# SURFACE PROPERTIES OF THE Pb-O-Bi SYSTEM

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## ABSTRACT

*The phenomena affecting the interactions between liquid metals and substrates vary for different liquid metals and their relevance depends on the characteristics of the structural material and on the operating conditions of the system. Corrosion and degradation of the mechanical properties of the structural materials in Heavy Liquid Metals are a key issue to demonstrate the technical feasibility of a sub-critical system using Pb-Bi, both as spallation target and coolant of an Acceleration Driven System (ADS). The knowledge of the surface properties of liquid Pb, Bi and Pb-Bi eutectic alloy (LBE) is the first step to investigate the interactions between steel components (as Fe, Cr, Mo, Ni) and the melts at the operating temperature in order to evaluate their effects and their influence on the efficiency of the system.*

*A prediction of surface properties (surface tension and surface segregation) of liquid Pb-Bi alloys as well as of some alloy compositions in the presence of oxygen is done. The models combines Gibbs's and Butler's equations having as the input data the Gibbs free energy data, surface tension reference data of pure components, oxygen solubility data, structural data (coordination number, molar volume) and temperature. The results obtained were compared with our own experimental data and with those reported in the literature.*

## INTRODUCTION

The renewed interest for Heavy Liquid Metals, essentially Lead and LBE, is strongly correlated with the great deal of interest displayed in recent years, worldwide, in ADS to transmute radioactive wastes in a possibly cleaner and safer way than at present [1]. The use of these melts for ADS requires an assessment of their thermodynamic, thermophysical, mechanical and nuclear properties in order to achieve compatibility with structural materials, both austenitic steels and ferritic / martensitic steels. In the last couple of decade a lot of work has been done to complete the knowledge of thermodynamic and thermophysical properties of the Pb-Bi liquid phase [2, 3, 4, 5, 6, 7, 8, 9, 10]. Among these results, many of them were obtained from studies dedicated to the LBE [3, 4, 6, 7, 8, 9, 10]. On the other side, concerning the surface properties of molten LBE, there are only a few papers [6, 7], while nobody reported the influence of oxygen on its surface tension. The effects of surface-active species on the surface tension of liquid metals and alloys are important in numerous industrial applications as well as for understanding the wetting behaviour of solid substrates by melts. A clear picture of wetting phenomena in such systems allows the predictions of the interface reactions when a liquid is put into contact with a solid phase [11, 12]. Accordingly, the knowledge of wetting characteristics of LBE in contact with a steel substrate is a prerequisite that is necessary for a systematic study of corrosion. The present authors reported their results on the wetting behaviour of the LBE alloy on the AISI 316L substrate, investigated under the *oxygen free* conditions in the temperature range 623-773 K [13]. Until now, there is a complete lack of the corresponding literature data on its wetting behaviour under an atmosphere with different oxygen contents.

The purpose of this study is to analyse the effect of oxygen on the surface tension of liquid Pb, Bi and LBE by using Tanaka's model [14]. This model combines the physical property data included in Butler's equation with the oxygen solubility data and it gives the same results as Belton's adsorption Equation [15]. In the case of the LBE alloys, the calculated results will be substantiated with our preliminary experimental data. The large drop method was selected to carry out the experiments in a wide range of oxygen partial pressures varying from $10^{-31}$ to 1 Pa and at temperatures ranging between 623 and 773 K.

## METHODOLOGY

### Experimental

Surface tension measurements were performed on the Bi-44.1at%Pb (LBE) by the large drop method [16]. The alloy specimens were prepared by mixing high purity bismuth and lead (99.9999% Marz-grade) for each nominal composition and pre-melted under a vacuum of $10^{-4}$ Pa at 723 K. The final composition was controlled by the EDS analysis. The experimental apparatus used for surface tension measurements has already been described in [17]. Before the test, the chamber was heated and degassed under a vacuum, and then the ArN60, Ar-5%$H_2$ and Ar-20%$O_2$ were opportunely mixed in a pre-chamber to obtained the working $PO_2$ measured by a solid state electrode (POAS-Setnag®). During the surface tension measurements, the sample of about 3 g was placed in a non-oriented monocrystalline alumina crucible (r = 5.5 mm) especially designed to avoid any chemical contamination and to maintain the axial symmetry of the drop [18]. The crucible with the sample was laid on an alumina holder sliding in the experimental apparatus. When the operative conditions (temperature, oxygen partial pressure) were reached, the sample was introduced into the centre of the furnace by a pushrod magnetic manipulator. The surface tension measurements were performed under static conditions by decreasing the temperature step by step under a fixed oxygen partial pressure ranging in

