Oxidation of Metals with Highly Reactive Vapors: Extension of Wagner Theory

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In this article, a theoretical analysis of the behavior of metallic materials at high temperature in the presence of gaseous oxygen is presented. A generalized Wagner approach is presented in the limiting scenario of highly reactive vapors, Wagner's theory being the lower limit for null reactivity. Oxygen transfer from the gas phase to the condensed phase is expressed in terms of oxygen effective pressure, accounting for the contribution of volatile oxides. The theoretical approach allows the prediction of the oxygen partial pressures in the feed gas corresponding to oxidation/deoxidation conditions. Such conditions can be different from those given by thermodynamic equilibrium by several orders of magnitude. Moreover, the actual oxygen partial pressure at the condensed phase interface can be expressed as a function of the feed-gas oxygen content, which is measurable. The theory is applicable for metals and nonmetallic materials, such as semiconductors, both in solid and liquid phase. An application to the molten silicon-oxygen system is presented.

I. INTRODUCTION

THE identification of the factors controlling gas transport at the liquid or solid interfaces as a function of the boundary conditions and the reactivity of surfaces assumes an important role in the definition of the efficiency of several technological processes. In particular, for high temperature processes, capillary phenomena, crystal growth, welding, etc., the studies on the interplay of all possible mechanisms of mass transport at/through the liquid-gas interface are of topical interest from a scientific and a technological point of view. The materials involved in these kinds of processes can be metals and nonmetals. For the sake of synthesis, the word "metal" is used hereafter in a generalized sense and includes semiconductors.

The presence of oxygen at the molten metal interface and the existence of oxygen fluxes, from/towards the atmosphere yielding adsorption/desorption mechanisms,[1] can strongly affect the performance of such processes. Moreover, vaporization phenomena, providing fluxes of metal and oxide vapors leaving the liquid surface, can modify the oxygen availability at the surface. In the case of metal vapors, if the boundary conditions are favorable from both the thermodynamic and kinetic points of view, there will be the possibility of reactions with the oxygen in the gas phase, in the vicinity of the surface.[2] In the case of oxide vapors, if highly volatile oxides are formed, such as SiO, SnO, Al_2O, etc., high oxygen fluxes leaving the liquid surface can be produced.[3] In both cases, the contamination of the surface itself could be reduced. Furthermore, it has been pointed out by different authors[4,5,6] that some anomalous trends of surface tension *vs* temperature can be justified by considering the different availability of oxygen near the surface as a function of temperature and gas flow rate.

Theoretical models, relating the mass exchange between liquid metals and the surrounding atmosphere at different oxygen partial pressures, both under inert gas carrier and Knudsen regime, have been developed,[7–11] which make possible an estimation of the degree of contamination of the surface and an explanation of the mechanism of the oxygen mass transfer at the liquid metal-gas interface. In the case of inert carrier gas flow, Ricci *et al.*[7] identified the conditions in which the metal vapor reactivity is sufficiently high for an oxidation reaction to take place in the gas phase, far from the surface. Castello *et al.*,[8] on the other hand, studied systems under low total pressures (Knudsen regime) and considered a double contribution of molecular oxygen and volatile oxides to the oxygen flux to/from the surface, the so called "oxygen effective pressure." Curves separating different oxidation/deoxidation regimes[12,13] were drawn, representing a very useful control tool for the degree of oxygen contamination of liquid metals. The fundamental concept of this last model is in complete agreement with the Wagner theory.[3] Hence, the work of Castello *et al.*[8] can be seen as an extension and generalization of such a theory, conceived for inert carrier gases containing oxygen to systems in the Knudsen regime.

Many theoretical and experimental studies on this subject are available in literature for solid materials.[14–17] In contrast, significantly less effort has been applied to the examination of such mechanisms and their effect in capillary phenomena at high temperature. In this article, previous models are seriously reconsidered in view of the description of such materials that produce highly reactive vapors and that form highly volatile oxides. Such a case is not difficult to verify: an approximated evaluation of the kinetics shows that such conditions are indeed encountered, *e.g.*, in the case of molten silicon.[18] However, accounting for chemical reactions produces a notable increase in the complexity of the model. To study effects of reactions in the simplest way, the limiting case of instantaneous reactions is assumed, *i.e.*, chemical equilibrium is reached instantaneously. So, fluxes were evaluated by considering a diffusional model with the local equilibrium constraints of oxidation reactions for the

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gaseous phase surrounding the condensed phase. The possibility of formation of fogs/aerosols of condensed oxides in the layer surrounding the sample is considered. So, the output of this model is obtained in cases of both homogeneous and heterogeneous layers (*i.e.*, aerosols are present) surrounding the metal sample, allowing the identification of the steady-state oxidation/deoxidation regimes at different oxygen partial pressures. Recently, a similar model has been presented[10,11] but with a major difference: the possibility of condensation of oxides in the gaseous layer was not considered. The present model is applicable to metals and nonmetallic materials, both in solid and liquid phase. The results presented here allow the prediction of all possible scenarios: the Wagner theory is the lower limit for null metal reactivity, while the present extension is the upper limit for "infinite" reactivity. Application to the Si-O system is considered.

II. THE MODEL

The model refers to the usual geometry of an experimental apparatus consisting of a tube-shaped, vacuum-tight chamber in which a sample of a pure metal or alloy is placed and where a gaseous flux of known composition is introduced.[11] The oxygen concentration in the gas flow can be controlled by mixing known amounts of this gas with an inert carrier or by using buffered gaseous mixtures. With reference to this experimental layout, the model is based on the following assumptions: (1) the temperature is uniform in a large region of the tube-shaped chamber surrounding the sample; (2) the total pressure is constant; (3) the gas flow around the metal sample can be considered as laminar ($\mathrm{Re}_d < 100$); (4) the surface of the metal sample is considered "plane," that is, the characteristic dimension d_d is "large" with respect to the gas diffusion layer dimension; (5) accumulation in the gas phase is neglected, so steady-state conditions in the gaseous layer are assumed; (6) the gas phase is assumed ideal; (7) molecular diffusion is assumed to be the process mainly controlling the exchange of matter between the sample and the surrounding atmosphere, *i.e.*, there is a layer δ surrounding the sample in which the transport mechanism is exclusively diffusional; (8) in the layer δ, the transport of oxygen, metal, and oxide vapors is taken into account and chemical reactions between the previously mentioned gaseous compounds are considered; and (9) owing to the very high reactivity between metal vapors and oxygen at high temperature, the chemical reactions are assumed instantaneous, *i.e.*, concentration profiles of the gaseous compounds fulfil the local chemical equilibrium conditions.

