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Oxygen transport phenomena at the liquid metal-vapour interface

E. ARATO[1,2], E. RICCI[2], P. COSTA[1,*]
[1]*DIAM, University of Genoa, Via Opera Pia, 15, 16145 Genova, Italy*
[2]*CNR-IENI - Department of Genoa, Via De Marini, 6, 16149 Genova, Italy*
E-mail: costa@diam.unige.it

A system made of an atmosphere, a liquid metal and an oxide phase at a given temperature and total pressure is zero-variant and allows only a particular set of partial pressures, compatible with thermodynamic equilibrium. For any different gas composition the system will show a tendency to evolution. Therefore, classical thermodynamics cannot give the answers to a number of problems of major interest, such as those concerning the conditions for interface saturation and oxide formation. Strictly speaking these are kinetic problems, but they can still be treated as pseudo-thermodynamic questions. The key to the problem is in considering the characteristic times of evolution, which suggest stationary state approximation for the condensed phases. In many instances, the evaluation of gas-atmosphere mass exchanges under stationary conditions makes it possible to determine the effective oxygen pressure at which the oxidation of the metal becomes evident. Surface tension measurements allow this condition to be detected with a good accuracy. According to experimental evidence, the effective oxygen pressure can be many orders of magnitude greater than the equilibrium value. The problem needs different theoretical approaches according to the molecular mechanisms involved. Moreover, from the experimental point of view, there are particularly delicate questions regarding the accuracy and the significance of the oxygen control and measurement.

List of symbols

a	stoichiometric coefficient in reaction (1) (-)
C	total concentration (kmol/m^3)
d	molecular diameter (m)
D	diffusivity (m^2/s)
f_{sh}	shape factor (-)
k	mass transfer coefficient, in terms of mol fractions (kmol/m^2 s)
K_{AC}	mass transfer coefficient ratio, see Equation 23
K_{d}	equilibrium constant of dissolution reaction (2), in terms of mol fractions (-)
K_{y}	equilibrium constant of oxidation reaction (1), in terms of mol fractions (-)
M	molecular weight (kg/kmol)
N	flux, relative to interface (kmol/m^2 s)
P	pressure (Pa)
Pe	Peclet number (-)
S	drop surface (m^2)
t	time (s)
T	absolute temperature (K)
v	gas velocity (m/s)
V	drop volume (m^3)
x	mol fraction in the liquid phase (-)
y	mol fraction in the gas phase (-)
β	condensation coefficient in Langmuir-Knudsen equation (-)
σ	surface tension (N/m)

Subscripts and superscripts

A	oxygen
B	metal
C	oxide
f	outlet
G	gaseous phase
i	refers to points close to the interface
I	inert gas
L	liquid phase
m	mean
s	saturation
σ	refers to interface (Gibbs interface)
o	inlet
$*$	effective

1. Introduction

Mass transport phenomena at the gas-metal interface play a very important role in several technological processes, such as crystal growth and welding. In particu-

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[*] Author to whom all correspondence should be addressed.

lar, 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. The mechanisms of the interaction between oxygen and the interfaces are very complex: convection, both inside the liquid phase and the surface (Marangoni flow) can affect diffusion; diffusion paths in the gas phase can be quite different according to whether Knudsen conditions (high vacuum) occur or not; moreover, oxidation phenomena can occur, with the formation of one or more oxides; oxides may form just at the interface or inside the gaseous layer close to the interface and, in their turn, they may undergo condensation phenomena or not. All these molecular events can have effects on interface behaviour. Surface tension measurement is a good and relatively simple way to study interface properties, their temporal change and their connections to transport and reaction rates.

This work is a review and reformulation of a number of theoretical and experimental studies developed by our group on the subject during the last 15 years [1–7]. During this period, numerous experiments have been carried out on a number of different metals and alloys: systematic surface tension measurements have been performed using the sessile drop method and acquisition times of a few seconds, so that the drop evolution has been successfully observed. At the same time, theoretical models, relating the mass exchange between liquid metals and the surrounding atmosphere, both under inert gas carrier and Knudsen regimes have been developed. In the case of inert carrier flow, the effects of oxidation reactions taking place in the gas phase have been considered; in the case of low total pressures the effect of oxide evaporation has been considered. In both cases the presence of oxidation phenomena contribute to maintaining interface cleanliness and then strongly affect the position of the curves separating the oxidation and de-oxidation regimes.

The fundamental concept of these descriptions is in complete agreement with Wagner's theory [8]: in fact, some of our works can be seen as an extension and generalisation of it [5, 6]. Here a further generalisation has been made to formally consider a number of distinct situations from a unique point of view, initially conceived for Knudsen regime conditions.

