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Dynamic surface tension measurements on a molten metal-oxygen system: The behaviour of the temperature coefficient of the surface tension of molten tin

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In order to point out the interactions of oxygen with a liquid metal and to study the influence of the actual operating conditions, dynamic surface tension measurements of a liquid test metal (tin), were performed under vacuum conditions by using the large drop method. This classical method has been improved by applying a new experimental procedure which allowed to obtain reliable surface tension measurements at high temperature as a function of time and varying the oxygen content. Further, complementary information on molten metal-oxygen interactions can be obtained. In particular, in this work, the trend of the surface tension temperature coefficient has been analysed as a function of different operative parameters, highlighting some crucial points such as the dependence of the temperature coefficient on the accuracy of the surface tension experimental data and the influence of the dissolved oxygen. It was demonstrated that the surface tension and its temperature coefficient do not depend on the quantity of dissolved oxygen when this is inside a certain range of values.

1. Introduction

The agreement between the existing experimental data on temperature coefficient of surface tension of metals is quite poor, notwithstanding its great influence on all aspects of thermocapillary phenomena [1], For example, the temperature coefficient of tin, which is the object of this study varies from a maximum value of −0.0476 to a minimum one of −0.222 (ignoring one source whose result was actually −0.48) [2]. The data reported in the literature suffer from experimental problems that are essentially due to the type of the measuring apparatus, the degree of measurement accuracy, the use of incorrect density data and, most often, the presence of impurities in the metal. This aspect must be seriously taken into consideration, particularly when using the sessile (large) drop technique, when the possibility that the liquid metal is contaminated is very high. Even in the case when an inert solid support is used, it still remains very difficult to perform experiments with an inert atmosphere.

However many works have been published in which the surface tension values have been determined in controlled atmospheres particularly poor in oxygen. Sometimes these values have been expressed as a function of the oxygen concentration of the metal by supposing equilibrium conditions and then using Sievert's Law [3]. It is known that such an approach is incorrect as the experimental test conditions are far from the thermodynamic equilibrium operating in a vacuum or at atmospheric pressure. Wagner's concept of the steady state for systems operating both at atmospheric pressure [4] and in the Knudsen regime [5, 6] has been improved [7, 8]. Indeed, the description of drop behaviour, under constant boundary conditions, includes the thermodynamic equilibrium at the gas-liquid interface; the stationary state for the diffusion and reaction phenomena through the gaseous layer surrounding the drop and the pseudo-stationary state for the liquid phase [9]. From these studies of material fluxes carried out for molten metal-atmosphere interfaces it emerges that a metal, under steady state conditions, is less subject to the chemical attack of oxygen than under thermodynamic equilibrium conditions. This fact has also been confirmed by correlated experimental data on surface tension as a function of oxygen partial pressure [10–14].

The trend of the surface tension of molten tin, chosen as test metal, as a function of the temperature and imposed oxygen partial pressure has been already studied and the results reported in our previous work [15], together with a detailed description of the experimental procedures adopted. In particular, it has been

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determined that the molten metal (tin) is in 'clean surface' conditions when the trend of the surface tension is linear as a function of the temperature and invariable with regard to the externally imposed oxygen pressure. For the sake of clarity it is reminded that the aim of this work is not the determination of the reference surface tension data of pure metals (tin in this case), and the term "clean surface" refers to a liquid metal surface free of any oxide films. The principal aim of this work, based on our previous one [15], is to examine the dependence of the temperature coefficient on each of the principal operating parameters, compared with data available in the literature and critically evaluated.