The following chemical species are considered: A (molecular oxygen), B (the metal), the corresponding j-oxides, C_j, and the inert gas, I.

Oxidation reactions with the following general stoichiometric form are considered:

$$\alpha_j A + B \leftrightarrow C_j \qquad [1]$$

The reaction scheme (Eq. [1]) has to be intended as a molecular balance and can be formally extended to any types of oxides. To do so, it is necessary to convert any stoichiometric form by assigning the value 1 to the stoichiometric coefficient of the metal, and accordingly, modifying all the related physicochemical parameters, such as the reaction equilibrium constants.

Whatever the mechanism of the oxidation reactions, the reaction kinetics of each chemical species can be formalized as

$$r_{C_j} = kf_j,\ r_A = -k \sum \alpha_j f_j; \quad r_B = -k \sum f_j \qquad [2]$$

where f_j is a function of the local values of T and c_i, according to the Arrhenius law and the kinetic mechanism of the jth reaction.

In the hypothesis of steady-state and by applying the dimensionless quantities:

$$\zeta = \frac{z}{\delta} \qquad \mathrm{x}_i = \frac{P_i}{P_B^s} = \frac{c_i}{c_B^s} \qquad i = I, A, B, 1, \ldots n$$

$$\Phi^2 = \frac{\delta^2 k}{D_A c_B^s} \qquad \Psi_B = \frac{D_B}{D_A}; \qquad \Psi_{C_j} = -\frac{D_{C_j}}{D_A} \qquad [3]$$

the dimensionless local balances on the layer can be written as

$$\nabla^2 x_A = \Phi^2 \sum_j \alpha_j f_j$$

$$\Psi_B \nabla^2 x_B = \Phi^2 \sum_j f_j \qquad [4]$$

$$\Psi_{C_j} \nabla^2 x_{C_j} = \Phi^2 f_j$$

completed by the algebraic constraint

$$x_I = x_{\mathrm{tot}} - x_A - x_B - \sum_j x_{C_j}$$

and with the boundary conditions given by

$$\zeta = 0 \qquad x_i = x_i^\sigma$$

$$\zeta = 1 \qquad x_i = x_i^\delta \qquad [5]$$

To define the boundary conditions at the liquid surface, local equilibrium is considered

$$A\ (\mathrm{g}) \leftrightarrow \underline{A} \quad B\ (\mathrm{l}) \leftrightarrow B\ (\mathrm{g}) \quad \alpha_j A\ (\mathrm{g}) + B\ (\mathrm{l}) \leftrightarrow C_j\ (\mathrm{g})$$

and then, at $\zeta = 0$,

$$x_A^\sigma = x_A^*; \quad x_B^\sigma = x_B^s = 1; \quad x_{C_j}^\sigma = \min\,(x_{C_j}^s, x_A^{*\alpha_j}/K_j) \qquad [6]$$

At a distance, δ, from the metal sample the concentration, c_i^0, of each component in the gas phase is constant; c_i^δ can be estimated from a material balance involving the oxygen supply, the gas outlet, and the gas fluxes through the layer surrounding the metal sample.[11] Here, we assume that at the distance, δ, from the sample, the gas composition equals the composition in the inlet, c_i^0. This implies no loss of generality: Ratto *et al.*[11] included the global balance to define boundary conditions of the system and showed that, when transport in the layer surrounding the sample is expressed as a function of inlet concentrations, the solution of the model is almost independent of the flow conditions and that to set $c_i^\delta = c_i^0$ is a totally acceptable assumption.

In order to consider the presence of oxidation reactions in the gas phase in the simplest way, local equilibrium condition of the oxidation reactions is imposed for the whole layer $P_{C_j}/(P_A^{\alpha_j} P_B) = K_{pj}$, which becomes, in dimensionless form

$$x_A^{\alpha_j} x_B = K_j x_{C_j} \quad \text{where} \quad K_j = (K_{p_j} P_B^{s a_j})^{-1}\ j = 1, \ldots n \qquad [7]$$

In this case, the system is bivariant (at constant P, T) and can be described with only two independent variables (*e.g.*,

x_A, x_B). In the opposite case of null reactions (Wagner theory[3]), all the terms on the right-hand side in the system of Eq. [4] are null.

However, in some central portions of the diffusion layer, the oxide with the lowest product, $K_j x^s_{C_j} P_B^{s(\alpha_j+1)} = K^s_j$, defined in the following as the saturation product, could condense. Indicating this kind of oxide with the subscript, *p*, the relationships of Eq. [7] become

$$x_{C_p} = x^s_{C_p} \qquad x_A^{\alpha_p} x_B = K_p x^s_{C_p} \tag{8}$$

making the system monovariant with a unique independent variable (*e.g.*, x_A).

In general, five different cases can occur in the layer:

(a) the entire layer is homogeneous;
(b) homogeneous layer ($0 < \zeta < \zeta^{(1)}$), then heterogeneous layer ($\zeta^{(1)} < \zeta < \zeta^{(2)}$) and the homogeneous layer again ($\zeta^{(2)} < \zeta < 1$);
(c) heterogeneous layer ($0 < \zeta < \zeta^{(1)}$) and then homogeneous layer ($\zeta^{(1)} < \zeta < 1$);
(d) homogeneous layer ($0 < \zeta < \zeta^{(1)}$) and then heterogeneous layer ($\zeta^{(1)} < \zeta < 1$);
(e) the entire layer will be heterogeneous.

Cases (d) and (e) are possible only if the carrier gas already contains metal vapors; otherwise, the partial pressures of the oxides in the carrier gas are null and an external layer must exist which is homogeneous, so that only cases (a), (b), and (c) can occur. Furthermore, the paths from cases (a) to (b) or (a) to (c) are given in a scale of increasing oxygen content of the carrier gas. When x^0_A increases sufficiently, at a given position in the layer, a condensed oxide will be formed: the occurrence of cases (b) or (c) depends on whether or not that position is at the interface. When a condensed oxide is formed in the boundary layer, different phenomena can take place: in extreme synthesis, oxides can either precipitate or remain in the layer as aerosol, as also observed experimentally. However, the local equilibrium of the condensed phase as aerosol in the diffusive layer is not easily attained. The conceptual limit given by the local equilibrium hypothesis (Eq. [8]), even if unlikely, is very useful since it allows a simple preliminary description of the effects of oxide condensation in the gas layer without the need of any description of nucleation phenomena.

In the following sections, the solution of the system of Eq. [4] for both homogeneous and heterogeneous cases is presented in detail. Furthermore, the asymptotic conditions for the system will be determined, corresponding to steady-state conditions (*i.e.*, constant composition) also in the condensed phase.