A system made of an atmosphere, a liquid metal and an oxide phase at given temperature and total pressure is zero-variant and only a particular set of partial pressures is compatible with its thermodynamic equilibrium. For any different gas composition the system shows a tendency to evolution until the disappearance of one or two phases. In particular, if the partial pressures of metal and oxide are kept very low, both condensed phases will disappear in the end, leaving only the gas phase.

Classical thermodynamics cannot go further, while a problem of relevant practical interest is what phase will disappear first according to the oxygen partial pressure imposed on the system. A quite similar problem regards the formation of an oxide phase on a metal phase: a partial pressure of oxygen greater than the equilibrium value should be sufficient to obtain the formation and growth of an oxide phase, while both condensed phases will tend to disappear in the long term. On the contrary, only under much more severe oxidising conditions does an oxide phase tend to form during evolution and the metal phase tend to disappear first, while under softer oxidising conditions the oxide phase does not form at all, in spite of classical thermodynamic indications.

Strictly speaking these are kinetic problems, depending on the extension of the phases and mechanisms of reaction and diffusion, but they can still be considered, from a certain point of view, as pseudo-thermodynamic questions.

The key to the problem is in considering the characteristic times of evolution, which suggest the stationary state approximation. In many instances, the evaluation of gas-atmosphere mass exchanges under stationary conditions makes it possible to predict whether the metal surface will remain clean or an oxide phase will form on it and then to evaluate an effective oxygen pressure at which the oxidation of metal becomes evident thanks to the appearance of an oxide phase. This effective oxygen pressure, according to experimental evidence, can be many orders of magnitude greater than the equilibrium value.

Starting from this generalised formulation a number of different cases will be considered. In terms of the operating conditions, the problem needs a number of different approaches according to the gas diffusion mechanisms (Fick or Knudsen), and the reactions occurring in the gas phase. In terms of the metal species, reference has mainly been made to tin, with some digression on aluminium and silicon. Finally, in terms of the experimental aspects, one of the most critical factors is the control of oxygen inside experimental apparatuses.

2. Thermodynamics

In the following only one oxide species is considered, but the discussion can easily be extended to a number of different oxides [9]. This simplified presentation maintains a great part of its validity if the term "oxide" is replaced by the term "the most stable oxide" in the thermodynamic equations [10] and the oxide fluxes are replaced with a sum that takes all the oxide contributions into account in the kinetic equations. In this sum all the terms are negligible except one, so that in this case the term "oxide" should be replaced by the term "the most volatile oxide" [11].

The equilibrium between a gaseous phase (atmosphere) and two incondensable phases (metal and oxide), involving four components (gaseous inert, metal B, oxygen A and an oxide compound C) with the reaction link

$$aA + B = C \quad K_{\mathrm{y}}(T, P) = y_{\mathrm{C}}/\left(y_{\mathrm{B}} y_{\mathrm{A}}^{\mathrm{a}}\right) \tag{1}$$

is bivariant. At a given temperature T and total pressure P the system becomes zerovariant and only a particular set of mole fractions

$$y_{\mathrm{C}} = y_{\mathrm{Cs}} \quad y_{\mathrm{B}} = y_{\mathrm{Bs}} \quad y_{\mathrm{A}} = y_{\mathrm{As}} = [y_{\mathrm{Cs}}/(K_{\mathrm{y}} y_{\mathrm{Bs}})]^{1/\mathrm{a}} \tag{2}$$

is compatible with the equilibrium. Correspondingly the concentration of oxygen in the liquid phase, according to the reaction

$$A = 2A_{\mathrm{L}} \quad K_{\mathrm{d}}(T, p) = x_{\mathrm{A}}/(y_{\mathrm{A}})^{1/2} \tag{3}$$

and to the Sievert's law, will be

$$x_{\mathrm{As}} = K_{\mathrm{d}}(y_{\mathrm{As}})^{1/2} = K_{\mathrm{d}}[y_{\mathrm{Cs}}/(K_{\mathrm{y}} y_{\mathrm{Bs}})]^{1/2\mathrm{a}} \tag{4}$$

Any set of gas compositions different from (2) is incompatible with the coexistence of the three phases under equilibrium conditions, so that the system, with arbitrary but constant boundary conditions for the gas phase, will exhibit a tendency to evolution until one or two phases disappear.