$10^{-12}$ Pa ≤ $PO_2$ ≤ 1 Pa. At each temperature (773, 723, 673, 623 K), measured by a Pt-Pt/Rh thermocouple, placed near the sample, the drop was allowed to equilibrate for a time of about 30 minutes. An automatic acquisition procedure (A.S.T.R.A.View) [19] was used giving the surface tension data in real time with an accuracy of ± 0.1%. The precision of measurements is improved by a high quality optical system with a CCD camera; in particular, the magnification factor is evaluated for each image utilised for the surface tension measurements.

The reported surface tension values represent the average of a large number of measurements. Each measured value shows a deviation of about ± 2 mN/m around the reported mean value. The density, as a function of temperature, was taken from the literature data [20].

## Modelling of Surface Tension of Liquid Metal – Oxygen System

It is well known that the surface tension of metallic melts is strongly affected by the degree of cleanliness of surface which depends on surrounding atmosphere and in particular on its oxygen content. The presence of highly reactive trace impurities, such as oxygen or sulphur, in the surrounding atmosphere affects to a great extent the surface tension of molten metals. An overview of surface tension data on pure liquid metals reported by Keene indicates an accuracy of about ± 5% and ± 50% in the case of surface tension experimental data and the temperature coefficients, respectively [21]. However, it is also important to underline from the experimental point of view that the surface tension values of pure metals, even if determined under strongly controlled atmosphere particularly poor in oxygen, so called *oxygen free* conditions, are never *free* of at least, weak tensioactive effects, caused by a small quantity of adsorbed oxygen [18].

Tanaka *et al* developed the models to calculate the surface tension of molten alloys, salt and oxide mixtures and the details are reported in [14, 22, 23]. The surface tension of liquid iron has been evaluated by a simple model based on Butler's equation, considering Fe-O system as Fe-FeO system [22]. Subsequently, the same type of model have been successfully applied to calculate the surface tension of liquid Co-O, Ni-O, Si-O and Cu-O systems [14]. In the present work Tanaka's model was applied to study the effect of oxygen on Pb-O, Bi-O and LBE-O melts, and, in the case of liquid metals, the obtained results were compared with literature data, while in the case of the LBE, a new set of surface tension experimental data was used for a comparison. In the following, only the basic equations of Tanaka's formalism are given. The evaluation of the surface tension of liquid metal-oxygen (*Me-O*) system is done assuming the existence of an associate molecule *MeO*, and thus the initial system is regarded as *Me-MeO* [14]. Butler's Equation for Me-MeO binary solution is given by:

$$\sigma = \sigma_{Me} + \frac{RT}{A_{Me}} \ln \frac{(1 - C^{s}_{MeO})}{(1 - C^{b}_{MeO})} + \frac{1}{A_{Me}} \overline{G}^{Ex,s}_{Me} (T, C^{s}_{MeO}) - \frac{1}{A_{Me}} \overline{G}^{Ex,b}_{Me} (T, C^{b}_{MeO}) \tag{1a}$$

or

$$\sigma = \sigma_{MeO} + \frac{RT}{A_{MeO}} \ln \frac{C^{s}_{MeO}}{C^{b}_{MeO}} + \frac{1}{A_{MeO}} \overline{G}^{Ex,s}_{MeO} (T, C^{s}_{MeO}) - \frac{1}{A_{MeO}} \overline{G}^{Ex,b}_{MeO} (T, C^{b}_{MeO}) \tag{1b}$$

