

Oxidation Conditions of Pure Liquid Metals and Alloys

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The evaluation of oxygen-liquid metal interactions is a topic of undoubted interest for different technological processes such as optimizing the preparation of binary alloys.

In such instances, productive processes can be more easily studied using theoretical approaches based on the study of mass-transport phenomena in liquid metal-gas systems. Therefore, a physico-mathematical method for analyzing the interaction of liquid metals or liquid binary alloys and their oxides has been developed.

The theoretical results of this analysis and the model validations performed up until now indicate that the behaviour of an alloy to oxidation tends to be similar to that of the less oxidizable component because the evaporation of a highly volatile oxide can prevent surface oxidation, even if the corresponding metal is present in low percentages.

This paper aims to provide a more systematic analysis of the behaviour of a number of different pure metals to oxidation and to determine which of them is most likely to contribute to keeping the surface of a binary alloy free of oxygen.

1. Introduction

Mass transport phenomena at the gas-metal interface play a very important role in several metallurgical processes, such as casting, brazing, welding, etc. In particular, the presence of oxygen and the existence of oxygen fluxes at the interface can strongly affect the properties of the interface itself and then the behaviour of such processes. In fact, it is impossible to avoid having traces of oxygen in the working atmosphere and so surface-contamination phenomena are often of great practical relevance. In such instances, productive processes can be more easily studied using theoretical approaches based on the study of mass transport phenomena in liquid metal-gas systems.

The mechanisms of the interaction between oxygen and the interface are very complex: convection, both inside the liquid phase and at the surface (Marangoni flow) can affect diffusion; the diffusion paths in the gas phase can be different according to whether Knudsen conditions (high vacuum) occur or not. Moreover, oxidation phenomena can occur, with the formation of one or more oxides; these oxides may form only at the interface or inside the gaseous layer close to the interface and, in their turn, they may or may not undergo condensation phenomena.

All these molecular events can have effects on interface behaviour. The measurement of the surface tension is a good and relatively simple way to study surface/interface properties, their temporal change and their connections to transport and reaction rates (Ricci et al. (2005)).

The effects of oxygen transport phenomena on the surface tension of pure metals (Arato et al. (2006), Castello et al. (1994), Fiori et al. (2003), Giuranno et al. (2006), Ratto et al. (2000), Ricci et al. (2008a)) and binary alloys (Arato et al. (2006), Ricci et al. (2008b)) have been thoroughly studied. The theoretical analysis of this problem has revealed that the liquid-atmosphere mass exchanges, under more realistic stationary conditions and dynamic transport processes, must be considered in determining the oxidation condition of a liquid metal system: in many cases, the combined effects of metal-atom and sub-oxide evaporation can hinder oxygen reaching the liquid surface, thus creating “cleaner” conditions, also in an atmosphere with an oxygen content higher than that foreseen by thermodynamics.

Various examples of metal systems (pure metals and binary alloys) and their interaction with oxygen reaching the surface are analysed in this paper by a theoretical approach that considers the relevant contribution of their volatile oxides. Moreover, in the theoretical treatment, the oxygen transport inside the liquid phase is also taken into account for pure metals and, under some approximations, for binary alloys.

The evolution of oxidation phenomena, as predicted by the diffusional model, has been experimentally investigated by dynamic surface tension measurements of different pure metals and binary systems. The experimental evidence is in good agreement with the theoretical behaviour foreseen under stationary-conditions.

2. The Theoretical Approach

2.1 Pure metals

The behaviour of some pure liquid metals and their interaction with oxygen reaching the surface has been analysed both theoretically and experimentally in several papers, by investigating the evolution of oxidation phenomena through dynamic surface tension measurements as a function of oxygen partial pressure. The details of the experimental procedures and apparatus have been given in (Ricci et al. (2005)).

It has been established that the behaviour of liquid metals to surface oxidation is linked to the nature of their oxides (Castello et al. (1994)). Metals forming low volatile oxides, are adequately described by thermodynamics. On the contrary, the description of oxidation phenomena of other metals requires a diffusional theoretical approach which considers the relevant contribution of the volatile oxides, under the steady state condition of the liquid phase. In this case, the liquid phase is still considered in equilibrium with the gas-liquid interface, but it exchanges oxygen and the volatile oxide with the atmosphere. Under the steady-state condition, the net exchange of oxygen has to be null and so the effective threshold value of the oxygen partial pressure between the oxidation-deoxidation regimes can be estimated, for both Fick and Knudsen regimes, by the equation:

$$P_{O_2\text{eff}} = P_{O_2s} + a P_{ox}^s \quad (1)$$

where, P_{O_2s} is the oxygen partial pressure at saturation, P_{ox}^s is the vapour pressure of the volatile oxide and, referring to oxidation reactions, a is the stoichiometric coefficient of

oxygen. Therefore, only metals having oxides of relatively low volatility ($P_{ox}^s \leq P_{O_2s}$), such as Cu, Ni, Bi, Ag, etc. (Ricci et al. (2008b)), which have effective pressure that coincides with the saturation pressure, behave, in terms of oxidation, as foreseen by thermodynamics. On the contrary, for many other metals, such as Sn, Al, Si, Pb, etc., the oxide volatility is very high ($P_{ox}^s \geq P_{O_2s}$) so that their stationary pure liquids show an effective oxygen pressure that roughly corresponds to the vapour pressure of their most volatile oxide at saturation.