When the oxide phase is not present, the system at given T and P is monovariant: for each oxygen molar fraction $y_{\mathrm{A}} < y_{\mathrm{As}}$ we have, at equilibrium,

$$\begin{aligned} &y_{\mathrm{B}} = y_{\mathrm{Bs}} \quad y_{\mathrm{C}} = K_{\mathrm{y}} y_{\mathrm{Bs}} y_{\mathrm{A}}^{\mathrm{a}} < y_{\mathrm{Cs}} \\ &x_{\mathrm{A}} = K_{\mathrm{d}}(y_{\mathrm{A}})^{1/2} < x_{\mathrm{As}} \qquad y_{\mathrm{A}} < y_{\mathrm{As}} \end{aligned} \tag{5}$$

In turn, when the liquid metal phase is not present, for each $y_{\mathrm{A}} > y_{\mathrm{As}}$ we have

$$y_{\mathrm{C}} = y_{\mathrm{Cs}} \quad y_{\mathrm{B}} = y_{\mathrm{Cs}}/(k_{\mathrm{y}} y_{\mathrm{A}}^{\mathrm{a}}) < y_{\mathrm{Bs}} \quad y_{\mathrm{A}} > y_{\mathrm{As}} \tag{6}$$

When the molar fractions of the metal and oxide in the gas phase are both kept very low, as it is often done in experimental conditions,

$$y_{\mathrm{B}} < y_{\mathrm{Bs}} \qquad y_{\mathrm{C}} < y_{\mathrm{Cs}} \tag{7}$$

the equilibrium condition is incompatible with the existence of condensed phases, so that they, if initially present, will disappear in the end, leaving only the gas phase.

Beyond classical thermodynamics, a number of major questions require attention, such as those raised in the introduction. For an effective and straightforward approach to these questions the key lies in considering the characteristic times of evolution, which suggest a stationary state (and not equilibrium) approximation for the condensed phases.

3. Characteristic times

With reference to a metal drop in an oxidising atmosphere, the most important characteristic times involved are the following:

- Interface time. It is always very low, for instance 10^{-4}–10^{-6} s, so that interfacial equilibrium conditions can always be invoked.
- Diffusion time around the drop (or gaseous diffusion time). This time is also low: a reference value of the order of 1 s can be obtained for a 1 cm diameter drop, atmospheric total pressure, 800 K temperature and low gas velocities (viscous flow conditions).
- Diffusion time inside the drop (or liquid diffusion time). Liquid diffusion is much slower than gaseous diffusion: a reference value under the above conditions and in the absence of convective circulation could be estimated in 10^2 s. As circulation is quite probable, diffusion times are very likely to be lower.
- Reaction time. Due to the very low solubility of oxides in liquid metal, it can be assumed that oxidation reactions only occur inside the gaseous phase or at the interface. As high temperatures are normally involved, reaction times can often be assumed to be much lower than diffusion times, so that local equilibrium in the gaseous layer can be assumed. On the other hand, as oxidation reactions are consistent with a bimolecular type of mechanism, when very low concentrations occur, reaction times can become much longer than diffusion times, so that reaction kinetics become negligible.
- Drop time. This is the time of evolution of the drop to a concentration stationary state and involves reaction and diffusion kinetics, so that it depends on the above characteristics and the oxygen capacity of the drop.
- Drop lifetime. When an equilibrium state is incompatible with the conditions imposed, the drop continues to lose mass until it disappears. This is always a much longer time than all the previous ones, so that pseudo-stationary configurations of the drop, with an almost constant composition field, can be often usefully studied.

In brief, the description of drop behaviour, under constant boundary conditions, includes the following assumptions.

- Thermodynamic equilibrium at the gas-liquid interface.
- Stationary state for the diffusion and reaction phenomena through the gaseous layer surrounding the drop. If the gaseous diffusion times are much higher than the reaction times, then the local equilibrium can be extended to the whole layer (instantaneous reactions). If, on the contrary, the gaseous diffusion times are much smaller than the reaction times, reference can be made to null kinetics.
- Pseudo-stationary state for the liquid phase. A true stationary state is achieved only after a transient period of the order of magnitude of the drop time. In some instances this time may be very long.