III. MODEL SOLUTION FOR HOMOGENEOUS LAYER

A layer, or a portion of it in which only the gaseous phase is present, is now considered. The description of the oxidation/deoxidation regimes for the liquid sample must account for the contributions of all chemical species containing oxygen. Hence, the total oxygen flux through the layer has to be considered:

$$\begin{aligned} N_{AT} &= N_A + \sum_j \alpha_j N_{C_j} \\ &= -(D_A \text{ grad } c_A + \sum_j \alpha_j D_{C_j} \text{ grad } c_{C_j}) \end{aligned} \tag{9}$$

which, defining the corresponding nondimensional quantity $n_{AT} = \dfrac{N_{AT}\delta}{D_A c^s_B} = -\text{grad } X_A$ where $X_A = (x_A - \sum_j \alpha_j \Psi_{C_j} x_{C_j})$, can be written in the following dimensionless form:

$$\text{grad } X_A = \text{grad } (x_A - \sum_j \alpha_j \Psi_{C_j} x_{C_j}) \tag{10}$$

In the same way, the dimensionless total metal flux can be defined as

$$\text{grad } X_B = \text{grad } (\Psi_B x_B - \sum_j \Psi_{C_j} x_{C_j}) = -n_{BT} \tag{11}$$

where $X_B = (\Psi_B x_B - \sum_j \Psi_{C_j} x_{C_j})$

By writing the local balances for the variables X_A and X_B, the unknown kinetic terms in the system of Eq. [4] are eliminated, obtaining

$$\begin{matrix} \nabla^2 X_A = 0 \\ \nabla^2 X_B = 0 \end{matrix} \Rightarrow \begin{matrix} \text{grad } X_A = \text{const} = B_1 \\ \text{grad } X_B = \text{const} = B_2 \end{matrix} \tag{12}$$

The constants B_1 and B_2 are easily derived from the boundary conditions:

$$\zeta = \zeta_1 \qquad x_A = x_{A1} \qquad x_B = x_{B1} \Rightarrow x_{C_j} = x_{C_j1}$$

$$\zeta = \zeta_2 \qquad x_A = x_{A2} \qquad x_B = x_{B2} \Rightarrow x_{C_j} = x_{C_j2}$$

where the values of x_{C_j1} and x_{C_j2} are determined by the equilibrium Eq. [7] and ζ_1 and ζ_2 are spatial boundaries for the homogeneous layer. In general, we have

$$B_1 = \frac{X_{A2} - X_{A1}}{\zeta_2 - \zeta_1} \quad \text{and} \quad B_2 = \frac{X_{B2} - X_{B1}}{\zeta_2 - \zeta_1} \tag{13}$$

When the homogeneous zone covers the whole layer, case (a) occurs, $\zeta_2 = 1$, $\zeta_1 = 0$; and the total fluxes are constant along the whole layer:

$$B_1 = X^0_A - X^\sigma_A \text{ and } B_2 = X^0_B - X^\sigma_B \tag{14}$$

Equations [12] and [13] show that the driving forces of the total oxygen and metal fluxes are the gradients of the variables X_A and X_B, *i.e.*, the gradient of the oxygen effective pressure:

$$P_{A_{\text{eff}}} = P_A + \sum_j \alpha_j \,.\, \Psi_{C_j} \,.\, P_{C_j} \tag{15}$$

and the gradient of the metal effective pressure:

$$P_{B_{\text{eff}}} = \Psi_B P_b + \sum_j \,.\, \Psi_{C_j} \,.\, P_{C_j} \tag{16}$$

A. *Asymptotic Behavior*

The vapor pressure of oxides at the surface, defined in Eq. [6], can be essential in determining the direction and the magnitude of the total fluxes expressed in Eqs. [12] and [13] and subsequently the average composition of the liquid metal. In fact, if y_A is the average value of the oxygen molar fraction inside the metal sample, the oxygen content inside the sample increases if the following conditions are attained:

$$\frac{dy_A}{dt} > 0 \quad \Leftrightarrow \quad (1 - y_A) \cdot \text{grad } X_{A \,\blacksquare\, \zeta=1} - y_A \cdot \text{grad } X_{B \,\blacksquare\, \zeta=1} > 0 \tag{17}$$

Inequalities (Eq. [17]) show that, even if the gas phase is under steady-state conditions, this does not necessarily imply that the liquid phase is also under steady-state conditions. In inequalities (Eq. [17]), the dynamic behavior of the average oxygen content of the metal sample can be interpreted by a sequence of pseudostationary states in the gas. Steady-state conditions also for the liquid correspond to the asymptotic behavior, *i.e.*, the composition y_A (and subsequently the oxygen partial pressure at the surface, which must be in equilibrium with the liquid phase) changes until the following equality is attained between fluxes:

$$\text{grad } X_A \,.\,_{\zeta=1} / \text{grad } X_B \,.\,_{\zeta=1} = y_A/(1 - y_A) \qquad [18]$$

The determination of the steady-state asymptotic conditions for the metal sample is very important for the prediction of the behavior of our system.

An entirely homogeneous layer, δ, is now considered. The condition of a totally homogeneous layer can always be fulfilled, provided that the oxygen concentration in the carrier gas is sufficiently low. By assuming, without loss of generality, that in the carrier gas no metal or oxide vapors are present:

$$x_B^0 = 0 \quad \Rightarrow \quad x_{C_j}^0 = 0 \quad j = 1 \ldots n \qquad [19]$$

considering equalities (Eq. [14]) and remembering boundary conditions (Eq. [6]) at the metal surface, Eq. [18] can be written as

$$x_A^0 = \left(x_A^\sigma - \sum_j \left(\alpha_j - \frac{y_A}{(1 - y_A)} \right) \Psi_{C_j} x_{C_j}^\sigma \right) - \frac{y_A}{(1 - y_A)} \Psi_B x_B^\sigma \qquad [20]$$

So, given the local equilibrium constraints; given the most likely situation in which no metal vapors are present in the feed gas; recalling that y_A is related to x_A^σ by an equilibrium law (*e.g.*, Sievert's law), and eventually, by some mass transfer equation inside the condensed phase, Eq. [20] is an algebraic relationship between the oxygen content of the feed-carrier gas, x_A^0, easily measurable, and the oxygen partial pressure at the interface, x_A^σ, at the asymptotic conditions. Furthermore, given the initial conditions of the system

$$x_A^0 \,(t = 0) \text{ and } x_A^\sigma \,(t = 0) \; [\Leftrightarrow y_A \,(t = 0)]$$

it can be immediately determined whether the oxygen content in the metal sample will increase (adsorption takes place during transient) or decrease (desorption takes place) by verifying the inequalities:

$$\begin{gathered} x_A^0 \,(t = 0) > h[x_A^\sigma \,(t = 0)] \Leftrightarrow \frac{dy_A}{dt} > 0; \\ x_A^0 \,(t = 0) < h[x_A^\sigma \,(t = 0)] \Leftrightarrow \frac{dy_A}{dt} < 0 \end{gathered} \qquad [21]$$