This effective oxygen pressure P_{O_2eff} , as a property of the system, can be many orders of magnitude greater than the equilibrium pressure P_{O_2s} , as shown for the Pb-O system in Figure 1. The evolution of oxidation phenomena has been experimentally investigated through dynamic surface tension measurements, as shown in the insert in Figure 1, where the imposed temperature of the liquid Pb was changed under a constant oxygen content in the surrounding atmosphere ($P_{O_2} \approx 5 \cdot 10^{-2}$ Pa) assured by ArN60 (purity of 99.9999%, $O_2 < 0.1$ ppm). The temperature modulation allowed some significant "inversions" in the surface tension behaviour to be noted (A and B points). The maximum surface tension (or inversion) points are assumed to correspond to the incoming oxidation points. The experimental conditions of inversion are linked to the oxygen tensio-active effect, but not necessarily to the formation of stable oxides on the surface and this effect is identified by the sign inversion (from negative to positive) of the temperature coefficient of the surface tension (Fiori et al. (2003)).

On the other hand, as saturation conditions strongly depend on temperature, a temperature modulation corresponds to a modulation of the saturation level and it is then equivalent to a modulation of the oxygen concentration in the liquid phase (Ricci et al. (2005)).

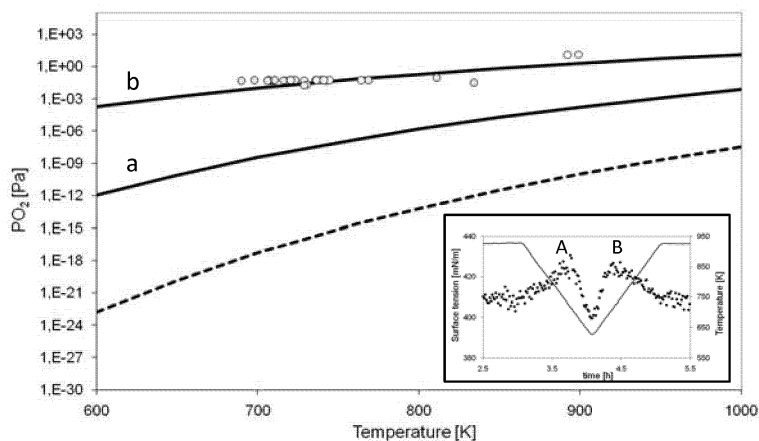


Figure 1: Effective Oxygen Pressure curve calculated for the Pb-O system (line a) (Knacke et al. (1991)) compared with the saturation pressure (broken line) and effective oxygen pressure considering liquid mass transport under the Fick regime (line b). Experimental points of oxidation-deoxidation under the Fick regime (\circ). Insert: Surface tension of Pb (\bullet) as a function of time t and temperature ($-$).

As often happens with these kinds of measurements, the differences between the experimental data and theoretical predictions are of some orders of magnitude: about 5 orders in this case (line a), but the difference is greatly reduced when the effect of the liquid mass transfer is considered (line b), by taking into account the diffusivity of oxygen and its solubility inside the liquid phase (Arato et al. (2006)).

In comparison with the thermodynamic predictions (broken line), where the differences are of some tens of orders of magnitude (about 12 in this case) the result can be considered very significant.

2.2 Binary alloys

The oxidation phenomena of a liquid binary system, such as the Bi-Pb alloys, may undergo drastic changes owing to the contribution of the evaporation phenomena: a metal, which is more oxidizable than another according to the thermodynamic description, in this case Pb become less oxidizable in practice (Arato et al. (2008)).

For this reason it is important to analyze both the saturation pressure P_{O_2s} (Knacke et al. (1991)) and the effective oxygen pressure P_{O_2eff} of the different metals to understand for which metal the classical thermodynamic approach is sufficient and for which, on the contrary, it is necessary to consider the evaporation of the volatile oxides by evaluating their vapour pressure P_{ox}^s (Knacke et al. (1991)).