4. The basic approach

In terms of a physico-mathematical description [12, 13], what has been said above can be schematised as follows. Assuming constant and uniform temperature and total pressure and a simple phase geometry (e.g. spherical), the transient behaviour of the metal phase

$$d(VC_{\mathrm{L}}x_{\mathrm{Am}})/\mathrm{d}t = -SN_{\mathrm{AL}} \tag{8}$$

$$d(VC_{\mathrm{L}})/\mathrm{d}t = -S(N_{\mathrm{AL}} + N_{\mathrm{BL}}) \tag{9}$$

thanks to the stationary interface assumption

$$N_{\mathrm{AL}} = N_{\mathrm{AG}} + aN_{\mathrm{CG}} = N_{\mathrm{AGT}} \tag{10}$$

$$N_{\mathrm{BL}} = N_{\mathrm{BG}} + N_{\mathrm{CG}} = N_{\mathrm{CGT}} \tag{11}$$

can be rearranged as

$$dx_{\mathrm{Am}}/\mathrm{d}t = -(S/VC_{\mathrm{L}})[(N_{\mathrm{AG}} + aN_{\mathrm{CG}})(1 - x_{\mathrm{Am}}) - (N_{\mathrm{BG}} + N_{\mathrm{CG}})x_{\mathrm{Am}}] \tag{12}$$

On a time scale greater than the diffusion and reaction times, the fluxes in the gas phase can be treated as constants (stationary gas layer assumption), only depending on the compositions on the two sides of the diffusion layer. A simple formal expression for this dependence can be

$$N_{\mathrm{AG}} = k_{\mathrm{AG}}(y_{\mathrm{Ai}} - y_{\mathrm{A}}) \quad N_{\mathrm{BG}} = k_{\mathrm{BG}}(y_{\mathrm{Bi}} - y_{\mathrm{B}}) \quad N_{\mathrm{CG}} = k_{\mathrm{CG}}(y_{\mathrm{Ci}} - y_{\mathrm{C}}) \tag{13}$$

but one has to bear in mind that the "transport coefficients" k_{AG}, k_{BG}, k_{CG} are often strongly dependent on gas compositions.

Under similar conditions a similar assumption can be made for the diffusion in the liquid phase

$$N_{\mathrm{AL}} = k_{\mathrm{AL}}(x_{\mathrm{Am}} - x_{\mathrm{Ai}}) + (C_{\mathrm{L}}x_{\mathrm{Ai}} - C_{\mathrm{G}}y_{\mathrm{Ai}})\mathrm{d}V/\mathrm{d}t \approx k_{\mathrm{AL}}(x_{\mathrm{Am}} - x_{\mathrm{Ai}}) \tag{14}$$

where the contribution due to drop evaporation can often be neglected or, at most, included in an effective transport coefficient.

Equations 10–14 can be used for different purposes. First of all, the system of stationary (10) and equilibrium conditions (5) (interface equilibrium assumption)

$$k_{\mathrm{AL}}(x_{\mathrm{Am}} - x_{\mathrm{Ai}}) = k_{\mathrm{AG}}(y_{\mathrm{Ai}} - y_{\mathrm{A}}) + ak_{\mathrm{CG}}(y_{\mathrm{Ci}} - y_{\mathrm{C}}) \tag{15}$$

$$y_{\mathrm{Bi}} = y_{\mathrm{Bs}} \quad y_{\mathrm{Ci}} = K_{\mathrm{y}}y_{\mathrm{Cs}}y_{\mathrm{Ai}}^{a} \quad x_{\mathrm{Ai}} = K_{d}(y_{\mathrm{Ai}})^{1/2} \quad (y_{\mathrm{Ai}} < y_{\mathrm{As}}) \tag{16}$$

makes it possible to calculate the interface composition (that is the set of four unknowns x_{Ai}, y_{Ai}, y_{Bi}, y_{Ci}) for a clean drop ($y_{\mathrm{Ai}} < y_{\mathrm{As}}$) if the bulk compositions of the phases x_{Am}, y_{A}, y_{B}, y_{C} are known. When the interface compositions and fluxes are known, Equation 12 allows us to follow the drop evolution over time. Moreover, the knowledge of the instantaneous composition of the three-dimensional phases close to the interface makes it possible to study the properties of the two-dimensional Gibbs interface [14]. Of particular interest are the dependence of the interface composition and surface tension on the gas and liquid composition and the question of whether they, under non-equilibrium conditions, depend on fluxes or not. If local equilibrium at the interface still holds up from this point of view, simple relationships, such as the following, are expected

$$x_{\mathrm{A}\sigma} = f_{\mathrm{x}}(x_{\mathrm{Ai}}) = f_{\mathrm{y}}(y_{\mathrm{Ai}}) \quad \sigma = f_{\sigma}(x_{\mathrm{A}\sigma}) \tag{17}$$

also in the presence of non-null fluxes crossing the interface. In this way the surface tension measurements can be related to local liquid and gas compositions and then to fluxes. In this interpretation fluxes do not directly affect surface tension, but show their importance in changing x_{Ai}, y_{Ai} and then $x_{\mathrm{A}\sigma}$, σ. It is worth remembering that full equilibrium between phases implies null fluxes. On the contrary, the presence of non-null net fluxes, according to the microscopic reversibility principle, does not contradict a close approach to local equilibrium at the interface.