From Eq. [20], it can clearly be deduced that, if highly volatile oxides exists, we have $x_A^0 \gg x_A^\sigma$ at the steady-state, *i.e.*, under these conditions a nearly clean metal surface can be maintained, also in the presence of a carrier gas 'rich' in oxygen. Furthermore, the molar fraction is usually $y_A \ll 1$, $y_A/(1 - y_A) \approx 0$. Additionally, since the object of this study, as well as the object of the Wagner theory, is to analyze metals with highly volatile oxides, $\frac{y_A}{(1 - y_A)} \,.\, \Psi_B \,.\, x_B^\sigma \ll \max_{j=1,n} [\alpha_j \,.\, \Psi_{C_j} \,.\, x_{C_j}^\sigma]$ will also be true. Therefore, the contribution of the condensed phase concentration can be ignored, obtaining

$$x_A^0 = \left(x_A^\sigma - \sum_j \alpha_j \Psi_{C_j} x_{C_j}^\sigma \right) = \left(x_A^\sigma - \sum_j \alpha_j \Psi_{C_j} \frac{x_B^s x_A^{\sigma^{\alpha_j}}}{K_j} \right) \qquad [22]$$

or equivalently, in terms of partial pressures:

$$(P_{A\text{eff}}^0 =) \; P_A^0 = P_A^\sigma + \sum_j \alpha_j \,.\, \Psi_{C_j} \,.\, K_{Pj} P_B^s P_A^{\sigma^{\alpha_j}} \; (= P_{A\text{eff}}^\sigma) \qquad [23]$$

B. *Discussion about the Extension of Wagner's Approach*

As discussed in the introduction, the results presented in this article represent the limiting scenario for infinite reactivity of the layer, δ, as a completion of the Wagner approach, where no reactions in the layer were considered. Wagner studied active/passive oxidation of solid silicon.[3] To do this, he considered the diffusive mass transfer of oxygen towards the solid surface and the transfer of gaseous SiO from the surface and obtained a curve, which is the analogue of Eq. [22]. In this way, he could explain the transition from active to passive oxidation of solid silicon as the partial pressure of oxygen passed a threshold value, corresponding to SiO saturation conditions. Hence, he explained active oxidation in terms of oxygen effective pressure, which is the fundamental concept of this work, too.

Furthermore, model hypotheses can easily be identified from his work:[3]

(1) Local equilibrium at the metallic surface.
(2) Chemical reactions in the gas phase were not considered, *i.e.*, negligible gas reactivity was assumed.
(3) Diffusion is described in terms of a mass transfer coefficient, which is proportional to the square root of the diffusivity, as in the penetration theory[19] (valid for $\text{Re}_d > 100$); so, the dimensionless ratios, Ψ, of this work are not exactly the same quantities as in Wagner. This slight difference does not seem to be very important in the sense that the present description of diffusion is justified by the hypothesis of $\text{Re}_d < 100$ and that the difference in model results due to this aspect is quantitatively very small.
(4) The presence of gaseous Si and SiO_2 was ignored. This is obvious because the vapor pressures of Si and SiO_2 are smaller than the vapor pressure of SiO by orders of magnitude. However, in the more generalized context of this article, the presence of all possible gaseous species must be accounted for.

In this article, we will refer to the Wagner approach as defined by the basic hypotheses 1 and 2, with the minor modification of hypothesis 3 ($\text{Re}_\alpha < 100$) and the generalization of hypothesis 4. With such a set of hypotheses, the system can easily be described by considering Eq. [4] with all the right-hand terms equal to 0 (no reaction takes place in the layer). This gives linear profiles for all chemical species from the boundary values in the carrier gas to the interface values. It is also possible, in this case, to define the total oxygen/metal fluxes in terms of the variables X_A and X_B, obtaining exactly the same Eqs. [20], [22], and [23]. So, when the layer is homogeneous, the two opposite scenarios with null/infinite reactivity, as well as every intermediate situation, give the same result as far as the asymptotic behavior of the metal sample is concerned (References

10 and 11). So it can be stated that Eq. [22] describes Wagner's results in a more general and formal way. However, the two scenarios are different, if the fluxes of the single chemical species are taken into account. In the Wagner approach, the profiles are linear, while for instantaneous reactions, the profiles deeply change, according to the flux enhancement induced by chemical reactions, and become strongly nonlinear as clearly shown in Section VI. Flux enhancement can have two main effects, whose thorough discussion seems to be beyond the scope of the present work.

(1) The characteristic times of the transient,[12] in which the system attains the asymptotic behavior, can dramatically change. Experimental observations of such characteristic times will be useful for the evaluation of the effect of gas reactivity and to evaluate which model can be more suitable.
(2) Another important effect must be expected when the total oxygen flow rate in the carrier gas is small. In such cases, the enhancement of the consumption of oxygen due to the reaction would lead to a very small oxygen concentration (almost equal to the interface one) in the outlet from the furnace. Such an effect would be less evident if reactions are ignored.[11]

It seems useful to underline that such effects can be relevant not only in the limiting case of instantaneous reactions, but also for the intermediate cases. The analysis of intermediate situations implies the study and identification of all possible kinetic mechanisms,[20,21] not only for homogeneous reactions, but also for the heterogeneous ones, for nucleation, etc.

IV. MODEL SOLUTION FOR THE HETEROGENEOUS LAYER

When an oxide ($j = p$) is in equilibrium with its condensed phase, the constraint of Eq. [13] must hold at each point in the layer and the system of Eq. [10] can be written in the form

$$\nabla^2 x_A = \Phi^2 \left[\sum_{j \neq p} \alpha_j f_j + \alpha_p f_p \right]; \quad \nabla^2 x_B = \frac{\Phi^2}{\Psi_B} \left[\sum_{j \neq p} f_j + f_p \right];$$

$$\nabla^2 x_{C_j} = \frac{\Phi^2}{\Psi_{C_j}} f_j \quad j \neq p; \quad \nabla^2 x_{C_p} = 0 \qquad [24]$$

From Eq. [24], it is possible to obtain the following invariant relationship after eliminating the unknown kinetic terms, performing some algebraic operations, and moving two integration steps along the spatial coordinate:

$$x_A - \sum_j (\alpha_j - \alpha_p)\Psi_{C_j} x_{C_j} - \alpha_p \Psi_B x_B = (X_A - \alpha_p X_B) = \mathbf{A} + \mathbf{B}\zeta \qquad [25]$$