2. Experimental results

2.1. Dependence of the temperature coefficient on the rate of the temperature variation

The extensive experimental data obtained under the Knudsen regime (total pressure less than 1 Pa) as reported in [15] show that in "clean surface" conditions, the surface tension trend is linear with the temperature and invariable with respect to the rate of the variation of the latter (1 K/min and 5 K/min) [16]. The results of tests performed at $PO_2 = 10^{-5}$ Pa [15] and by subjecting the sample to a specific thermal cycle (−1 K/min from $T_{in} = 915$ K to $T_{fin} = 590$ K; one hour at constant temperature of 590 K, then at +1 K/min from $T_{in} = 590$ K to $T_{fin} = 915$ K) confirm this feature. The sequence was repeated at the rate of 5 K/min. The surface tension data referred to the four time periods show a remarkable linear trend in each segment ($R_2 > 0.99$). The temperature coefficient has an absolute value much lower than that of other sources [2] and its variations are insignificant.

2.2. Dependence of the temperature coefficient on externally imposed PO_2

When the externally imposed PO_2 was increased, the system evolved in the direction of surface oxidation with a consequent diminution of the surface tension value, in agreement with the prediction of a previously developed theoretical model [5] and confirmed by experimental data already reported in [15].

As the PO_2 increases, the temperature domain in which the surface tension trend is linear [16] becomes narrower. However, in the linear field the temperature coefficient is univocal. In fact, when the PO_2 is increased the temperature of inversion of the sign of the temperature coefficient reaches ever-higher temperatures, but the part of the data that precedes the inversion does not seem to be affected by the variation of the imposed oxygen partial pressure. This can be seen in Fig. 1 where surface tension data are reported as a function of temperature for four different tests conducted at different PO_2 and decreasing temperature (−5 K/min) from $T_{in} = 910$ K to $T_{fin} = 600$ K. In the linear part the surface tension data have an uncertainty of 1% and the temperature coefficient does not change with the PO_2, within the limits of a low experimental scatter. Moreover, when all the tests characterised by a temperature coefficient value varying from about −0.074 to −0.058 are taken into consideration, it is impossible to discern any trend that connects the temperature coefficient value with the value of the PO_2.

2.3. Dependence of the temperature coefficient on the oxygen concentration dissolved in the molten metal

When the tests performed under operative surface deoxidation conditions (see Ref. [15]) are considered, other information can be obtained. In these tests the samples that had relatively large amounts of dissolved oxygen, and were tested with the thermal cycles until the surface tension inversion point disappeared, presented a surface tension trend as a function of the temperature which, in its linear part, coincided for all the cycles. As an example, in Fig. 2 the data of the initial part of a test performed at $PO_2 = 10^{-5}$ Pa are reported. During this test the surface tension inversion points (indicated in the figure by *) occurred at ever-lower temperatures until disappearing after 70 hours [15]. The test was carried out by subjecting the sample to a series of identical thermal cycles consisting of a period at constant temperature of 940 K, a period at decreasing temperature

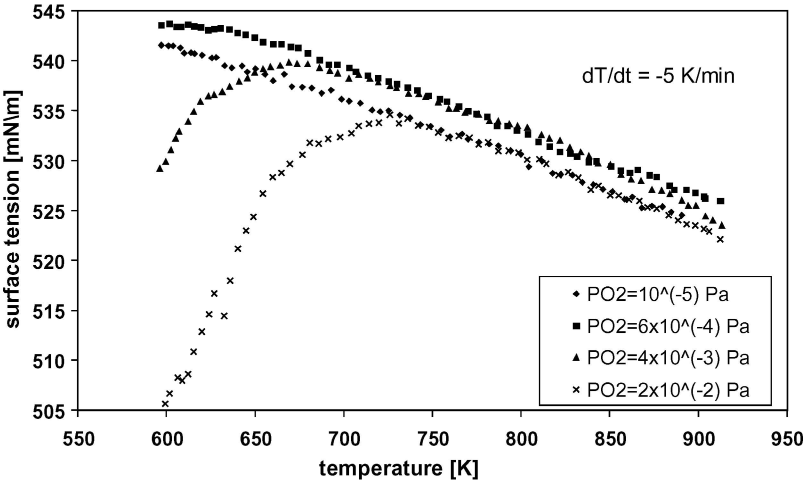

Figure 1 Surface tension of tin versus temperature at varying PO_2; $dT/dt = 5$ K/min.