In Equation (1a-b) $T$, $\sigma_i$, $A_i$, $C^{j}_{i}$ and $\overline{G}^{Ex,j}_{Me}$ ( $i$ = *Me*, *MeO*; $j$ = *b*, *s*) are temperature, surface tension, surface area, molar fraction and partial Gibbs excess energy of component *i*,

σ

respectively. The superscripts $j$ indicate the bulk or surface phase. The surface area, $A_i$ is calculated as:

$$A_i = LN_0^{1/3} V_\mathrm{i}^{2/3} \tag{2}$$

where $N_0$, $V_\mathrm{i}$ and $L$ are Avogadro's number, molar volume and structural factor, respectively. The last one is taken 1.091 for liquid metals and 1.0 for molten salts and oxides.

In a Me-MeO molten system for the activity of a solvent (Me) obeys Raoult's law, while for that of a solute (MeO), the Henry's law is held. Accordingly, in Equation (1a), the terms describing the partial Gibbs excess energy of molten metal in both phases are equal to zero, and the corresponding term in Equation (1b), for an oxide (MeO) at infinite dilution is:

$$\overline{G}_{MeO}^{Ex,b}(T, C_{MeO}^{b}) = RT \ln \gamma_{MeO}^{b,0} \tag{3}$$

where $\gamma_{MeO}^{b,0}$ is the activity coefficient of MeO at infinite dilution. Thermodynamic analysis shows its large positive value [14] that indicates repulsive interaction with liquid metal. Taking into account the basic hypotheses of demixing solution model [24], the partial Gibbs excess energy of MeO and Me in the bulk phase can be expressed by:

$$\overline{G}_{MeO}^{Ex,b}(T, C_{MeO}^{b}) = 1 - \frac{1}{n} - \ln n + \frac{W_{Me-MeO}}{RT} \tag{4}$$

$$\overline{G}_{Me}^{Ex,b}(\mathrm{T}, C_{MeO}^{b}) = RT \ln \gamma_{Me}^{b} = 0 \tag{5}$$

In Equation (4) the cluster size, $n$, is assumed to be common in both, the surface and the bulk phase.

Depending on the stoichiometry of oxide, its activity coefficient can be calculated from the mole fraction of MeO, $C_{MeO}^{b,sat}$, saturated in liquid Me, which can be obtained from the data on oxygen saturation in liquid Me, $C_{O}^{b,sat}$, as follows

$$RT \ln \gamma_{MeO}^{b,0} = RT \ln\left(\frac{1}{C_{MeO}^{b,sat}}\right) = RT \ln\left(\frac{1 - C_{O}^{b,sat}}{C_{O}^{b,sat}}\right) \quad \text{for MeO = MeO type oxide} \tag{6a}$$

$$= RT \ln\left(\frac{1 - C_{O}^{b,sat}}{2C_{O}^{b,sat}}\right) \quad \text{for MeO = Me}_2\text{O type oxide} \tag{6b}$$

$$= RT \ln\left(\frac{2(1 - C_{O}^{b,sat})}{C_{O}^{b,sat}}\right) \quad \text{for MeO = MeO}_2\text{ type oxide} \tag{6c}$$

$$= RT \ln\left(\frac{3(1 - C_{O}^{b,sat})}{2C_{O}^{b,sat}}\right) \quad \text{for MeO = Me}_2\text{O}_3\text{ type oxide} \tag{6d}$$

Combining Equation (4) and Equation (6) the interaction energy term, $W_{Me\text{-}MeO}$, can be calculated. To obtain the corresponding energy parameter in the surface phase, the last one should be multiplied by the reduced coordination factor, β [14]. Since $C^{b}_{MeO} << 1$, taking into account the previous equations, Equation (1a-b) can expressed by:

$$\sigma = \sigma_{Me} + \frac{RT}{A_{Me}}\ln(1 - C^{s}_{MeO}) = \sigma_{MeO} + \frac{RT}{A_{MeO}}\ln\frac{C^{s}_{MeO}}{C^{b}_{MeO}} + \frac{1}{A_{MeO}}W_{Me-MeO}(\beta - 1) \qquad (7)$$