Therefore, since the heterogeneous layer with local equilibrium of the oxidation reactions is monovariant, with the single algebraic, Eq. [25], the system is completely determined. In other words, concentration profiles, and subsequently the fluxes of all chemical species, can be directly determined by simultaneously solving Eq. [25] and the equilibrium relationships (Eq. [7]) with the constraint (Eq. [8]), for any given boundary conditions, *e.g.*, if x_{A1} and x_{A2} are known. In particular, the following relationship can be written:

$$\mathbf{B} = \frac{(X_A - \alpha_p X_B)_2 - (X_A - \alpha_p X_B)_1}{\zeta_2 - \zeta_1} \qquad [26]$$

For a totally heterogeneous layer, *i.e.*, for case (e), Eq. [26] degenerates into

$$\mathbf{B} = (X_A - \alpha_p X_B)^0 + (X_A - \alpha_p X_B)^\sigma \qquad [27]$$

Furthermore, starting from Eq. [25] and after a few steps, the expressions for the total oxygen and metal fluxes as a function of the integration constant, **B**, and of the local concentrations of the different chemical species can be obtained:

$$\text{grad } X_A = \mathbf{B} \frac{x_A - \sum_j \alpha_j(\alpha_j - \alpha_p)\Psi_{C_j} x_{C_j}}{x_A + \alpha_p^2 \Psi_B x_B - \sum_j (\alpha_j - \alpha_p)^2 \Psi_{C_j} x_{C_j}}$$

$$\text{grad } X_B = -\mathbf{B} \frac{\Psi_B \alpha_p x_B + \sum_j (\alpha_j - \alpha_p) \Psi_{C_j} x_{C_j}}{x_A + \alpha_p^2 \Psi_B x_B - \sum_j (\alpha_j - \alpha_p)^2 \Psi_{C_j} x_{C_j}} \qquad [28]$$

By using Eqs. [26] to [28], the fluxes at the boundaries of the layer can easily be calculated. In this case, the total fluxes are not constant along the layer and these equations allow an evaluation to be made only at the boundaries or as a function of x_A.

Furthermore, the quantity, Q_p, can be defined, which represents the production rate of the condensed oxide in the layer: $Q_p = \dfrac{\text{grad } X_{A \cdot 1} - \text{grad } X_{A \cdot 2}}{\alpha_p} = \text{grad } X_{B \cdot 2} - \text{grad } X_{B \cdot 1}$.

A. *Asymptotic Behavior*

Considering an entirely heterogeneous layer, the condition of Eq. [18], should always be imposed for the total fluxes at the interface, which becomes, after combining Eq. [28] and eliminating the common denominators and the constant, **B**:

$$x_A^\sigma - \sum_j \left(\alpha_j - \frac{y_A}{(1 - y_A)} \right) (\alpha_j - \alpha_p)\Psi_{C_j} x_{C_j}^\sigma + \frac{y_A}{(1 - y_A)} \alpha_p \Psi_B x_B^\sigma = H(x_A^\sigma) = 0 \qquad [29]$$

As in the homogeneous case, the terms containing y_A of Eq. [29] can be ignored in most cases, obtaining

$$\left(x_A^\sigma - \sum_j \alpha_j(\alpha_j - \alpha_p)\Psi_{C_j} x_{C_j}^\sigma \right) = H\,(x_A^\sigma) = 0 \qquad [30]$$

Given the boundary condition $x_B^\sigma = x_B^s$ and the equilibrium constraints, Eq. [12], the function, H, depends only on x_A^σ. So Eqs. [29] and [30] are verified only for a fixed value of x_A^σ, which does *not* depend on the oxygen concentration in the carrier gas. So, for a heterogeneous layer, relationships, such as Eq. [20] or [22], which relate the concentrations in the carrier gas and at the interface, are no longer valid, but the interface conditions remain constant and do not depend on the actual concentration of the carrier gas. Finally, it seems useful to remark that Eqs. [29] and [30] also hold true for case (c) of mixed layers.

V. MIXED LAYER

Case (b) is here discussed, which is the most general and includes all other cases. The mixed layer structure can be defined by the positions.

1. $0 < \zeta < \zeta^{(1)}$: The layer is homogeneous. It can be defined by the relationships of Eqs. [12] and [13] and by the constants $\mathbf{B}_1^{(1)}$ and $\mathbf{B}_2^{(1)}$.
2. $\zeta^{(1)} < \zeta < \zeta^{(2)}$: The layer is heterogeneous. It can be defined by the relationships of Eqs. [26] to [28] and by the constant $\mathbf{B}$.
3. $\zeta^{(2)} < \zeta < 1$: The layer is homogeneous. It can always be defined by the relationships of Eqs. [12] and [13], but another two constants have to be considered ($\mathbf{B}_1^{(2)}$ and $\mathbf{B}_2^{(2)}$).

To find the asymptotic solution in this case, the sublayer $0 < \zeta < \zeta^{(1)}$ must be considered. After some calculations and ignoring the terms containing y_A, the following system of equations can easily be obtained:

$$\begin{cases} \left(x_A^{(1)} - \sum_j \alpha_j(\alpha_j - \alpha_p)\Psi_{C_j} x_{C_j}^{(1)} \right) = H(x_A^{(1)}) = 0 \\ x_A^{(1)} - \sum_j \alpha_j \Psi_{C_j} x_{C_j}^{(1)} = x_A^{\sigma} - \sum_j \alpha_j \Psi_{C_j} x_{C_j}^{\sigma} \end{cases} \qquad [31]$$

where the superscript (1) indicates the concentration at the spatial location $\zeta^{(1)}$. The system of Eq. [31] also holds for case (d).

So, as in the entirely heterogeneous layer, the asymptotic condition can be fulfilled only for a fixed value of x_A^{σ}, which does not depend on the actual oxygen content of the carrier gas. So, also in this case, the asymptotic behavior predicted for infinite reactivity of the layer is different from that predicted by applying the Wagner hypotheses and, by varying the oxygen concentration in the carrier gas, the interface concentration is not altered (this can be explained by an increase of the production rate of the condensed oxide in the heterogeneous layer). With this, the two extreme scenarios are clearly defined. This means that, for an intermediately reactive layer in which condensed oxides are present, the production rate of condensed oxides would not be able to maintain the interface composition constant as the carrier gas composition is increased, but, in all cases, the interface oxygen composition would be smaller than expected following the Wagner approach.