Instead, if the solution to (15), (16) is $y_{\mathrm{Ai}} > y_{\mathrm{As}}$ this means that a super saturation of the interface occurs and an oxide phase has formed or tends to form. In particular, the incoming oxidation condition ($y_{\mathrm{Ai}} = y_{\mathrm{As}}$, $y_{\mathrm{Ci}} = y_{\mathrm{Cs}}$) can be assumed to occur when the bulk gas oxygen content is

$$y_{\mathrm{A}}^{*} = y_{\mathrm{As}} + (ak_{\mathrm{CG}}/k_{\mathrm{AG}})(y_{\mathrm{Cs}} - y_{\mathrm{C}}) + (k_{\mathrm{AL}}/k_{\mathrm{AG}})(x_{\mathrm{As}} - x_{\mathrm{Am}}) \tag{18}$$

Up to now, the liquid composition has been considered as a variable. On the other hand, on a time scale greater than the drop time, the stationary drop assumption can be used and the composition inside the drop can be treated as almost constant over time ($\mathrm{d}x_{\mathrm{Am}}/\mathrm{d}t = 0$). In such instances interface compositions and incoming oxidation conditions no longer depend on the liquid bulk composition and Equation 12 can be written

$$N_{\mathrm{AGT}}/N_{\mathrm{CGT}} = x_{\mathrm{Am}}/(1 - x_{\mathrm{Am}}) = [k_{\mathrm{AG}}(y_{\mathrm{Ai}} - y_{\mathrm{A}}) + ak_{\mathrm{CG}}(y_{\mathrm{Ci}} - y_{\mathrm{C}})]/[k_{\mathrm{BG}}(y_{\mathrm{Bs}} - y_{\mathrm{B}}) + k_{\mathrm{CG}}(y_{\mathrm{Ci}} - y_{\mathrm{C}})] \tag{19}$$

In such a way, Equations 15, 16 and 19 make it possible to calculate the interface composition as well as the liquid composition for a stationary drop.

The incoming saturation condition for a stationary drop can easily be deduced from Equation 19, yielding

$$[k_{\mathrm{AG}}(y_{\mathrm{As}} - y_{\mathrm{A}}) + ak_{\mathrm{CG}}(y_{\mathrm{Cs}} - y_{\mathrm{C}})]/[k_{\mathrm{BG}}(y_{\mathrm{Bs}} - y_{\mathrm{B}}) + k_{\mathrm{CG}}(y_{\mathrm{Cs}} - y_{\mathrm{C}})] = x_{\mathrm{As}}/(1 - x_{\mathrm{As}}) \tag{20}$$

As the solubility of oxygen is usually very low ($x_{\mathrm{As}} \ll 1$), Equation 20 can be written for most metals as

$$k_{\mathrm{AG}}(y_{\mathrm{As}} - y_{\mathrm{A}}) + ak_{\mathrm{CG}}(y_{\mathrm{Cs}} - y_{\mathrm{C}}) = 0 \tag{21}$$

The same result is obtained from Equation 15 putting $x_{\mathrm{Ai}} = x_{\mathrm{Am}} = x_{\mathrm{As}}$ and neglecting the drop evaporation in Equation 14. In its turn, for a saturated stationary drop, Equation 18 now becomes

$$y_{\mathrm{A}}^{*} = y_{\mathrm{As}} + (ak_{\mathrm{CG}}/k_{\mathrm{AG}})(y_{\mathrm{Cs}} - y_{\mathrm{C}}) \tag{22}$$

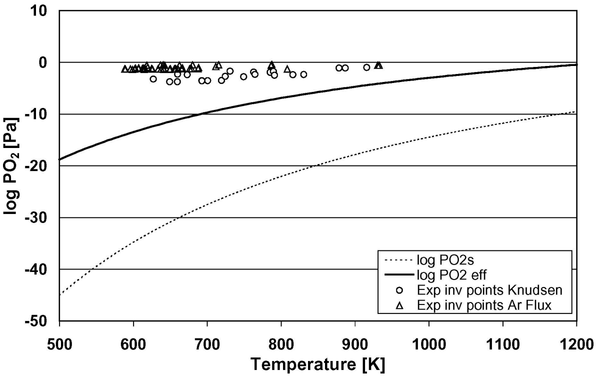

Figure 1 Experimental data for tin under vacuum (Knudsen regime) [20] and atmospheric pressure flux (presented at HTC 2004 by E. Arato). Equilibrium [broken curve, calculated by Equation 2] and effective [bold curve, calculated by Equation 24] pressure curves versus temperature are also reported. [Exp. inv. points = Experimental inversion (saturation) points].