# RESULTS AND DISCUSSION

## The Pb-O and Bi-O Melts

Based on the thermodynamic studies and on the corresponding phase diagrams of the Pb-O [10, 25] and the Bi-O [27] the effect of the oxygen partial pressure on the surface tension of both melts was calculated by Tanaka's model (Equation 7) taking into account the stoichiometry of the oxides, i.e., PbO (Equation 6a) and $Bi_2O_3$ (Equation 6d). The dependences of the surface tension of liquid Pb and Bi vs oxygen partial pressure are shown in Figures 1 and Figure 2, respectively.

The surface tension of liquid Pb [7], PbO [23], Bi [29] and $Bi_2O_3$ [23], the oxygen solubility data [8], the molar volumes and other physical properties [20] of these molten metals were taken as the input data for the calculations of the surface tension isotherms. In all calculations the reduced coordination factor was taken as β =0.2, while the cluster size parameter = 4 exhibits the best agreement with the activity data [9].

In the case of Pb-O melts (Figure 1), in order to compare the experimental data [26] with the corresponding calculated values, for each temperature (T=623 K and T=773 K), two isotherms were computed; the first one (Figure 1, full line) was obtained by own Pb-surface tension measurements [7], assuming the surrounding atmosphere with oxygen partial pressure of $P=^{10-31}$ Pa as *oxygen free*, as indicate the squares in Figure 1. The other one (Figure 1, dashed line) was calculated using Pb - surface tension data [26]. At each temperature, the surface tension literature data obtained under oxygen partial pressures of the order $10^{-38}$, $10^{-27}$ and $10^{-14}$ Pa [26] exhibit a some scatter with respect to the calculated curves, probably associated with experimental difficulties. An exception represents the surface tension data σ = 426.2 measured under the highest $O_{2-}$ pressure of $P = 5.4 \cdot 10^{-14}$ Pa, that fits well the calculated value. The tensioactive effect of oxygen on Pb-melts is more pronounced at lower temperature.

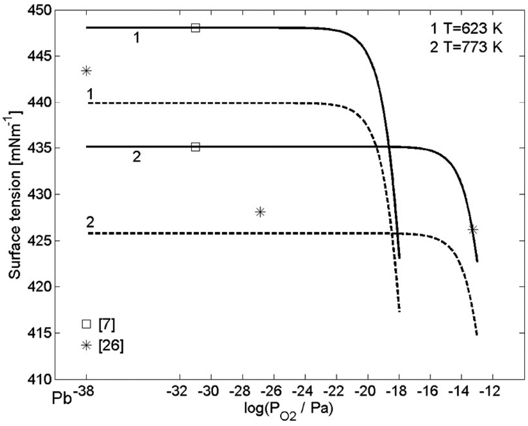

Figure1: Effect of $O_2$-Content on the Surface Tension in Pb-O Melts at 623 and 773 K

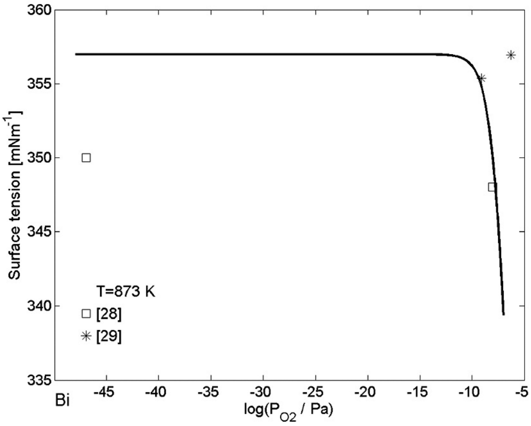

Figure 2: Effect of $O_2$-Content on the Surface Tension in Bi-O Melts at 873 K

The effects of oxygen on Bi-O melts have been analysed from literature data at T=873 K. The surface tension isotherm was calculated to compare the experimental data [28, 29]. A sharp decrease in Bi-surface tension was obtained for oxygen partial pressure higher than $P=10^{-8}$ Pa, in agreement with both experimental data sets [28, 29].