VI. APPLICATION TO LIQUID SILICON

The theory here presented can be applied identically for both solid and liquid phases. In this section, this theory is applied to a significant technological case: molten silicon.[22,23] By specifying the general definitions given in Section II for the Si-O system, we have the following.

1. Oxidation reactions in the gas phase:[24]

$$\mathrm{Si} + \mathrm{O_2} \leftrightarrow \mathrm{SiO_2} \qquad K_{p1}\,(1750\ \mathrm{K}) = 1.41 \cdot 10^{10}\ \mathrm{Pa^{-1}}$$

$$\mathrm{Si} + \frac{1}{2}\,\mathrm{O_2} \leftrightarrow \mathrm{SiO} \qquad K_{p2}\,(1750\ \mathrm{K}) = 5.56 \cdot 10^{10}\ \mathrm{Pa^{-0.5}}$$

2. Vapor pressures of metal and oxides and saturation products for oxides at 1750 K:

$$P_B^s = P_{\mathrm{Si}}^s = 1.04 \cdot 10^{-1}\ \mathrm{Pa}$$

$$P_{C1}^s = P_{\mathrm{SiO_2}}^s = 1.67 \cdot 10^{-4}\ \mathrm{Pa} \qquad K_{\mathrm{SiO_2}}^s = 1.18 \cdot 10^{-14}\ \mathrm{Pa^2}$$

$$P_{C2}^s = P_{\mathrm{SiO}}^s = 3.55 \cdot 10^{2}\ \mathrm{Pa} \qquad K_{\mathrm{SiO}}^s = 6.48 \cdot 10^{-9}\ \mathrm{Pa^{1.5}}$$

3. Saturation pressures of oxygen at 1750 K:

$$P_{\mathrm{O_2}}^{\mathrm{sat}}\,(\mathrm{SiO_2}) = \frac{P_{\mathrm{SiO_2}}^s}{K_{p1} P_{\mathrm{Si}}^s} = 1.14 \cdot 10^{-13}\ \mathrm{Pa}$$

$$P_{\mathrm{O_2}}^{\mathrm{sat}}\,(\mathrm{SiO}) = \left(\frac{P_{\mathrm{SiO}}^s}{K_{p2} P_{\mathrm{Si}}^s} \right)^2 = 3.85 \cdot 10^{-15}\ \mathrm{Pa}$$

4. Diffusion coefficients at 1750 K:

$$D_{\mathrm{O_2}} = 3.84 \cdot \mathrm{cm^2 s^{-1}}$$

$$D_{\mathrm{SiO_2}} = 2.23 \cdot \mathrm{cm^2 s^{-1}} \qquad \Psi_{\mathrm{SiO_2}} = -0.58$$

$$D_{\mathrm{Si}} = 3.51 \cdot \mathrm{cm^2 s^{-1}} \qquad \Psi_{\mathrm{Si}} = 0.914$$

$$D_{\mathrm{SiO}} = 2.84 \cdot \mathrm{cm^2 s^{-1}} \qquad \Psi_{\mathrm{SiO}} = -0.739$$

With such input data, the system of Eq. [4] can be solved, as well as the asymptotic behavior. First of all, let us consider the asymptotic behavior of the Si-O system.

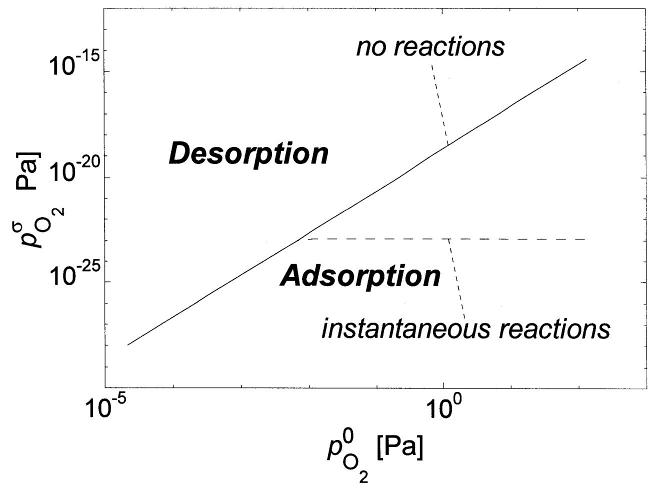


Fig. 1—Curves $P^{\sigma}_{\mathrm{O_2}}$ *vs* $P^{0}_{\mathrm{O_2}}$ at the asymptotic behavior for silicon in the two limit cases of absence of reactions and instantaneous reactions. T = 1750 K.

In Figure 1, at a fixed temperature two curves are plotted for the relationship, $P^{\sigma}_{\mathrm{O_2}}$ *vs* $P^{0}_{\mathrm{O_2}}$, one calculated with Eq. [22] for the Wagner approach, the other computed with Eqs. [22] and [31] for instantaneous reactions in the layer. First of all, it is worth noting that the oxygen concentration in the feed gas is larger than the one at the surface by several orders of magnitude. This is the effect of the oxygen effective pressure mechanism and explains why it is possible to maintain an oxygen-free surface with a feed gas relatively rich in oxygen. As expected, if the layer is homogeneous (bottom left part of the figure), the Wagner approach and our approach give the same result, while the two curves diverge when condensed oxides are present. Moreover, the curve for null reactions is allowed to reach saturation conditions at

Table I. Experimental Data of Huang *et al.*[25] and Transformation by Means of Eq. [22] (T = 1688 K)

$P^0_{O_2}$ Huang *et al.*[25] (Pa)	$P^\sigma_{O_2}$ Eq. [22] (Pa)	Surface Tension (mN/m)
0, 1	9.8×10^{-22}	824
8.03	6.3×10^{-18}	810
16	2.5×10^{-17}	809
28	7.7×10^{-17}	792
42	1.7×10^{-16}	789