Equation 18 and its limit form (20), or the approximate one (22), are important tools in studying the behaviour of a metal liquid interface. First of all, while classical thermodynamics indicates that the three-phase equilibrium can occur only when $y_A = y_{As}$, so that the existence of an oxide phase requires $y_A > y_{As}$, Equation 18 states that reference must be made to an "effective" oxidation condition y^*_A instead of the thermodynamic oxidation condition y_{As}. As the difference between y^*_A and y_{As} may involve several orders of magnitude, this conclusion is not only a marginal correction, but the theoretical key to understand a large set of experimental findings. This point of view, firstly intuited by Wagner, can now be considered as a systematic and quantitative approach to a number of scientific and practical questions involving gas-metal and oxide-metal interfaces. In Figs 1 and 2 some results are reported for tin and aluminium under various conditions.

In particular, Equation 18 shows that the incoming oxidation condition is different from the saturation condition for two distinct reasons. The first one depends on oxide evaporation, the second one on mass transfer inside the drop. For a clean drop ($x_{Am} < x_{Ai}$) in a clean atmosphere ($y_C < y_{Ci}$) these two effects cooperate to raise y^*_A over y_{As}. As x_{Am} approaches the stationary value for which ($x_{Am} = x_{Ai}$), y^*_A decreases until only the first phenomenon remains significant, according to Equation 22. The differences between the expected and measured values in Fig. 1 can be attributed to the liquid mass transfer in a non-stationary drop [15].

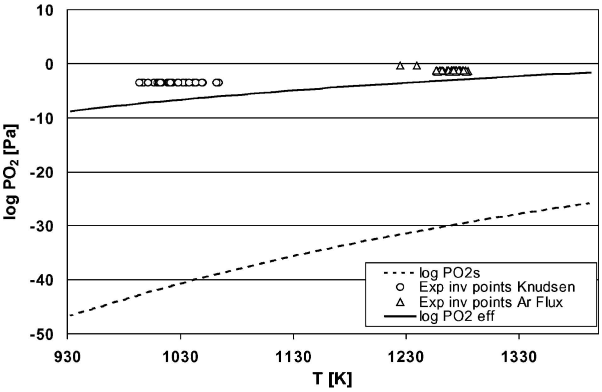

Figure 2 Experimental data for aluminium (presented at HTC 2004 by D. Giuranno [21]) under vacuum (Knudsen regime) and atmospheric pressure (flux). Equilibrium [broken curve, calculated using Equation 2] and effective [bold curve, calculated by Equation 24] pressure curves versus temperature are also reported. [Exp. inv. points = Experimental inversion (saturation) points].

It is useful to remember that both the above-mentioned phenomena are irreversible and are then regulated by kinetic laws, so that y^*_A, unlike y_{As}, is to be considered as a dynamic parameter, depending on a number of variables (besides temperature and pressure, bulk composition of the phases, flow field of the phases, etc.). On the other hand, as Equation 22 indicates, liquid mass transfer phenomena are not important as far as stationary conditions are concerned; moreover in many experimental conditions the gas phase can be assumed to be very clean ($y_C \ll y_{Cs}$). These reference conditions define an incoming oxidation parameter (effective oxidation molar fraction K_{AC})

$$y^*_{As} = y_{As} + K_{AC} y_{Cs} \quad K_{AC} = a k_{CG}/k_{AG} \tag{23}$$

which no longer depends on the composition of the phases. In addition, the dynamic parameters still present appear as a ratio, so that their dependence on the velocity field is weak and can be neglected. Within this approximation, the parameter K_{AC} depends only on molecular gas phase properties, such as diffusivities, or mean free paths or, more analytically, on the mass and size of the molecules. So, y^*_{As} and its corresponding partial pressure (effective oxidation pressure P^*_A)

$$P^*_A = P y^*_A = P_{As} + K_{AC} P_{Cs} \tag{24}$$

can be considered as pseudo-thermodynamic parameters, or, better, properties of the system that are univocally defined by the operating conditions (temperature and total pressure) and the nature of the metal. However, these properties can be operatively defined within uncertainty ranges larger than those of the true thermodynamic parameters or molecular transport properties.

5. Particular cases

The use of equations such as (23) needs the knowledge of transport coefficients (k_{AG}, k_{CG}) or, at least, their mutual ratio (K_{AC}). The values and functional dependences of transport coefficients are, in turn, strongly affected by operating conditions, in particular total pressure.