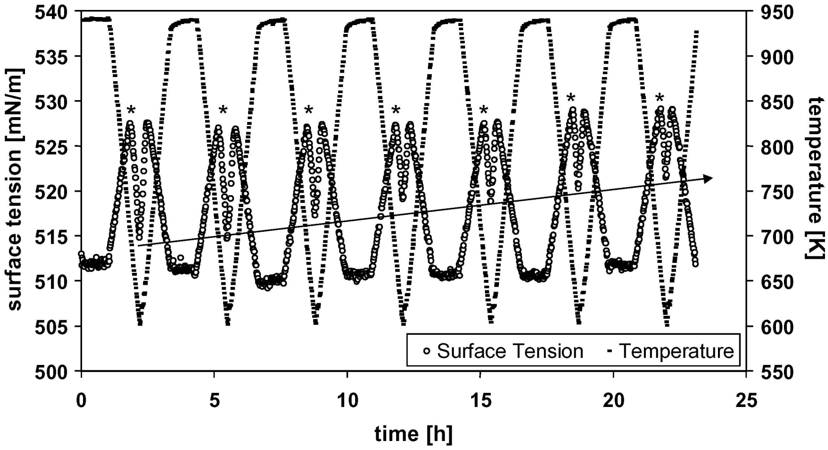

Figure 2 Surface tension of tin and temperature versus time when subjecting the sample to a series of identical thermal cycles. Inversion points are indicated by $*(PO_2 = 10^{-5}$ Pa).

(-5 K/min) from $T_{in} = 940$ K to $T_{fin} = 600$ K, and a period at increasing temperature ($+5$ K/min) from $T_{in} = 600$ K to $T_{fin} = 940$ K.

The fundamental point is that the entire test was carried out in surface deoxidation conditions, for which reason the trend reported in the figure is not correlated to the value of PO_2 inside the test chamber, but is linked to the initial concentration of the dissolved oxygen in the metal sample. The inversion point marks a concentration threshold of dissolved oxygen in the drop above which oxygen manifests its tensioactive character in relation to tin. This threshold concentration should correspond to the saturation level of oxygen in the metal, and the point at which it begins to form an oxide on the metal surface. When the temperature is reduced, the solubility of oxygen is also reduced [17] until it reaches its saturation concentration on the surface and in the bulk. In fact, when lowering the temperature, if the drop is "clean", surface tension increases at first, according to the behaviour of pure liquid, then as saturation is approached [9], the oxygen content in the liquid surface increases and the surface tension begins to decrease. The maximum surface tension for a decrease in temperature or the minimum surface tension when temperature increases corresponds to incoming oxidation points.

As the system is in surface deoxidation conditions, the oxygen level inside the sample falls over time and, in the test considered, after 70 hours its concentration is such that even at the minimum test temperature (600 K) it is not sufficient to saturate the drop and form an oxide film. The trend further shows that the liquid metal drop with a relatively high oxygen content does not immediately achieve equilibrium with the surrounding atmosphere: the exchange of mass occurring at the interface brings the metal to steady state conditions with its surroundings only after many hours. This behaviour is confirmed by studying in more detail the dependence of the temperature coefficient on the oxygen concentration dissolved in the metal. For this reason a selection of experimental data of surface tension vs temperature is given in Fig. 3. The series are identified according to their temporal sequence, (the trend over time is also presented), and differ only with respect to the moment at which the inversion in the sign of the temperature coefficient occurred. In the linear part that characterises the trends before the inversion point, all the tests are very similar: independent of their timing within the 70 hours of the tests and independent of whether the temperature was increasing or decreasing. The experimental findings are very significant: (a) the surface tension data do not vary by more than 2 mN/m in the linear section;