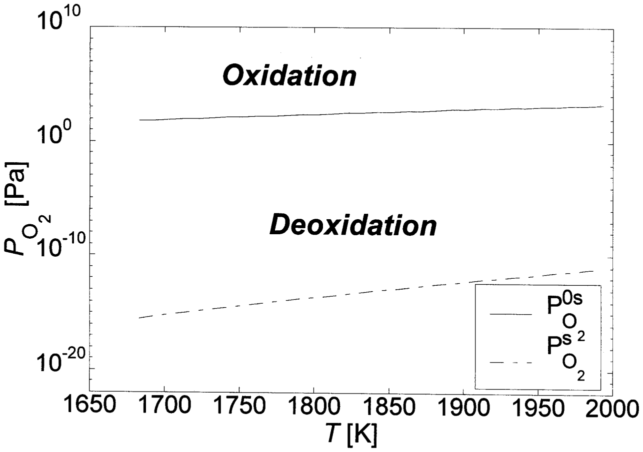
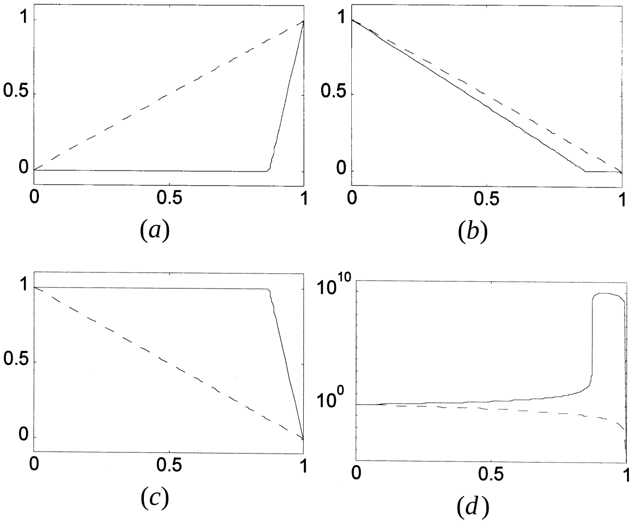


Fig. 2—Saturation curves for the asymptotic behavior ($P^{0s}_{O_2}$ *vs* T) and ($P^s_{O_2}$ *vs* T) for the Si-O system in the limit case of absence of reactions.

the surface (actually, the line ends up at top right of the plot for saturation conditions), while in the case of instantaneous reactions with mixed layer, surface concentration does not change while the oxygen in the feed gas is increased, implying that saturation cannot be reached. This is obviously a conceptual limit, which will never occur in practice and the region between the two curves is the band in which the real asymptotic curve is placed. In all cases, it will always be possible to reach saturation for a sufficiently large amount of oxygen in the feed. Curves $P^\sigma_{O_2}$ *vs* $P^0_{O_2}$ are very important, since they allow the estimation of the real concentrations at the liquid surface, when the oxygen concentration in the feed gas is measured. This also allows the interpretation of nonhomogeneous, literature, surface tension measurements at different oxygen partial pressures provided by different authors under a unifying scenario, where in some cases the inlet P_{O_2}, and in other cases the P_{O_2} at the outlet[5,25] are measured. The full discussion of such aspects is the subject of another study,[11] where the effectiveness of the approach based on the oxygen effective pressure is verified using experimental data. For example, we report in Table I, the case of Huang *et al.*,[25] regarding silicon surface tension measurements at different oxygen partial pressures. Measurements were preformed in the feed gas. Raw values of oxygen partial pressure by Huang *et al.* are larger than saturation values by several orders of magnitude. By applying oxygen effective pressure approach (second column of Table I), however, it was possible to demonstrate that such high values in the inlet correspond to oxygen content at the surface well below saturation.

Figure 1 also allows outlining the behavior of the sample during the transient. If the point representing the initial conditions of the experimental setup is below the curve corresponding to the actual reaction regime, adsorption takes place at the surface, and the liquid will increase its oxygen content until the asymptotic curve is reached; if the coordinates of the initial conditions are above the curve, desorption takes place.



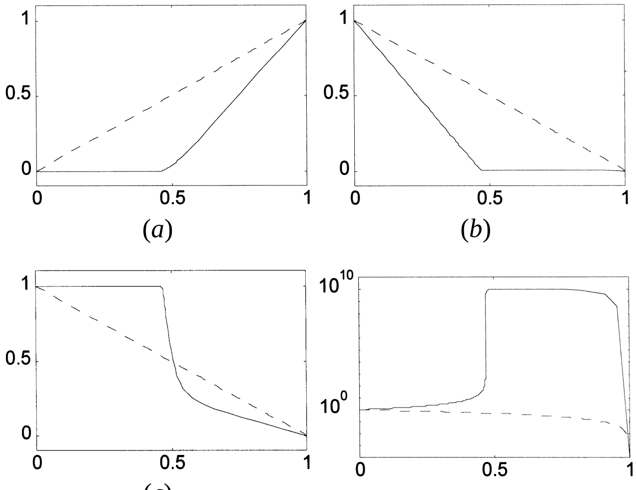
(*a*) (*b*) (*c*) (*d*)

Fig. 3—Pressure profiles *vs* ζ at the asymptotic behavior. T = 1750 K, $P^0_{O_2} = 7 \cdot 10^{-3}$ Pa. Solid lines = instantaneous reactions, case (a). Dashed lines = no reaction (Wagner approach). (*a*) $P_{O_2}/P^0_{O_2}$. (*b*) P_{Si}/P^s_{Si}. (*c*) P_{SiO}/P^σ_{SiO}. (*d*) Semilog-*y* $P_{SiO_2}/P^\sigma_{SiO_2}$.

In Figure 2, the transition between oxidation/deoxidation conditions is shown as a function of the temperature in the case of negligible reactions. The solid curve represents the transition for $P^0_{O_2}$ between the (passive) oxidation regime above the curve and the deoxidation (active oxidation in Wagner's notation) regime below the curve. The dashed curve is the thermodynamic saturation curve. The curve ($P^{0s}_{O_2}$ *vs* T) is the envelope of the *x*-coordinates of the saturation endpoints of the curves $P^\sigma_{O_2}$ *vs* $P^0_{O_2}$ with null reactions (top right in Figure 1) at different temperatures and has been computed by applying Eq. [23] with the right-hand side terms at saturation conditions. Analogous behavior was calculated in Reference 8 for liquid silicon under Knudsen regime. Furthermore, such a curve is analogous to the curves for solid silicon studied by many authors.[3–16] The major interest for capillary phenomena is addressed to the behavior under active oxidation, *i.e.*, when the liquid metal surface is oxide-free, so this curve is very useful to identify the suitable operating conditions at different temperatures. Comparing Figures 1 and 2 also allows a qualitative evaluation of the saturation oxygen effective pressure in the general case of reacting gas layer. Since the real $P^\sigma_{O_2}$ *vs* $P^0_{O_2}$ curve lies between the two curves plotted in Figure 1, saturation conditions will be reached for larger values of $P^0_{O_2}$, implying that the ($P^{0s}_{O_2}$ *vs* T) curve in Figure 2, obtained for null reactions, is the lowest, *i.e.*, conservative, limit for oxidation conditions to take place in the sample.

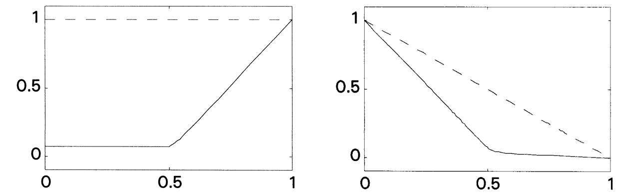
To better clarify the difference between the Wagner approach and the present approach, the concentration profiles obtained solving Eq. [4] along the spatial coordinate, ζ, are considered in Figures 3 through 5.