5.1. Low pressures

At very low total pressure, when the mean free paths of molecules are longer than the dimensions of the operating chamber, the Knudsen diffusion regime occurs and attention must primarily be paid to interfacial reactions and oxide evaporation. So the "transport coefficients" are the coefficients of the Langmuir-Knudsen equation for a surface under vacuum, so that

$$K_{AC} = (\beta_A/\beta_C)(M_C/M_A)^{1/2} \tag{25}$$

The case of aluminium in a vacuum, (Fig. 2), represents a good confirmation of Equations 23 and 25.

5.2. High pressures; no reaction in the gas phase

When an inert gas maintains the total pressure at relatively high values, Fick diffusion occurs and gas phase reactions can play an important role. In the absence of reactions, the integration of the local mass balance and the transport equation in the gas layer close to the liquid leads to

$$K_{AC} = aD_C/D_A = [(M_C + M_I)/(M_A + M_I)]^{1/2} \times [(d_A + d_I)/(d_C + d_I)]^2 \quad (26)$$

As shown in Fig. 1, tin at atmospheric pressure tends to confirm Equations 23 and 26, just as the data for tin in a vacuum tend to confirm Equations 23 and 25. As K_{AC} values, according to Equations 25 and 26, are always of the order of unity, the calculated P_A^* curves in Fig. 1 for Fick and Knudsen diffusion are practically superimposed. The measured values for P_A^* are higher than the calculated ones and the differences are larger for atmospheric pressure data.

5.3. High pressures, oxide formation in the gas phase

The occurrence of the oxidation reaction (1) in the gas layer can significantly alter the effective transport coefficients, which must be corrected with the introduction of "exaltation factors". On the other hand, by using the reaction invariants, the ratio K_{AC} can be shown to be independent of exaltation factors and can still be expressed as in the former case. In other words, the result (26) is substantially independent of the oxidation reaction kinetics: very slow or "frozen" reactions and very quick or "equilibrium" reactions both lead to the same incoming oxidation conditions.

5.4. High pressures, oxide formation and condensation in the gas phase

By using the local condition for instantaneous oxide condensation as the condition for gas saturation at the gas-liquid interface, it is possible to obtain

$$y_{AG}^* \approx (1 + 1/a)y_{As} + (aD_C/D_A)y_{Cs} > y_A^* \quad (27)$$

from which it follows that the condition for gas saturation with incoming oxide condensation requires a more oxidant bulk gas phase than that required for liquid saturation (23), (26). In the presence of a unique oxide the gas saturation with oxide condensation can only follow the saturation of the liquid and Equation 26 for incoming liquid saturation still holds true.

5.5. High pressures, formation of more than one oxide

The existence of a second oxide may change the interface behaviour. The first term on the right hand side of Equation 27 may become negative, so that the gas saturation might be encountered before the liquid saturation. While increasing y_A, a limit value for x_{Ai} may be encountered $[(x_{Ai})_{max} < x_{As}]$ corresponding to a still-clean liquid surface. A greater y_A value will not further change the composition of the interface liquid; all that will occur is an increase in the oxide condensation phenomena in the gas phase. Under such conditions, the theory should foresee that the interface will remain clean whatever the oxygen content of the gas phase is, while the degree of oxygen contamination of the interface cannot exceed the saturation limit. This seems to be the case of silicon [5, 6, 16, 17].

6. Experimental questions

A number of difficulties have already been encountered or can be expected in making high-temperature measurements of liquid metals. In this paper particular attention is paid only to the time scale of the phenomena and to the control of the oxygen content inside the bulk-gas phase.

6.1. Checking the drop time

In using the stationary drop assumption one must be aware that the time scale of the required measurements is greater than the drop time. It is also worth considering a comparison between Equation 22 (incoming saturation for a stationary drop) and Equation 18 written for $x_{Am} = 0$ (incoming saturation for a completely clean and, therefore, non-stationary drop). The differences in y_A^* and then the uncertainty of the dependence of this parameter on the liquid composition are due to liquid transport phenomena. If the drop time is low, experimental uncertainties depending on drop composition are low too and, moreover, approach zero in the short saturation time. On the other hand, if the drop time is high these uncertainties are high and high times are required for reaching the stationary state. In order to obtain reliable and usable results, different experimental procedures have to be adopted according to the length of the drop time.

In the case of tin (Fig. 1) the drop time might be several hundreds of hours and the stationary drop assumption would not be at all realistic for most known experimental data. A significant advance can be made by considering the liquid phase mass transfer. As said, the difference between the predicted and measured values in Fig. 1 can be attributed to liquid mass transfer in a non-stationary drop [15].