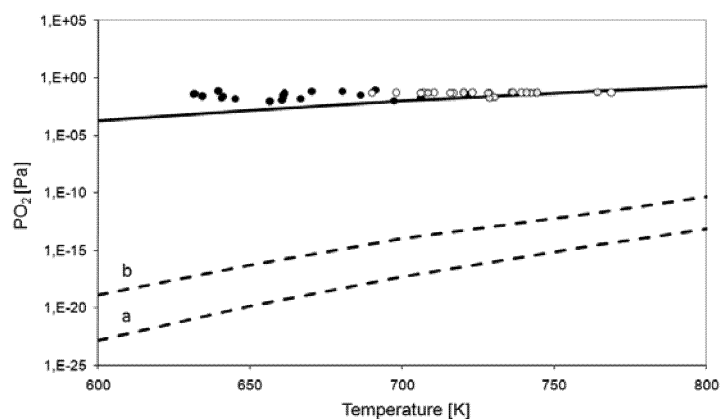


Figure 2: Effective Oxygen Pressure curve calculated for the Pb–O system (bold line) (Knacke et al. (1991)) taking into account the liquid mass transport under the Fick regime (Arato et al. (2006)) and compared to the saturation pressure corresponding to the formation of the stable oxides, PbO (line a) and Bi₂O₃ (line b). Experimental points of oxidation-deoxidation under the Fick regime for pure liquid Pb (○) and Bi-44.1at%Pb alloy (●).

In Figure 2 the saturation pressure P_{O_2s} of the two metals, Pb (curve a) and Bi (curve b), are shown. From a thermodynamic point of view, Pb should be more oxidizable than Bi: the saturation pressure of Pb is some orders of magnitude lower than that of Bi.

On the contrary, in terms of volatility, only the volatile oxide of lead, i.e. PbO, can be considered: the lead oxide evaporation is mainly responsible for maintaining the

cleanness of the alloy surface, as indeed shown in Figure 2 where, the eutectic alloy (Bi-44.1at%Pb) of the Bi-Pb system behaves towards oxidation like Pb.

Moreover, checking the oxygen distribution between gas, interface and liquid, then the role of liquid mass transfer phenomena by the evaluation of the diffusivity of oxygen inside the liquid phase (Arato et al. (2006)), it is possible to infer that the system will behave like Pb over a wide composition range (see also Figure 3), Pb being the less oxidizable component according to the definition of the effective oxygen pressure. In other words, the behaviour of an alloy to oxidation tends to be similar to the constituent which behaves as the less oxidizable one because the evaporation of a highly volatile oxide, combined with the diffusion of oxygen inside the liquid phase, can prevent surface oxidation, even if the corresponding metal is present in low percentages.

This theoretical conclusion is substantially confirmed by the experimental data, as shown in Figure 3. In this figure, the experimental data for the detected oxygen tensio-active effect, observed at 762 K, are shown as a function of the alloy composition, together with the calculated effective oxygen pressure (line a): the differences between the experimental data and theoretical predictions are of some orders of magnitude, while, a satisfactory description is reached when the effect of the liquid mass transfer is considered (line b), as a further refinement of the present analysis. In comparison with the thermodynamic predictions (broken line), where the differences are of some tens of orders of magnitude, the result can be considered very significant.

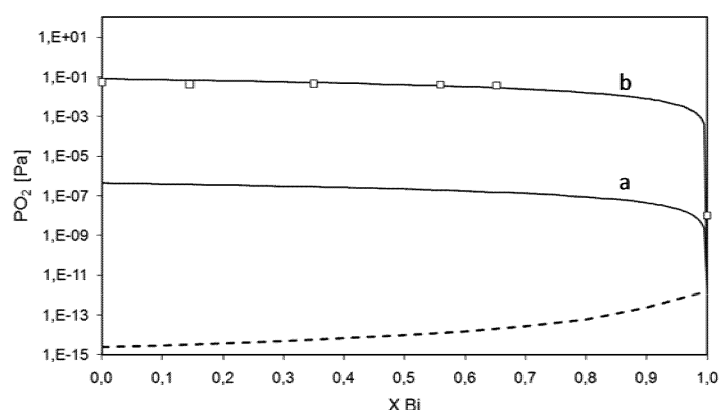


Figure 3: Effective oxygen pressure calculated for Bi-Pb alloys at the temperature $T = 762$ K as a function of the alloy composition (line a) and compared with the effective oxygen pressure calculated by taking into account the liquid mass transport under the Fick regime (line b) (Arato et al. (2006)) and the saturation pressure calculated for the binary system (broken line). Experimental points of oxidation-deoxidation under the Fick regime (\square).

3. Conclusions

The phenomena of oxygen transport at a molten metal-atmosphere interface, and particularly the mechanisms whereby a molten metal or alloy surface is kept clean even

in the presence of atmospheric oxygen impurities, play a very important role in many technological processes. From the results obtained with our models, it is possible to straightforwardly and qualitatively explain the mechanisms that keep a molten metallic system “oxygen-free”, despite the thermodynamic driving force. The experimental results for several pure metals and some binary alloys using dynamic surface tension measurements demonstrate that the experimental oxidation–deoxidation transitions occur at values of oxygen partial pressure higher than the thermodynamic ones, due to the non-negligible contribution of the linked oxygen as volatile oxides and the oxygen dissolved inside the liquid phase.

Moreover, in the case of a binary system, the theoretical results indicate that the behaviour of the alloy towards oxidation tends to be similar to that of the less oxidizable component: in many instances, as experimentally demonstrated on Bi-Pb system, the existence of a volatile oxide prevents surface oxidation, even if the corresponding metal is only present in very low percentages.

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