## The LBE-O Melts

A simple Tanaka's model [14], evaluated for the thermodynamic prediction of surface tension as function of oxygen content has also been applied on the LBE-O melt, with temperature restriction, at which β - PbO phase coexists with LBE (T=823 K) [10]. Taking into account that in the liquid Pb-Bi phase under *oxygen-free* conditions, Bi-atoms segregate to the surface over the whole composition range [7, 13], the surface oxygen saturation range is close to the Bi-O system. Accordingly, in the present work, the same type of calculation on the quasi binary LBE-$Bi_2O_3$ system was done at 823 K, and the results obtained are compared with own surface tension experimental data measured at 723 and 773 K.

As in the case of Pb and Bi pure metals, the surface tension of liquid LBE [7], its oxygen solubility data [8] together with LBE-molar volume, calculated from the density data

[6] and its melting temperature [2] together with the corresponding data on the $Bi_2O_3$ were taken as the input data. At T=823 K, the calculated values (Figure 3) showed a sharp decrease in the LBE-surface tension for the oxygen partial pressures higher than $10^{-9}$ Pa, that is in contrast with the experimental data, obtained at lower temperatures. The experimental data exhibit similar behaviour, and seems that in this temperature range and for indicated oxygen partial pressures, a drop in the LBE-surface tension was not observed. A large difference between the two type of data principally can be attributed to the difficulties of performing surface tension determinations using controlled values of oxygen present in the gas phase [18, 28].

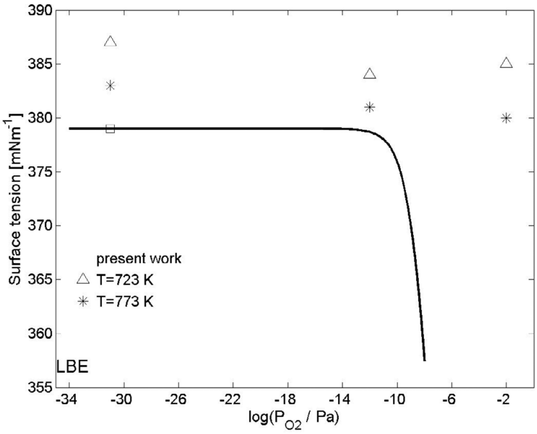

Figure 3: Effect of $O_2$-Content on the Surface Tension in LBE-O Melts at 723 and 773 K

In addition, when dealing with high-temperature measurements of metallic systems, vaporisation phenomena generally occur and have to be taken into account. For those molten metals that form volatile oxides, such as Pb forming PbO, there will also be a flow of metal oxides leaving the liquid surface. In this case, the oxygen transfer from the gas phase to the condensed phase must account for the double contribution of molecular oxygen and the oxygen linked as oxide [18]. In fact, purification processes by means of oxide and sub-oxide evaporation at high temperature are extensively used in metal refining.

To have a complete approach to the study of oxygen interactions with the liquid metal and of its influence on the material properties, in particular the surface properties, it is clear that a correlation needs to be established between the kinetics of vapour fluxes and thermodynamic equilibrium [17].

## CONCLUSIONS

The adsorption behaviour of oxygen in liquid Lead, Bismuth and the LBE has been analysed by the surface tension measurements. The thermodynamic approach to describe the tensioactive effect of oxygen on the surface tension of pure molten metals is, in many cases consistent with literature data, although some scatter among the two type of data can be observed, such as in the case of liquid Pb and Bi. As concerns the surface tension of molten LBE-alloy, the calculated values are similar to that of Bi-O melts. Preliminary experimental data on the LBE exhibit similar behaviour at both temperature, T=723 and 773 K, while to have a complete understanding of LBE-surface properties, other measurements are needed. Furthermore, in the cases of liquid alloys, a large scatter between the experimental data and the corresponding theoretical values calculated by the thermodynamic models, can be reduced taking into account the mass transport in a gas phase.

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