7			1550	1790	1.23_9	0.2	1.56_9
G1327												80	76.8	4			1620	1840	0.99_8	0.24	1.39_4
G160795	0.09	0.27	1.17		0.09			0.02	0.005			70	62	10	44	102	1690	1870	1.48_8	0.06	1.58_7
G160700			1.28									150	141.2	11	40		1630	1780	0.90_3	0.4	1.56_3
G160698			1.21									60	52.8	9			1660	1815	1.10_4	−0.01	1.08_8

TABLE II Austenitic steels: composition and results of measurements

Austenitic	composition (wt%)									Composition (ppm)				T range°C		Measured values linear fit		$\gamma_{(\mathrm{calc})}$ N · m^{-1}
Steel	C	Si	Cr	Ni	Mo	Mn	Ti	Al	P	S	Ca	$O_{(\mathrm{total})}$	N	min	max	Intercept N · m^{-1}	Slope $(\times 10^3\ \mathrm{N}\, cdot\ \mathrm{m}^{-1}.\mathrm{K}^{-1})$	@1650 °C
V304 LS	0.06	0.57	18.1	8.4		1.06	<0.01	<0.01	0.032	30	1			1576	1805	1.72_8	−0.03	1.67_9
V304HS	0.06	0.41	18.3	8.4		0.86	<0.01	<0.01	0.024	80	1			1579	1781	1.28_2	0.17	1.56_3
V316LS	0.05	0.54	17.6	11.7	2.1	0.84	<0.02	<0.02		10	20			1583	1810	2.16_6	−0.24	1.770
V316HS	0.06	0.8	17.5	11.8	2.2	0.81	<0.01	<0.01	0.028	50	5			1572	1801	1.25_9	0.20	1.58_9
KR1	0.019	0.61	18.2	10.2	0.18	1.07	0.19	0.003	0.023	20		60	260	1564	1769	1.830	−0.10	1.66_5
KR2	0.036	0.62	18.3	9.1	0.16	1.07	0.2	0.003	0.025	30			370	1534	1751	2.12_8	−0.27	1.68_3
KR4	0.036	0.59	18.4	9.3	0.22	1.13	0.15	0.003	0.024	50			280	1586	1780	1.77_5	−0.06	1.67_6
KRA 304	0.02	0.4	18.3	10.2		1.75			0.033	100				1550	1890	0.95_3	0.31	1.46_5
KRB 304	0.024	0.42	18.31	10.62		1.62			0.023	30				1600	1810	1.99_5	−0.12	1.79_7
A304LS	0.04	0.57	18.4	9.1	0.69	1.6			0.032	36						1.73_3	−0.04	1.67_2
A304HS	0.04	0.49	18.6	8.3	0.09	1.42			0.024	84						1.090	0.33	1.63_5
A316LS	0.04	0.54	16.3	10.2	2.53	1.54			0.031	12				1619	1823	2.32_7	−0.40	1.66_7
A316HS	0.07	0.36	15.7	9.55	2.85	1.78			0.04	120						0.94_8	0.37	1.55_9
Mat 18 304										18				1572	1796	2.07_4	−0.20	1.74_4
Mat 30 304										30				1560	1823	1.88_7	−0.10	1.72_2
Mat 77 304										77				1605	1848	1.32_5	0.17	1.60_6
WI 3CL	0.036	0.46	16.8	10.8	2.32	1.59	<0.01	0.12	0.027	60				1535	1877	1.500	0.08	1.62_7
IC60	0.064	0.37	18.1	8.7	0.25	1.43	<0.01	0.007	0.02	110				1550	1860	1.02_1	0.33	1.55_9
IC77	0.016	0.31	16.5	11.4	2.16	1.55	<.01	0.008	0.029	110				1585	1857	1.03_2	0.29	1.51_4
IC155	0.043	0.21	16.8	11.7	2.53	1.71	<0.01	0.005	0.028	50						1.46_7	0.12	1.660
IC158	0.043	0.5	16.8	11.3	2.46	1.61	0.018	0.009	0.03	70						1.450	0.06	1.55_2

$d\gamma/dT$ is very sensitive to scatter in individual measurement points in small sample populations, and the addition of calcium to the ferritic steels increases scatter in the measurements: Calcium can form a solid oxide on the surface of the measurement sample; this oxide will become soluble at temperatures above ca. 1650°C, but below that temperature it will form a raft or skin which can dampen the oscillations, the effect of which is to lower the measured surface tension value, and therefore give a more positive $d\gamma/dT$. In the industrial process, these skins may reduce the thermocapillary flow at the surface, form slag spots, and are known to increase porosity in welds [5]. The majority of values fall within ±5% of the equations, which, given the accuracy of the measurement (±2.5%) plus limits of ±5 ppm for the determination of sulphur, and the effects of segregation producing varying quantities sample to sample, we feel is acceptable.

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