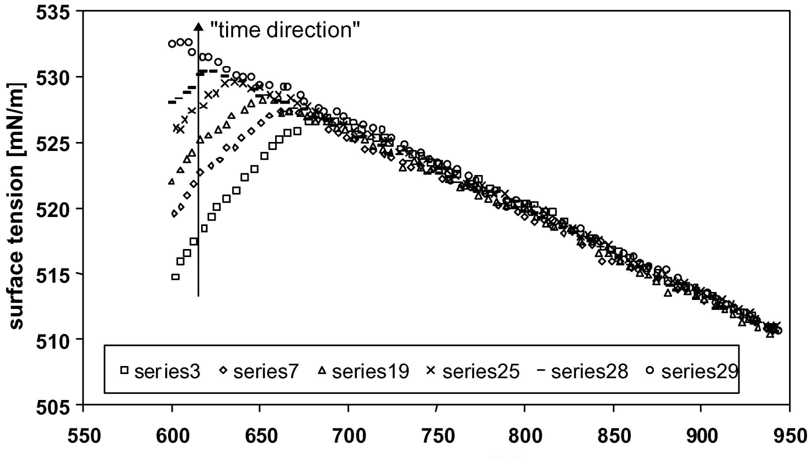

Figure 3 Surface tension of tin as a function of temperature from a selection of decreasing temperature segments of the test reported in Fig. 2 (exp.time = 70 h).

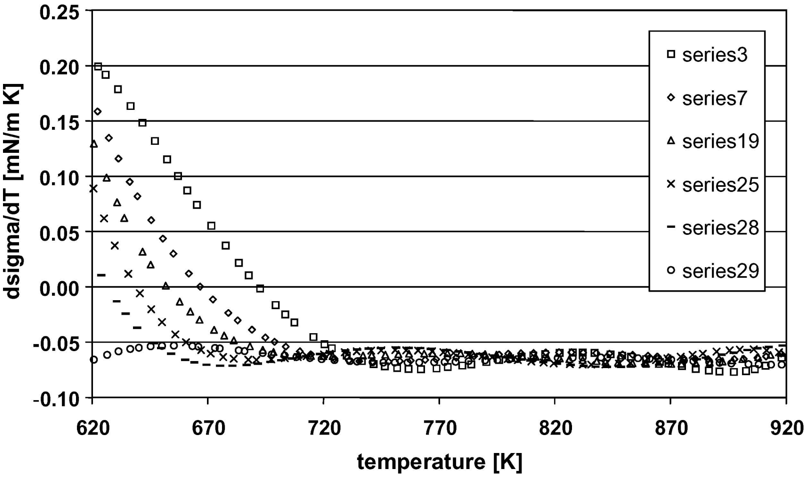

Figure 4 Temperature coefficient of surface tension data reported in Fig. 3.

(b) the temperature coefficient of the surface tension of tin is independent of dissolved oxygen concentration for a finite range of this concentration. In Fig. 4 the temperature coefficient is reported as a function of the temperature for the same series of measurements reported in Fig. 3. That coefficient was obtained by fitting the experimental data with a polynomial of the sixth degree. The use of a function of the sixth degree was an arbitrary choice that, however, allowed us to obtain a very good approximation of the experimental points (>99.5%). From the functions obtained in this way it was possible to determine the temperature coefficient, necessarily amplifying the error of the data. The procedure should be more accurate than the linearisation of the experimental data in the part concerning the "clean" drop, a common and convenient practice when only a few experimental data are available. It can be seen that before the inversion the temperature coefficient at each point calculated, was confined to a range that goes from −0.075 to −0.055 (mN/mK); then, at low temperature, it tends to rise for drops with a high oxygen content up to values of +0.25 (mN/m K). The fitting procedure loses its accuracy at the extremes of the temperature range: the temperature coefficient values are reported for 620 K $< T <$ 920 K.