6.2. The Peclet number

The oxygen content can be measured at the gas inlet (y_{Ao}) or gas outlet (y_{Af}) of the test chamber or at an intermediate point in the chamber, but measured values do not usually coincide with the mean value at a distance

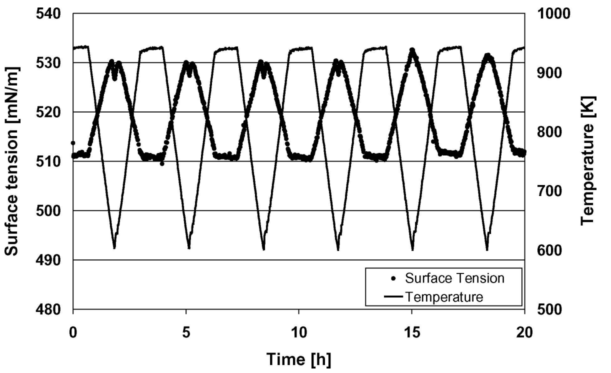

Figure 3 An example of oxygen content control by means of temperature modulation for tin under Knudsen regime.

δ from the interface (y_A) or with the interface value (y_{Ai}). The simplest way to take this fact into account, at least roughly, is to consider the parameter

$$\mathrm{Pe} = (\delta v / D_A E_A) f_{sh} \tag{28}$$

which is related to the flow conditions and geometry of the test chamber. This parameter, the Peclet number, can be unambiguously defined only in a few, particular, experimental conditions, such as viscous flow ($\delta = R_d$), no reactions ($E_A = 1$), a very simple geometry and a "well mixed" situation where $y_A \approx y_{Af}$.

A measure of the inlet oxygen level y_{Ao} allows a good estimation of interface saturation; the link between y_{Ao} and x_{Ai} is stable [5]; that is it is less dependent on the Peclet number and a very rough estimation of Pe will also lead to a reasonably good estimation of the order of magnitude of x_{Ai}. On the contrary, a measurement of the oxygen level in the gas outlet does not allow any reliable evaluation: the link between y_{Af} and x_{Ai} is very sensitive to the Peclet number.

A particular recommendation is to take care in positioning the oxygen sensors inside the experimental apparatus and in interpreting their measurements as indications of the real interface conditions. Some apparently great differences between diverse sets of experimental data can be reconciled using a unique interpretative approach. An example is the case of silicon [5, 18, 19]. Recent experimental results show, however, that these effects are much less important for tin [20]. Some significant effects for aluminium in a vacuum have been observed [21].

6.3. Obtaining saturation

Experimental techniques employed to control the oxygen content around liquid samples are of some interest too. At least two different techniques can be used for the purpose.

For instance, a more oxidising atmosphere can be achieved by simply increasing the oxygen input. When trying to control the oxygen content great difficulties may be encountered in regulating the inlet devices, especially in tests in a vacuum. This problem cannot be completely solved by using buffer mixtures.

In many instances the simplest way passes through a temperature control: as saturation conditions strongly depend on temperature, a temperature modulation corresponds to a saturation modulation and it is then equivalent to an oxygen level modulation. An example of temperature modulation for tin at atmospheric pressure is reported in Fig. 3.

7. Conclusions

The simple and generalised physico-mathematical description of interfacial evolution presented in this paper further advances our understanding of interfacial saturation phenomena for liquid metals.

The first, fundamental, step in the right direction was made when the close system and equilibrium assumption was rejected and reference was made to a drop as an open system and the related temporal invariance conditions (stationary drop assumption).

The step sequence towards better control of interfacial saturation phenomena can be illustrated by the following points, with reference to tin in a vacuum at about 600 K. The equilibrium assumption leads to a huge underestimation (up to 32 o.m.) of the oxygen concentration (or partial pressure) corresponding to the interface saturation. The stationary drop assumption leads to an underestimation of about 8 o.m.; the improvement over the former assumption is evident and confirms that the system is far from equilibrium; however the discordances with experimental data are still quite significant. Recent developments in the consideration of liquid-phase mass transfer have led to substantially better estimations.

For aluminium in a vacuum at about 1000 K the equilibrium assumption leads to an underestimation of about 40 o.m.; the stationary drop assumption leads to a substantially correct estimation. The extension of this system to other alloys is under way.

At present, the interpretation of surface tension dynamic measurements on a clean drop, in terms of the oxygen excess concentration of the interface, also appears to be an attainable objective.

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