In Figures 3 and 4, the pressure profiles of the four chemical species are shown for the case of instantaneous reactions



(*a*) (*b*) (*c*) (*d*)

Fig. 4—Pressure profiles *vs* ζ at the asymptotic behavior. $T = 1750$ K, $P^0_{O_2} = 1 \cdot 10^{-1}$ Pa. Solid lines = instantaneous reactions, case (b). Dashed lines = no reaction (Wagner approach). (*a*) $P_{O_2}/P^0{}_{O2}$. (*b*) P_{Si}/P^s_{Si}. (*c*) P_{SiO}/P^σ_{SiO}. (*d*) Semilog-*y* $P_{SiO_2}/P^\sigma_{SiO_2}$.



(*a*) (*b*)

Fig. 5—Profiles for oxygen and metal effective pressures *vs* ζ at the asymptotic behavior. $T = 1750$ K. (*a*) $P^{eff}_{O_2}/P^0_{O_2}$. (*b*) $P^{eff}_{Si}/P^{eff^\sigma}_{Si}$. Dashed lines = instantaneous reactions, case (a) ($P^0_{O_2} = 7 \cdot 10^{-3}$ Pa) and no reaction. Solid lines = instantaneous reactions, case (b) ($P^0_{O_2} = 1 \cdot 10^{-1}$ Pa).

(solid lines) and for the Wagner approach (dashed lines). In Figure 3, the layer is fully homogeneous, *i.e.*, case (a), while in Figure 4 the layer is mixed, *i.e.*, case (b). Concentration profiles for instantaneous reactions are strongly not linear, while they are linear for null reactions. Following the concept that we consider the two extreme opposite situations, it can be stated that the real concentration profiles lay in the region between the two curves. In Figure 3(d), a very sharp maximum at $\zeta = 0.91$ for the SiO_2 concentration can be seen (the less volatile oxide), visible only in the logarithmic scale. In Figure 4(d), again in logarithmic scale, the heterogeneous portion of the layer due to condensation of SiO_2 is very clearly visible, characterized by the plateau in the interval $\zeta \in (0.49,0.63)$.

In Figure 5, profiles of the oxygen and metal effective pressures are shown. Since asymptotic conditions are considered, the gradient of the oxygen effective pressure at the surface of the sample ($\zeta = 0$) is always null. Profiles of effective pressures in Figure 5 are always linear for homogeneous layers, both for null and instantaneous reactions, while they become nonlinear for instantaneous reactions in the case of heterogeneous layers. Considering a fully homogeneous layer, even if the same results as in the Wagner approach are obtained for effective pressures and for the relationship $P^\sigma_{O_2}$ *vs* $P^0_{O_2}$ at the asymptotic behavior (Figure 1), the fluxes of each chemical specie are completely different. In particular, for instantaneous reactions, fluxes at the liquid surface (metal evaporation) and at the boundary with the carrier gas (oxygen consumption) will be enhanced. This may have important effects as far as the characteristic times and the outlet composition are concerned. Such effect of flux enhancing will be even stronger in the case of partially heterogeneous layers.

VII. CONCLUSIONS

In this article, an extension of the Wagner theory has been applied for the analysis of oxidation conditions of materials when the gas surrounding the sample is highly reactive. As a limiting hypothesis, instantaneous reactions are assumed and subsequently local equilibrium of all oxidation reactions over the whole layer. A fundamental result of this work is the derivation of the expression of the curves of the asymptotic behavior of the system. With these curves, it is possible to predict whether the system is under oxidizing or deoxidizing conditions. Two scenarios can occur: when the gaseous layer remains homogeneous, *i.e.*, no oxide reaches the saturation point in the layer, the expression of the asymptotic curve given by Eq. [22] holds true for both null and instantaneous reactions, as well as for any intermediate situation. Hence, Eq. [22] can be seen as the generalized expression of the Wagner theory for any type of reactivity of metal vapors. On the other hand, when an oxide reaches saturation point inside the layer, the curves representing the asymptotic conditions diverge. In this case, the present results indicate the region in which any other possible asymptotic curve, representing an intermediate situation, can be placed.

This article has raised a number of problems, which need further attention and consideration.

1. The study of characteristic times of the transient to attain asymptotic behavior.
2. The analysis of the layer with intermediately active reactions.

Moreover, further developments in the experimental analysis, in particular, surface tension measurements in dynamic conditions as a function of oxygen partial pressure and/or temperature, are needed in order to observe and understand the response of liquid metals to the presence of oxygen. The results of such research are important for the correct interpretation of and as a guide to the experimental analysis and for technological development, especially in high-tech processes, such as the production of single crystals, semiconductors, and materials for advanced applications.

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NOMENCLATURE

c_i	concentration of the *i*th compound, mol cm^{-3}
d_d	metal sample characteristic dimension

D	diffusivity, cm^2 s^{-1}
f_j	function (of T and c_i) in the reaction kinetics expression of the jth oxide
k	constant common to all reaction kinetics, cm^3 mol^{-1} s^{-1}
K_{pj}	equilibrium constant for the jth reaction
K_j	dimensionless equilibrium constant for the jth reaction
K_j^s	saturation product for the jth oxide, defined as $P^s_{C_j}/K_{pj}$
I	inert gas (He, Ar, . . .)
n	total number of oxides
n_i	dimensional molar flux
N_i	molar flux, mol cm^2 s^{-1}
P_i	partial pressure, atm
r_i	reaction rate of the ith compound, mol cm^{-3} s^{-1}
Re_d	Reynolds number of the metal sample.
x_i	concentration of the ith chemical specie, normalized with respect to c_B^s
X_A	dimensionless total effective oxygen concentration
X_B	dimensionless total effective metal concentration
y	molar fraction in the condensed phase
z	spatial coordinate with origin at the interface and perpendicular to it, cm.

Greek Letters

α_j	oxygen stoichiometric coefficient in the jth oxidation reaction
ζ	dimensionless spatial coordinate with origin at the interface and perpendicular to it
δ	diffusive layer
Φ	Thiele modulus
Ψ	diffusivity, normalized with respect to D_A

Superscripts

0	carrier gas
σ	metal surface
s	saturation
$*$	equilibrium with the condensed phase

Subscripts

i	index for all chemical species, A, B, C_j
j	index for oxides
p	index for the oxide with minimum solubility product
eff	effective pressure
$\overline{\qquad}$	in the liquid phase

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