3. Discussion and conclusions

A comparison of the temperature coefficient values for tin in the literature shows that they vary greatly [2]. It could be that the lower absolute values are due to contamination by oxygen or other tensioactive species. Bearing in mind that at constant oxygen partial pressure the theory [5] foresees that oxygen is more readily available to the liquid surface at relatively low temperatures than at relatively high ones, it can therefore be assumed that the surface tension data obtained at high temperatures are more 'reliable' than data obtained at lower ones. The latter are affected by the tensioactive effect of oxygen and show lower values than what expected for pure metal. Similarly, they also show lower absolute values for the temperature coefficient. According to these considerations, Passerone *et al.* [12]. having experimentally obtained surface tension data for tin in the temperature range 505–1000 K, determined the value of the temperature coefficient using only the data at the higher temperatures (>770 K).

In this work we have underlined that the surface tension value (and consequently also the temperature coefficient value) does not depend on the quantity of oxygen dissolved up a threshold concentration. The fact that surface tension values higher than the ones reported here, are often found in the literature, could possibly be explained by the following:

1. The oxygen concentration range inside which the surface tension of tin does not vary has a lower threshold.
2. Extrapolating the temperature coefficient obtained from high-temperature data to low temperatures can provide wrong results.
3. The temperature coefficient is extremely sensitive to: (a) the scatter in the surface tension values; (b) the number of the surface tension experimental points in a certain temperature range.
4. The presence of other chemical species can also influence the surface tension data.

Considering the first point, all the tests conducted in the temperature range from about 600 to 950 K, where the surface tension trend is clearly linear with the temperature, the temperature coefficient is between −0.074 and −0.058 (mN/mK). For practical reasons we have defined a drop that has constant $d\gamma/dT$, with a typical value between −0.074 and −0.058, as having a 'clean surface'. But the literature presents values up to −0.13 for the tin temperature coefficient. It must therefore be concluded that all the tests in [15] have been conducted on drops containing a certain quantity of dissolved oxygen. For this reason, the term 'clean surface' was used to define a surface free of tin oxide but not free of adsorbed oxygen . The lower value of the temperature coefficient can be connected to the use of purer metal samples than those used in this work. For example, Passerone *et al.* [12] report different temperature coefficients for tin under different atmospheres: authors calculated a value of −0.16 in vacuum; a value of −0.074 in a test chamber at atmospheric pressure fed with helium +5% hydrogen; a value of −0.13 in an atmosphere of helium and at a 'very low oxygen partial pressure', values that have been proposed as reference data. The results of Ricci *et al.* [18] are consistent with those obtained in this study: acquiring surface tension data in continuum, in high vacuum, varying the temperature by 5 K/min and operating with $PO_2 = 10^{-3}$ Pa or with $PO_2 = 10^{-15}$ Pa, temperature coefficient values that range from -0.076 to -0.067 were obtained.

Because PO_2 values below 10^{-7} Pa were not used for any of the tests performed, a certain level of oxygen contamination of the sample has to be reasonably supposed. Thus, the reason why the surface tension coefficient obtained here probably differs from its lower value available in the literature is the presence of oxygen. However on the basis of Gibbs' equation it remains quite difficult to explain how a liquid metal whose surface adsorbs oxygen has a linear surface tension trend as a function of temperature, as is theoretically predicted for a pure metal.

Independently of the degree of purity of the metal the main result obtained here is the invariance of the value of the surface tension temperature coefficient for liquid tin with respect to the quantity of dissolved oxygen when the latter is inside a finite range.

So, as conclusions, it is possible to remark that:

– the surface tension of the liquid and its temperature coefficient are of particular importance as they can influence all aspects of thermocapillary phenomena and the findings reported in the literature are often at variance.

– the temperature coefficient of the surface tension is extremely sensitive to a number of hardly controllable parameters, and strongly dependent on the precision of the surface tension data;

– in a liquid metal, a definite range of dissolved oxygen concentrations exists, where the liquid surface tension and its temperature coefficient are independent of oxygen content.

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